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Dynamical Extensions of Band Theory: Non-Hermitian contributions and topological stabilization

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The present doctoral dissertation was submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy of the University of Cyprus. It is a product of original work of my own, unless otherwise mentioned through references, notes, or any other statements.

Kyriakou Kyriakos

Περίληψη

Υποκινούμενοι από την αυξανόμενη σημαντικότητα των επιφανειακών (ή γενικότερα συνοριακών) φαινομένων σε τοπολογικές καταστάσεις της Συμπυκνωμένης Ύλης, και σε συνδυασμό με την εμπλοκή γεωμετρικών και τοπολογικών εννοιών στην Κβαντομηχανική, η παρούσα διατριβή αφιερώνεται στην αναδιατύπωση και επέκταση ορισμένων θεμελιωδών εννοιών, οι οποίες με τη σειρά τους επιφέρουν σημαντικές μετρήσιμες συνέπειες.

Έχουμε αναθεωρήσει τη λεγόμενη Μοντέρνα Θεωρία της Τροχιακής Μαγνήτισης, ορίζοντας καινούργιες ποσότητες, οι οποίες οφείλονται σε ένα μη-Ερμιτιανό φαινόμενο, το οποίο αποδίδεται σε ανώμαλους τελεστές που σπάνε το πεδίο ορισμού της Ερμιτιανής Χαμιλτονιανής. Ως αποτέλεσμα, συνεισφορές από τα άκρα οι οποίες έχουν αγνοηθεί στο παρελθόν, λαμβάνονται αυστηρά και αναλυτικά υπόψη. Αυτές αναμένεται να δίνουν πολύ μεγάλες συνεισφορές στην τροχιακή μαγνήτιση, όποτε υπάρχουν διασταυρώσεις ενεργειακών ζωνών μαζί με τάση Hall λόγω ανισορροπίας στη συσσώρευση των ηλεκτρονίων σε απέναντι άκρα του υλικού.

Παρόμοια επιχειρήματα με μη-Ερμιτιανές συνεισφορές έχουμε εφαρμόσει και στη φυσική του σπιν. Δείχνουμε πώς μπορεί κανείς να ορίσει μια κβαντική εξίσωση κίνησης για το σπιν, χωρίς να είναι απαραίτητη η ύπαρξη τοπικού νόμου διατήρησης, σε αντίθεση με την καθιερωμένη πρακτική. Σε αυτό το πλαίσιο, έχουμε ορίσει το ενδογενές ρεύμα του σπιν ως τη χρονική παράγωγο της συσχέτισης μεταξύ της θέσης και του σπιν του ηλεκτρονίου. Το ενδογενές ρεύμα του σπιν είναι απαλλαγμένο από οποιεσδήποτε επιπλοκές, λαμβάνει ρητά υπόψη τις συμβολές από τα άκρα, και για συστήματα στα οποία δεν ασκούνται τοπικές ροπές στρέψης δίνει μηδενική τιμή.

Επιπλέον, έχουμε κάνει μια επέκταση του γνωστού θεωρήματος Hellmann-Feynman, σε μια διευρυμένη μορφή η οποία μπορεί να εφαρμοστεί σε χρονικά εξαρτώμενες καταστάσεις και χρονικά εξαρτώμενες παραμέτρους. Ο προκύπτων τύπος της επέκτασης έχει βρεθεί ότι δίνει τις αναμενόμενες τιμές των φυσικών μεγεθών σαν συνάρτηση γενικευμένων καμπυλοτήτων του Berry και συνεισφορών από τα άκρα του συστήματος λόγω και πάλι ενός αναδυόμενου μη-Ερμιτιανού φαινομένου. Με εφαρμογή της επέκτασης έχουμε βρει τις κβαντικές εξισώσεις κίνησης του ηλεκτρονίου οι οποίες επεκτείνουν τις αντίστοιχες ημικλασικές. Η εφαρμογή του θεωρήματος στη μελέτη της μεταφοράς σωματιδίων σε μη-αδιαβατικό όριο, δείχνει ότι η κβάντωση καταρρέει εξαιτίας μιας μη τετριμμένης Aharonov-Anandan φάσης. Ομοίως, η εφαρμογή του θεωρήματος στη μελέτη της πόλωσης των ηλεκτρονίων, αναδεικνύει την ύπαρξη μιας επιφανειακής μη-Ερμιτιανής συνεισφοράς η οποία

δεν έχει ληφθεί υπόψη μέχρι στιγμής στη λεγόμενη Μοντέρνα Θεωρία της Πόλωσης.

Χρησιμοποιώντας μια ορθοκανονική βάση αναλύσαμε περαιτέρω την επέκταση του θεωρήματος Hellmann-Feynman. Έχουμε βρει ένα τύπο για τις αναμενόμενες τιμές των φυσικών μεγεθών που εξαρτάται τόσο από τη δυναμική εξέλιξη μέσω των συντελεστών του αναπτύγματος, όσο και από την τοπολογία του στιγμιαία κατειλημμένου χώρου Hilbert. Είναι ενδιαφέρον το γεγονός ότι τα μετρήσιμα μεγέθη αποκτούν εξάρτηση από μη-Αβελιανές καμπυλότητες Berry όποτε η κβαντική κατάσταση καταλαμβάνει περισσότερες από μία διαστάσεις του χώρου Hilbert. Η μορφή αυτών των μη-Αβελιανών καμπυλοτήτων μοιάζει με τους τανυστές του πεδίου Yang-Mills. Στο πλήρως δυναμικό όριο, όταν όλοι οι συντελεστές του αναπτύγματος εξελίσσονται πλήρως συζευγμένοι μεταξύ τους, αυτές οι μη-Αβελιανές καμπυλότητες του Berry δίνουν μηδέν. Με την εφαρμογή αυτής της επέκτασης, μπορούμε να δικαιολογήσουμε τα θεωρητικά αποτελέσματα που έχουν προκύψει τα τελευταία χρόνια στις μελέτες μεταφοράς σε δυναμικά συστήματα τα οποία είναι εκτός ισορροπίας (π.χ. συστήματα Floquet), όπου έχει βρεθεί ότι η αγωγιμότητα, καθώς και η μεταφορά σωματιδίων, δίδονται ως ολοκληρώματα των καμπυλοτήτων Berry σταθμισμένα από τις πιθανότητες των καταλήψεων.

Αυτή η διατριβή δίνει μια καινούργια προοπτική για ουσιαστική εμπλοκή των μη Ερμιτιανών φαινομένων, της τοπολογίας και της δυναμικής εξέλιξης, μέσα σε ένα εννοιολογικό πλαίσιο που είναι κατάλληλο για θεωρητικές μελέτες στη Φυσική της Συμπυκνωμένης Ύλης, και ως τέτοια, ευχόμαστε να συμβάλει στο να ακολουθηθούν αυτές οι μέθοδοι και από άλλα μέλη της κοινότητας στο μέλλον.

Abstract

Motivated by the increased importance of boundary effects in topological states of Condensed Matter, combined with the involvement of geometric and topological concepts within a quantum mechanical framework, this dissertation is dedicated to the reformulation and extension of some fundamental concepts, which in turn lead to important measurable consequences.

We have reconsidered the so called Modern Theory of Orbital Magnetization by defining additional quantities that incorporate a non-Hermitian effect due to anomalous operators that break the domain of definition of the Hermitian Hamiltonian. As a result, overlooked boundary contributions to the observable are rigorously and analytically taken into account. These are expected to give giant contributions to orbital magnetization whenever band crossings occur along with Hall voltage due to imbalance of electron accumulation at opposite boundaries of the material.

We have also applied similar arguments with non-Hermitian contributions to spin physics. We show how one can set up a global quantum equation of motion for the spin transport processes without any local conservation law being necessary, in contrast to the established practice. In this framework, we have defined the intrinsic spin current operator as the time derivative of the correlation between electron's position and electron's spin. This intrinsic spin current is free from any complications, it explicitly takes into account boundary contributions, and for systems that lack local spin-torques turns zero value.

In addition, we have made a dynamical extension of the standard Hellmann-Feynman theorem to one that can be applied to time-dependent states with time-dependent parameters. The resulting formula for the dynamics of the observables is found to have profound connections to generalized Berry curvatures as well as to boundary contributions due to an emerging non-Hermitian effect. By way of application we have derived the quantum equations of motion of the electron which extends the standard semiclassical counterpart. Application of the theorem to the study of particle transport in the non-adiabatic limit, shows that the quantization breaks down due to a non-trivial Aharonov-Anandan phase. Similarly, application of the theorem to the study of the electric polarization indicates that there is a boundary non-Hermitian contribution that has been so far overlooked in the so called Modern Theory of Polarization.

By using an orthonormal basis we have analyzed further the dynamical extension of the Hellmann-Feynman theorem. We have found a formula for the observables that depends

on the dynamics through the expansion coefficients together with the topology of the instantaneous occupied Hilbert space. Interestingly, the observables acquire dependence on non-Abelian Berry curvatures when the quantum state occupies more than one dimensions in Hilbert space. The form of these non-Abelian Berry curvatures resembles the Yang-Mills field strength tensors. In the fully dynamical limit, when all expansion coefficients evolve in time coupled to each other, these non-Abelian Berry curvatures turn to zero. By way of application of this extension we can justify the theoretical results that have come out in the last few years in non-equilibrium transport studies (i.e. of Floquet systems), where they find that the conductivity as well as the particle transport, are given as integrals of Berry curvatures weighted by the occupation numbers.

Our dissertation gives a new perspective for an essential engagement of boundary non-Hermitian effects, topology and dynamics, in a single theoretical framework that is appropriate for theoretical studies of Condensed Matter Physics, and as such we hope that it will contribute in making these methods followed up by other members of the community in the future.

Dedication

“ To humans that spend time of their life on the hard pursuit of creation: from the beginning of new ideas to the establishment of new scientific knowledge.”

Acknowledgments

First and foremost, I would like to offer my sincere thanks to Dr. Moulopoulos Konstantinos for his kind support and continuous guidance for all these years. There were times that he was more than just a supervisor, and his sincere faith on me was always an extra motivation when needed. Discussing physics with him was one of the most enjoyable things to do.

Finally, I would like to acknowledge the support of my parents and sister for always believing in me and encouraging me to achieve my goals.

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Chapter 1

Introduction

For decades, the application of differential geometry and algebraic topology has been restricted to either the curved spacetime of general relativity or gauge theories in particle physics. This was until 1984 when Michael Berry [17] discovered the geometric phase accompanying adiabatic evolutions around closed loops. Barry Simon [123] interpreted this result in terms of the holonomy in a Hermitian line bundle and realized the topological origin of the integer quantum Hall effect [135]. He identified the integer values of conductivity[1] as the first Chern numbers which are topological invariants related to closed surfaces. The discoveries of Michael Berry and Barry Simon mark the beginning of a new era in the theoretical studies of condensed matter physics. The involvement of geometry and topology by means of quantum mechanics sharpened our understanding and led to numerous discoveries[2].

Quantization of particle transport [134] for a time-periodic and adiabatic evolution was justified due to topology. Reformulation of the electric polarization by engaging geometric phases [75, 101, 109] was carried out in the 1990s (although the role of the Berry phase in this theory was not immediately apparent, it facilitated the reinterpretation of macroscopic polarization later on [114, 111]). Reformulation of the orbital magnetization [133, 33] by using geometric concepts was performed in mid 2000s. An extension of the semiclassical equations of motion was made [35, 130], and an additional term that depends on geometric details, called the anomalous velocity, has finally confirmed a fifty-year-old idea concerning the interpretation of the anomalous Hall effect [73].

Generally, topological states of matter are inherently related to non-integrable geometric phases, and as such are realized for example in Chern and topological insulators [61, 106], as well as in Dirac and Weyl semimetals [137, 6]. The special properties of such states of matter like the Chern number, can be traced back to geometric quantities like the Berry curvature, in the same spirit as the Gauss-Bonnet theorem which connects the Euler characteristic of a

[1] The theoretical explanation of the integer quantized Hall conductance in the presence of a magnetic field was first made in 1982 by the quartet of Thouless, Kohmoto, Nightingale and den Nijs [135] with a perturbation calculation, where they found the integer values (appropriately coined later as the TKNN invariant) without using topological arguments.

[2] These discoveries go by the name Topological Phases, and their great importance is reflected in the 2016 Nobel Prize in Physics (awarded to D. J. Thouless, J. M. Kosterlitz and F. D. M. Haldane).

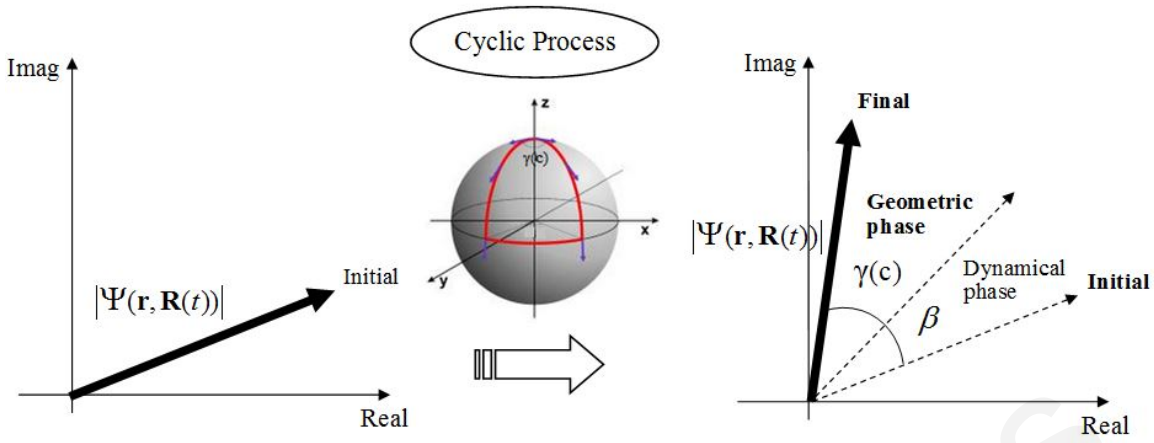

Figure 1.1: At the end of a cyclic process the (final) modulus of the wavefunction $\Psi(\mathbf{r},\mathbf{R}(t))$ remains the same to the initial but the wavefunction acquires a dynamical β plus a geometric $\gamma(c)$ phase.

surface to the Gaussian curvature.

1.1 Geometric Phases

In classical and quantum mechanics, the geometric phase is a phase difference acquired over the course of a cycle when a system is subject to a cyclic process as shown in Fig.1.1.

The geometric phases occur whenever there are parameters characterizing a wave in the vicinity of some sort of singularity or hole. The first to observe the occurrence of a geometric phase when dealing with closed loops in a parameter space was S. Pancharatnam [102] in 1956. He discovered the geometric phase in the context of optical polarization. He discussed the interference of two polarized beams, one of them having been transported around a closed loop on the Poincare sphere (the space of polarization states) with respect to the other. Moreover, he was able to express the result in terms of the solid angle described by the normal vector along the loop. In 1959 Y. Aharonov and D. Bohm [2] realized that the electromagnetic scalar and vector potentials, which were introduced in classical electrodynamics mainly for convenience, have physically meaningful consequences in quantum mechanics. Although measurable quantities cannot depend directly on the potentials due to gauge freedom, Y. Aharonov and D. Bohm discovered that the electronic wave function acquires a measurable (geometric) phase shift when transported along a circuit threaded by a line of magnetic flux. Speaking in terms of geometry, the magnetic vector potential and field in the Aharonov-Bohm effect correspond to the connection and curvature, respectively. At the same time, the geometric phase appeared at a different end in a more subtle way, in the study of Jahn-Teller effect in molecular systems. It manifested itself as a change of sign in the electronic wavefunction during a cyclic evolution of the nuclear coordinates around a conical intersection of the potential energy surfaces. The original idea was limited to systems where the wavefunctions could be chosen as real. Hence, the interpretation of the sign change of a

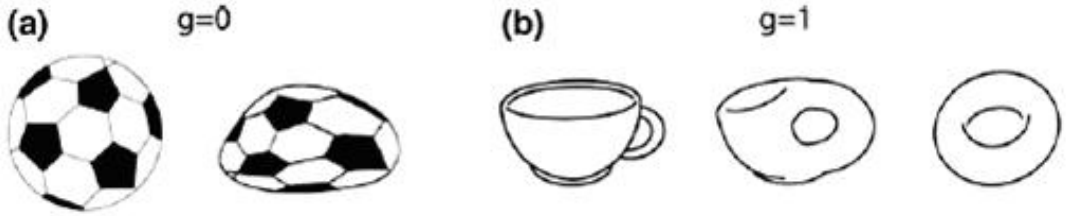

Figure 1.2: Spherical and crumpled balls have the same genus of $g = 0$, in (a), but both the donut and the coffeecup with one hole in (b) are characterized by $g = 1$. Adapted from [16].

real wavefunction as the special case of a phase change of a complex wavefunction was not apparent, and the geometric phase that was underlying the entire problem was not identified as such. It was not until the publication of C. Mead and D. Truhlar [93] in 1979, when the double-valuedness of the electronic wavefunction caused by the sign change was resolved by introducing a vector potential in the electronic Hamiltonian. This vector potential seemed to originate from a fictitious magnetic flux line at the location of the conical intersection of two energy levels in the parameter space of nuclear coordinates. Because of this analogy, the phenomenon is called the molecular Aharonov-Bohm effect. In fact, this method introduced geometric phases as a generalization of the Born-Oppenheimer approximation in molecules if one allows for the nuclei to move slowly.

1.2 Topology in condensed matter

Topology is the abstract study of continuity. It introduces mathematical structures which remain unchanged under continuous deformation. For this reason it is often called "rubber sheet" geometry as it focuses on features that do not change when continuous changes are made to the parameters of the system. In conventional band theory, one only needs to calculate the dispersion relation $E_n(\mathbf{k})$ in order to study the transport properties. For example, the electron's velocity $\mathbf{v}$ is simply given by the gradient of the electron's energy $\mathbf{v} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_n(\mathbf{k})$. On the other hand, in topologically non-trivial states of matter, the latter relation turns out to be inadequate and is enhanced by extra terms $\boldsymbol{\mathcal{T}}_n(\mathbf{k})$ resulting to $\mathbf{v} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_n(\mathbf{k}) + \boldsymbol{\mathcal{T}}_n(\mathbf{k})$. The extra terms capture the topology of the Hilbert space and mathematically are attributed to the singularities of the wavefunctions. These singularities form nodal lines (also called dislocation lines) in 3D configuration space or points in 2D. Along these nodal lines the phase of the wavefunction is undetermined and its modulus is normally zero. Each nodal line is characterized by a topological integer that is also called topological charge. The number of dislocation lines that penetrates only once a closed surface, in a way can be thought as the genus g that counts the number of holes of a surface as shown in Figure 1.2. The study of this kind of singularities is made either by Dirac string method, where one explicitly deals with the singularities, or with the fiber-bundle method where one deals with overlap spaces and the strings are avoided. The Dirac string method although a bit more complicated, is intuitively more instructive for one to highlight the in-

volvement of non-integrable phases. In this framework, we outline in what follows the Paul Dirac's [43] monopole charge study in real space $\mathbf{r}$, and then describe a counterpart study in parameter space $\mathbf{R}$.

First, we discuss the analyticity of the wavefunction and it's single-valuedness, in order to connect as simply as possible the topological states of matter with the related singularities of the wavefunctions. In this respect we consider the space

$$(\mathbf{r}, \mathbf{R}, t)$$

where $\mathbf{r}$ is the position vector, $\mathbf{R}$ is a three-dimensional continuous vector parameter, and t is time. We assume a wavefunction that defines the map

$$(\mathbf{r}, \mathbf{R}, t) \longmapsto \Psi(\mathbf{r}, \mathbf{R}, t) \tag{1.1}$$

for a closed system

$$\iiint_V |\Psi(\mathbf{r}, \mathbf{R}, t)|^2 \, d^3r = 1. \tag{1.2}$$

Position coordinates

If the wavefunction is globally single-valued over position coordinates, it satisfies

$$\oint_C \boldsymbol{\nabla}\Psi(\mathbf{r}, \mathbf{R}, t) \cdot d\mathbf{r} = 0 \tag{1.3}$$

for any closed circuit that fulfills two conditions stated below. We consider for simplicity a scalar wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t) = |\Psi(\mathbf{r}, \mathbf{R}, t)| \, e^{iS(\mathbf{r}, \mathbf{R}, t)}$, where $|\Psi(\mathbf{r}, \mathbf{R}, t)|$ is its modulus and $S(\mathbf{r}, \mathbf{R}, t)$ its phase. Taking into account that the wavefunction is single-valued but the phase is defined modulo 2π, it results to the first condition

$$\oint_C \boldsymbol{\nabla} S(\mathbf{r}, \mathbf{R}, t) \cdot d\mathbf{r} = 2\pi n \tag{1.4}$$

where n is an integer. The latter equation implies that, when $n \neq 0$ there exist a nodal line where the phase is undetermined[3]. The modulus of the wavefunction, must satisfy the Schwarz integrability condition globally over space coordinates $\boldsymbol{\nabla} \times \boldsymbol{\nabla}|\Psi(\mathbf{r}, \mathbf{R}, t)| = 0$, due to the normalization constraint Eq. (1.2). Applying the Stokes theorem in the arbitrary circuit of Eq. (1.3) gives

$$i \iint_S \Psi(\mathbf{r}, \mathbf{R}, t) \, \boldsymbol{\nabla} \times \boldsymbol{\nabla} S(\mathbf{r}, \mathbf{R}, t) \cdot d\mathbf{a} = 0. \tag{1.5}$$

[3] Applying the Stokes theorem for the arbitrary closed circuit gives $\iint_S \boldsymbol{\nabla} \times \boldsymbol{\nabla} S(\mathbf{r}, \mathbf{R}, t) \cdot d\mathbf{a} = 2\pi n$, implying that there is a nodal line along the points where $\boldsymbol{\nabla} \times \boldsymbol{\nabla} S(\mathbf{r}, \mathbf{R}, t) \neq 0$ for $n \neq 0$.

This implies that $\Psi(\mathbf{r},\mathbf{R},t)$ has to be zero at the dislocation lines where the phase is undetermined $\boldsymbol{\nabla}\times\boldsymbol{\nabla}S(\mathbf{r},\mathbf{R},t)\neq 0$ which is the second constraint. Although the phase is not globally integrable, it does not cause any complications due to the constraint $\Psi(\mathbf{r},\mathbf{R},t)\,\boldsymbol{\nabla}\times\boldsymbol{\nabla}S(\mathbf{r},\mathbf{R},t)=0$. For example, in the Hydrogen atom the wavefunction is zero along the entire z axis whenever the electron has a well-defined angular momentum. Therefore, an infinite nodal line is present and extends all over the z axis, from the lower boundary of the system to the upper boundary. This defines the topologically trivial states with quantized angular momentum, that is the states where each nodal line crosses twice the enclosing surface of the system.

Dirac string

An exceptional, non-trivial case was encountered in the seminal work of Paul Dirac [43] in his study about the motion of an electron around a magnetic monopole charge. He introduced a vector potential $\mathbf{A}(\mathbf{r})$ by a global, singular $U(1)$ phase transformation with a non-integrable phase. That is, he assumed $\Phi(\mathbf{r},t)=e^{i\Lambda}\,\Psi(\mathbf{r},t)$ where Λ cannot be expressed as a function of $(\mathbf{r},t)$ with definite value at each point, but, has definite derivatives satisfying $\boldsymbol{\nabla}\Lambda=\frac{e}{\hbar c}\mathbf{A}(\mathbf{r})$. The phase Λ is undefined along the nodal line characterized by $\boldsymbol{\nabla}\times\boldsymbol{\nabla}\Lambda=\frac{e}{\hbar c}\mathbf{B}(\mathbf{r})\neq 0$, where $\mathbf{B}(\mathbf{r})$ is tangential to the nodal line. This nodal line is unobservable, provided that it coincides with a nodal line of $\Psi(\mathbf{r},t)$, as well as it satisfies $\oint\boldsymbol{\nabla}\Lambda\cdot d\mathbf{r}=2\pi n$. Therefore, viewing the nodal line as an infinitesimal flux tube with the magnetic field $\mathbf{B}(\mathbf{r})$ coming from south pole as depicted in Figure 1.3, and assuming that this nodal line penetrates only once the surface enclosing the system, he concluded that the magnetic flux over a closed surface is quantized

$$\frac{e}{\hbar c}\oiint_S\mathbf{B}(\mathbf{r})\cdot d\mathbf{a}=\oiint_S\boldsymbol{\nabla}\times\boldsymbol{\nabla}\Lambda\cdot d\mathbf{a}=\oint_{C\to 0}\boldsymbol{\nabla}\Lambda\cdot d\mathbf{r}=2\pi n,$$

where C is the infinitesimal closed curve enclosing the nodal line and n is an integer. Equivalently, this magnetic flux can be attributed to a magnetic monopole charge q_m that is situated at the end of the nodal line where $\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\times\boldsymbol{\nabla}\Lambda\neq 0$ and creates an effective spherically symmetric magnetic field $\mathbf{B}_{\text{eff}}(\mathbf{r})$ as shown in Figure 1.3. Therefore the magnetic charge is quantized in units of $q_m=n\frac{\hbar c}{2e}$.

String in parameter space

Similar arguments of the Dirac string approach in real space, are commonly found in the topological states of matter, where the role of the magnetic field is given to the Berry curvature and the role of vector potential to the Berry connection. For example, in topological states of matter one frequently finds the map

$$(\mathbf{r},\mathbf{R})\longmapsto\Psi(\mathbf{r},\mathbf{R})\longmapsto i\iiint_V\Psi^*(\mathbf{r},\mathbf{R})\,\boldsymbol{\nabla}_{\boldsymbol{R}}\Psi(\mathbf{r},\mathbf{R})dV=\mathbf{A}(\mathbf{R}) \tag{1.6}$$

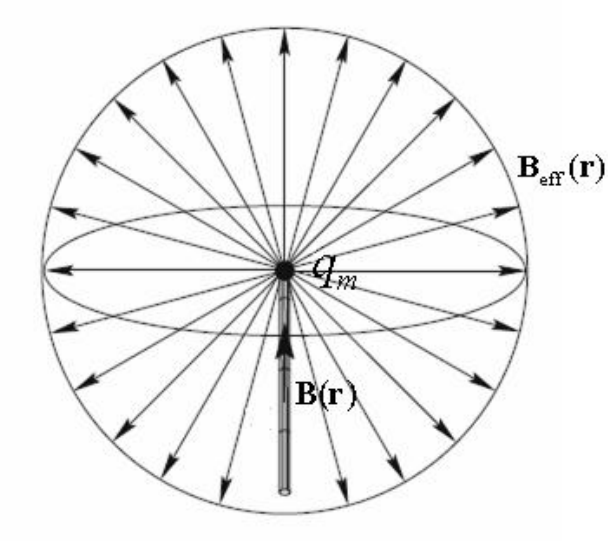

Figure 1.3: Magnetic field of the singular Dirac potential.

where $\mathbf{A}(\mathbf{R})$ is the Berry connection. Intuitively one expects that singularities of the wavefunction created by variation of the parameter $\mathbf{R}$ will be inherited to the Berry connection. Therefore, one can follow the Dirac steps of derivation but in parameter space, namely, introduce a Berry connection $\mathbf{A}(\mathbf{R})$ by a global singular $U(1)$ phase transformation with a non-integrable phase. In this framework we assume $\Phi(\mathbf{r},\mathbf{R}) = e^{i\Lambda}\,\Psi(\mathbf{r},\mathbf{R})$, where the phase Λ cannot be expressed as a function of $\mathbf{R}$ with definite value at each point, but, has definite derivatives satisfying $\boldsymbol{\nabla}_{\mathbf{R}}\Lambda = \mathbf{A}(\mathbf{R})$. This vector field is singular along the nodal line $\boldsymbol{\nabla}_{\mathbf{R}} \times \boldsymbol{\nabla}_{\mathbf{R}}\Lambda \neq 0$, but is unobservable provided that it coincides with a nodal line of $\Psi(\mathbf{r},\mathbf{R})$ as well as it satisfies $\oint \boldsymbol{\nabla}_{\mathbf{R}}\Lambda \cdot d\mathbf{R} = 2\pi n$. Therefore, for a nodal line that penetrates once a closed surface in parameter space, one finds

$$\oiint_S \boldsymbol{\mathcal{B}}(\mathbf{R}) \cdot d\mathbf{a} = \oiint_S \boldsymbol{\nabla} \times \boldsymbol{\nabla}\Lambda \cdot d\mathbf{a} = \oint_{C\to 0} \boldsymbol{\nabla}\Lambda \cdot d\mathbf{R} = 2\pi n$$

where $\boldsymbol{\mathcal{B}}(\mathbf{R}) = \boldsymbol{\nabla}_{\mathbf{R}} \times \mathbf{A}(\mathbf{R})$ is the so-called Berry curvature, C is the infinitesimal closed curve enclosing the nodal line, and n is a topological invariant integer called first Chern number. In this framework, monopoles are also possible to exist in parameter space provided that the Berry connection $\mathbf{A}(\mathbf{R})$ and the wavefunctions (according to Eq. (1.6)), have some kind of singularities. A monopole (antimonopole) charge in parameter space (the $\mathbf{k}$ space in Solid State Physics) is situated at the end (beginning) of a nodal line which coincides with a band-touching point in the Brillouin zone.

Monopoles are realized in crystal momentum (parameter) space in band theory, in the topological states of matter, in contradistinction to real space. A reason that may cause this dissimilarity may be due to the wavefunctions that need not be single-valued globally over parameter coordinates (in contrast to real space). Therefore, the single-valuedness over real

space coordinates Eq. (1.5) can be relaxed in parameter space

$$\oint_C \boldsymbol{\nabla}_{\mathbf{R}}\Psi(\mathbf{r},\mathbf{R})\cdot d\mathbf{R} = i\iint_S \Psi(\mathbf{r},\mathbf{R})\,\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\nabla}_{\mathbf{R}}S(\mathbf{r},\mathbf{R},)\cdot d\mathbf{a}_{\mathbf{R}} \neq 0. \tag{1.7}$$

This kind of multivalued functions does not affect the observables in the canonical formulation, since the operators $(\mathbf{r},\mathbf{p})$ do not act on the parameter coordinates. If we accept that this is the case, then, the nodal lines in parameter space $\mathbf{R}$ need not coincide with the zeros of the wavefunction, and as such are presumably much easier to be realized in crystal momentum space.

Two plausible questions now arise. What are the theoretical tools that probe these topological effects and how are these effects explicitly taken into account as part of observables' formulas? The probe of these effects is usually made by studying the geometric phases in the framework of Michael Berry's phase [17], but the explicit connection to observables is still somewhat unclear. Perhaps the most known result so far that explicitly relates an observable with a curvature, was given by Ming-Che Chang and Qian Niu [35] in 1996, and Ganesh Sundaram and Qian Niu [130] in 1999, who enhanced the semiclassical equations of motion by incorporating Berry curvature corrections.

An explicit engagement of Berry curvatures in the formulas of observables will come out as a part of this dissertation, originating from a derivation of two dynamical extensions of the Hellmann-Feynman theorem that takes into account boundary contributions due to non-Hermitian effects. The dynamical extensions give one the ability, in the simplest manner possible, to explicitly probe the dynamics and the topology of the embedded Hilbert space.

1.3 Semiclassical Equations of Motion

In the semiclassical approach, each electron is described by a wave packet constructed from a single band Bloch functions under the following condition. The spread $\Delta\mathbf{k}$ of the wave packet in the momentum space should be small compared with the dimensions of the Brillouin zone, so that it is meaningful to speak of the momentum $\mathbf{k}$ of the electron. This requirement implies that in real space the spread $\Delta\mathbf{r}$ of the wave packet is on the scale of hundreds of unit cells. Therefore, in order for the semiclassical description to be valid, external perturbations must vary slowly over the dimensions of $\Delta\mathbf{r}$. The wave packet can be written as

$$|\,W(\mathbf{r}_c,\mathbf{k}_c)\,\rangle = \iiint_{BZ} a_n(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_c)}\,|\,u_n(\mathbf{k})\,\rangle \tag{1.8}$$

where $\mathbf{r}_c$ and $\mathbf{k}_c$ are the wave packet centers in real and momentum space respectively, $a_n(\mathbf{k})$ is the expansion coefficients whose exact form is not important as long as the above requirement on the wave packet spread is satisfied, and $|u_n(\mathbf{k})\rangle$ is the periodic part of the Bloch function $|\Psi_n(\mathbf{k})\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}\,|u_n(\mathbf{k})\rangle$. The spirit of the semiclassical model is that the fast varying periodic lattice potential is taken into account by the use of the Bloch functions $|u_n(\mathbf{k})\rangle$ while the slowly varying external perturbations are treated semiclassically. In the

presence of weak electric $(\mathbf{E})$ and magnetic $(\mathbf{B})$ fields, the equation of motion of the wave packet center is usually given in the following form [8]

$$\frac{d\mathbf{r}_c}{dt} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k_c}} E_n(\mathbf{k}_c) \tag{1.9}$$

$$\hbar\frac{d\mathbf{k}_c}{dt} = e\mathbf{E} + \frac{e}{c}\frac{d\mathbf{r}_c}{dt} \times \mathbf{B} \tag{1.10}$$

where $E_n(\mathbf{k}_c)$ is the unperturbed band energy of the electron. According to this set of equations, the electron dynamics is *solely* determined by the band energy. In fact, the quantity $E_n(\mathbf{k}_c)$ is so important that techniques developed to calculate the band structure have become an independent field in Solid State Physics. The wave packet is expanded in the basis of the cell functions $|u_n(\mathbf{k})\rangle$ which are the eigenstates of the following effective Hamiltonian

$$H(\mathbf{k}) = \frac{1}{2m}(-i\hbar\boldsymbol{\nabla} + \hbar\mathbf{k})^2 + V_{crys}(\mathbf{r}). \tag{1.11}$$

If the electron adiabatically moves from $\mathbf{k}_1$ to $\mathbf{k}_2$, which can be done by simply applying an electric field, the electron's wavefunction will acquire an extra geometrical type of phase. M. C. Chang and Q. Niu [35] in 1996, and G. Sundaram and Q. Niu [130] in 1999, were the first to enhance the above semiclassical equations of motion by incorporating Berry curvature corrections. They use an effective Lagrangian of the motion with generalized variables the electron's main position and the electron's main crystal momentum, whereas the external (electric and magnetic) fields were taken into account as perturbations. Under the approximations that: (i) the external fields vary slowly over the spatial extension of the wave packet, and (ii) the fields do not cause excitations (adiabatic approximation), and by employing a time-dependent variational principle for the trial wave packet, they found the two extended semiclassical equations of motion

$$\frac{d\mathbf{r}_c}{dt} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k_c}} \widetilde{E}_n(\mathbf{k}_c) - \frac{d\mathbf{k}_c}{dt} \times \boldsymbol{\mathcal{B}}_n(\mathbf{k}_c) \tag{1.12}$$

$$\hbar\frac{d\mathbf{k}_c}{dt} = e\mathbf{E} + \frac{e}{c}\frac{d\mathbf{r}_c}{dt} \times \mathbf{B}, \tag{1.13}$$

where

$$\boldsymbol{\mathcal{B}}_n(\mathbf{k}_c) = i\,\langle \boldsymbol{\nabla}_{\mathbf{k}_c} u_n(\mathbf{k}_c)| \times |\boldsymbol{\nabla}_{\mathbf{k}_c} u_n(\mathbf{k}_c)\rangle \tag{1.14}$$

is the Berry curvature evaluated with respect to the cell periodic states. In this framework, they found that the electron acquires an extra velocity that is proportional to the Berry curvature $-\frac{d\mathbf{k}_c}{dt} \times \boldsymbol{\mathcal{B}}_n(\mathbf{k}_c)$ which is sometimes referred to as the "anomalous velocity" of the electron. As we shall see, a part of our work described below leads to even further extensions of the above equations of motion that involve additional types of Berry quantities (that can be interpreted as electric field in $\mathbf{k}$-space).

1.4 Outline of the dissertation

Motivated by the increased importance of boundary effects in topological states of matter, combined with the involvement of geometric and topological concepts within a quantum mechanical framework, this dissertation is dedicated to the reformulation and extension of some fundamental concepts, which in turn lead to important measurable consequences. The outcomes of this dissertation are briefly reviewed below:

□ **Theoretical study of orbital magnetization**

We reconsider the modern theory of orbital magnetization by defining additional quantities that incorporate a non-Hermitian effect due to anomalous operators that break the domain of definition of the Hermitian Hamiltonian. As a result, boundary contributions to the observable are rigorously and analytically taken into account. In this framework, we extend the standard velocity operator definition in order to incorporate an anomaly of the position operator that is inherent in band theory, which results in an explicit boundary velocity contribution. Using the extended velocity, we define the electrons' intrinsic orbital circulation and we argue that this is the main quantity that captures the orbital magnetization phenomenon. As evidence of this assertion, we demonstrate the explicit relation between the nth band electrons' collective intrinsic circulation and the approximated, evaluated with respect to Wannier states, local and itinerant circulation contributions that are frequently used in the modern theory of orbital magnetization. A quantum mechanical formalism for the orbital magnetization of extended and periodic topological solids (insulators or metals) is re-developed without any Wannier-localization approximation or heuristic extension [33]. It is also shown that, as a result of the non-Hermitian effect, an emerging covariant derivative enters the one-band (adiabatically deformed) approximation $\mathbf{k}$-space expression for the orbital magnetization. In the corresponding many-band (unrestricted) $\mathbf{k}$-space formula, the non-Hermitian effect contributes an additional boundary quantity which is expected to give locally (in momentum space) giant contributions whenever band crossings occur along with Hall voltage, due to imbalance of electron accumulation at the opposite boundaries of the material.

□ **Theoretical study of boundary contributions with application to spin current**

We show how one can set up a global quantum equation of motion for transport processes, without any local conservation law being necessary (in contrast to the established practice), provided that additional boundary operators are taken into account and the system is closed. The global quantum equation of motion: (i) provides a way for defining operators in an extended manner, (ii) leads to a bulk-boundary relation for stationary states (having the form of a gain-loss balance equation that relates the boundary rate of change of an observable with its corresponding bulk change), as well as, (iii) gives a way for defining linear approximation dissipation equations near equilibrium. By employing the extended definition of an operator,

we first review the spin current definition [121] and show that, together with the bulk spin generation, spin generation over the boundaries has to also be zero, in order for their operator to have a well defined value; the spin generation over the boundaries is explicitly attributed to a non-Hermitian boundary operator and has not been pointed out in this manner so far. We then define the intrinsic spin current operator as the time derivative of a correlation function between electron's position and electron's spin. The intrinsic spin current has two parts, the bulk part and a boundary one, the latter attributed to the non-Hermitian effect. Its value is always well-defined without any constraints being involved whatsoever. For any stationary state, there exists a gain-loss detailed balance relation that explicitly relates the bulk intrinsic spin current with the corresponding boundary one, while, for systems that lack local spin-torques (in a given direction), the spin current turns zero value (provided that the state under consideration has a well-defined spin in the given direction) due to the position and spin being uncorrelated.

□ **Derivation of a dynamical Hellmann-Feynman theorem and application to topological transport processes**

On could argue in general that topological quantum states of matter are studied and classified by two different kinds of methods. Within the first kind, one examines the phases that are accumulated during cyclic processes with respect to parameters that vary with time, whereas in the second kind of methods, one explicitly studies an observable's expectation value by using time-dependent linear response methods. In the first kind of methods the quantities involved are Berry connections which are gauge-dependent quantities, whereas in the second kind the quantities involved are Berry curvatures that are gauge-invariant quantities. It is fair to state that, although in this work none of these has been followed, we have still derived results on expectation values of observables to all orders in the fields (no linear response assumption). By just using quantum dynamics in an appropriate way, we have derived an extended and dynamical Hellmann-Feynman (HF) theorem for general non-adiabatic processes. The theorem is derived for a time-dependent vector parameter and takes into account boundary contributions due to an emerging non-Hermitian effect. We present therefore a formula for the observables that explicitly depends on generalized Berry curvatures and takes into account boundary contributions. We show that, when dealing with states that are labeled by time-dependent parameters (as for example in the extended HF theorem that we have derived), it creates a complication in the standard (in band theory) way of transformation between the discrete sum over static parameters (such as crystal momentum) to a counterpart Riemann integral over continuous variables. We resolve this issue by taking into account the arbitrary Jacobian of transformation between the initial value of a parameter and the time-evolved one. This way of transformation engages measurable consequences when the parameter velocity-field behaves as a compressible fluid field. This complication is precisely the "paradox" that appears in the semiclassical modification of density of states [149], which has not been realized or identified in this manner.

Several applications of the theorem showing its usefulness are made:
(i) We have derived a generalized Maxwell type of equation (in parameter space) with monopole sources, where the fields are the generalized Berry curvatures of the theorem. For flux preserving motions, the generalized Maxwell type of equation takes the familiar form of Faraday's law accompanied by a current that has two parts, the first part being the monopole current whereas the second being a divergenceless free part. The current satisfies a continuity equation leading to conservation of the total monopole charge of the system. This Maxwell type of equation is a generalization of the Maxwell type of equation that is found in the last few years [70] in the study of Weyl semimetals, which has arisen by heuristic analogy to the electromagnetic induction law and without any detailed derivation.
(ii) We have studied the particle transport in the adiabatic limit (Thouless pump) as well as in dynamical and non-adiabatic limit. By using the extended velocity operator we have confirmed that the quantization of the particle transport in the adiabatic limit is a boundary effect. This is accomplished by using the dynamical HF theorem together with the non-Hermitian boundary velocity. In the counterpart study of the non-adiabatic transport we find that the quantization of the particle transport breaks down due to a non-trivial (non-integrable) Aharonov-Anandan phase.
(iii) We have reconsidered the electric polarization in the framework of the so-called modern theory of polarization. We have shown that there is a boundary contribution that has been overlooked. This boundary contribution is zero only when the Bloch states satisfy periodic boundary conditions (over the realistic boundaries of the material) during the adiabatic driving, thus no voltage must be present during the adiabatic cyclic evolution.
(iv) We have derived two sets of quantum equations of motion for the electron without any localization or adiabatic approximation involved. One is for spinless motion and the other for spinfull one. These quantum equations of motion are extensions of the semiclassical ones [130] that where derived by means of a time-dependent variational method, applied to a trial localized wavepacket under the adiabatic approximation. The electron's velocity that we found depends explicitly on two generalized Berry curvatures as well as on a non-Hermitian boundary term. We argue that the spinfull quantum equations of motion can be applied to the quantum anomalous Hall effect. Based on the spinfull equations of motion, and by showing explicitly the approximations involved, we have derived a modification of the density of states for a spinfull motion. In comparison to the semiclassical counterpart modification, the magnetic field is replaced by the total magnetic field, that is, the externally applied field plus the effective one due to spin-orbit coupling; at the same time, the modification takes into account an extra term that involves the monopole charges which were discarded in the semiclassical study.

□ Derivation of a dynamical HF theorem in a complete and orthonormal basis accompanied by applications

The dynamical extension of the Hellmann-Feynman theorem that we have made, although practical and useful, cannot extract analytically the combined information of (i) the dynamics captured by the expansion coefficients and (ii) the topology of the Hilbert space that is instantaneously occupied. On the other hand, during the last few years a lot of theoretical as well as experimental work is carried out in the study of time-dependent and non-equilibrium systems, where topological patterns of behavior may emerge under certain constraints. Therefore, by using an orthonormal basis we have further analyzed the dynamical extension of the Hellmann-Feynman theorem. We have found a formula for the observables that depends on emerging non-Abelian curvatures as well as on non-Hermtian boundary contributions. The formula has an inherited gauge structure that is attributed solely to the dimensions of the Hilbert space that are instantaneously occupied, irrespectively of the energy scale of the quantum system. Therefore, the gauge structure comes up either when the electron is spinless and not relativistic or when it is a spinfull and high energy one. It is remarkable that the form of these non-Abelian Berry curvatures resembles the Yang-Mills field strength tensors. In the fully dynamic limit, when all expansion coefficients evolve in time coupled one to each other, these non-Abelian Berry curvatures turn to zero. On the other hand, whenever only one dimension of the available Hilbert space is at every instant occupied, then, the gauge structure is lost and the observables are given by Abelian curvatures. By way of application of this extension we can justify the theoretical results that have come out the last few years in non-equilibrium transport studies, where they find that the conductivity, as well as the particle transport, are given as integrals of Berry curvatures weighted by the occupation numbers.

We should probably stress that all the new quantities emphasized above have indeed been defined for the first time in this work. All interpretations and results are based on these quantities and have been derived during the period of carrying out this dissertation. In particular, the non-Hermitian effect (that had earlier been noted as a “paradox” in the Ehrenfest theorem, and is here also encountered in the Hellmann-Feynman theorem) stands out as something that seems to have been entirely overlooked in the Solid State literature, various cases where it shows up deserving further investigation.

Chapter 2

Orbital magnetization

As we already declared in the Introduction, we shall begin with the orbital magnetization[1] as the observable under investigation and we shall see that this leads to results - especially on subtle boundary contributions - that have largely been ignored in the literature.

Boundary effects are ubiquitous in condensed matter systems. However, how these effects influence bulk quantities such as the bulk orbital magnetization $\mathbf{M}$ seems to be still unclear [38, 92, 20]. Circular dichroism measurements have confirmed the existence of surface states with non-trivial orbital moment textures in $\mathbf{k}$-space [104, 74] due to Orbital Rashba Effect [103], while gigantic orbital magnetization values are predicted to occur in the vicinity of band crossings at the surfaces of sp alloys [54]. A simple and direct method to link boundary properties with bulk quantities, if found, would conceptually give a direct realization of a bulk-boundary correspondence in a general sense. Hints of such a link have appeared but they have not yet been combined in a single theoretical framework for condensed matter systems. In the chemists' community the link between boundary effects and "bulk" quantities seems to have been studied in detail and is formalized as surface integrals (fluxes) of certain generalized currents in the so-called atomic theorems [13, 12, 15] that determine atom properties viewed as parts (fragments) of a molecule; for example, the atomic dielectric polarization [15] and atomic magnetic susceptibility [14] have been determined within that method. In the mathematical physics community the connection between boundary effects and bulk quantities can be attributed to anomalous operators that break the domain of definition of the Hamiltonian operator, thereby leaving residues either in the Ehrenfest theorem [47, 48, 66] or in the Hellmann-Feynman [49] theorem; these can be converted into space coordinate surface integrals (for 3D systems) over the system's boundaries. In this paper we rigorously take into account these boundary residues as non-Hermitian effects in order to model the boundary contributions to the orbital magnetization of non-interacting electrons.

In general, anomalous operators act on states that belong within a given Hilbert space, where the Hamiltonian is assumed Hermitian and the system is closed, and they produce

[1] This chapter is adapted from K. Kyriakou and K. Moulopoulos [81] which is currently under review in Physical Review B.

states that are outside this given Hilbert space; this leads to emergent non-Hermiticity in the Hamiltonian which is precisely the above mentioned boundary residue.

One of the most common examples of such an anomalous operator (that leaves a boundary residue in the Ehrenfest theorem) is the position operator $\mathbf{r}$ whenever periodic boundary conditions at the ends of the system are adopted for the wavefunctions. In Solid State Physics one usually bypasses this kind of anomaly as in Ref.[110] by redefining a proper (periodic) operator for the electrons' position that does not leave any boundary residue and by working with its expectation value. In this work we deal with this problem in a direct way, that is we maintain the standard electrons' expectation value $\langle \mathbf{r} \rangle$ as defined within the Schrödinger picture (despite the fact that the electrons' position expectation value $\langle \mathbf{r} \rangle$ becomes undefined within the Bloch representation in the thermodynamic limit, its displacement $\Delta\langle \mathbf{r} \rangle$ after a finite time interval is always a well-defined quantity as shown in Appendix A) and simply extend the standard velocity operator by adding to it an extra operator term that takes into account the non-Hermitian effect of the Hamiltonian operator. The expectation value of the added operator term is determined entirely from the boundaries of the system and it rigorously gives a boundary velocity contribution for the electron (although formalized in a bulk framework).

Therefore, having in mind the evolution of the quantum state under consideration as well as the position operator expectation value within the Schrödinger picture, we are led to define the velocity operator in an extended form as, $\mathbf{v}_{ext} = \mathbf{v} + \mathbf{v}_b$ where $\mathbf{v}$ is the standard velocity operator as given in the literature (which can be viewed as a bulk property) and $\mathbf{v}_b$ is the added boundary operator term that takes into account the non-Hermitian effect. In this fashion, the extended velocity operator expectation value $\langle \mathbf{v}_{ext} \rangle$ is always equal to the rate of change of the electrons' position expectation value $\langle \mathbf{v}_{ext} \rangle = \dfrac{d}{dt}\langle \mathbf{r} \rangle$ irrespectively of the system's size or the boundary conditions to be imposed on the wavefunction; it should be noted that the latter equality is not guaranteed if the boundary velocity operator is not taken into account, and this has been the source of paradoxes[66].

The above boundary velocity $\mathbf{v}_b$ expectation value, can be used as a probe with respect to transport properties that are carried by the system's boundaries. However, although the boundary velocity expectation value $\langle \mathbf{v}_b \rangle$ is well defined and not zero within Bloch representation in the thermodynamic limit, the expectation value of certain observable operators involved in orbital magnetization calculations in the literature, can be undefined, e.g. the position operator expectation value $\langle \mathbf{r} \rangle$ and the circulation operator expectation value $\langle \mathbf{r} \times \mathbf{v} \rangle$. Such subtle behaviors, as well as relevant consequences with respect to the modern theory of orbital magnetization, are presented in Sec.2.1.3 and summarized in Table 2.1.

Orbital magnetization is the quantity to be crucially affected by the above non-Hermitian effect and it is this observable that is the focus of our treatment. Before we start, let us note that, although in conventional materials the orbital magnetization is only of the order of a few per cent of the total magnetization, in materials with topologically nontrivial band structures the electrons' collective orbital magnetization can be larger than spin magnetization which

has been confirmed in experiments [131, 58, 107], owing to large orbital magnetization contribution arising from the effective reciprocal space monopoles near the band crossings.

Nowadays, the so-called modern theory of orbital magnetization $\mathbf{M}$ has been argued to have come to a mature stage [132]. Three main methods for deriving the bulk orbital magnetization formula in the context of modern theory are currently widespread: a quantum mechanical method with direct calculation of circulating currents for trivial band insulators in the presence of boundaries [133, 33], a semiclassicall wave packet approximation method [149, 148, 35] and one that takes the derivative of free energy with respect to magnetic fields under periodic boundary conditions [120, 37]. In the first of the above methods two incompatible features had to be overcome in order for the magnetization to be a genuine bulk property, namely adoption of periodic boundary conditions (PBCs) and usage of the circulation operator $\mathbf{r} \times \mathbf{v}$ in the Bloch representation. This was done with the aid of the Wannier representation which can be rigorously employed in normal insulators with zero Chern number.

Furthermore, it has been argued that bulk behavior of observables in crystalline materials is ensured when computing within PBCs. In spite of this belief, and contrary to what has been stated in the literature [112, 19], the system by construction has a "terminated" boundary surface (assuming a 3D material), the one on which PBCs are imposed; boundary contributions due to non-Hermitian effects are therefore generally not ruled out, especially whenever observables incorporate anomalous operators, such as the position operator that enters the expressions for the electron's magnetic and electric dipolar moment.

In the spirit of re-examining the orbital magnetization formula within a quantum mechanical theoretical framework that takes into account boundary effects and at the same time relaxes the Wannier-localization approximation, we were motivated to define a circulation operator that contains the extended velocity operator in the form $\frac{1}{2}(\mathbf{r} \times \mathbf{v}_{ext} - \mathbf{v}_{ext} \times \mathbf{r})$, in order to analytically determine the orbital magnetization of a system of effectively non-interacting electrons (i.e. in a density functional theory framework). Although this circulation operator takes into account boundary contributions as a consequence of the extended velocity operator $\mathbf{v}_{ext}$, its expectation value is still problematic in the Bloch representation within PBCs and it becomes undefined for extended systems in the thermodynamic limit (see Appendix A).

In spite of the undefined expectation value of the latter circulation operator in periodic and extended systems, and to our surprise, we found out that it can always be decomposed into two distinct parts, namely, an intrinsic one that has a definite value and an extrinsic one that carries the undefined value. The intrinsic one has an intensive and bulk behavior that properly counts the local and circulating probability micro-currents embodied in the (generally) extended wavefunction's structure with boundary contributions being explicitly taken into account due to the non-Hermitian effect.

Specifically, the expectation value of the intrinsic orbital circulation is found to have the following properties: (i) it does not depend on the system's size and has a finite value within

PBCs in the Bloch representation in the thermodynamic limit, (ii) it carries information about the electrons' orbital circulating probability micro-currents which are encoded as structured wavefunction in real space (for free electrons and plane waves it becomes zero), (iii) its value does not depend on the position origin (as long as the shift of the origin can be attributed to a unitary transformation of the wavefunction) and (iv) it takes into account boundary contributions as a consequence of the non-Hemitian effect.

Although we do not use any Wannier states in this work, we nevertheless demonstrate how an explicit relation between the electrons' nth band collective intrinsic circulation (evaluated with respect to Bloch eigenstates) and a starting point formula of the modern theory of orbital magnetization (namely, the electrons' collective circulation evaluated with respect to Wannier states) can be established. This is accomplished by using the standard velocity, the newly defined boundary velocity and the intrinsic circulation and by assuming that each Bloch eigenstate satisfies the periodic gauge. In this respect, we expand each Bloch eigenstate into the basis of localized bulk Wannier states and localized surface orbitals, and as a result the nth band electrons' collective intrinsic circulation (initially evaluated with respect to Bloch eigenstates) acquires two distinct contributions which are the same as the ones given in Ref.[133], that is, the collective local circulation contribution (LC) plus the collective itinerant circulation contribution (IC), the latter being, in our formulation, explicitly attributed to the new boundary velocity. It is important to re-emphasize that, using the relation between the boundary and the standard velocity, the IC can be recast in a form that can be evaluated as a bulk property.

In this framework we propose that the intrinsic circulation is the proper quantity that encodes the electrons' intrinsic orbital behavior in periodic (or moderately disordered) and extended systems, without the need of any approximation, and as such it must be employed in a rigorous quantum mechanical theoretical framework for calculating the orbital magnetization.

In the fashion described above, we exploit the intrinsic orbital circulation in order to model the orbital magnetization of non-interacting electrons and as such we use it to derive two quantum mechanical formulas, one as an $\mathbf{r}$-space and another one as a "reciprocal" $\mathbf{k}$-space formula, both being relaxed from any Wannier-localization approximation.

The $\mathbf{r}$-space formula is derived for an extended system within PBCs over the terminated boundaries, giving therefore the bulk orbital magnetization.

In the derivation of the $\mathbf{k}$-space expression we relax the PBCs constraint, and as a consequence, certain interesting features emerge. Namely, a covariant derivative appears in the one-band (adiabatically deformed) approximation formula for the orbital magnetization as an emerging operator, and survives due to the non-Hermitian effect that is attributed to the anomalous momentum gradient operator $\partial_{\mathbf{k}}$ that enters the static (off-diagonal) Hellmann-Feynman theorem that we derive in Appendix C. In the many-band (unrestricted) formula the non-Hermitian effect contributes an additional boundary quantity which explicitly depends on the off-diagonal matrix elements of the boundary velocity operator $\mathbf{v}_b$ as well as

on a new boundary momentum gradient operator $\mathbf{k}_b$ (defined in Eq. (2.46)). The latter additional boundary quantity, is expected to give locally (in momentum space) giant orbital magnetization contributions (due to its structure) whenever band crossings occur along with Hall voltage as a consequence of boundary conditions that may generally break the standard Born-von Kármán periodicity.

The theoretical method that we propose can be employed either for calculating the built-in orbital magnetization of solids in the absence of external fields [133, 33] or for calculating the induced orbital magnetization as a response to external fields, e.g. to an electric field [90]. In this work we determine the built-in magnetization in solids when time reversal symmetry is assumed to be broken, either from a staggered magnetic field that averages to zero over the unit cell, or through spin-orbit coupling to a background of ordered local moments.

2.1 Definitions

2.1.1 Extended velocity operator

By taking into account the evolution of the state under consideration, and by demanding that the velocity operator expectation value must always be equal with the rate of change of the electrons' expectation value $\frac{d}{dt}\langle \mathbf{r} \rangle$, it is necessary to define the velocity operator in an extended theoretical framework as,

$$\mathbf{v}_{ext} = \mathbf{v} + \mathbf{v}_b \tag{2.1}$$

where,

$$\mathbf{v} = \frac{i}{\hbar}\left[H(\mathbf{r},t), \mathbf{r}\right] \tag{2.2}$$

is the standard velocity operator and

$$\mathbf{v}_b = \frac{i}{\hbar}\big(H(\mathbf{r},t)^+ - H(\mathbf{r},t)\big)\mathbf{r} \tag{2.3}$$

is the boundary velocity operator.

The introduction of this new operator $\mathbf{v}_b$ is rather naturally motivated by Refs.[47, 48] and its expectation value is not zero only whenever the position operator becomes anomalous due to the non-Hermitian effect, in which case there are paradoxes first noted in Ref.[66].

For closed systems $\langle \Psi(t) | \Psi(t) \rangle = 1$, the Hamiltonian is Hermitian $H(\mathbf{r},t)^+ = H(\mathbf{r},t)$ with respect to the states that belong within the domain of its definition and these states form the given Hilbert space. The non-Hermitian effect emerges whenever the state $\mathbf{r}\Psi(\mathbf{r},t)$ does not belong within the given Hilbert space, that is $H(\mathbf{r},t)^+(\mathbf{r}\Psi(\mathbf{r},t)) \neq H(\mathbf{r},t)\,(\mathbf{r}\Psi(\mathbf{r},t))$, which is a characteristic property of all wavefunctions $\Psi(\mathbf{r},t)$ that satisfy PBCs over the system boundaries.

Although the expectation value of the boundary velocity operator Eq. (2.3) given by

$$\langle \mathbf{v}_b \rangle = \frac{i}{\hbar}(\langle H(\mathbf{r},t)\Psi(t)|\,\mathbf{r}\Psi(t)\rangle - \langle \Psi(t)|\,H(\mathbf{r},t)\mathbf{r}\Psi(t)\rangle) \tag{2.4}$$

is by definition a bulk quantity, due to space-volume integration (assuming a 3D system) in position representation, it can always and equivalently be evaluated as a boundary quantity due to the structure (and symmetry) of the integrands that allows an integration by parts.

In this respect, by working in position representation, for real scalar and vector potentials and after a straightforward integration by parts, the expectation value of Eq. (2.3) is given in the form

$$\langle \mathbf{v}_b \rangle = -\oiint_S \mathbf{r}\,(\mathbf{J}_{pr}(\mathbf{r},t)\cdot d\mathbf{S}) + \frac{i\hbar}{2m}\oiint_S |\Psi(\mathbf{r},t)|^2 d\mathbf{S} \tag{2.5}$$

with S being the terminated boundary surface of the system where the boundary conditions are imposed, and $\mathbf{J}_{pr}(\mathbf{r},t) = \text{Real}[\Psi(\mathbf{r},t)^* \mathbf{v}\, \Psi(\mathbf{r},t)]$ is the standard local probability current density (for a spinless electron). The general form of Eq. (2.5) can be further reduced for periodic systems. Specifically, by assuming a wavefunction $u(\mathbf{r},t)$ that is cell-periodic in the bulk and at the same time satisfies Born-von Kármán periodic boundary conditions over the material's boundaries, Eq. (2.4) takes the form

$$\langle \mathbf{v}_b \rangle = \frac{i}{\hbar}\left(\langle H(\mathbf{r},t)u(t)|\,\mathbf{r}u(t)\rangle_{cell} - \langle u(t)|\,H(\mathbf{r},t)\mathbf{r}u(t)\rangle_{cell}\right) \tag{2.6}$$

where we have used the normalization convention $\langle u(t)|u(t)\rangle_{cell} = 1$, as well as the fact that $u(\mathbf{r},t)$ belongs within the domain of definition of the Hamiltonian, that is, $\langle H(\mathbf{r},t)u(t)|\,u(t)\rangle - \langle u(t)|\,H(\mathbf{r},t)u(t)\rangle = 0$. By then exploiting the symmetry of the integrands and performing integration by parts, Eq. (2.6) takes the simplified form

$$\langle \mathbf{v}_b \rangle = -\oiint_{cell} \mathbf{r}\,(\mathbf{J}_{pr}(\mathbf{r},t)\cdot d\mathbf{S}) \tag{2.7}$$

that is valid for periodic systems.

The first term of Eq. (2.5) can be seen as a position-weighted probability flux through the boundaries of the system, while the second and purely imaginary part, cancels a possible imaginary remnant part of the standard velocity operator expectation which is given by

$$\langle \mathbf{v} \rangle = \iiint_V \mathbf{J}_{pr}(\mathbf{r},t)dV - \frac{i\hbar}{2m}\oiint_S |\Psi(\mathbf{r},t)|^2 d\mathbf{S}. \tag{2.8}$$

By adding Eq. (2.5) and Eq. (2.8), that is $\langle \mathbf{v}_{ext} \rangle = \langle \mathbf{v} \rangle + \langle \mathbf{v}_b \rangle$ we see that $\langle \mathbf{v}_{ext} \rangle$ is always a real quantity as expected (see discussion below).

The boundary velocity operator can also be useful in the study of materials with strong spin-orbit coupling interaction if a modification of its expectation value form is made, that is, by taking into account the spin dependence of the standard velocity operator (as an outcome of the non-relativistic limit of the Dirac equation) $\mathbf{v} = \frac{1}{m}\mathbf{\Pi} + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma} \times \nabla V(\mathbf{r})$ that en-

ters the local probability current density $\mathbf{J}_{pr}(\mathbf{r},t)=\text{Real}[\Psi(\mathbf{r},t)^{\dagger}\mathbf{v}\,\Psi(\mathbf{r},t)]$ which now must be evaluated with respect to spinors.

With the aid of Eq. (2.1) – (2.3), the extended velocity operator can be recast in the form

$$\mathbf{v}_{ext}=\frac{i}{\hbar}(H(\mathbf{r},t)^{+}\mathbf{r}-\mathbf{r}H(\mathbf{r},t)), \tag{2.9}$$

and the equality $\langle\mathbf{v}_{ext}\rangle=\frac{d}{dt}\langle\mathbf{r}\rangle$ holds irrespectively of the position operator behavior (hence irrespective of the boundary conditions). By the definition as given in Eq. (2.9) and by working in the position representation $\mathbf{r}^{+}=\mathbf{r}$, we can easily deduce that the extended velocity operator is always a Hermitian operator $\mathbf{v}_{ext}^{+}=\mathbf{v}_{ext}$ and its expectation value is always real, in agreement with a summation of Eq. (2.5) and (2.8) without the need of any specific boundary conditions to be imposed, which is also valid even for open systems where the Hamiltonian is not a Hermitian operator.

A simple and intuitive criterion to demonstrate the necessity of introducing the extended velocity operator is as follows: Consider a stationary and extended plane wave state of a free electron of mass m with well defined momentum $\hbar\mathbf{k}$ in a finite volume V. The system is assumed to be closed, that is the electrons' wavefunction is normalized to unity at every instant t within the volume V, $\langle\Psi(t)|\Psi(t)\rangle=1$. In this fashion, the electrons' displacement $\Delta\langle\mathbf{r}\rangle$ must always be smaller than (or equal to) the systems' size. Using the standard velocity definition $\mathbf{v}=\frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{r}]$ the elctrons' displacement acquires the value $\Delta\langle\mathbf{r}\rangle=\frac{\hbar\mathbf{k}}{m}t$ which will eventually lead the electron out of the system. This paradox is bypassed within the extended velocity operator definition, as it turns out that the boundary velocity contributes an equal magnitude and opposite sign than the bulk electrons' velocity $\langle\mathbf{v}\rangle$ resulting in zero displacement $\Delta\langle\mathbf{r}\rangle=0$ at every instant t for the assumed stationary state. In fact, the extended velocity operator guarantees that every stationary state (irrespectively of the static potentials) will always produce zero displacement for the electron, that is $\frac{d}{dt}\langle\mathbf{r}\rangle=\langle\mathbf{v}_{ext}\rangle=\langle\mathbf{v}\rangle+\langle\mathbf{v}_{b}\rangle=0$, as expected from the trivial fact that the position operator expectation value is a static quantity with respect to any stationary state.

In this fashion, we can develop a simple and direct method to link boundary effects with bulk properties as a form of a bulk-boundary correspondence in a general sense for every stationary state, namely $\langle\mathbf{v}\rangle_{n}=-\langle\mathbf{v}_{b}\rangle_{n}$ where n indexes the Hamiltonian eigenstate; this is an example, therefore, of a bulk formulation that properly takes into account boundary currents that are rigorously related to the bulk band structure.

There are two important features of the extended velocity operator $\mathbf{v}_{ext}$ that can be deduced from its off-diagonal matrix elements with respect to the (generally time-dependent) Hamiltonian instantaneous eigenstates $|n(t)\rangle$. These are derived by direct application of Eq. (2.9) and Eq. (2.1) and are given by

$$\langle m(t)|\mathbf{v}|n(t)\rangle+\langle m(t)|\mathbf{v}_{b}|n(t)\rangle=\frac{i}{\hbar}(E_{m}(t)-E_{n}(t))\,\langle m(t)|\mathbf{r}|n(t)\rangle \tag{2.10}$$

where, the off-diagonal matrix elements of the boundary velocity operator are explicitly calculated (after a straightforward integration by parts) as

$$\langle m(t)|\mathbf{v}_b|n(t)\rangle = -\frac{1}{2}\oiint_S \mathbf{r}\left((\mathbf{v}\,\psi_m)^\dagger\psi_n + \psi_m^\dagger\,\mathbf{v}\,\psi_n\right)\cdot d\mathbf{S} \;+\; \frac{i\hbar}{2m}\oiint_S \psi_m^\dagger\,\psi_n\,d\mathbf{S}, \quad (2.11)$$

$\psi_n = \psi_n(\mathbf{r},t) = \langle\mathbf{r}|n(t)\rangle$ are the Hamiltonian's instantaneous eigenfunctions and $\mathbf{v}$ is the velocity operator given by Eq. (2.2). Eq. (2.11) can be viewed as the off-diagonal counterpart of Eq. (2.5).

The two important features then follow. First, the off-diagonal position matrix elements in Eq. (2.10) will explicitly be involved in the many-band (unrestricted) formula of the orbital magnetization that we will derive in this article; therefore, boundary contributions due to the off-diagonal boundary velocity matrix elements will explicitly be taken into account. Second, the off-diagonal position matrix elements in Eq. (2.10) are proportional to the electrons' transition dipole moment, therefore the emission and absorption of photons can be rigorously related with boundary properties owing to the off-diagonal boundary velocity matrix elements.

Generalizing the results of this subsection we point out that, whenever one defines an operator in an extended way $\boldsymbol{\mathcal{O}}_{ext}$ so that its expectation value $\langle\boldsymbol{\mathcal{O}}_{ext}\rangle$ is equal with the rate of change of the expectation value of a given Hermitian operator $\mathbf{G}$, that is $\langle\boldsymbol{\mathcal{O}}_{ext}\rangle = \frac{d}{dt}\langle\mathbf{G}\rangle$, the definition of $\boldsymbol{\mathcal{O}}_{ext}$ can be consistently given by the Ehrenfest theorem, as long as a corresponding boundary operator $\boldsymbol{\mathcal{O}}_b$ is taken into account. The expectation value of the boundary operator $\langle\boldsymbol{\mathcal{O}}_b\rangle$ is extremely sensitive to the boundary conditions of the wavefunction and takes a nonzero value only whenever the given Hermitian operator $\mathbf{G}$ (entering the theorem) becomes anomalous due to the non-Hermitian effect. Specifically, by working in position representation, due to symmetry of the integrand, after a straightforward integration by parts, the expectation value $\langle\boldsymbol{\mathcal{O}}_b\rangle$ is always cast in the form of a boundary integral (assuming real scalar and vector potentials) of a generalized current $\mathbf{J}_G$ flux as

$$\langle\boldsymbol{\mathcal{O}}_b\rangle = \frac{i}{\hbar}\langle\Psi(t)|\left(H(\mathbf{r},t)^+ - H(\mathbf{r},t)\right)\mathbf{G}\,|\Psi(t)\rangle = \oiint_S \mathbf{J}_G\,dS \quad (2.12)$$

where the generalized current density $\mathbf{J}_G$ is given by

$$\mathbf{J}_G = -\frac{1}{2}\mathbf{n}\cdot\left((\mathbf{v}\Psi(\mathbf{r},t))^\dagger + \Psi(\mathbf{r},t)^\dagger\mathbf{v}\right)\mathbf{G}\Psi(\mathbf{r},t). \quad (2.13)$$

The wavefunction $\Psi(\mathbf{r},t)$ entering Eq. (2.13) can be either the electrons' two component spinor wavefunction for spinfull electron (and this will be nontrivially useful in solids with strong spin-orbit interaction) or the scalar wavefunction for spinless electron motion (where the generalized current has the same structure but with the dagger operation † being replaced by the complex conjugation $*$ operation only) and $\mathbf{n}$ is the unit vector locally normal to the surface S. For the special case of $\mathbf{G} = \mathbf{r}$ and either spinlfull or spinless electron motion, by analytically calculating the directional velocity operator $\mathbf{n}\cdot\mathbf{v}$ action on $\mathbf{G}\Psi(\mathbf{r},t)$ within

Eq. (2.13) and Eq. (2.12), we recover Eq. (2.5). Alternatively, if we choose $\mathbf{G}$ to be the identity operator I, then $\mathbf{J}_G$ becomes the usual probability current $\mathbf{J}_{pr}$ and for a closed system Eq. (2.12) becomes zero, which is consistent with the conservation of total probability (valid for states belonging within the Hilbert space of closed systems).

2.1.2 Intrinsic and extrinsic orbital circulation

In order to define the electrons' intrinsic and extrinsic orbital circulation for an extended and periodic system, we first choose to define a Hermitian circulation operator as

$$\mathbf{C} = \frac{1}{2}(\mathbf{r} \times \mathbf{v}_{ext} - \mathbf{v}_{ext} \times \mathbf{r}) \tag{2.14}$$

namely the electrons' orbital circulation operator that employs the extended velocity operator; it is therefore designed to take into account the inherited anomaly of the position operator when computing circulating currents in periodic systems. The circulation operator always behaves as a Hermitian operator $\mathbf{C}^+ = \mathbf{C}$ irrespectively of the wavefunctions' boundary conditions as evidenced from Eq. (2.14) and Eq. (2.1). With the aid of Eq. (2.1) –(2.3) and $\mathbf{r} \times \mathbf{r} = 0$, the circulation operator can be recast in the forms

$$\mathbf{C} = \frac{i}{2\hbar}\mathbf{r} \times \left(H(\mathbf{r},t)^+ + H(\mathbf{r},t)\right)\mathbf{r}$$

and

$$\mathbf{C} = \mathbf{r} \times \mathbf{v} + \frac{1}{2}\mathbf{r} \times \mathbf{v}_b.$$

It is interesting to note that in the latter form of $\mathbf{C}$ the $\frac{1}{2}\mathbf{r} \times \mathbf{v}_b$ term is an anti-Hermitian operator that has imaginary expectation value which exactly cancels any remnant imaginary part of the $\mathbf{r} \times \mathbf{v}$ term expectation value. Direct calculation gives the orbital circulation operator $\mathbf{C}$ expectation value form, which is found to be

$$\langle\Psi(t)|\,\mathbf{C}\,|\Psi(t)\rangle = \mathrm{Im}[\,i\,\langle\Psi(t)|\,\mathbf{r} \times \mathbf{v}\,|\Psi(t)\rangle\,] = \iiint_V \mathbf{r} \times \mathbf{J}_{pr}(\mathbf{r},t)dV \tag{2.15}$$

where the quantum state under consideration $|\Psi(t)\rangle$ is normalized within the volume V of the system. In spite of the cautious definition of the circulation operator in order to take into account the possible anomaly of the position operator for periodic systems, it is shown in Appendix A that its expectation value $\langle\mathbf{C}\rangle$ with respect to a Bloch eigenstate does not quite lead to any theoretical progress as it becomes undefined for an extended system in the thermodynamic limit.

Motivated, however, by classical mechanics, either by rigid body dynamics or by continuous medium (hydrodynamical) theories, we find out that the expectation value of the circulation operator $\langle\mathbf{C}\rangle$ can always be decomposed into two distinct parts. Namely, an intrinsic circulation part $\langle\mathbf{C}_{intr}\rangle$ that always has an intensive and bulk behavior (with well defined value within Bloch representation in the thermodynamic limit) and an extrinsic circulation

part $\langle \mathbf{C}_{extr} \rangle$ that has an extensive and position origin-dependent behavior (with undefined value within Bloch representation in the thermodynamic limit). The definitions of the intrinsic and extrinsic circulations are given by

$$\langle \Psi(t) | \, \mathbf{C}_{intr} \, | \Psi(t) \rangle = \mathrm{Im}[\, i \, \langle \Psi(t) | \, (\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{v} \, | \Psi(t) \rangle \,] = \iiint_V (\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{J}_{pr}(\mathbf{r}, t) dV \tag{2.16}$$

and

$$\langle \Psi(t) | \, \mathbf{C}_{extr} \, | \Psi(t) \rangle = \mathrm{Im}[\, i \, \langle \Psi(t) | \, \langle \mathbf{r} \rangle \times \mathbf{v} \, | \Psi(t) \rangle \,] = \iiint_V \langle \mathbf{r} \rangle \times \mathbf{J}_{pr}(\mathbf{r}, t) dV \tag{2.17}$$

respectively, where V is the volume of the system and $\langle \mathbf{r} \rangle = \iiint_V \mathbf{r} \, |\Psi(\mathbf{r}, t)|^2 dV$ is the position operator expectation value that takes an undefined value within Bloch representation in the thermodynamic limit (as shown in Appendix A).

The intrinsic circulation $\langle \mathbf{C}_{intr} \rangle$ has no ambiguity and is a position origin-independent quantity whenever the shift of the position origin causes a U(1) transformation for the scalar wavefunction (assuming a spinless electron). The origin-independence is a consequence of the combined transformation (under a shift of the position origin) of the operator $((\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{v})$ and the U(1) transformation of the wavefunction that compensate each other. For spinfull electrons the velocity operator acquires spin-dependence and, as long as the shift of the position origin can be described by an SU(2) transformation of the spinor wavefunction, the intrinsic circulation remains a position origin-independent quantity without any ambiguity.

The electrons' intrinsic orbital circulation as given by Eq. (2.16) has an inherited boundary contribution which is revealed when taking into account Eq. (2.1) and Eq. (2.5) – (2.8). In the special case of a stationary state $|\Psi_n(t)\rangle$ the electrons' intrinsic orbital circulation has the explicit boundary dependence given in

$$\langle \Psi_n(t) | \, \mathbf{C}_{intr} \, | \Psi_n(t) \rangle = \iiint_V \mathbf{r} \times \mathbf{J}_{pr(n)}(\mathbf{r}) dV - \langle \mathbf{r} \rangle_n \times \oiint_S \mathbf{r} \, (\mathbf{J}_{pr(n)}(\mathbf{r}) . d\mathbf{S}). \tag{2.18}$$

Assuming an extended Bloch eigenstate $\Psi_n(\mathbf{r}, t, \mathbf{k})$ that obeys PBCs over the boundaries of the system (and is normalized within its volume V), and in spite of the position operator (undefined) expectation value $\langle \mathbf{r} \rangle$ that explicitly enters Eq. (2.16), we find after a straightforward calculation shown in Appendix A that the electrons' intrinsic orbital circulation takes a well-defined value at the infinite volume limit $V \to \infty$, given by

$$\langle \Psi_n(t, \mathbf{k}) | \, \mathbf{C}_{intr} \, | \Psi_n(t, \mathbf{k}) \rangle = \iiint_{V_{cell}} (\mathbf{r} - \langle u_n(\mathbf{k}) | \, \mathbf{r} \, | u_n(\mathbf{k}) \rangle_{cell}) \times \mathbf{J}_{pr(n)}(\mathbf{r}, \mathbf{k}) dV \tag{2.19}$$

with $u_n(\mathbf{r}, \mathbf{k})$ the cell periodic eigenstates, where all space integrals have been truncated (due to symmetry of the integrands) and evaluated within a unit cell of volume V_{cell}, the local

probability current density being determined with respect to a Bloch eigenstate. It is evident from Eq. (2.19) that the intrinsic circulation is a bulk and intensive quantity of a periodic and extended system. On the contrary, the extrinsic circulation as given from Eq. (2.17), takes an undefined value for a periodic and extended system (owing to the position operator expectation value); it is therefore not a proper quantity to model any bulk or boundary property of such a periodic and extended system. We note that, in deriving Eq. (2.19) we have assumed the normalization convention $\langle \Psi_n(\mathbf{k}) | \Psi_n(\mathbf{k}) \rangle = \langle u_n(\mathbf{k}) | u_n(\mathbf{k}) \rangle_{cell} = 1$, that is we have assumed a Bloch state in the form $|\Psi_n(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} e^{i\mathbf{k}.\mathbf{r}} |u_n(\mathbf{k})\rangle$ where N is the total number of the unit cells enclosed within the volume V of the system.

Summarizing, and with Eq. (2.16) as well as Eq. (2.19) in mind, we can conclude that the quantity $(\mathbf{r} - \langle \mathbf{r} \rangle) \times \mathbf{J}_{pr}(\mathbf{r}, t)$ is a well defined local intrinsic circulation density, even if it is computed with respect to an extended Bloch state in the thermodynamic limit where the electrons' position expectation value acquires an undefined value.

Physical meaning of the intrinsic orbital circulation

A physically and intuitively important feature of the intrinsic orbital circulation is that it is a quantity that properly counts the circulating probability micro-currents embodied in the wavefunction's structure. In order to clarify this feature in a simple manner let as consider two spinless and free electron motions in 3D space: one electron with well defined linear momentum vector $\hbar\mathbf{k}$ and another one with partially well defined linear momentum vector, e.g. only its z component $\hbar k_z \mathbf{e}_z$ (with k_x and k_y being undetermined). We assume that each electron is in an extended state motion that is normalized within a volume V. The free electron motion with well defined linear momentum vector $\hbar\mathbf{k}$, hence with a plane wave form for the wavefunction, has a local probability current density that is a homogeneous vectorial quantity proportional to $\hbar\mathbf{k}/m$. On the contrary, the free electron motion with partially well defined linear momentum $\hbar k_z \mathbf{e}_z$ has a local probability current density that is an inhomogeneous vectorial quantity with a constant z component proportional to $\hbar k_z/m$. Using Eq. (2.16), we can easily find that the intrinsic orbital circulation of the free electron motion with well defined linear momentum $\hbar\mathbf{k}$ is zero (due to the homogeneous local probability current density), while the intrinsic orbital circulation of the free electron with partially well defined linear momentum $\hbar k_z \mathbf{e}_z$ is non-vanishing (due to the inhomogeneous local probability current density) and takes contributions only from the x and y non-constant components of the local probability current density that may constitute a vortex circulating probability micro-current field on the planes normal to $\mathbf{e}_z$ (with free electron vortex state being an example, see below).

Considering such a structured wavefunction, its phase is indeterminate on the dislocation lines (in 3D space) where the modulus of the wavefunction takes a zero value. The intrinsic orbital circulation of the electron as given by Eq. (2.16) becomes zero, namely, $\iiint_V \mathbf{r} \times \mathbf{J}_{pr}(\mathbf{r}, t) dV - \langle \mathbf{r} \rangle \times \iiint_V \mathbf{J}_{pr}(\mathbf{r}, t) dV = 0$ whenever, in the simplest scenario, the local probability current density is zero (the gradient of the wavefunction's phase is zero)

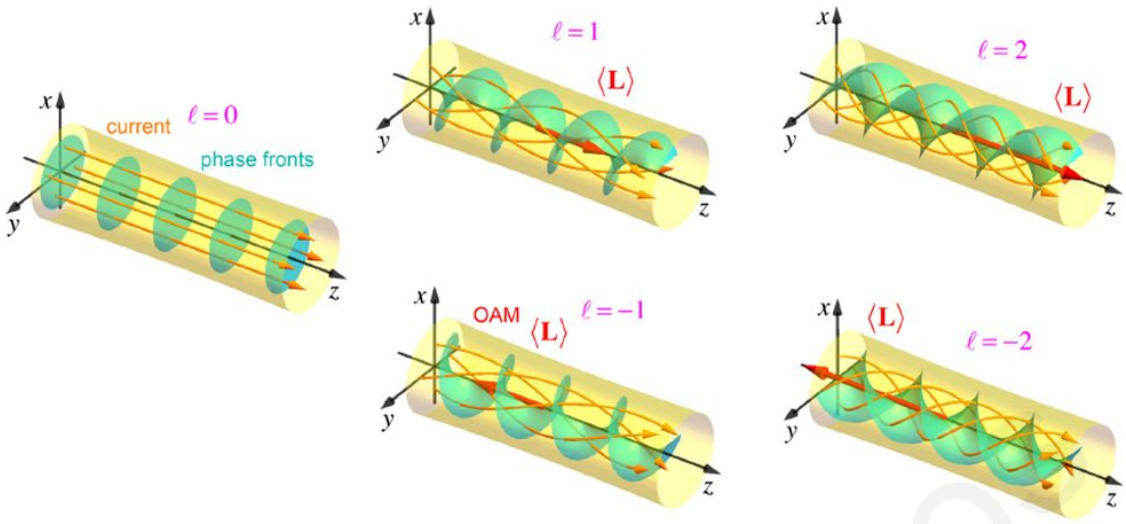

Figure 2.1: Vortex beams propagating along the z-axis carrying intrinsic longitudinal orbital angular momentum $\langle \mathbf{L}_z \rangle = \hbar\,\ell$ per particle. The 3D schematics show the phase fronts (cyan) and probability-current streamlines (orange) for beams with different vortex charges. Adapted from [21].

or whenever the local probability current density is a homogeneous quantity (the gradient of the wavefunction's phase has a constant and well-defined value), therefore the wavefunction is structureless. On the contrary, in structured wavefunctions the electrons' intrinsic orbital circulation is generally not zero and has two competing contributions as given in Eq. 2.16, which are explicitly dependent on the local probability current density field. The bigger the difference of these two competing contributions the bigger the electrons' intrinsic orbital circulation, which occurs for example whenever the internal structure of the wavefunction has such a symmetry that makes some of the components of $\iiint_V \mathbf{J}_{pr}(\mathbf{r},t)dV$ become zero. The latter symmetry feature is found in the free electron motion that are described by vortex states [86, 21] illustrated in Fig. 2.1, where the electron has well defined linear momentum $\hbar k_z \mathbf{e}_z$ only in the z direction and at the same time has a well defined canonical orbital angular momentum along the same direction (characterized by the azimuthal index l). Due to the rotational (azimuthal) symmetry of the wavefunction, the azimuthal component of $\iiint_V \mathbf{J}_{pr}(\mathbf{r},t)dV$ becomes zero.

Structured wavefunctions appear naturally in motions under external potentials, e.g. in atomic orbitals with nonzero mechanical angular momentum or in Landau states in a magnetic field. In this respect, we generally expect that the ionic environment will in principle produce structured and extended cell periodic electronic wavefunctions $u_n(\mathbf{r},\mathbf{k})$, with the dislocation lines being periodically ordered in the bulk owing to the periodicity of $u_n(\mathbf{r},\mathbf{k})$, while spiraling probability micro-currents around those lines can be taken into account by Eq. (2.16) and Eq. (2.19). Intrinsic orbital circulation is the starting point quantity for the microscopic understanding of the orbital magnetization origin and as such will be used in the following to model the orbital magnetization in band theory without the need of any Wannier-localization approximation.

Table 2.1: Matrix elements evaluated with respect to Bloch eigenstates in the thermodynamic limit.

Operator	**Matrix element**	**Value**	**Origin**	**Boundary Velocity is**
$\mathbf{r}$	$\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle$	undefined	dependent	well defined
$\mathbf{r}$	$\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_m\rangle \quad n\neq m$	well defined	independent	well defined
$\mathbf{r}\times\mathbf{v}$	$\langle\psi_n\vert\,\mathbf{r}\times\mathbf{v}\,\vert\psi_n\rangle$	undefined	dependent	well defined
$\frac{i}{\hbar}\mathbf{r}\times H_k\sum_m^{HS}\vert u_m\rangle\langle u_m\vert\,\mathbf{r}$	$\frac{i}{\hbar}\sum_m^{HS}\langle u_n\vert\,\mathbf{r}\,\vert u_m\rangle\times E_m\langle u_m\vert\,\mathbf{r}\,\vert u_n\rangle$	well defined	independent	zero
$\mathbf{r}-\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle$	$\langle\psi_m\vert\,(\,\mathbf{r}-\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle)\,\vert\psi_m\rangle$	well defined	independent	well defined
$(\mathbf{r}-\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle)\times\mathbf{v}$	$\langle\psi_n\vert\,(\mathbf{r}-\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle)\times\mathbf{v}\,\vert\psi_n\rangle$	well defined	independent	well defined
$\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle\times\mathbf{v}$	$\langle\psi_n\vert\,\langle\psi_n\vert\,\mathbf{r}\,\vert\psi_n\rangle\times\mathbf{v}\,\vert\psi_n\rangle$	undefined	dependent	well defined

Physical meaning of the extrinsic orbital circulation

The extrinsic orbital circulation $\langle\,\mathbf{C}_{extr}\,\rangle = \mathrm{Im}[\,i\,\langle\,\mathbf{r}\,\rangle\times\langle\,\mathbf{v}\,\rangle\,]$ is an extensive quantity that counts the circulation of the global probability current $\langle\,\mathbf{v}\,\rangle$ with respect to a specific position origin. It does not carry any tractable information about the structure of the wavefunction or the circulating probability micro-currents (due to being a position origin dependent quantity), and has an undefined value within Bloch representation in the thermodynamic limit (owing to the position operator expectation value being undefined).

2.1.3 Subtle behaviors and relevant consequences within Bloch representation

The scope of this subsection is ultimately to facilitate a comparison of our results (derived in later sections) with the literature, and more specifically (i) to point out the behavior of operators (with respect to their expectation values and position origin dependence) that are commonly used in the modern theory of orbital magnetization, and (ii) to show some subtle consequences that emerge due to implicit Hermiticity assumptions that were silently made during calculations in recent theoretical works [92, 20, 19].

The expectation value of the position operator with respect to a Bloch eigenstate $\langle\psi_n(\mathbf{k})\vert\,\mathbf{r}\,\vert\psi_n(\mathbf{k})\rangle$ turns out to be an undefined value in the thermodynamic limit, as shown by Eq. (A.4) derived in Appendix A. On the other hand, the corresponding off-diagonal matrix elements $\langle\psi_n(\mathbf{k})\vert\,\mathbf{r}\,\vert\psi_m(\mathbf{k})\rangle$ given by Eq. (A.5) (also derived in Appendix A) remain well defined quantities. In this respect we also note that the matrix elements of the operator $(\,\mathbf{r}-\langle\psi_n(\mathbf{k})\vert\,\mathbf{r}\,\vert\psi_n(\mathbf{k})\rangle)$, evaluated with respect to any Bloch state, have a well defined value in the thermodynamic limit. This can be shown by taking the expectation value with respect to $\vert\psi_m(\mathbf{k}')\rangle$, that is $(\,\langle\psi_m(\mathbf{k}')\vert\,\mathbf{r}\,\vert\psi_m(\mathbf{k}')\rangle-\langle\psi_n(\mathbf{k})\vert\,\mathbf{r}\,\vert\psi_n(\mathbf{k})\rangle)$, which by using the 3D ana-

logue of Eq. (A.12), shows that the undefined terms cancel each other and, as a result, the expectation has a well defined value.

The same pattern, that is, the undefined terms canceling each other, is what makes the intrinsic circulation $\mathrm{Im}[i\,\langle\psi_n(\mathbf{k})|\,(\mathbf{r}-\langle\psi_n(\mathbf{k})|\,\mathbf{r}\,|\psi_n(\mathbf{k})\rangle)\times\mathbf{v}\,|\psi_n(\mathbf{k})\rangle]$ have a well defined value in the thermodynamic limit. On the other hand, the real part of the circulation operator expectation value $\mathrm{Im}[\,i\,\langle\psi_n(\mathbf{k})|\,\mathbf{r}\times\mathbf{v}\,|\psi_n(\mathbf{k})\rangle\,]$, is an undefined quantity as shown by Eq. (A.11). For what follows it is worth pointing out that, in all the above mentioned calculations, no constraint is assumed with respect to the boundary velocity expectation value.

By then using the Bloch form of the considered state as well as $\mathbf{v}=\frac{i}{\hbar}\,[H(\mathbf{r}),\mathbf{r}]$ and $\mathbf{r}\times\mathbf{r}=0$, the circulation operator takes the form $-\frac{1}{\hbar}\mathrm{Im}[\,\langle u_n(\mathbf{k})|\,\mathbf{r}\times H_k(\mathbf{r},\mathbf{k})\,\mathbf{r}\,|u_n(\mathbf{k})\rangle\,]$ where $H_k(\mathbf{r},\mathbf{k})=e^{-i\mathbf{k}.\mathbf{r}}H(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}$. Assuming then that the state $\mathbf{r}\,|u_n(\mathbf{k})\rangle$ can be expanded in the complete orthonormal basis of the cell periodic eigenstates $|u_m(\mathbf{k})\rangle$, that is, using the closure relation $I=\sum_{m}^{\mathrm{HS}}|u_m(\mathbf{k})\rangle\,\langle u_m(\mathbf{k})|$ and acting from the left on the above state $\mathbf{r}\,|u_n(\mathbf{k})\rangle$, the circulation operator becomes

$$-\frac{1}{\hbar}\sum_{m}^{\mathrm{HS}}\mathrm{Im}[\,\langle u_n(\mathbf{k})|\,\mathbf{r}H_k(\mathbf{r},\mathbf{k})|u_m(\mathbf{k})\rangle\times\langle u_m(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle\,]$$

which has far reaching consequences. Firstly, the latter operator is now transformed into a well defined quantity due to taking the form

$$-\frac{1}{\hbar}\sum_{m\neq n}^{\mathrm{HS}}\mathrm{Im}[\,\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_m(\mathbf{k})\rangle E_m(\mathbf{k})\times\langle u_m(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle\,],$$

where we have used $\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle\times\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle=0$. This is the basic idea behind the theoretical work made in Refs [92, 20, 19] which, however, was performed in a slightly different way. Specifically, these works used a spectral resolution of the Hamiltonian $H(\mathbf{r})=IH(\mathbf{r})I$, where the closure is given by $I=\sum_{m}^{\mathrm{HS}}|\phi_m\rangle\,\langle\phi_m|$ and $|\phi_m\rangle$ are the orbitals. As a result of this spectral resolution, the (undefined) diagonal matrix elements of the position operator are excluded from their circulation operator formula.

The subtle consequence of the above two calculations, is that one unintentionally assumes that the state $\mathbf{r}\,|\phi_n\rangle$ belongs within the domain of $H(\mathbf{r})$, that is, certain boundary conditions for $\phi_n(\mathbf{r})$ are assumed which guarantee that the wavefunction $\mathbf{r}\phi_n(\mathbf{r})$ also belongs within the domain of definition of the Hamiltonian, and as a result the non-Hermitian boundary velocity Eq. (2.4) becomes zero. Specifically, the identification $\mathbf{r}\,|\phi_n\rangle=\sum_{m}^{\mathrm{HS}}C_m\,|\phi_m\rangle$ is the one that enforces the state $\mathbf{r}\,|\phi_n\rangle$ to belong within the domain of the Hamiltonian and the boundary velocity expectation value to become zero. This is evident when one (i) takes the inner product of $\mathbf{r}\,|\phi_n\rangle$ with $\frac{i}{\hbar}\langle\phi_n|\big(H(\mathbf{r})^{+}-H(\mathbf{r})\big)$, (ii) uses Eq. (2.3) for the definition

of the boundary velocity operator $\mathbf{v}_b$, and (iii) exploits the fact that the states $|\phi_n\rangle$ belong within the domain of definition of $H(\mathbf{r})$ which finally gives

$$\langle\phi_n|\,\mathbf{v}_b\,|\phi_n\rangle = \frac{i}{\hbar}\langle\phi_n|\big(H(\mathbf{r})^+ - H(\mathbf{r})\big)\,\mathbf{r}\,|\phi_n\rangle = \frac{i}{\hbar}\sum_m^{\text{HS}} C_m\,\langle\phi_n|\big(H(\mathbf{r})^+ - H(\mathbf{r})\big)|\phi_m\rangle = 0.$$

In this framework, the method of calculation used by Refs [92, 20, 19], enforced on one hand the circulation operator to have a well defined value, but, on the other hand, unwillingly, they induced Hermiticity which sweeps away boundary contributions to the orbital magnetization; in this respect, the conclusion about the irrelevance of the boundary on the orbital magnetization of metals that was made by Ref. [92], although reasonable, is rather unjustified. We also point out that, due to the above mentioned spectral resolution of the Hamiltonian (performed within the circulation operator) the orbitals $|\phi_n\rangle$ that were assumed in Refs [92, 20, 19] , must have zero standard (bulk) velocity expectation value $\langle\phi_n|\,\mathbf{v}\,|\phi_n\rangle = 0$ owing to the relation $\langle\phi_n|\,\mathbf{v}\,|\phi_n\rangle = -\langle\phi_n|\,\mathbf{v}_b\,|\phi_n\rangle$ that holds for any stationary eigenstate of the Hamiltonian.

To demonstrate at a glance the various subtleties hidden in the literature, in Table 2.1 we summarize the behavior of certain operators that are related to the modern theory of orbital magnetization: we summarize their values, their position origin dependence, as well as relevant boundary constraints. The presented values are results of calculations performed with respect to Bloch eigenstates in the thermodynamic limit.

2.1.4 Decomposition of the intrinsic orbital circulation into local (LC) and itinerant circulation (IC) contributions

At this point it is useful to make a connection between the one electron's intrinsic circulation as given by Eq. (2.16) and the decomposition of the nth band collective electrons' circulation that was made in a rather ambiguous way, namely, to local circulation (LC) and itinerant circulation (IC) in the seminal work of Ref. [133] in order to model the orbital magnetization of normal insulators within a quantum mechanical method. Therein, they started from the assumption that each electron's eigenstate can be represented by an exponentially localized Wannier function (thus the Bloch states that they used satisfy the periodic gauge $|\Psi_n(\mathbf{k}+\mathbf{G})\rangle = |\Psi_n(\mathbf{k})\rangle$ and have zero Chern invariant) and they began their calculation with a collective circulation computed with respect to these Wannier functions, turning at the end of their calculation to the Bloch eigenstates. In the present work we follow an opposite route, that is we start our calculation from the one electron's intrinsic circulation Eq. (2.16) without any gauge assumptions (restrictions) with respect to the Bloch eigenstates, and using those states as building blocks in the many-body Slater determinant wavefunction we determine analytically the electrons' (ground state) collective orbital magnetization. By then taking into account the above mentioned relation between the standard and the boundary velocity for stationary states $\langle\mathbf{v}\rangle_n = -\langle\mathbf{v}_b\rangle_n$, the electrons' intrinsic circulation with respect

to a Bloch eigenstate $\Psi_n(\mathbf{r},t,\mathbf{k})$ is given by

$$\langle\Psi_n(\mathbf{k})|\,\mathbf{C}_{intr}\,|\Psi_n(\mathbf{k})\rangle = \mathrm{Im}[\,i\,\langle\Psi_n(\mathbf{k})|\,\mathbf{r}\times\mathbf{v}\,|\Psi_n(\mathbf{k})\rangle\,] + \mathrm{Im}[\,i\,\langle\mathbf{r}\rangle_n \times \langle\Psi_n(\mathbf{k})|\,\mathbf{v}_b\,|\Psi_n(\mathbf{k})\rangle\,]. \tag{2.20}$$

In order to establish the connection with Ref. [133] method we assume that the Bloch eigenstates $\Psi_n(\mathbf{r},t,\mathbf{k})$ entering Eq. (2.20) satisfy the periodic gauge and we expand it as

$$|\Psi_n(\mathbf{k})\rangle = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{i\mathbf{k}.\mathbf{R}}\,|n,\mathbf{R}\rangle = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_I} e^{i\mathbf{k}.\mathbf{R}_I}\,|n,\mathbf{R}_I\rangle + \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_S} e^{i\mathbf{k}.\mathbf{R}_S}\,|n,\mathbf{R}_S\rangle \tag{2.21}$$

where N is the number of primitive cells of the system, $|n,\mathbf{R}_I\rangle$ is the nth band Wannier function in the bulk cell $\mathbf{R}$ and $|n,\mathbf{R}_S\rangle$ is the nth surface localized orbital on the surface cell $\mathbf{R}_S$. By then taking into account that the expectation value of the boundary velocity $\langle\Psi_n(\mathbf{k})|\,\mathbf{v}_b\,|\Psi_n(\mathbf{k})\rangle$ is determined by a boundary integral, that is, only the boundary localized orbitals $|n,\mathbf{R}_S\rangle$ enter into the expansion of the expectation value

$$\langle\Psi_n(\mathbf{k})|\,\mathbf{v}_b\,|\Psi_n(\mathbf{k})\rangle = \frac{1}{N}\sum_{\mathbf{R}_{S'}}\sum_{\mathbf{R}_S} e^{i\mathbf{k}.(\mathbf{R_S}-\mathbf{R'_S})}\,\langle n,\mathbf{R}'_S|\,\mathbf{v}_b\,|n,\mathbf{R}_S\rangle\,, \tag{2.22}$$

we calculate the nth band collective electrons' intrinsic circulation given by $\mathbf{C}_{n(coll)} = \frac{V}{(2\pi)^3}\iiint_{BZ}\langle\Psi_n(\mathbf{k})|\,\mathbf{C}_{intr}\,|\Psi_n(\mathbf{k})\rangle\,d^3k$, which takes the form

$$\begin{aligned}\mathbf{C}_{n(coll)} &= \sum_{\mathbf{R}}\langle n,\mathbf{R}|\,\mathbf{r}\times\mathbf{v}\,|n,\mathbf{R}\rangle \\ &\quad+\sum_{\mathbf{R}'}\sum_{\mathbf{R}}\sum_{\mathbf{R}'_S}\sum_{\mathbf{R}_S}\delta_{\mathbf{R}'+\mathbf{R}'_S,\mathbf{R}+\mathbf{R}_S}\,\langle n,\mathbf{R}'|\,\mathbf{r}\,|n,\mathbf{R}\rangle\times\langle n,\mathbf{R}'_S|\,\mathbf{v}_b\,|n,\mathbf{R}_S\rangle\,.\end{aligned} \tag{2.23}$$

Assuming then that the crystal has inversion symmetry in the bulk $\langle n,-\mathbf{R}_I|\,\mathbf{r}\,|n,-\mathbf{R}_I\rangle = -\langle n,\mathbf{R}_I|\,\mathbf{r}\,|n,\mathbf{R}_I\rangle$, that is $\sum_{\mathbf{R}_I}\langle n,\mathbf{R}_I|\,\mathbf{r}\,|n,\mathbf{R}_I\rangle = 0$, as well as that for $\mathbf{R}'_S\neq\mathbf{R}_S$ the matrix elements $\langle n,\mathbf{R}+\mathbf{R}_S-\mathbf{R}'_S|\,\mathbf{r}\,|n,\mathbf{R}\rangle$ can be taken as zero, the nth band electrons' collective intrinsic circulation takes the approximate form

$$\mathbf{C}_{n(coll)} = \sum_{\mathbf{R}}\langle n,\mathbf{R}|\,\mathbf{r}\times\mathbf{v}\,|n,\mathbf{R}\rangle \;+\; \sum_{\mathbf{R}_S}\langle n,\mathbf{R}_S|\,\mathbf{r}\,|n,\mathbf{R}_S\rangle\times\langle n,\mathbf{R}_S|\,\mathbf{v}_b\,|n,\mathbf{R}_S\rangle \tag{2.24}$$

where the first term on the right hand side of Eq. (2.24) gives the electrons' nth band collective local circulation contribution (LC) and the second term the collective itinerant circulation contribution (IC) illustrated in Fig. 2.2, as given respectively in Ref. [133].

In Ref. [133] and [33] they notice that the itinerant circulation (IC) contribution that involves only the surface WFs can always be calculated as a bulk quantity that involves the bulk WFs, and they emphasize that this is quite remarkable and one of their central results. Their finding is explained whenever in the starting Eq. (2.20) we use the bulk

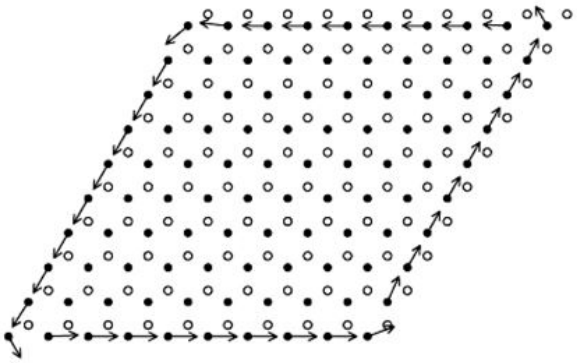

Figure 2.2: The itinerant current $\langle n, \mathbf{R}_S| \mathbf{v}_b |n, \mathbf{R}_S\rangle$ (indicated by arrows) associated with each nth surface localized orbital centered at $\langle n, \mathbf{R}_S| \mathbf{r} |n, \mathbf{R}_S\rangle$ which is used by [133] in order to calculate their itinerant surface contribution (IC) to the orbital magnetization. Adapted from [133].

expression Eq. (2.4) for the boundary velocity expectation value and at the same time replace $\langle H(\mathbf{r})\Psi_n(\mathbf{k})| \mathbf{r}\Psi_n(\mathbf{k})\rangle$ with its equal $\langle \Psi_n(\mathbf{k})| \mathbf{r}H(\mathbf{r})\Psi_n(\mathbf{k})\rangle$, which is true for all stationary states according to Eq. (2.9) (and the vanishing of its expectation value). Therefore, with the aid of the extended velocity operator and the intrinsic circulation definitions, we can elucidate and rigorously explain the origin of the heuristic partitioning of the orbital magnetization that was made in Ref.[133] and [33].

2.2 Orbital magnetization quantum formulas

In this section we use the electrons' intrinsic orbital circulation presented in Sec. 2.1 in order to derive quantum mechanical formulas for the orbital magnetization of non-interacting electrons by accounting for the circulating probability micro-currents. The formulas that we derive are applicable either to conventional or to topological crystalline materials, under periodic or realistic boundary conditions for the electrons' wavefunctions, while any localization assumptions are absent.

In a system of non-interacting electrons we can define the (single-eigenstate) orbital magnetization $\mathbf{M}_n(\mathbf{k})$ per electron as

$$\mathbf{M}_n(\mathbf{k}) = \frac{\mathbf{m}_n(\mathbf{k})}{V} = \frac{e}{2cV} \langle \Psi_n(t,\mathbf{k})| \mathbf{C}_{intr} |\Psi_n(t,\mathbf{k})\rangle \tag{2.25}$$

where $\mathbf{m}_n(\mathbf{k})$ is the electrons' orbital magnetic moment, $\Psi_n(\mathbf{r},t,\mathbf{k})$ is a Bloch eigenstate, V is the volume of the system, c is the speed of light and $e<0$ is the electron charge.

2.2.1 r-space orbital magnetization quantum formula

In the derivation of the $\mathbf{r}$-space formula we do not take into account the realistic boundary contributions to the orbital magnetization due to the realistic wavefunctions' boundary con-

ditions; rather we provide a formula that has a bulk character. Namely, we calculate the orbital magnetization within PBCs which are imposed on the wavefunction over a "terminated" boundary surface of the (3D) material in the thermodynamic limit.

Using Eq. (2.19) for the electrons' intrinsic orbital circulation and Eq. (2.25) for the orbital magnetization per electron, as well as the collective electrons' ground state magnetization (assumed to be evaluated with respect to a many-body Slater determinant wavefunction) given by $\mathbf{M}=\frac{1}{(2\pi)^3}\sum_{E_n\leq\mu}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathbf{m}_n(\mathbf{k})\,d^3k$, where μ is the Fermi energy and $f_n(\mathbf{k},\mu)$ is the occupation function, the bulk orbital magnetization of spinless and non-interacting electrons is given by

$$\mathbf{M}=\frac{e}{2c(2\pi)^3}\sum_{E_n\leq\mu}\iiint_{BZ} f_n(\mathbf{k},\mu)\left(\iiint_{V_{cell}}(\mathbf{r}-\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle_{cell})\times\mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})dV\right)d^3k \tag{2.26}$$

where all expectation value position-integrals are truncated (due to symmetry) and carried out within a primitive cell of volume V_{cell} as shown in Appendix A. The orbital magnetization $\mathbf{r}$-space formula is the first major result in this work and the integrand of Eq. (2.26) can be seen as a local orbital magnetization density with respect to real space.

We re-emphasize that, although the position operator that enters Eq. (2.16) has by itself an undefined expectation value $\langle\mathbf{r}\rangle$ within Bloch representation, its problematic behavior does not show up and it effectively behaves as a well defined operator when it appears within Eq. (2.16) and subsequently within Eq. (2.26). Therefore, the position operator does not have to be "sandwiched" between the ground-state projector and its complement as done in Ref. [19] in order to get a well defined local expression for the electrons' orbital magnetization with respect to periodic and extended states, but this can be realized in a straightforward manner with Eq. (2.26).

As evidenced from Eq. (2.26), the orbital magnetization acquires significant value whenever the difference between the two competing contributions gets as large as possible. We therefore expect that the orbital magnetization will have significant contributions from those states that possess some kind of rotational symmetry within the unit cell that results in $\iiint_{V_{cell}}\mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})dV\rightarrow 0$. Although we have considered spinless electrons, the orbital magnetization as given by Eq. (2.26) is a property that silently carries an explicit spin dependence. In crystals with strong spin-orbit interaction the velocity operator acquires spin dependence $\mathbf{v}=\frac{1}{m}\mathbf{\Pi}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V_{cry}(\mathbf{r})$ which is inherited in the local probability current density $\mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})=\text{Real}[\Psi_n(\mathbf{r},\mathbf{k})^{+}\mathbf{v}\Psi_n(\mathbf{r},\mathbf{k})]$ that enters Eq. (2.26). Therefore, in materials with strong spin-orbit interaction where the spin degree of freedom is essential, the orbital magnetization is directly influenced (apart from the wavefunctions) by the crystal force field that interacts with the electron.

2.2.2 k-space orbital magnetization quantum formula

In this subsection we derive an orbital magnetization formula that is valid for general boundary conditions for the electrons' wavefunction. Boundary contributions are explicitly taken into account as a consequence of the emergent non-Hermitian effect.

In order to derive the $\mathbf{k}$-space formula we assume that, each electrons' motion is described from a (generally) extended and stationary form eigenstate (normalized within the volume of the material) in the form $|\Psi_n(t,\mathbf{k})\rangle = e^{-\frac{1}{\hbar}E_n(\mathbf{k})t}e^{i\mathbf{k}.\mathbf{r}}|u_n(\mathbf{k})\rangle$ and no Wannier-localization approximation is involved. The bulk values of each (position representation) wavefunction $u_n(\mathbf{r},\mathbf{k})$ are assumed to be periodic (with respect to any direct lattice vector translation $\mathbf{R}$), while we relax this property near the boundaries of the material in order to take into account the realistic boundary contributions. We derive below a $\mathbf{k}$-space orbital magnetic formula $\mathbf{m}_n(\mathbf{k})$ for each electron, starting from

$$\mathbf{m}_n(\mathbf{k}) = \frac{e}{2c}\mathrm{Im}[\, i\,\langle\Psi_n(t,\mathbf{k})|\,(\mathbf{r}-\langle\mathbf{r}\rangle_n)\times\mathbf{v}\,|\Psi_n(t,\mathbf{k})\rangle\,] \tag{2.27}$$

(*cf.* Eqs (2.16) and (2.25)), and by straightforward generalization we provide the collective orbital magnetization formula for non-interacting electrons calculated with respect to a many-body Slater determinant wavefunction. The formula we derive will explicitly incorporate $\mathbf{k}$ derivatives (with the thermodynamic limit assumed), thus we are cautious from the very beginning against possible $\mathbf{k}$-dependent ambiguities of our final result. For this reason we consider the dynamical phase as well as an arbitrary $\mathbf{k}$-dependent phase (due to gauge freedom) for the wavefunctions from the very beginning of our derivation. Therefore, the Bloch type quantum eigenstates that we consider (for each electron) have the form $|\Psi_n(t,\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\,e^{i\Theta_n(t,\mathbf{k})}\,|u_n(\mathbf{k})\rangle$, where $\Theta_n(t,\mathbf{k})$ is the dynamical phase augmented by an additional $\mathbf{k}$-dependent gauge phase. The $\Theta_n(t,\mathbf{k})$ phase has explicit form, for a static H, given by $\Theta_n(t,\mathbf{k}) = -\frac{1}{\hbar}E_n(\mathbf{k})t + \Lambda(\mathbf{k})$.

By taking into account the above Bloch type eigenstate for each electron, the standard velocity operator as given by Eq. (2.2), and the Schrödinger equation that evolves the quantum eigenstate, the action of the standard velocity operator on the Bloch type eigenstate is given, as analytically derived in Appendix B, by

$$\mathbf{v}\,|\Psi_n(t,\mathbf{k})\rangle = -\frac{1}{\hbar}\,e^{i\mathbf{k}.\mathbf{r}}e^{i\Theta_n(t,\mathbf{k})}\,(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle + \frac{1}{\hbar}\partial_{\mathbf{k}}E_n(\mathbf{k})\,|\Psi_n(t,\mathbf{k})\rangle\,. \tag{2.28}$$

where $H_k(\mathbf{r},\mathbf{k}) = e^{-i\mathbf{k}.\mathbf{r}}H(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}$. In view of Eq. (2.27), the orbital magnetic moment for each electron is given by

$$\mathbf{m}_n(\mathbf{k}) = -\frac{e}{2c\hbar}\mathrm{Im}[\, i\,\langle u_n(\mathbf{k})|\,(\mathbf{r}-\langle\mathbf{r}\rangle_n)\,\times\,(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,]. \tag{2.29}$$

It is now helpful to see the origin of the electron's orbital magnetic moment Eq. (2.27) and Eq. (2.29); a comparison with the semi-classical counterpart of a localized wave packet

[148] will be made at the end of this subsection after Eq. (2.49). In virtue of Eq. (2.27) and Eq. (2.19), the orbital magnetic moment is always a well defined quantity even if the wavefunction is an extended one and the volume V of the system infinite. It is a quantity that emerges due to the circulating probability micro-currents embodied in the wavefunction's (bulk as well as boundary) structure. For free electron and plane wavefunction, namely, a wavefunction with a well defined crystal momentum $\hbar\mathbf{k}$, the electron's orbital magnetic moment Eq. (2.27) becomes zero. In virtue now of Eq. (2.29), where Eq. (2.28) has been used, although the orbital magnetic moment holds its above mentioned physical origin, is now also explicitly dependent on the remnant non-Hermitian boundary term $(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle$ of the Hellmann-Feynman theorem, a fact first noticed in Ref. [49]. Specifically, by taking the inner product of Eq. (2.28), with $\langle\Psi_n(t,\mathbf{k})|$, the electrons standard velocity expectation value is found to be

$$\langle u_n(\mathbf{k})|\mathbf{v}|u_n(\mathbf{k})\rangle = \frac{1}{\hbar}\partial_{\mathbf{k}} E_n(\mathbf{k}) - \frac{1}{\hbar}\,\langle u_n(\mathbf{k})|\,(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle\,, \tag{2.30}$$

where the second term on the right side of Eq. (2.30) is precisely the non-Hermitian boundary term of Ref. [49], which emerges due to the momentum gradient operator $\partial_{\mathbf{k}}$ that becomes anomalous. In this respect, despite the fact that the electron's orbital magnetic moment Eq. (2.27) is an intensive quantity, when we transform it into a $\mathbf{k}$-derivative formula, Eq. (2.29), this is dominated by the remnant boundary term $(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle$.

We then express the action of the operator $\mathbf{r} - \langle\mathbf{r}\rangle_n$ on the eigenstate $|u_n(\mathbf{k})\rangle$ as a $\mathbf{k}$-derivative formula, and then substitute the result in Eq. (2.29). This is done by taking into account that the time-independent eigenstate $|u_n(\mathbf{k})\rangle$ can be recast in the form $|u_n(\mathbf{k})\rangle = e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\,|\Psi_n(\mathbf{k})\rangle$, where the time-dependence has been eliminated. In this manner, the action of the position operator on the eigenstate $|u_n(\mathbf{k})\rangle$ is expressed as a $\mathbf{k}$-derivative given by

$$\mathbf{r}\,|u_n(\mathbf{k})\rangle = i\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle - \partial_{\mathbf{k}}\Lambda(\mathbf{k})\,|u_n(\mathbf{k})\rangle - i\,e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\,|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,. \tag{2.31}$$

Accordingly, the expectation value of the position operator $\mathbf{r}$ with respect to the eigenstate $|u_n(\mathbf{k})\rangle$ takes the form

$$\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle = \mathbf{A}_{nn}(\mathbf{k}) - \partial_{\mathbf{k}}\Lambda_n(\mathbf{k}) - i\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,, \tag{2.32}$$

where $\mathbf{A}_{nn}(\mathbf{k}) = i\,\langle u_n(\mathbf{k})|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle$ is the Abelian Berry connection. By acting with Eq. (2.32) on $|u_n(\mathbf{k})\rangle$ and then subtracting the product from Eq. (2.31) we obtain the identity

$$\begin{aligned}(\,\mathbf{r} - \langle\mathbf{r}\rangle_n)\,|u_n(\mathbf{k})\rangle \;\;=\;\; & (\,i\partial_{\mathbf{k}} - \mathbf{A}_{nn}(\mathbf{k}))\,|u_n(\mathbf{k})\rangle - i\,e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\,|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle \\ & + i\,e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,|\Psi_n(\mathbf{k})\rangle\,.\end{aligned} \tag{2.33}$$

The first two terms on the right hand side of Eq. (2.33) can be recast in the form,

$$(\, i\partial_{\mathbf{k}} - \mathbf{A}_{nn}(\mathbf{k}))\,|u_n(\mathbf{k})\rangle = i\widetilde{\partial}_{\mathbf{k}}\,|u_n(\mathbf{k})\rangle \tag{2.34}$$

where

$$\widetilde{\partial}_{\mathbf{k}} = (\,1 - |u_n(\mathbf{k})\rangle\langle u_n(\mathbf{k})|\,)\,\partial_{\mathbf{k}} \tag{2.35}$$

is the one-band covariant derivative that will explicitly enter the final many-body orbital magnetization formula as an emerging operator, and as such has never shown up in the literature of modern theory of orbital magnetization. In this fashion, Eq. (2.33) takes the form

$$\begin{aligned}(\,\mathbf{r} - \langle\mathbf{r}\rangle_n)\,|u_n(\mathbf{k})\rangle \;&=\; i\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle - i\,e^{-i\mathbf{k}.\mathbf{r}}\,e^{-i\Lambda(\mathbf{k})}\,|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle \\ &\quad + i\,e^{-i\mathbf{k}.\mathbf{r}}\,e^{-i\Lambda(\mathbf{k})}\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,|\Psi_n(\mathbf{k})\rangle\,.\end{aligned} \tag{2.36}$$

We then expand the state $|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle$ of Eq. (2.36) on the complete basis of the Bloch eigenstates $|\psi_m(\mathbf{k}')\rangle$ using the identity operator $I = \sum_m^{\mathrm{HS}} \iiint_{BZ} d^3k'\,|\psi_m(\mathbf{k}')\rangle\,\langle\psi_m(\mathbf{k}')|$, that is we use $|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle = \sum_m^{\mathrm{HS}} \iiint_{BZ} d^3k'\,\langle\psi_m(\mathbf{k}')|\partial_{\mathbf{k}}\psi_n(\mathbf{k})\rangle\,|\psi_m(\mathbf{k}')\rangle$. By then taking into account that the operator $(\mathbf{r} - \langle\mathbf{r}\rangle_n)$ is by definition Hermitian (without the need of any specific boundary conditions to be imposed) owing to the position representation that we are working in $(\mathbf{r}^+ = \mathbf{r})$ and to the reality of the position operator expectation value $\langle\mathbf{r}\rangle_n$, we let it act on the left to the eigenstate $\langle u_n(\mathbf{k})|$ in Eq. (2.29), which is carried out by taking the Hermitian conjugate of Eq. (2.36) and then plugging it into Eq. (2.29). In this respect and as analytically shown in Appendix B, Eq. (2.29) takes the form (B.14), namely

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) \;&=\; -\frac{e}{2c\hbar}\mathrm{Im}\left[\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\,\times\,(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle\right] \\ &\quad -\frac{e}{2c\hbar}\sum_{m\neq n}\mathrm{Im}\left[\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle\times\langle u_m(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,\right],\end{aligned} \tag{2.37}$$

which, by using the identity $(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle = (H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle$, takes the form

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) \;&=\; -\frac{e}{2c\hbar}\mathrm{Im}\left[\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\,\times\,(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))\,|\widetilde{\partial}_{\mathbf{k}}u_n\right\rangle\right] \\ &\quad -\frac{e}{2c\hbar}\sum_{m\neq n}\mathrm{Im}\left[\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle\times\langle u_m(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n\rangle\,\right].\end{aligned} \tag{2.38}$$

Now, some further analysis is in order concerning the off-diagonal elements in Eq. (38). As rigorously shown in Appendix C, by deriving an off-diagonal Hellmann-Feynman the-

orem that takes into account non-Hermitian corrections, the off-diagonal matrix elements $\langle \Psi_n(\mathbf{k}) | \partial_{\mathbf{k}} \Psi_m(\mathbf{k}) \rangle$ are found to be emergent non-Hermitian boundary quantities, that are given by

$$\langle \psi_n(\mathbf{k}) | \partial_{\mathbf{k}} \psi_m(\mathbf{k}) \rangle = \frac{\mathbf{S}_{nm}(\mathbf{k})}{(E_n(\mathbf{k}) - E_m(\mathbf{k}))} \tag{2.39}$$

where the matrix elements of the non-Hermitian term $\mathbf{S}_{nm}(\mathbf{k})$ are always transformed after an integration by parts (due to symmetry of the integrands) into a boundary quantity that is given by

$$\mathbf{S}_{nm}(\mathbf{k}) = \frac{i\hbar}{2} \oiint_S \mathbf{n} \cdot \big((\mathbf{v}\, \psi_n)^* + \psi_n^*\, \mathbf{v} \big)\, \partial_{\mathbf{k}} \psi_m \, dS, \tag{2.40}$$

where $\mathbf{S}_{nm}(\mathbf{k})$ is defined as

$$\begin{aligned} \mathbf{S}_{nm}(\mathbf{k}) &= \langle H(\mathbf{r}) \psi_n(\mathbf{k}) | \partial_{\mathbf{k}} \psi_m(\mathbf{k}) \rangle - \langle \psi_n(\mathbf{k}) | H(\mathbf{r}) \partial_{\mathbf{k}} \psi_m(\mathbf{k}) \rangle \\ &= \big\langle \Psi_n(\mathbf{k}) \big| \big(H(\mathbf{r})^+ - H(\mathbf{r}) \big) \, \partial_{\mathbf{k}} \Psi_m(\mathbf{k}) \big\rangle \, . \end{aligned} \tag{2.41}$$

By then using the considered Bloch eigenstate $|\Psi_m(\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\, e^{i\Lambda(\mathbf{k})}\, |u_m(\mathbf{k})\rangle$ in the non-Hermitian boundary term expression $\mathbf{S}_{nm}(\mathbf{k})$, we transform the non-Hermitian boundary term and express it in a form that is evaluated only by the use of the cell periodic eigenstates. Straightforward calculation shows that

$$\mathbf{S}_{nm}(\mathbf{k}) = \hbar \, \langle u_n(\mathbf{k}) |\, \mathbf{v}_b \, | u_m(\mathbf{k}) \rangle + \langle u_n(\mathbf{k}) |\, \mathbf{k}_b \, | u_m(\mathbf{k}) \rangle \, , \tag{2.42}$$

where,

$$\langle u_n(\mathbf{k}) |\, \mathbf{v}_b \, | u_m(\mathbf{k}) \rangle = \frac{i}{\hbar} (\langle H_k(\mathbf{r}, \mathbf{k}) u_n(\mathbf{k}) |\, \mathbf{r} u_m(\mathbf{k}) \rangle - \langle u_n(\mathbf{k}) |\, H_k(\mathbf{r}, \mathbf{k}) \mathbf{r} u_m(\mathbf{k}) \rangle) \tag{2.43}$$

are the off-diagonal matrix elements of the boundary velocity operator $\mathbf{v}_b$ defined as

$$\mathbf{v}_b = \frac{i}{\hbar} \, \big(H_k(\mathbf{r}, \mathbf{k})^+ - H_k(\mathbf{r}, \mathbf{k}) \big) \, \mathbf{r}, \tag{2.44}$$

while

$$\langle u_n(\mathbf{k}) |\, \mathbf{k}_b \, | u_m(\mathbf{k}) \rangle = \langle H_k(\mathbf{r}, \mathbf{k}) u_n(\mathbf{k}) |\, \partial_{\mathbf{k}} u_m(\mathbf{k}) \rangle - \langle u_n(\mathbf{k}) |\, H_k(\mathbf{r}, \mathbf{k}) \partial_{\mathbf{k}} u_m(\mathbf{k}) \rangle \tag{2.45}$$

are the off-diagonal matrix elements of the boundary momentum gradient "operator" defined as

$$\mathbf{k}_b = \big(H_k(\mathbf{r}, \mathbf{k})^+ - H_k(\mathbf{r}, \mathbf{k}) \big) \, \partial_{\mathbf{k}} \, , \tag{2.46}$$

where the Hamiltonian $H_k(\mathbf{r}, \mathbf{k})$ is the standard $H_k(\mathbf{r}, \mathbf{k}) = e^{-i\mathbf{k}.\mathbf{r}} H(\mathbf{r}) e^{i\mathbf{k}.\mathbf{r}}$ and $u_m \equiv u_m(\mathbf{r}, \mathbf{k})$ are the cell-periodic eigenfunctions. In position representation and after an integration by parts, both the above off-diagonal matrix elements are always transformed (due

to symmetry of the integrands) to boundary quantities given by

$$\begin{aligned}\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle &= -\frac{1}{2}\oiint_S \mathbf{n}\cdot\big(\,(\mathbf{v}\,u_n)^* + u_n^*\,\mathbf{v}\,\big)\,\mathbf{r}\,u_m\,dS \\ &= -\frac{1}{2}\oiint_S \mathbf{r}\,\big((\mathbf{v}\,u_n)^* u_m + u_n^*\mathbf{v}\,u_m\,\big)\cdot d\mathbf{S} + \frac{i\hbar}{2m}\oiint_S u_n^*\,u_m\,d\mathbf{S}\end{aligned} \tag{2.47}$$

(which comes out from Eq. (2.11)), and

$$\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_m(\mathbf{k})\rangle = \frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\big(\,(\mathbf{v}\,u_n)^* + u_n^*\,\mathbf{v}\,\big)\,\partial_{\mathbf{k}}u_m\,dS \tag{2.48}$$

respectively, where $u_m = u_m(\mathbf{r},\mathbf{k})$ are cell-periodic in the bulk. We note that Eq. (2.47) and Eq. (2.48) are not zero *only whenever* the position operator $\mathbf{r}$ and the momentum gradient operator $\partial_{\mathbf{k}}$ become anomalous respectively. For example, for bulk localized states (defined as the ones that the wavefunction $u_m(\mathbf{r},\mathbf{k})$ and all of its derivatives are zero over the materials boundaries) both operators behave as normal operators and have zero matrix elements, $\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle = 0$ and $\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_m(\mathbf{k})\rangle = 0$ respectively. On the other hand, for extended states that satisfy PBSs over the material boundaries $\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle \neq 0$ while $\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_m(\mathbf{k})\rangle = 0$. We also point out that the matrix elements $\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle$ and $\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_m(\mathbf{k})\rangle$, thus also their sum $\mathbf{S}_{nm}(\mathbf{k})$, can equally be computed as bulk quantities whenever the integrations by parts are not performed.

Using Eq. (2.38) and Eq. (2.39) we find the second major result in this work, namely the $\mathbf{k}$-space orbital magnetic moment of each electron $\mathbf{m}_n(\mathbf{k})$ that is given by

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) = &-\frac{e}{2c\hbar}\mathrm{Im}\left[\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\,\times\,\left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\right)\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle\right] \\ &-\frac{e}{2c\hbar}\sum_{m\neq n}\mathrm{Im}\left[\frac{1}{\left(E_n(\mathbf{k}) - E_m(\mathbf{k})\right)}\,\mathbf{S}_{nm}(\mathbf{k})\times\langle u_m(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\right]\end{aligned} \tag{2.49}$$

.

It is worth noticing that, due to the off-diagonal Hellmann-Feynman theorem Eq. (C.6), the combination of the off-diagonal matrix elements $(\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_m(\mathbf{k})\rangle)$, where $\mathbf{A}_{mn}(\mathbf{k}) = i\,\langle u_m(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle$ is the non-Abelian Berry connection, turns out to be a boundary-dependent quantity that emerges due to the non-Hermitian effect and is given by

$$i\,\langle\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle = (\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_m(\mathbf{k})\rangle) = i\frac{\mathbf{S}_{nm}(\mathbf{k})}{(E_n(\mathbf{k}) - E_m(\mathbf{k}))}, \tag{2.50}$$

which can be viewed as a new result in the Berry phase literature showing the role of the non-Hermitian effect on Berry curvatures.

By using Eq. (2.49) we can now make a comparison with the semi-classical electron's orbital magnetic moment given by Ref. [148]. In that framework, the electron's state $|W_o\rangle$,

is a localized wave packet state, composed of one band Bloch states. The wave packet is sharply centered in $\mathbf{k}$-space around the wave vector $\mathbf{k}_c$ and its center of mass is well defined and given by $\langle W_o|\,\mathbf{r}\,|W_o\rangle = \mathbf{r}_c$. Due to the self rotation of the wave packet around its center of mass, they found that the electron acquires an intrinsic orbital magnetic moment given by $\mathbf{m}_n(\mathbf{k}_c) = \frac{ie}{2c\hbar}\langle\partial_{\mathbf{k}_c}u_n(\mathbf{k}_c)|\times(H_{k_c}(\mathbf{k}_c)-E_n(\mathbf{k}_c))\,|\partial_{\mathbf{k}_c}u_n(\mathbf{k}_c)\rangle$ where they have use the convention $e>0$. If we assume that the electron's state is a bulk state, as well as that the electron completely avoids the boundaries of the system where it is enclosed, hence the wavefunction $u_n(\mathbf{r},\mathbf{k})$ and all of its derivatives are zero over the boundaries, then, all non-Hermitian boundary terms become zero. In this respect, letting $\mathbf{S}_{nm}(\mathbf{k})=0$ in Eq. (2.49) we find $\mathbf{m}_n(\mathbf{k}) = -\frac{e}{2c\hbar}\mathrm{Im}\left[\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle\Big]$ where we have used $(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle = (H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle$. Furthermore, by using the one-band covariant derivative Eq. (2.35), we make the replacement $\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right| = \langle\partial_{\mathbf{k}}u_n(\mathbf{k})| + \langle u_n(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\langle u_n(\mathbf{k})|$ in the above approximated $\mathbf{m}_n(\mathbf{k})$ which results into

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) \;=\; & -\frac{e}{2c\hbar}\mathrm{Im}\left[\langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\right]\\ & -\frac{e}{2c\hbar}\mathrm{Im}\left[\langle u_n(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\times\langle u_n(\mathbf{k})|\,(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\right].\end{aligned}$$

The term $\langle u_n(\mathbf{k})|\,(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle$ in the above equation, is also a non-Hermitian boundary term, which by assumption is also zero. In this respect, for the assumed bulk states, defined as the ones that the electron completely avoids the boundaries, the electron's magnetic moment is given by

$$\mathbf{m}_n(\mathbf{k})|^{Bulk}_{Localized\ State} = -\frac{e}{2c\hbar}\mathrm{Im}\left[\langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\right] \tag{2.51}$$

which is a form that has the same structure as the real part of semi-classical electron's orbital magnetic moment $\mathrm{Re}[\mathbf{m}_n(\mathbf{k}_c)] = \mathrm{Im}[i\,\mathbf{m}_n(\mathbf{k}_c)]$ of Ref. [148].

It is evident that, the semi-classical electron's orbital magnetic moment $\mathbf{m}_n(\mathbf{k}_c)$ does not explicitly take into account contributions from the realistic boundaries of a material, and as a consequence, the electrons' magnetization formulas that are derived by semi-classical means do not take into account such boundary contributions. We expect that our more general result Eq. (2.49) will be able to provide such contributions.

Moreover, our own result for the electrons' orbital magnetic moment formula Eq. (2.49) satisfies the two basic invariant properties, namely it is invariant with respect to gauge transformations of the form $u_n(\mathbf{k})\to e^{if_n(\mathbf{k})}u_n(\mathbf{k})$ and with respect to a shift of the zero of the Hamiltonian $H_k(\mathbf{r},\mathbf{k})\to H_k(\mathbf{r},\mathbf{k})+\epsilon$; we expect therefore that the many body orbital magnetization formula that we derive further below will share the same invariant properties.

At this point it is useful to make some further remarks that may be important. In the modern theory of orbital magnetization, they implement by heuristic argument the many-band covariant derivative [90, 113, 91] in order to make their final orbital magnetization

formulas gauge invariant. In a different context, namely in the study of the polarization current produced by a homogeneous but time-dependent electric field [126], the many-band covariant derivative is also implemented in the time dependent Schrödinger equation in order to consider in a gauge invariant manner the action of the position operator on the time-dependent and cell-periodic states.

As will be explicitly shown in the next subsection a boundary contribution that is encoded by the one-band covariant derivative is hidden within the first term of the right hand side of our Eq. (2.49) and it is attributed to the emerging momentum gradient operator $\partial_{\mathbf{k}}$ anomaly.

Having in mind that the combination of $(\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})| \mathbf{r} |u_m(\mathbf{k})\rangle)$ is the one that rigorously and explicitly gives the boundary contributions, if one does not take into account the off-diagonal position matrix elements $\langle u_n(\mathbf{k})| \mathbf{r} |u_m(\mathbf{k})\rangle$ within Eq. (2.50), thus contributions coming from the boundaries are lost, then it is evident from Eq. (2.50) (if this is substituted into Eq. (2.38)) that the magnetization will explicitly be expressed in terms of the many-band covariant derivative which will appear as an emerging *operator* within our formulation; it should be noted that the latter many-band covariant derivative is frequently used in the literature of the orbital magnetization in a heuristic manner that is based on the gauge invariance argument. This is therefore another possible deficiency of the heuristically found results in the literature that are based on the gauge invariance argument, namely that they ignore the off-diagonal position matrix elements $\langle u_n(\mathbf{k})| \mathbf{r} |u_m(\mathbf{k})\rangle$.

Finally, let us in what follows use our general result Eq. (2.49) (or Eq. (2.38)) to provide a general result for the total orbital magnetization and apply it to particular cases, by always keeping an eye on corresponding results in the literature. (The total final result is Eq. (2.55) below.) Let us, however, first start with the simplest one-band case.

One-band formula

In the one-band formula we assume that each combination of the off-diagonal matrix elements $(\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})| \mathbf{r} |u_m(\mathbf{k})\rangle)$ can be neglected, due to

$$\frac{\mathbf{S}_{nm}(\mathbf{k})}{(E_n(\mathbf{k}) - E_m(\mathbf{k}))} \to 0$$

which is a good approximation for conventional insulators with large band gap and negligible boundary contributions as evidenced from Eq. (2.40) and Eq. (2.42). If we assume that in Eq. (49) each of the non-Hermitian effect terms $\mathbf{S}_{nm}(\mathbf{k})$ is zero, then $\hbar \langle u_n(\mathbf{k})| \mathbf{v}_b |u_m(\mathbf{k})\rangle = -\langle u_n(\mathbf{k})| \mathbf{k}_b |u_m(\mathbf{k})\rangle$ must be satisfied, which in the simplest scenario is fulfilled whenever the electrons completely avoid the boundaries of the material and at the same time no band-crossings exist in the Brillouin zone.

In a different point of view, the assumption of zero value for the off-diagonal matrix elements, namely, $(\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})| \mathbf{r} |u_m(\mathbf{k})\rangle) = 0$ (*cf.* Eq. (2.50)) can be attributed to adiabatically deformed Bloch eigenstates $|\Psi_m(\mathbf{k})\rangle$ with respect to crystal momentum differentiation, that is, $|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle = \langle \Psi_m(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle |\Psi_m(\mathbf{k})\rangle$. The latter equality is satisfied

whenever each one of the off-diagonal amplitudes $\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle$ is zero which defines the restriction $\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle = 0$ for $n \neq m$. Substituting $\Psi_m(\mathbf{r},\mathbf{k}) = e^{i\mathbf{k}.\mathbf{r}}u_m(\mathbf{r},\mathbf{k})$ in the latter adiabatically deformed restriction we find the former assumption of zero value for each one of the off-diagonal matrix elements $(\mathbf{A}_{nm}(\mathbf{k}) - \langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_m(\mathbf{k})\rangle)$.

In this respect and within the one-band (adiabatically deformed) approximation, the many-body electron orbital magnetization (Eq. (2.49)) is given by

$$\mathbf{M} = -\frac{e}{2c\hbar(2\pi)^3}\sum_{E_n\leq\mu}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathrm{Im}\left[\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\times\left(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\right)\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle\right]d^3k \tag{2.52}$$

which satisfies the two basic invariant properties, namely, it is gauge invariant and invariant with respect to a shift of the zero of the Hamiltonian.

Although we have apparently dropped out any boundary contributions of the orbital magnetization by approximating the off-diagonal matrix elements $\mathbf{S}_{nm}(\mathbf{k})$ values as zero, there still exists an explicit boundary contribution within Eq. (2.52) which is attributed to the one-band covariant derivative. Specifically, if we use the definition of the one-band covariant derivative as given by Eq. (2.35) we can recast the integrand of Eq. (2.52) in the following form

$$\begin{aligned}\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right|\times\left(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\right)\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle &= \langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times\left(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\right)|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\\ &-i\,\mathbf{A}_{nn}(\mathbf{k})\times\langle u_n(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,.\end{aligned} \tag{2.53}$$

The second term on the right hand side of Eq. (2.53) gives a non-zero boundary contribution to the orbital magnetization only whenever the non-Hermitian effect with respect to the momentum gradient operator emerges, that is

$$\begin{aligned}\langle u_n(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle &= -\left\langle u_n(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k})^+ - H_k(\mathbf{r},\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle\\ &= -\frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\left((\mathbf{v}\,u_n)^*+u_n^*\,\mathbf{v}\right)\partial_{\mathbf{k}}u_n\,dS \neq 0\end{aligned} \tag{2.54}$$

where $u_n = u_n(\mathbf{r},\mathbf{k})$ are the cell-periodic eigenfunctions. If we further assume within a stricter approximation that the position operator $\mathbf{r}$ and the momentum gradient operator $\partial_{\mathbf{k}}$ are separately normal operators, that is the expectation value of the boundary momentum gradient operator $\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_n(\mathbf{k})\rangle$ is zero, $\langle u_n(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle = 0$, we can replace the covariant derivative entering Eq. (2.52) with the normal derivative that yields the orbital magnetization formula that was derived in Ref. [133] but with the correct opposite sign between the Hamiltonian operator and the energy. Alternatively, if one assumes from the beginning a solid with one band denoted by n then, the sum in the second term on the right side of Eq. (2.38), will not be present due to the one band closure rela-

tion $I = \iiint_{BZ} d^3k' \, |\psi_n(\mathbf{k}')\rangle \langle \psi_n(\mathbf{k}')|$, that must be used in Eq. (B.12) and subsequently in Eq. (B.13) leading to Eq. (4.31).

Many-band formula

In the many-band formula we don't a priori make any assumption with respect to the behavior of the position operator $\mathbf{r}$ and the momentum gradient operator $\partial_{\mathbf{k}}$, thus no restrictions for the wavefunctions' boundary conditions are made; the goal is to derive a general formula applicable to non-interacting electrons within topological materials, insulators or semimetals. In this respect, and because of Eq. (2.49), the many-band orbital magnetization formula of non-interacting electrons within a periodic solid is given by

$$\mathbf{M} = C_\phi \sum_{E_n \leq \mu} \iiint_{BZ} f_n \, \mathrm{Im} \left[\left\langle \widetilde{\partial}_{\mathbf{k}} u_n(\mathbf{k}) \right| \times \left(H_k(\mathbf{r}, \mathbf{k}) - E_n(\mathbf{k}) \right) \left| \widetilde{\partial}_{\mathbf{k}} u_n(\mathbf{k}) \right\rangle \right] d^3k$$
$$+ C_\phi \sum_{E_n \leq \mu} \sum_{m \neq n} \iiint_{BZ} f_n \, \mathrm{Im} \left[\frac{\mathbf{S}_{nm}(\mathbf{k})}{\left(E_n(\mathbf{k}) - E_m(\mathbf{k}) \right)} \times \langle u_m(\mathbf{k})| \, H_k(\mathbf{r}, \mathbf{k}) - E_n(\mathbf{k}) \, |\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle \right] d^3k \tag{2.55}$$

where $C_\phi = -\dfrac{e}{2c\hbar(2\pi)^3}$ and $f_n = f_n(\mathbf{k}, \mu)$, which is valid for arbitrary boundary conditions on the wavefunctions $u_m(\mathbf{r}, \mathbf{k})$. Orbital magnetization many-band formula Eq. (2.55) is the major result of this work; it rigorously provides within a quantum mechanical theoretical framework, and without any Wannier-localization approximation or heuristic extension [33], the manner in which one could generally model the orbital magnetization of periodic topological solids.

The energy differences in the denominator of the second term on the right hand side of Eq. (2.55) captures the possible local (in momentum space) gigantic orbital magnetization contributions in the vicinity of band crossings. These gigantic orbital magnetization contributions are predicted to occur only whenever band crossings exist along with an imbalance of electron accumulation at the opposite boundary surfaces of the material that creates a Hall voltage.

In order to verify the need of the presence of a Hall voltage, we will show that within PBSs for the wavefunctions (thus with no electron accumulation occurring) no gigantic local contribution of the orbital magnetization is possible even if the material is topological. Within PBCs the momentum gradient operator $\partial_{\mathbf{k}}$ does not break the domain of definition of the Hamiltonian, that is the wavefunctions $u_n(\mathbf{r}, \mathbf{k})$ and $\partial_{\mathbf{k}} u_n(\mathbf{r}, \mathbf{k})$ both satisfy periodic boundary conditions in $\mathbf{r}$-space. Indeed, the latter periodicity of $\partial_{\mathbf{k}} u_n(\mathbf{r}, \mathbf{k})$ can be deduced from the periodicity $u_n(\mathbf{r} + \mathbf{L}, \mathbf{k}) = u_n(\mathbf{r}, \mathbf{k})$, where $\mathbf{L}$ is the length of the material, by differentiating both sides with respect to the momentum $\mathbf{k}$ (which is treated as an independent parameter in the assumed thermodynamic limit) that gives $\partial_{\mathbf{k}} u_n(\mathbf{r} + \mathbf{L}, \mathbf{k}) = \partial_{\mathbf{k}} u_n(\mathbf{r}, \mathbf{k})$. In this fashion, each one of the matrix elements $\langle u_n(\mathbf{k})| \, \mathbf{k}_b \, |u_m(\mathbf{k})\rangle$ is zero due to symmetry, and any emergence of the non-Hermitian effect owing to the momentum gradient operator $\partial_{\mathbf{k}}$

anomaly is prohibited. We point out that the absence of this non-Hermitian effect is invariant with respect to twisted boundary conditions of the form $u_n(\mathbf{r}+\mathbf{L},\mathbf{k}) = e^{if(\mathbf{L},\mathbf{k})}u_n(\mathbf{r},\mathbf{k})$ as long as the system is closed.

By recasting the $\langle u_m(\mathbf{k})|\, H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle$ term entering the right hand side of Eq. (2.55) in the form

$$\begin{aligned}\langle u_m(\mathbf{k})|\, H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle \;&=\; (E_m(\mathbf{k}) - E_n(\mathbf{k}))\langle u_m(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle \\ &\quad - \langle u_m(\mathbf{k})|\,\mathbf{k}_b\,|u_n(\mathbf{k})\rangle\,, \end{aligned} \tag{2.56}$$

as well as by taking into account the non-Hermitian boundary term as given by Eq. (2.42)

$$\mathbf{S}_{nm}(\mathbf{k}) = \hbar\,\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle + \langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_m(\mathbf{k})\rangle\,,$$

then, under periodic boundary conditions the boundary momentum gradient "operator" $\mathbf{k}_b$ matrix elements given by Eq. (2.48) are zero $\langle u_m(\mathbf{k})|\,\mathbf{k}_b\,|u_n(\mathbf{k})\rangle = 0$, and the multi-band and unrestricted orbital magnetization formula Eq. (2.55) takes the form

$$\begin{aligned}\mathbf{M} \;=\; &-\frac{e}{2c\hbar(2\pi)^3}\sum_{E_n\le\mu}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathrm{Im}\left[\,\langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,\right]d^3k \\ &+\frac{e}{2c(2\pi)^3}\sum_{E_n\le\mu}\sum_{m\neq n}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathrm{Im}\left[\,\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle\times\langle u_m(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,\right]d^3k\end{aligned} \tag{2.57}$$

where we have also replaced the one-band covariant derivative with the normal one

$$\left\langle\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle = \langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle \tag{2.58}$$

due to $\langle u_n(\mathbf{k})|\,\mathbf{k}_b\,|u_n(\mathbf{k})\rangle = 0$ in accordance with Eq. (2.53) and Eq. (2.54).

It is now clear from Eq. (2.57) that, whenever a Hall voltage is zero owing to periodic boundary conditions, the orbital magnetization cannot acquire local gigantic values, even if the material is topological with non-trivial band structure crossings, while whenever imbalance of electron charge is formed, local gigantic orbital magnetization contributions near the band crossings are generically expected to occur.

It is also interesting to point out that, whenever the material's realistic boundary conditions are periodic, by expanding the cell periodic functions in a Fourier series over all reciprocal lattice vectors $\mathbf{G}$, namely, $u_n(\mathbf{r},\mathbf{k}) = \sum_{\mathbf{G}} C_n(\mathbf{k},\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{r}}$, it is evident that $\partial_{\mathbf{k}}u_n(\mathbf{r},\mathbf{k})$ is periodic in space (as well as $u_n(\mathbf{r},\mathbf{k})$ and the Hamiltonian $H_k(\mathbf{r},\mathbf{k})$). By then using the normalization convention $\langle\Psi_n(t,\mathbf{k})|\Psi_n(t,\mathbf{k})\rangle = \langle u_n(\mathbf{k})|u_n(\mathbf{k})\rangle_{cell} = 1$, that is, assume a Bloch state in the form $|\Psi_n(t,\mathbf{k})\rangle = \frac{1}{\sqrt{N}}\,e^{-\frac{1}{\hbar}E_n(\mathbf{k})t}\,e^{i\mathbf{k}.\mathbf{r}}\,|u_n(\mathbf{k})\rangle$, we replace $|u_n(\mathbf{k})\rangle \to \frac{1}{\sqrt{N}}\,|u_n(\mathbf{k})\rangle$ in all terms in Eq. (2.57) (the initially assumed eigenstate was nor-

malized over the volume V without taking into account the cell normalization convention, therefore it defers by a factor $\frac{1}{\sqrt{N}}$) and exploiting the symmetry of the integrands, the orbital magnetization formula it truncates into the form

$$\mathbf{M} = -\frac{e}{2c\hbar(2\pi)^3}\sum_{E_n\leq\mu}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathrm{Im}\left[\,\langle\partial_{\mathbf{k}}u_n(\mathbf{k})|\times\left(H_k(\mathbf{r},\mathbf{k})-E_n(\mathbf{k})\right)|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle_{cell}\,\right]d^3k$$
$$+\frac{e}{2c(2\pi)^3}\sum_{E_n\leq\mu}\sum_{m\neq n}\iiint_{BZ} f_n(\mathbf{k},\mu)\,\mathrm{Im}\left[\,\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle_{cell}\times\langle u_m(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle_{cell}\,\right]d^3k$$

where all space integrals are performed within one primitive cell, and the off-diagonal matrix elements of the boundary velocity are given by

$$\langle u_n(\mathbf{k})|\,\mathbf{v}_b\,|u_m(\mathbf{k})\rangle = -\frac{1}{2}\oiint_{cell}\mathbf{r}\left((\mathbf{v}\,u_n)^*u_m+u_n^*\mathbf{v}\,u_m\right)\cdot d\mathbf{S} \tag{2.59}$$

in accordance with Eq. (2.47), where we have taken into account that $u_n(\mathbf{r},\mathbf{k})$ are periodic over the unit cell boundaries. Eq. (2.59) can be thought as the $\mathbf{k}$-space analog of Eq. (2.26).

It is worth comparing (i) the orbital magnetization formula of periodic solids that is given by Eq. (2.57) with the one that was proposed in Ref.[33] by a heuristic argument, as well as, (ii) compare the general orbital magnetization formula Eq. (2.55) with the one derived in Ref. [92], where they propose a theoretical approach to discriminate the separate contributions of the total magnetization, that is, the one contribution coming from the bulk states and the other coming from the surface states.

(i) Orbital magnetization formula Eq. (2.57), is relaxed from any Wannier localization approximation as well as from the periodic gauge approximation, and it is therefore valid for topological materials as long as the electrons' wavefunctions satisfy periodic boundary conditions (zero Hall voltage) over the materials boundaries. The heuristic extension of the orbital magnetization formula [133] by an additional term, assumed to be proportional to the chemical potential, that was made in Ref. [33] in order to model the orbital magnetization of Chern insulators and metals, is rigorously given by the second term of the right hand side of Eq. (2.57). This term has explicit boundary contributions due to the off-diagonal matrix elements of the boundary velocity operator $\mathbf{v}_b$ which are not zero due to the emerging non-Hermitian effect of the position operator $\mathbf{r}$ that becomes anomalous within periodic boundary conditions, as should be expected.

(ii) In Ref. [92] they use the standard circulation operator together with the spectral resolution of the Hamiltonian, and as a result of this spectral resolution, the (undefined) diagonal matrix elements of the position operator are excluded from the circulation operator formula; one can therefore evaluate the standard circulation operator expectation value (even in the thermodynamic limit within PBCs), hence one can calculate the orbital magnetization. Due to the spectral resolution within the circulation operator, the assumed orbitals must satisfy $\langle\phi_n|\,\mathbf{v}\,|\phi_n\rangle = -\langle\phi_n|\,\mathbf{v}_b\,|\phi_n\rangle = 0$ owing to $\langle\phi_n|\,\mathbf{v}_b\,|\phi_n\rangle = 0$, therefore, the orbitals that are

taken into account indeed describe bound bulk states. Then, Ref. [92] extracted their result from the semi-classical orbital magnetization formula given in Ref. [149], and they stated that the remaining part gives the boundary contribution of the orbital magnetization. The theoretical method that they use rests on the argument that the semi-classical orbital magnetization formula given in Ref. [149] correctly gives the total (bulk and boundary) orbital magnetization of non interacting electrons. We argue that this may not be entirely true due to the approximations that are made during the derivation of the Ref. [149] orbital magnetization formula. First, as we have shown in the derivation of Eq. (2.51), the structure of the semi-classical electron's orbital magnetic moment can be attained by the unrestricted quantum formula Eq. (2.49) whenever the electron's state is a localized bulk state, that is, when the electron completely avoids the boundaries of the system where it is enclosed. Therefore, the orbital magnetization that is evaluated only by taking into account the electron's semi-classical orbital magnetic moment, does not account for magnetization contributions coming from all possible states, i.e. does not take into account topologically non trivial extended states. On the other hand, the semi-classical orbital magnetization formula given in Ref. [149], namely as the derivative of the electrons' total energy with respect to the magnetic field (at zero magnetic field), besides the contribution coming from the electrons' intrinsic orbital moment, it also acquires two extra terms that come up due to the modified density of states. One is attributed to the explicit magnetic field dependence of the density of states and the other is due to the resulting change in the Fermi volume. The two extra terms cannot carry any topologically non trivial information, on one hand due to the localized wavepacket employed, and on the other hand due to the explicit assumption $\boldsymbol{\nabla}_k \cdot \boldsymbol{\Omega}_n(\mathbf{k}) = 0$, where $\boldsymbol{\Omega}_n(\mathbf{k})$ is the Berry curvature, that was made in Ref. [149] for deriving the modified density of states (hence Berry type of monopoles, crucial for the non trivial topology, were ignored). In this framework, these two extra terms most probably represent corrections to the semi-classical orbital magnetization formula and do not carry any topologically non trivial information. We argue therefore that, although the method followed in Ref. [92] is reasonable, the findings do not represent the orbital magnetization of topologically non trivial surface states, but they instead provide trivial corrections to the orbital magnetization for non localized states. This discussion here is given so that our results Eq. (2.55) or Eq. (2.57) can be directly compared with the state of the art results.

Chapter 3

Defining operators in an extended framework: The spin current

The general viewpoint and methodology of the previous Chapter, and in particular the definition of appropriate boundary operators that reflect the non-Hermitian effect, is here applied to spin physics. The coherent accumulation and motion of magnetic moments associated with the spin of electrons, is a central concept of spintronics in condensed matter systems in the quest of processing and storing information within the spin degree of freedom. The pure motion of spins has the unique property that it uses minimal charge carriers to deliver substantial angular momentum, thus generating the least possible Joule heat. In spite of the primary importance of coherent spin accumulation and spin transport, there does not exist up to now a generally accepted agreement on the correct definition of the corresponding operators, namely, the spin-accumulation rate of change operator and the spin-current operator [108, 40, 128, 121, 125, 24, 44, 4, 23]. The reason for this controversy is that in any closed system that lacks spin-rotation invariance (which i.e. can be broken by spin-orbit interaction or by spin-spin interactions) it does not exist any given direction in the material along which the spin is conserved $S_n\Psi(\mathbf{r},t) \neq \pm\frac{\hbar}{2}\Psi(\mathbf{r},t)$, where $S_n = \mathbf{S}\cdot\boldsymbol{n}$ is the projection of the spin in the given direction $\boldsymbol{n}$; therefore, no local spin magnetization conservation law can be derived in a form of a continuity equation, and as a consequence it is said that, no quantum mechanical spin-current operator can unambiguously be well-defined. The technical reason for this discrepancy is the bulk source term $\Psi^\dagger(\mathbf{r},t)\frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{S}]\Psi(\mathbf{r},t) \neq 0$ that enters the local continuity equation which breaks the conservation of spin density $\Psi^\dagger(\mathbf{r},t)\mathbf{S}\Psi(\mathbf{r},t)$ with respect to position coordinates, in contrast to the electron charge density $\Psi^\dagger(\mathbf{r},t)e\Psi(\mathbf{r},t)$ that is conserved. Most of the theoretical methods used so far with respect to the proper definition of the spin-current operator, use the local spin density and rely on local continuity-like equations with bulk source terms; while the divergence term of certain quantities entering them is introduced without any rigorous and explicit consideration of the material's boundaries with respect to operator's behavior and to its macroscopic expectation values.

In our point of view, and as we will actually show, the bulk source terms are not quite a problem in the quest of the proper definition of an observable's operator; rather an expected

term, namely the divergence term entering the local continuity-like equation (commonly used in the quest of the spin current operator) is a real "problem". In particular, the divergence term is an emerging quantity that comes up due to the non-Hermitian effect and is generally overlooked in the standard theory of Hermitian operator's definition within Schrödinger picture, that is, its coordinate (volume) integration is frequently set to zero which is rarely the case.

Doubts about the reality of the dissipationless spin transport in equilibrium ground-states in Rashba mediums as an outcome of the conventional spin current have been raised [108, 125, 129]. By using a local continuity-like equation with a source term, Ref. [128] show that in order to completely describe the transport of the spin density $\frac{d}{dt}\Psi^{\dagger}(\mathbf{r},t)\,\mathbf{S}\,\Psi(\mathbf{r},t)$ one has to introduce the angular spin current density apart from the linear spin current. By using a restrictive assumption, namely, that the expectation value of the bulk spin torque is zero, as well as that the spin torque density over the system's boundaries can be neglected, Ref. [121] have proposed an alternative spin current operator. This is defined as the time derivative of the spin displacement operator $\frac{d(\mathbf{r}S_z)}{dt}$ (where the Heisenberg picture is implied and the z component of the spin is used), with the effective spin current density $\mathrm{Re}\Psi^{\dagger}(\mathbf{r})\frac{d(\mathbf{r}S_z)}{dt}\Psi(\mathbf{r})$ satisfying a continuity equation and supporting important conclusions concerning conservation of spin currents [127, 155, 147]. Compared to the conventional spin current, the Ref. [121] definition is more complete as it explicitly takes into account an additional contribution, which depends explicitly on the spin torque and is given by $\frac{1}{2}\left(\mathbf{r}\,\tau_z(\mathbf{r},t)+\tau_z(\mathbf{r},t)\,\mathbf{r}\right)$ where $\tau_z(\mathbf{r},t)$ is the spin torque in the z direction. As we will show, and based on our extended theoretical framework for defining operators, the boundary spin torque density that is neglected by Ref. [121], is rigorously attributed to a non-Hermitian effect boundary term that has not pointed out yet and we explicitly define it in this work. This boundary term gives the expectation value of a boundary spin torque, which must be zero in order for this spin current operator to have a well defined value. In this respect, whenever both limitations are satisfied, the time derivative of the spin displacement operator has a well-defined value in periodic systems (where the spin torque $\tau_z(\mathbf{r},t)$ is a periodic quantity) with respect to Bloch states in the thermodynamic limit. On the contrary, if any one of the spin torque expectation values, either the bulk or the boundary one, is not zero, then, this spin current behaves as an extensive quantity of a periodic system and scales linearly with the system's size, therefore has an undefined value. As a matter of fact and as we will show, the two limitations for the validity of this spin current are attributed to its definition, that is, it is an observable that is generally origin dependent unless the bulk and the boundary spin torques expectation values happen to be zero. In this respect, the vanishing of the bulk and the boundary spin torques, makes this spin current operator behave as a proper, intensive operator.

The purpose of this chapter is twofold, first to show a rigorous and unambiguous theoretical framework within Schrödinger picture of how one may define operators (in closed systems) in an extended manner without the need of any conservation law by defining additional boundary operators that take into account the non-Hermitian effect terms, and second,

to provide a rigorous definition for the intrinsic spin-current operator.

In this quest we will show that: (i) the boundary contributions are explicitly attributed to anomalies of the spin and position operators, (ii) the boundary contributions are encoded by boundary operators that we will explicitly define, (iii) the expectation values of the boundary operators are extremely sensitive to the boundary conditions of the spinor wavefunctions (as they are calculated by boundary integrals), and finally, (iv) for stationary states of closed systems, there exist a quantum mechanical relation between the bulk and the boundaries that has the form of a gain-loss detailed balance relation; whenever the bulk of the system behaves as a source, the boundaries operates as a sink and *vice versa*.

Motivated by classical mechanics continuous medium (hydrodynamical) theories, where angular momentum cannot be transferred (propagate) within a medium whenever the resultant local torque is zero in each medium position at every instant, we expect that, in quantum systems, the spin density of an equilibrium state can propagate only whenever local, non zero spin-torques, exist within the system. In this framework, we are defining the intrinsic spin current operator as the time derivative of the correlation function between position and spin. The expectation value of the intrinsic spin current operator have three basic properties, namely: (i) its value is independent of the position origin, (ii) it has a well defined value without any restrictions with respect to periodic systems and Bloch representation in the thermodynamic limit, and finally, (iii) for systems that lacks local spin-torques (in the bulk and over boundaries), the value of the intrinsic spin current turns to zero with respect to a stationary state (provided that the stationary state is a spin eigenstate also); in other words, whenever the correlation between position and spin is a constant quantity, then, the intrinsic spin current turns to zero.

In the chemists' literature, although they had never defined any operator in an extended manner, they had explicitly taken into account boundary contributions in the so-called atomic theorems [11, 13, 12] in order to determine atom properties viewed as parts (fragments) of a molecule. This was made within the quantum action principle generalized to an open system, that explicitly gives boundary and "bulk" contributions. The boundary contributions are formalized as surface integrals (fluxes) of certain generalized currents and have been used for example in the determination of atomic dielectric polarization [15] and atomic magnetic susceptibility [14].

In the mathematical physics literature, paradoxes related to anomalous operators entering the Ehrenfest theorem have been noticed [47, 48, 66], but to date there has not appeared any generally accepted theoretical framework for taking into account these operator anomalies, within quantum formulas that provide observables in condensed matter systems. Specifically, every assumed closed system $\langle\Psi(t)|\Psi(t)\rangle = 1$ evolves by a Hamiltonian that is Hermitian $H(\mathbf{r},t)^{+} = H(\mathbf{r},t)$ with respect to the states $\Psi(\mathbf{r},t)$ that belong within the domain of its definition D_H, which form the given Hilbert space. An operator $\mathbf{G}$ that enters the Ehrenfest theorem causes the non-Hermitan effect, whenever the states $\mathbf{G}\Psi(\mathbf{r},t)$ do not belong within the given Hilbert space, that is, $H(\mathbf{r},t)^{+}(\mathbf{G}\Psi(\mathbf{r},t)) \neq H(\mathbf{r},t)\,(\mathbf{G}\Psi(\mathbf{r},t))$, which is true

whenever the states $\mathbf{G}\Psi(\mathbf{r},t)$ and $\Psi(\mathbf{r},t)$ do not satisfy the same boundary conditions, and, as result a residue term remains in the theorem [47, 48, 66].

In this chapter, we are rigorously considering these residue terms in the Ehrenfest theorem within a theoretical framework that takes into account the non-Hermitian effect contributions that are explicitly attributed to additional boundary operators that we define. We will show that, for every closed system and in position representation, a boundary operator expectation value is explicitly evaluated by a boundary integral over the terminated boundaries of the system; such a boundary operator therefore rigorously gives an additional boundary contribution to the quantum equation of motion of the observable's expectation value.

A common paradigm of such an anomalous operator is the position operator $\mathbf{r}$ whenever periodic boundary conditions (Born-von Kármán) are adopted for the wavefunctions $\Psi(\mathbf{r}+\mathbf{L},t)=\Psi(\mathbf{r},t)$. These boundary conditions make the position operator $\mathbf{r}$ an anomalous operator due to the fact that the state $\mathbf{r}\Psi(\mathbf{r},t)$ breaks the periodicity, that is, $(\mathbf{r}+\mathbf{L})\Psi(\mathbf{r}+\mathbf{L},t)\neq\mathbf{r}\Psi(\mathbf{r},t)$.

On the the other hand for spinor wavefunctions $\Psi(\mathbf{r},t)=(\Psi_1(\mathbf{r},t),\ \Psi_2(\mathbf{r},t))^T$, the spin $\mathbf{S}$ (matrix) operator behaves as a normal operator and preserves the periodic boundary conditions owing to $\mathbf{S}\Psi(\mathbf{r}+\mathbf{L},t)=\mathbf{S}\Psi(\mathbf{r},t)$, not leaving therefore any non-Hermitian boundary residue in the Ehrenfest theorem. But, if one assumes a less restrictive boundary condition, namely, periodic boundary condition for the probability density of the spinor wavefunction $\Psi^\dagger(\mathbf{r}+\mathbf{L},t)\Psi(\mathbf{r}+\mathbf{L},t)=\Psi^\dagger(\mathbf{r},t)\Psi(\mathbf{r},t)$, then, the spinor wavefunction is periodic up to an $SU(2)$ phase. Specifically, assuming a domain of definition D_H where each spinor wavefunction is periodic up to a specific $SU(2)$ phase, then, each spinor wavefunction within the domain must satisfy

$$\Psi(\mathbf{r}+\mathbf{L},t)=e^{-i\frac{\mathbf{S}\cdot\boldsymbol{n}}{\hbar}\varphi}\Psi(\mathbf{r},t)=U(S_n,\varphi)\Psi(\mathbf{r},t), \tag{3.1}$$

where $\boldsymbol{n}$ is the direction about which the spinor wavefunction is rotated by an angle φ. Therefore, a quantum state $\mathbf{S}\Psi(\mathbf{r},t)$ belongs to the domain of the boundary conditions (given by Eq. (3.1)), when it satisfies $\mathbf{S}\Psi(\mathbf{r}+\mathbf{L},t)=U(S_n,\varphi)\mathbf{S}\Psi(\mathbf{r},t)$. Acting on both sides of Eq. (3.1) with $\mathbf{S}$ gives

$$\mathbf{S}\Psi(\mathbf{r}+\mathbf{L},t)=U(S_n,\varphi)\mathbf{S}\Psi(\mathbf{r},t)+[\mathbf{S},U(S_n,\varphi)]\Psi(\mathbf{r},t), \tag{3.2}$$

thus, the quantum state $\mathbf{S}\Psi(\mathbf{r},t)$ breaks the boundary conditions when $[\mathbf{S},U(S_n,\varphi)]\neq 0$. In this framework, the spin operator $\mathbf{S}$ becomes anomalous and leaves a (non-Hermitian) residue term in the Ehrenfest theorem which we will explicitly take into account. It is useful to note that this non-Hermitian effect of the spin $\mathbf{S}$ operator can be used as a probe (detector) for the spin Hall effect, where different spin orientations over the material's boundaries are present (due to bulk spin torques that are exerted on the electron's wavefunction as a result of strong spin-orbit interaction) but the probability density is periodic.

Provided that the non-Hermitian effect boundary term in the Ehrenfest theorem is taken

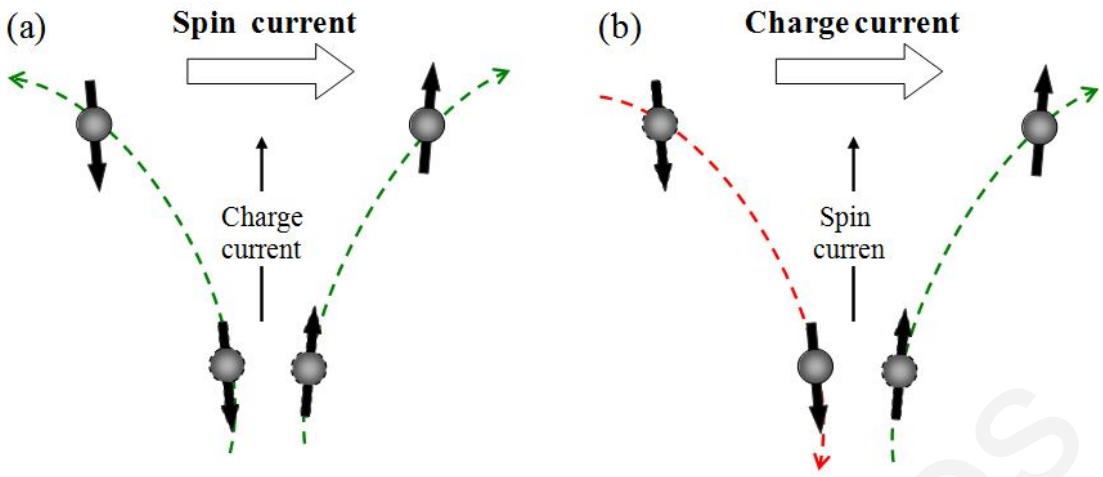

Figure 3.1: Interacting charge and spin currents. In (a) a longitudinal charge current is converted into transverse spin current by the Spin Hall effect. In (b) a longitudinal spin current is converted into transverse charge current by the inverse Spin Hall effect.

into account, one can unambiguously set up a self-consistent quantum equation of motion (with respect to the expectation value) for any spin dependent quantity. In this framework, for equilibrium, stationary and pure states, the expectation value of any extended operator is always zero (which is not generally true for the standard bulk operators), therefore, one can work in a quantum mechanical framework (as a counterpart of the statistical mechanical one) and derive reciprocal factors that relate the charge current to a produced spin current (spin Hall effect) and *vice versa*, relating therefore the spin current to a produced charge current (inverse spin Hall effect) [121, 56, 142, 71] as depicted in Fig.3.1. Specifically, for a quantum system that is near equilibrium and evolves irreversibly into equilibrium, where all extended operators have zero expectation value, one can employ a phenomenological linear dissipation approximation equation for the time derivative of an extended operator expectation value, and then derive Onsager reciprocal relations [99, 100, 32] between (different) coupled transport processes.

3.1 Operators within Schrödinger picture

3.1.1 Extended operator

By taking into account, (i) the time-evolution of the state under consideration (in Schrödinger picture), and (ii) the boundary conditions of the (spinor) wavefunction that belongs within a given Hilbert space D_H (of closed systems $\frac{d}{dt}\langle\Psi(t)|\Psi(t)\rangle = 0$), we suggest that one may readily define an operator $\boldsymbol{\mathcal{O}}_{ext}$ in an extended theoretical framework by using the equation of motion

$$\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \frac{d}{dt} \langle \mathbf{G} \rangle \,. \tag{3.3}$$

The equation Eq. (3.3) is always valid without any subtleties or restrictions involved provided that, in the definition of the extended operator $\boldsymbol{\mathcal{O}}_{ext}$, an additional, boundary operator

$\boldsymbol{\mathcal{O}}_b$ that emerges due to a possible non-Hermitian behavior of the Hamiltonian $H(\mathbf{r},t)$ is always taken into account. In this framework, the extended operator is given by

$$\boldsymbol{\mathcal{O}}_{ext} = \boldsymbol{\mathcal{O}} + \boldsymbol{\mathcal{O}}_b \tag{3.4}$$

where

$$\boldsymbol{\mathcal{O}} = \frac{i}{\hbar}\left[H(\mathbf{r},t), \mathbf{G}\right] + \frac{d\mathbf{G}}{dt} \tag{3.5}$$

is the standard (bulk) operator and

$$\boldsymbol{\mathcal{O}}_b = \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\right)\mathbf{G} \tag{3.6}$$

is the boundary operator. Although the explicit form of $H(\mathbf{r},t)^{+}$ may not be found when the given Hermitian operator $\mathbf{G}$ becomes anomalous (therefore we cannot define it as a regular operator), we can always evaluate the expectation value of the boundary operator $\langle\boldsymbol{\mathcal{O}}_b\rangle$ by employing the explicit form of the Hamiltonian operator $H(\mathbf{r},t)$. In this fashion, we assume a one electron spinfull Hamiltonian $H(\mathbf{r},t)$ given by

$$H(\mathbf{r},\mathbf{t}) = \frac{1}{2m}\boldsymbol{\Pi}(\mathbf{r},t)^2 + V(\mathbf{r},t) - \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t) + \boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})\cdot\boldsymbol{\Pi}(\mathbf{r},t) \tag{3.7}$$

where, $\boldsymbol{\Pi}(\mathbf{r},t) = \mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)$ is the kinematic momentum operator and $\boldsymbol{\sigma}$ the vector Pauli matrix. The third term on the right of Eq. (3.7) is the Zeeman term representing the interaction of the electron's spin with the magnetic field, while $\boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})$ in the fourth term represents the interaction of the electron's spin with the orbital motion. For the non-relativistic limit of the Dirac equation and pure spin-orbit interaction, that term is given by

$$\boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma}) = \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V(\mathbf{r},t). \tag{3.8}$$

As analytically shown in Appendix D: by (i) working in the position representation, (ii) using the explicit form of the Hamiltonian operator Eq. (3.7), and by (iii) taking into account that the scalar and vector potentials are real quantities, after a straightforward integration by parts (assuming a 3D system), the volume integration giving the expectation value of the boundary operator $\langle\boldsymbol{\mathcal{O}}_b\rangle$ is always transformed to a surface integral of a generalized vector current $\mathbf{J}_{\mathbf{G}}(\mathbf{r},t,\mathbf{n})$ over the terminated boundary surface S of the system (on which the boundary conditions of the spinor wavefunctions are imposed), given by

$$\begin{aligned}\langle\boldsymbol{\mathcal{O}}_b\rangle &= \frac{i}{\hbar}\left(\langle H(\mathbf{r},t)\Psi(t)|\mathbf{G}\Psi(t)\rangle - \langle\Psi(t)|H(\mathbf{r},t)\mathbf{G}\Psi(t)\rangle\right)\\ &= -\oiint_S \mathbf{J}_{\mathbf{G}}(\mathbf{r},t,\mathbf{n})\,ds.\end{aligned} \tag{3.9}$$

The generalized vector current $\mathbf{J_G}(\mathbf{r},t,\mathbf{n})$ is given from

$$\mathbf{J_G}(\mathbf{r},t,\mathbf{n}) = \frac{1}{2}\mathbf{n}\cdot\left((\mathbf{v}\Psi(\mathbf{r},t))^\dagger + \Psi(\mathbf{r},t)^\dagger\mathbf{v}\right)\mathbf{G}\Psi(\mathbf{r},t), \tag{3.10}$$

where $\mathbf{v}$ is the standard (bulk) velocity operator given by

$$\mathbf{v} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}\right] = \frac{\mathbf{\Pi}(\mathbf{r},t)}{m} + \boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma}) \tag{3.11}$$

and $\mathbf{n}$ is a unit vector that is locally normal to the boundary surface that encloses the system.

Due to the structure of the generalized vector current, that is $\mathbf{J_G}(\mathbf{r},t,\mathbf{n}) = (\mathbf{n}\cdot\mathbf{a})\mathbf{b}$, where $\mathbf{a} = \frac{1}{2}\left((\mathbf{v}\Psi(\mathbf{r},t))^\dagger + \Psi(\mathbf{r},t)^\dagger\mathbf{v}\right)$ and $\mathbf{b} = \mathbf{G}\Psi(\mathbf{r},t)$, it can always be rewritten as $\mathbf{J_G}(\mathbf{r},t,\mathbf{n}) = \mathbf{n}\cdot\overleftrightarrow{\mathbf{J}}_\mathbf{G}(\mathbf{r},t)$ where $\overleftrightarrow{\mathbf{J}}_\mathbf{G}(\mathbf{r},t)$ is a generalized second rank (Cartesian) tensor current that is given by the dyadic product of the vectors $\mathbf{a}$ and $\mathbf{b}$ and is denoted as $\mathbf{a}\,\mathbf{b}$. In this respect, the generalized tensor current is given by

$$\overleftrightarrow{\mathbf{J}}_\mathbf{G}(\mathbf{r},t) = \frac{1}{2}\left((\mathbf{v}\Psi(\mathbf{r},t))^\dagger + \Psi(\mathbf{r},t)^\dagger\mathbf{v}\right)\mathbf{G}\Psi(\mathbf{r},t) \tag{3.12}$$

and the expectation value of the boundary operator can be recast in the form of a flux of a generalized tensor current given by

$$\langle\boldsymbol{\mathcal{O}}_b\rangle = -\oiint_S d\mathbf{s}\cdot\overleftrightarrow{\mathbf{J}}_\mathbf{G}(\mathbf{r},t). \tag{3.13}$$

We note that, whenever the operator $\mathbf{G}$ that enters the Ehrenfest theorem is a scalar operator, the (second rank) tensor generalized current Eq. (3.12) is truncated to a (first rank) vector quantity.

Although our findings are based on the model Hamiltonian Eq. (3.7) which is continuous and quadratic in momentum (due to the kinetic energy), they can be modified and used to topological materials with linear dispersion relation. In this framework, we may ignore the kinetic energy term in Eq. (3.7) and use the approximated model Hamiltonian

$$H(\mathbf{r},\mathbf{t}) = \boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})\cdot\mathbf{\Pi}(\mathbf{r},t) + V(\mathbf{r},t) - \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t),$$

where the ferromagnetic properties of the solid can likewise be model with a mean Zeeman-like filed that acts on the electrons' spins. In this approximation, the expectation value of the boundary operator $\langle\boldsymbol{\mathcal{O}}_b\rangle$ is readily evaluated by Eq. (3.12) – (3.13) and the velocity operator is given by $\mathbf{v} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}\right] = \boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})$.

The simplest example to see the necessity of the boundary operator $\boldsymbol{\mathcal{O}}_b$ is the motion of a spinless and free electron. If we assume that the motion is described by a common eigenstate of the Hamiltonian $H(\mathbf{r})$ and momentum $\mathbf{p}$, thus the electron has a well defined energy E and momentum $\hbar\mathbf{k}$, then, by using $\mathbf{G} = \mathbf{r}$ in Eq. (3.3), we deduce that the equation of motion of the electron's main position $\frac{d}{dt}\langle\mathbf{r}\rangle = 0$ is not satisfied if we don't

take into account the boundary velocity expectation value, owing to $\langle \mathbf{p} \rangle = \hbar \mathbf{k} \neq m \frac{d}{dt} \langle \mathbf{r} \rangle$. Specifically, explicit calculation of the bulk velocity operator expectation value Eq. (3.9) gives $\langle \boldsymbol{\mathcal{O}}_b \rangle = -\hbar \mathbf{k}$, verifying that the expectation value of the extended (velocity) operator operator is zero $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \frac{d}{dt} \langle \mathbf{r} \rangle = 0$, as it should be for every stationary state according to Eq. (3.3). Similarly, after a time lapse T, the change of an operator $\mathbf{G}$ expectation value is correctly evaluated without any ambiguities by taking into account the extended operator definition

$$\Delta \langle \mathbf{G} \rangle = \int_{t}^{t+T} \langle \boldsymbol{\mathcal{O}}_{ext} \rangle \, dt. \tag{3.14}$$

At this point, it is helpful to see the physical as well as the mathematical origin of the boundary operator with respect to closed systems $\frac{d}{dt} \langle \Psi(t) | \Psi(t) \rangle = 0$. In this framework, we assume that, the potentials are created by known sources so that, either they are inside the system, or they lie in the environment and their potentials penetrate into the system:

(i) From a physical point of view we argue that, in every closed quantum system, the boundary operator expectation value $\langle \boldsymbol{\mathcal{O}}_b \rangle$ captures the exchange of the observable in question between the system and its environment. Specifically, in every closed system of indistinguishable particles we may have entering and leaving particles, provided that the net particles' number always remains constant. Each entering or leaving particle may carry different, i.e. momentum, angular momentum, spin or kinetic energy, which may result in a change of the system's global observable quantity in quest, but without changing the net particle's number of the particles. In this framework, we may define two categories of closed quantum systems, namely, the ones that are closed and isolated and the ones that are closed but not isolated. In the former ones, the wavefunction as well as all its spatial derivatives are zero over the system's boundaries, thus, the boundary operator expectation value with respect to any arbitrary operator $\mathbf{G}$ always turns zero value as evidence from Eq. (3.12) –(3.13); in topological systems, it seems that this is rarely the case. On the other hand, the latter ones, closed but not isolated systems, fulfill only the basic requirement, that is, the system's net particle number is held fixed. In this respect, by replacing $\mathbf{G} \to I$ in Eq. (3.3) and assuming $\frac{d}{dt} \langle \Psi(t) | \Psi(t) \rangle = 0$, as well as by taking into account the time evolution of the quantum system (thus the potentials are being taken into account), one finds the condition $\left\langle \boldsymbol{\mathcal{O}}_b^{(I)} \right\rangle = - \oiint_S d\mathbf{s} \cdot \mathbf{J}_I(\mathbf{r}, t) = 0$ which all closed systems must satisfy. Those wavefunctions $\Psi(\mathbf{r}, t)$ that fulfill proper boundary conditions over the system's boundaries and satisfy $\left\langle \boldsymbol{\mathcal{O}}_b^{(I)} \right\rangle = 0$, form the given Hilbert space of closed systems, or equivalently, form the domain of definition of the Hermitian Hamiltonian D_H. Although these systems are closed, their isolation is broken whenever there exist a nonzero outgoing (or incoming) boundary current of a physical quantity, such as momentum, orbital angular momentum, spin or kinetic energy. This phenomenon is captured by the corresponding boundary operators that result into non zero currents $\langle \boldsymbol{\mathcal{O}}_b \rangle = - \oiint_S d\mathbf{s} \cdot \overleftrightarrow{\mathbf{J}}_{\mathbf{G}}(\mathbf{r}, t) \neq 0$. Therefore, for any physical quantity, the boundary operator expectation value Eq. (3.13) represents the outgoing (or incoming) boundary current of the observable quantity in ques-

tion, the standard bulk operator expectation value Eq. (3.5) represents the creation (or sink) of this current within the bulk, and the extended operator expectation value Eq. (3.4) gives the net, global current of this physical quantity for the system.
(ii) From a mathematical point of view [47, 48], the boundary operator is attributed to an emerging non-Hermitian effect due to the operator $\mathbf{G}$ that breaks the domain of definition of the Hermitian Hamiltonian. In this language, $H(\mathbf{r},t)^{+}\Psi(\mathbf{r},t) = H(\mathbf{r},t)\Psi(\mathbf{r},t)$ with respect to the spinor wavefunctions $\Psi(\mathbf{r},t)$ that satisfies certain boundary conditions and fulfills $\left\langle \boldsymbol{\mathcal{O}}_b^{(I)} \right\rangle = 0$. On the other hand, the wavefunctions $\mathbf{G}\Psi(\mathbf{r},t)$ may satisfy such different boundary conditions over the system's boundaries, that they don't belong within the given Hilbert space of the closed system. In this fashion, the Hamiltonian $H(\mathbf{r},t)$ will not be Hermitian with respect to these states, which is locally indicated by the inequality $H(\mathbf{r},t)^{+}\mathbf{G}\Psi(\mathbf{r},t) \neq H(\mathbf{r},t)\,\mathbf{G}\Psi(\mathbf{r},t)$. In order to verify that the wavefunctions $\mathbf{G}\Psi(\mathbf{r},t)$ indeed lie outside the given Hilbert space of the assumed closed system, we have to integrate over the system's coordinates the local quantity

$$\Psi(\mathbf{r},t)^{+}H(\mathbf{r},t)^{+}\mathbf{G}\Psi(\mathbf{r},t) - \Psi(\mathbf{r},t)^{+}H(\mathbf{r},t)\,\mathbf{G}\Psi(\mathbf{r},t).$$

This volume integration, denoted in bra-ket notation as

$$\langle\, H(\mathbf{r},t)\Psi(t)|\mathbf{G}\Psi(t)\rangle - \langle\Psi(t)|H(\mathbf{r},t)\mathbf{G}\Psi(t)\rangle\,,$$

is equal (up to physical constants) with the boundary operator expectation value Eq. (3.9). This indicates that $\langle\boldsymbol{\mathcal{O}}_b\rangle$ is not zero only whenever the action of the operator $\mathbf{G}$ creates wavefunctions that lie outside the given Hilbert space of the Hermitian Hamiltonian; we can therefore say that the boundary operator expectation value is not zero owing to an emerging non-Hermitian effect.

Each extended defined operator Eq. (3.4), can be expressed in a more compact form. Namely, by expanding the commutation relation in Eq. (3.5), and by using Eqs. (3.6) and (3.4), it is recast in the form

$$\boldsymbol{\mathcal{O}}_{ext} = \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+}\mathbf{G} - \mathbf{G}H(\mathbf{r},t)\right) + \frac{d\mathbf{G}}{dt}, \tag{3.15}$$

which for closed and isolated systems that satisfy $H(\mathbf{r},t)^{+}\mathbf{G}\Psi(\mathbf{r},t) - H(\mathbf{r},t)\,\mathbf{G}\Psi(\mathbf{r},t) = 0$, is reduced to the standard, textbook definition of an observable operator.

Furthermore we point out that, by examining Eq. (3.3) we can deduce that any extended operator expectation value $\langle\boldsymbol{\mathcal{O}}_{ext}\rangle$, is always a real quantity with respect to the given Hilbert space, provided that the operator $\mathbf{G}$ is Hermitian with respect to the given boundary conditions of the system, that is, it satisfies $\langle\mathbf{G}\Psi(t)|\Psi(t)\rangle - \langle\Psi(t)|\mathbf{G}\Psi(t)\rangle = 0$. Such is for example the case when the operator $\mathbf{G}$ is, the position operator $\mathbf{r} = \mathbf{r}^{+}$ (working in position representation is implied), or the spin operator $\mathbf{S} = \mathbf{S}^{+}$ (due to Pauli matrices satisfying $\sigma_i = \sigma_i^{+}$), or any symmetric combination of position and spin operators. For these exam-

ples $\mathbf{G}=\mathbf{G}^{+}$, and the extended operator is Hermitian $\boldsymbol{\mathcal{O}}_{ext}=\boldsymbol{\mathcal{O}}_{ext}^{+}$ as evidenced from Eq. (3.15).

By assuming that the operator $\mathbf{G}$ is always a Hermitian operator with respect to any arbitrary states, which do not necessarily belong to the same Hilbert space, that is, $\langle\Phi(t)|\mathbf{G}\Psi(t)\rangle=\langle\mathbf{G}\Phi(t)|\Psi(t)\rangle$, it is easy to show by straightforward calculation that, the standard bulk expectation value $\langle\boldsymbol{\mathcal{O}}\rangle=\frac{i}{\hbar}\langle\Psi(t)|H(\mathbf{r},t)\mathbf{G}\Psi(t)\rangle-\frac{i}{\hbar}\langle\Psi(t)|\mathbf{G}H(\mathbf{r},t)\Psi(t)\rangle$ and the non-Hermitian boundary expectation value

$$\langle\boldsymbol{\mathcal{O}}_{b}\rangle=\frac{i}{\hbar}\langle H(\mathbf{r},t)\Psi(t)|\mathbf{G}\Psi(t)\rangle-\frac{i}{\hbar}\langle\Psi(t)|H(\mathbf{r},t)\mathbf{G}\Psi(t)\rangle\,,$$

satisfy $\langle\boldsymbol{\mathcal{O}}\rangle-\langle\boldsymbol{\mathcal{O}}\rangle^{*}=-(\langle\boldsymbol{\mathcal{O}}_{b}\rangle-\langle\boldsymbol{\mathcal{O}}_{b}\rangle^{*})$. Therefore, even if $\langle\boldsymbol{\mathcal{O}}\rangle$ has a complex expectation value, its imaginary part is canceled by the imaginary part of $\langle\boldsymbol{\mathcal{O}}_{b}\rangle$ when the two expectation values are added to give the extended operator $\langle\boldsymbol{\mathcal{O}}_{ext}\rangle$ expectation value.

At this point it is also interesting to note a dual picture, that can show up when the system does not exchange any observable quantity in question with the environment but, at the same time it does not have constant particle number. We can formalize this dual picture by taking into account Eq. (3.15) as well as Eqs. (3.3) – (3.6), and by remaining within cases with system's spinor wavefunctions $\Psi(\mathbf{r},t)$ as follows. We assume an effective Hamiltonian $H_{\text{eff}}(\mathbf{r},t)$ that has the form

$$H_{\text{eff}}(\mathbf{r},t)=H(\mathbf{r},t)+K \tag{3.16}$$

and which is enforced to satisfy

$$H_{\text{eff}}(\mathbf{r},t)^{+}\mathbf{G}\Psi(\mathbf{r},t)=H_{\text{eff}}(\mathbf{r},t)\,\mathbf{G}\Psi(\mathbf{r},t),$$

behaving therefore as a Hermitian operator with respect to $\mathbf{G}\Psi(\mathbf{r},t)$ spinor wavefunctions. The K operator is defined by taking advantage of Eq. (3.9) and the above mentioned Hermiticity of the effective Hamiltonian. Thus, K is defined by

$$\langle\boldsymbol{\mathcal{O}}_{b}\rangle=-\frac{i}{\hbar}\left(\langle K\Psi(t)|\mathbf{G}\Psi(t)\rangle-\langle\Psi(t)|K\mathbf{G}\Psi(t)\rangle\right). \tag{3.17}$$

Taking now into account that $\langle H(\mathbf{r},t)\Psi(t)|\Psi(t)\rangle-\langle\Psi(t)|H(\mathbf{r},t)\Psi(t)\rangle=0$, we see that $\langle H_{\text{eff}}(\mathbf{r},t)\Psi(t)|\Psi(t)\rangle-\langle\Psi(t)|H_{\text{eff}}(\mathbf{r},t)\Psi(t)\rangle$ is equal to $\langle K\Psi(t)|\Psi(t)\rangle-\langle\Psi(t)|K\Psi(t)\rangle$ and the conclusion drawn is simple. If the defined operator K satisfies $\langle K\Psi(t)|\Psi(t)\rangle-\langle\Psi(t)|K\Psi(t)\rangle\neq 0$, then the effective Hamiltonian will not be Hermitian with respect to $\Psi(\mathbf{r},t)$, that is, $H_{\text{eff}}(\mathbf{r},t)^{+}\Psi(\mathbf{r},t)\neq H_{\text{eff}}(\mathbf{r},t)\,\Psi(\mathbf{r},t)$ and (i) the system will behave as an open one with respect to the effective Hamiltonian, namely

$$\frac{d^{(\text{ef})}}{dt}\langle\Psi(t)|\Psi(t)\rangle=-\frac{i}{\hbar}\left(\langle H_{\text{eff}}(\mathbf{r},t)\Psi(t)|\Psi(t)\rangle-\langle\Psi(t)|H_{\text{eff}}(\mathbf{r},t)\Psi(t)\rangle\right)\neq 0$$

as well as (ii) the effective equation of motion of the observable $\mathbf{G}$ will be given from Eq. (3.15) by replacing $H_{\text{eff}}(\mathbf{r},t)^{+}\mathbf{G}=H_{\text{eff}}(\mathbf{r},t)\mathbf{G}$, where by definition the boundary ex-

pectation value is zero $\langle \boldsymbol{\mathcal{O}}_b \rangle_{\text{ef}} = 0$. In this framework, the effective system is certainly behaving as an isolated one with respect to the current of the observable quantity $\mathbf{G}$ over the system's boundaries, while it may behave as an open one with respect to the system's particle number. Specifically, whenever the expectation value of the defined operator K is an imaginary quantity, that is, $\langle K\Psi(t)|\Psi(t)\rangle - \langle \Psi(t)|K\Psi(t)\rangle \neq 0$, then the K operator is an anti-hermitian operator with respect to $\Psi(\mathbf{r},t)$ wavefunctions, and the effective system also behaves as an open one. A simple example to achieve this, and at the same time satisfy Eq. (3.17), is by employing a purely imaginary scalar potential, that is, $K = iV_K(\mathbf{r},t)$ where $V_K(\mathbf{r},t)$ is a real quantity. The imaginary scalar potential has to be chosen in order to satisfy $\langle \boldsymbol{\mathcal{O}}_b \rangle = -\frac{2}{\hbar}\langle \Psi(t)|V_K(\mathbf{r},t)\mathbf{G}\Psi(t)\rangle$, while the time evolution of the effective system's particle number is governed by $\frac{d^{(\text{ef})}}{dt}\langle \Psi(t)|\Psi(t)\rangle = -\frac{2}{\hbar}\langle \Psi(t)|V_K(\mathbf{r},t)|\Psi(t)\rangle$. In this simple example it is evident that each one expectation value, namely, $\langle \boldsymbol{\mathcal{O}} \rangle$ and $\langle \boldsymbol{\mathcal{O}}_b \rangle$, are separately purely real quantities, although it is generally only their sum that should be a real quantity. These conclusions pose now the opposite question. Given an open system whose time evolution is governed by the static non-Hermitian Hamiltonian $H_{\text{eff}}(\mathbf{r})$, under what conditions can it have all of its energy expectation values real? The answer is given by means of Eq. (3.16) which indicates that, whenever $\langle \Psi(t)|K\Psi(t)\rangle = 0$, then the two expectation values coincide $\langle \Psi(t)|H_{\text{eff}}(\mathbf{r})\Psi(t)\rangle = \langle \Psi(t)|H(\mathbf{r})\Psi(t)\rangle$ and the initially assumed open system behaves as a closed one $\frac{d^{(ef)}}{dt}\langle \Psi(t)|\Psi(t)\rangle = 0$.

In summary, whenever one deals with closed systems, then, by using our extended theoretical framework for defining operators within Schrödinger picture Eq. (3.4), the rate of change of an observable $\mathbf{G}$ expectation value is rigorously given by

$$\frac{d}{dt}\langle \mathbf{G} \rangle = \langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \langle \boldsymbol{\mathcal{O}} \rangle + \langle \boldsymbol{\mathcal{O}}_b \rangle \,, \tag{3.18}$$

and this equation, together with Eqs. (3.5) – (3.6), as well as Eq. (3.13), have been be used as the building blocks of this work. Firstly, in order to define our intrinsic spin current operator, and secondary, in order to review the currents defined in Ref. [128] and Ref. [121], that were both derived by local means and without taking into account any non-Hermitian effect term whatsoever.

3.1.2 Extended operator's equation of motion

By using Eq. (3.18), as well as by assuming that the operator $\mathbf{G}$ is Hermitian with respect to the Hilbert space of the assumed closed system (the observable's expectation value $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle$ being therefore a real quantity) we can deduce two important properties. That is: (i) for those quantum states that the extended operator has stationary expectation value $\frac{d}{dt}\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$, we can deduce an explicit relation between the standard (bulk) and the boundary operator expectation values and, (ii) for irreversible and non-equilibrium quantum states that are near equilibrium, where the extended operator expectation value satisfies the approximated linear

dissipation equation $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle = -k_{ij} \langle \mathcal{O}^j_{ext} \rangle$, with k_{ij} being phenomenological transport coefficients (where repeated indices denote summation), we can form reciprocal relations between phenomenological transport coefficients.

Stationary expectation values

The steady states that are giving stationary expectation values with respect to an extended operator, can be separated into two groups, namely, the ones in which $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$, and those in which $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \boldsymbol{C}$ where $\boldsymbol{C}$ is a constant vector quantity.

In the first group, by assuming that the operator $\mathbf{G}$ is time-independent, it is evident that the relation $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$ is satisfied whenever the system is in a stationary eigenstate of a static Hamiltonian, that is $|\Psi(t)\rangle = exp(-\frac{i}{\hbar} E_n\, t)\, |n\rangle$, where n indexes the band energy, and the system is therefore in an equilibrium state. In these equilibrium states $\langle \mathbf{G} \rangle_n = \boldsymbol{g}$, where $\boldsymbol{g}$ is a constant quantity, which results into $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle_n = 0$. As evidenced from Eq. (3.18), any such stationary state satisfies a bulk-boundary relation given by

$$\langle \boldsymbol{\mathcal{O}} \rangle_n = - \langle \boldsymbol{\mathcal{O}}_b \rangle_n \,, \tag{3.19}$$

where the operator $\mathbf{G}$ is assumed to be static. In this framework, Eq. (3.19) forms a strict balance relation in a type of a gain and loss between the standard (bulk) and the non-Hermitian effect (boundary) contributions with respect to the global "current" of the observable $\mathbf{G}$ denoted as $\frac{d}{dt}\langle \mathbf{G} \rangle$, and it states that, whenever the bulk of the system behaves as a source, the boundaries operates as a sink and *vice versa*. By defining the isolated stationary states (in a macroscopic sense with respect to the system's boundaries) as the ones that satisfy $\langle \boldsymbol{\mathcal{O}}_b \rangle_n = 0$, we can deduce from Eq. (3.19) that the standard (bulk) operator, evaluated with respect to such states, satisfies $\langle \boldsymbol{\mathcal{O}} \rangle_n = 0$, thus the boundary operator expectation value can be used as a probe (detector) of such isolated states.

In the second group where $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \boldsymbol{C}$, the system has to be in such a state that satisfies $\frac{d}{dt}\langle \mathbf{G} \rangle = \langle \boldsymbol{\mathcal{O}} \rangle + \langle \boldsymbol{\mathcal{O}}_b \rangle = \boldsymbol{C}$. The latter equation suggests that the expectation value of $\mathbf{G}$ must be equal to $\langle \mathbf{G} \rangle = \boldsymbol{g} + \boldsymbol{C}.t$, where $\boldsymbol{g}$ is also a constant. By assuming again that the operator $\mathbf{G}$ is time-independent, as well as that the Hamiltonian $H(\mathbf{r})$ is static, then, by taking into account that the system is in a superposition of Hamiltonian's eigenstates $|\Psi(t)\rangle = \sum_n C_n\, exp(-\frac{i}{\hbar} E_n\, t)\, |n\rangle$, by explicit calculation we see that by no means we cannot satisfy the equation

$$\begin{aligned} \frac{d}{dt}\langle \Psi(t)|\, \mathbf{G}\, |\Psi(t)\rangle \;\; = \;\; & \sum_n \sum_m C_n C^*_m \frac{d}{dt} exp(-\frac{i}{\hbar}(E_n - E_m)\, t) \\ & \times \langle m|\, \mathbf{G}\, |n\rangle = \boldsymbol{C} \end{aligned}$$

with $\boldsymbol{C}$ non-zero constant. On the other hand, if the operator $\mathbf{G}$ has an explicit linear time-dependence, namely, $\frac{d\mathbf{G}}{dt} = \boldsymbol{C}$, where $\boldsymbol{C}$ is the above mentioned constant, then, if the system

is in a single stationary eigenstate $|n\rangle$ of the Hamiltonian, the second restriction $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = \boldsymbol{C}$ is satisfied $\frac{d}{dt}\langle \Psi(t)| \, \mathbf{G} \, |\Psi(t)\rangle = \left\langle n \left| \frac{d\mathbf{G}}{dt} \right| n \right\rangle = \boldsymbol{C}$. In this framework, there exist a bulk-boundary relation

$$\langle \boldsymbol{\mathcal{O}} \rangle_n - \boldsymbol{C} = - \langle \boldsymbol{\mathcal{O}}_b \rangle_n \tag{3.20}$$

with respect to any operator $\mathbf{G}$ that has linear time dependence.

Reciprocal relations

By using Eq. (3.18) and the extended operator definition $\boldsymbol{\mathcal{O}}_{ext}$, we can always form a quantum equation of motion for an operator's $\mathbf{G}$ expectation value without any subtleties concerning emerging non-Hermitian behaviors being involved. In example, for $\mathbf{G} = \mathbf{r}$ and within periodic boundary conditions for the wavefunctions, the quantum equation of motion of the position operator expectation value $\frac{d}{dt}\langle \mathbf{r} \rangle$ cannot be satisfied by only taking into account the standard bulk velocity operator $\frac{i}{\hbar}[H(\mathbf{r},t), \mathbf{r}]$, rather it is satisfied only when the boundary operator is also taken into account, that is $\frac{d}{dt}\langle \mathbf{r} \rangle = \langle \boldsymbol{\mathcal{O}}_{ext} \rangle$. In this respect, we are asking a plausible question: given the equation of motion of an extended operator expectation value $\frac{d}{dt}\langle \boldsymbol{\mathcal{O}}_{ext} \rangle$, can we draw conclusions concerning its irreversible equation of motion towards the values $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$ and $\frac{d}{dt}\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$? In other words, an initially equilibrium system is perturbed and then left alone; can we make approximate estimates with respect to the irreversible process that returns the system back to an equilibrium, stationary eigenstate of a static Hamiltonian? The answer is yes within a linear approximation dissipation equation, that is, near $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$. We take a Taylor expansion of $\frac{d}{dt}\langle \boldsymbol{\mathcal{O}}_{ext} \rangle$ near equilibrium, and assume that each component of $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle$ has the function form $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle = f^i(\langle \mathcal{O}^x_{ext} \rangle , \langle \mathcal{O}^y_{ext} \rangle , \langle \mathcal{O}^z_{ext} \rangle)$. The expansion around the equilibrium value $\langle \boldsymbol{\mathcal{O}}_{ext} \rangle = 0$ gives $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle = -k_{ij} \langle \mathcal{O}^j_{ext} \rangle - \lambda_{ijk} \langle \mathcal{O}^j_{ext} \rangle \langle \mathcal{O}^k_{ext} \rangle + \cdots$ where repeated indices denotes summation, k_{ij} and λ_{ijk} are phenomenological transport coefficients and $f^i(0,0,0) = 0$. Within a linear dissipation approximation, the above expansion is reduced into $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle = -k_{ij} \langle \mathcal{O}^j_{ext} \rangle$, where $\frac{d}{dt}\langle \mathcal{O}^i_{ext} \rangle$ can be thought as the generalized "force" that cause the time evolution of $\langle \mathcal{O}^j_{ext} \rangle$. In matrix notation, the irreversible, linear quantum equation of motion takes the form

$$\frac{d}{dt} \begin{pmatrix} \langle \mathcal{O}^x_{ext} \rangle \\ \langle \mathcal{O}^y_{ext} \rangle \\ \langle \mathcal{O}^z_{ext} \rangle \end{pmatrix} = - \begin{pmatrix} k_{xx} & k_{xy} & k_{xz} \\ k_{yx} & k_{yy} & k_{yz} \\ k_{zx} & k_{zy} & k_{zz} \end{pmatrix} \begin{pmatrix} \langle \mathcal{O}^x_{ext} \rangle \\ \langle \mathcal{O}^y_{ext} \rangle \\ \langle \mathcal{O}^z_{ext} \rangle \end{pmatrix} . \tag{3.21}$$

Due to $\langle \mathcal{O}^j_{ext} \rangle$ being real quantities, it is evident that the phenomenological transport coefficients k_{ij} are also real quantities, therefore, the matrix composed of the coefficients is a real

matrix. We are interested in the irreversible, attenuating solutions of the above matrix equation, that is we seek solutions of the form $\left\langle \mathcal{O}^{j}_{ext}(t \to \infty) \right\rangle = 0$. The general solution form of the above matrix equation, is given by $\left(\langle \mathcal{O}^{x}_{ext} \rangle\,,\ \langle \mathcal{O}^{y}_{ext} \rangle\,,\ \langle \mathcal{O}^{z}_{ext} \rangle\right)^{T} = e^{-\lambda t}\,(c_1,\ c_2,\ c_3)^{T}$ where c_i and λ are constants. By substituting this form in Eq. (3.21) we end up with the eigenvalue equation

$$\begin{pmatrix} k_{xx}-\lambda & k_{xy} & k_{xz} \\ k_{yx} & k_{yy}-\lambda & k_{yz} \\ k_{zx} & k_{zy} & k_{zz}-\lambda \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_2 \end{pmatrix} = 0. \tag{3.22}$$

Taking now into account that, the elements k_{ij} of the matrix $\mathcal{K}$ in Eq. (3.21) are all real quantities, then, in order for all eigenvalues λ to be all purely real and at least one positive, so that there exists an exponential attenuating solution for each $\left\langle \mathcal{O}^{j}_{ext} \right\rangle$, it is necessary that the matrix $\mathcal{K}$ has to be a Hermitian one, therefore, $k_{ij} = k_{ji}$. In this respect, within a linear dissipation approximation equation (with respect to the time evolution of the extended operator's expectation value Eq. (3.21)), one can justify a quantum mechanical theoretical framework to derive Onsager reciprocal relations [99, 100] for irreversible transport processes.

Mixed States

Although all of our prior theoretical analysis resides on pure states, it is easy to extend the way that one can define an operator in an extended manner for a mixed states (within Schrödinger picture).

When the system is in a mixed state, the ensemble average of $\mathbf{G}$ is given by

$$[\mathbf{G}] = \sum_i w_i \left\langle \Psi_{(i)}(t) \right| \mathbf{G} \left| \Psi_{(i)}(t) \right\rangle$$

where w_i weights the expectation values of the ensemble members and satisfies $\sum_i w_i = 1$. Then, we may define the ensemble average extended value as $[\boldsymbol{\mathcal{O}}_{ext}\,] = \dfrac{d}{dt}[\mathbf{G}]$, which is given by

$$[\boldsymbol{\mathcal{O}}_{ext}\,] = \sum_i \frac{dw_i}{dt} \left\langle \Psi_{(i)}(t) \right| \mathbf{G} \left| \Psi_{(i)}(t) \right\rangle + \sum_i w_i \left\langle \Psi_{(i)}(t) \right| \boldsymbol{\mathcal{O}}_{ext} \left| \Psi_{(i)}(t) \right\rangle \tag{3.23}$$

where $\left\langle \Psi_{(i)}(t) \right| \boldsymbol{\mathcal{O}}_{ext} \left| \Psi_{(i)}(t) \right\rangle = \dfrac{d}{dt} \left\langle \Psi_{(i)}(t) \right| \mathbf{G} \left| \Psi_{(i)}(t) \right\rangle$ is given from Eq. (3.18) and $\dfrac{dw_i}{dt}$ accounts for the time evolution of the populations. Choosing a convenient complete orthonormal base $I = \sum_n |n\rangle\langle n|$, then, Eq. (3.23) is recast in the form

$$[\boldsymbol{\mathcal{O}}_{ext}\,] = \sum_n \langle n| \,\mu\, \mathbf{G} + \rho\, \boldsymbol{\mathcal{O}}_{ext} \,|\, n\rangle \tag{3.24}$$

where μ is the population density matrix operator given by

$$\mu = \sum_i \frac{dw_i}{dt} \left|\Psi_{(i)}(t)\right\rangle \left\langle\Psi_{(i)}(t)\right| \tag{3.25}$$

and ρ is the density matrix given from

$$\rho = \sum_i w_i \left|\Psi_{(i)}(t)\right\rangle \left\langle\Psi_{(i)}(t)\right|. \tag{3.26}$$

Within this framework, whenever the populations acquires a static value $\frac{dw_i}{dt} = 0$, the ensemble average extended value $[\boldsymbol{\mathcal{O}}_{ext}]$ may also acquire a stationary value $\boldsymbol{C}$, that is, $[\boldsymbol{\mathcal{O}}_{ext}] = \frac{d}{dt}[\mathbf{G}] = \boldsymbol{C}$, where we may assume that for $\boldsymbol{C} = 0$ the ensemble is "unpolarized". Therefore, whenever the ensemble average extended value gets a static value, there exists an involved bulk-boundary relation that is given by

$$\sum_n \langle n|\, \rho\, \boldsymbol{\mathcal{O}}\, |\, n\rangle = \boldsymbol{C} - \sum_n \langle n|\, \rho\, \boldsymbol{\mathcal{O}}_b\, |\, n\rangle \tag{3.27}$$

even though the system may not be in the lowest energy configuration.

3.1.3 Local continuity-like equations

Although it is an operator's expectation (global) value that represents the observable, it is instructive to make a connection with the methodology that is mainly followed in the theoretical works that concerns the spin transport [128, 121, 125, 24, 44, 23, 155]. In these methods, the starting point formulas are local, continuity-like equations with respect to the rate of change of the observable's $\mathbf{G}$ density. Based on our work, a local continuity-like equation can be derived by using the expectation value equation Eq. (3.18) in position representation, as well as by taking into account Eq. (3.13) and Eq. (3.5). In this respect, the expectation value Eq. (3.18) when calculated over position coordinates, has the local solution (due to the assumed volume V of the system being arbitrary) that can be expressed in a form of a local, continuity-like equation given by

$$\Psi^\dagger(\mathbf{r},t)\left(\frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{G}\right] + \frac{d\mathbf{G}}{dt}\right)\Psi(\mathbf{r},t) - \boldsymbol{\nabla}\cdot\overleftrightarrow{\mathbf{J}}_{\mathbf{G}}(\mathbf{r},t) = \frac{d}{dt}\Psi^\dagger(\mathbf{r},t)\mathbf{G}\Psi(\mathbf{r},t). \tag{3.28}$$

We note that Eq. (3.28) can also be derived by local means. This is done by: (i) taking the time derivative of the density of the observable $\Psi^\dagger(\mathbf{r},t)\mathbf{G}\Psi(\mathbf{r},t)$, (ii) using the time-dependent equation for the evolution of the spinor wavefunction $i\hbar\frac{d}{dt}\Psi(\mathbf{r},t) = H(\mathbf{r},\mathbf{t})\Psi(\mathbf{r},t)$, (iii) using the assumed Hamiltonian given by Eq. (3.7), and (iv) performing algebraic manipulations such as the ones made in the integrands of the expressions in the appendix D.

The first thing to note in the local Eq. (3.28), is that the divergence term $\boldsymbol{\nabla}\cdot\overleftrightarrow{\mathbf{J}}_{\mathbf{G}}(\mathbf{r},t)$ should be absent within the standard definition of Hermitian operators (assuming zero non-

Hermitian effect) rather than the bulk source-term (which is thought to be the problem in the literature). In this respect, and although we are considering closed systems, the bulk source-term cannot be ignored and naturally breaks the continuity equation for the density of the observable Eq. (3.28) when the expectation value $\langle\Psi(t)|\,\mathbf{G}\,|\Psi(t)\rangle$ is not zero. The breaking of the local conservation does not lead to any theoretical problem with respect to a proper definition of an observable's operator (also noticed by [125] in the quest of the proper definition of the spin current operator), contrary to what is commonly stated in the literature [128, 121, 24, 44]. As a matter of fact, Eq. (3.28) provides a local, quantum mechanical, micro-balance equation for the density of an observable (in analogous manner as in hydrodynamical theories) which takes into account the evolution of the state under consideration as well as the bulk and the boundary sources.

In summary, the divergence term can be viewed as the source term that produces the boundary time-evolution of the observable's expectation value $\langle\Psi(t)|\,\mathbf{G}\,|\Psi(t)\rangle$ which is not zero only whenever the operator $\mathbf{G}$ becomes anomalous, while the bulk source-term can be viewed as the one that produces the standard, bulk time-evolution. In spite the fact that the local balance equation Eq. (3.28) breaks the local conservation law, an alternative local equation for the observable's density, that satisfies a local conservation law, can be derived. This can be done by defining a local current density (flux) of the observable as $\mathbf{J}(\mathbf{r},t)=\frac{d}{dt}\Psi^{\dagger}(\mathbf{r},t)\mathbf{G}\Psi(\mathbf{r},t)$, and a local density by $\rho(\mathbf{r},t)=-\boldsymbol{\nabla}\cdot\big(\Psi^{\dagger}(\mathbf{r},t)\mathbf{G}\Psi(\mathbf{r},t)\big)$, which clearly satisfy a local conservation law

$$-\boldsymbol{\nabla}\cdot\mathbf{J}(\mathbf{r},t)=\frac{d\rho(\mathbf{r},t)}{dt}. \tag{3.29}$$

The latter conservation law Eq. (3.29) resembles the polarization current of classical electrodynamics, with the polarization current density given by $\mathbf{J}_{\mathbf{p}}(\mathbf{r},t)=\frac{d\mathbf{P}(\mathbf{r},t)}{dt}$ and the polarization charge density from $\rho_p(\mathbf{r},t)=-\boldsymbol{\nabla}\cdot\mathbf{P}(\mathbf{r},t)$, where $\mathbf{P}(\mathbf{r},t)$ is the polarization of the medium.

It is now helpful to see the usage of the local Eq. (3.28) for some observable operators:
(i) The particle's local number density is defined as $\Psi^{\dagger}(\mathbf{r},t)\Psi(\mathbf{r},t)$ and the rate of change of the local number density by $\frac{d}{dt}\Psi^{\dagger}(\mathbf{r},t)\Psi(\mathbf{r},t)$; in this respect, by replacing the $\mathbf{G}$ in Eq. (3.28) with the identity operator $\mathbf{G}\rightarrow I$, and for assumed closed system $\oiint_S d\mathbf{s}\cdot\mathbf{J}_I(\mathbf{r},t)=0$, Eq. (3.18) gives the particle number conservation with respect to those states that belongs within the domain of definition of the Hermitian Hamiltonian, that is $\frac{d}{dt}\langle\Psi(t)|\Psi(t)\rangle=0$, irrespectively of whether the quantum state under consideration is a stationary (equilibrium) state or a non-equilibrium state.
(ii) For an assumed closed system the particle's local position density is defined as $\Psi^{\dagger}(\mathbf{r},t)\,\mathbf{r}\,\Psi(\mathbf{r},t)$ and the rate of change of the particle's local position density by $\frac{d}{dt}\Psi^{\dagger}(\mathbf{r},t)\,\mathbf{r}\,\Psi(\mathbf{r},t)$. Therefore, by replacing $\mathbf{G}$ with the position operator $\mathbf{r}$ in the local Eq. (3.28), the particle's position expectation value time derivative $\frac{d}{dt}\langle\Psi(t)|\,\mathbf{r}\,|\Psi(t)\rangle$

given by Eq. (3.18), acquires two explicit contributions, namely, the one due to the standard bulk velocity operator $\frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{r}]$ expectation value, and a boundary one, due to the non-Hermitian effect term given by Eq. (3.13). A simple example to show the necessary presence of the boundary non-Hermitian effect velocity part is given as follows: Consider a stationary and extended plane wave state of a free electron of mass m with well defined momentum $\hbar\mathbf{k}$ in a finite volume V. The system is assumed to be closed, that is the electrons' wavefunction is normalized to unity at every instant t within the volume V, $\langle\Psi(t)|\Psi(t)\rangle = 1$. In this respect, the electrons' displacement $\Delta\langle\mathbf{r}\rangle$ must always be smaller than (or equal to) the systems' size. Using the standard velocity definition $\mathbf{v} = \frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{r}]$ the elctrons' displacement acquires the value $\Delta\langle\mathbf{r}\rangle = \frac{\hbar\mathbf{k}}{m}t$ which will eventually lead the electron out of the system; this paradox is bypassed by taking into account the non-Hermitian velocity part that, as it turns out, contributes an equal magnitude and opposite sign than the bulk electrons' velocity $\langle\mathbf{v}\rangle$ resulting in zero displacement $\Delta\langle\mathbf{r}\rangle = 0$ at every instant t for the assumed stationary state.

It is worthwhile to point out that, although the system is assumed closed with fixed number of electrons, the particle's main position $\langle\Psi(t)|\,\mathbf{r}\,|\Psi(t)\rangle$ is not a conserved quantity (with respect to space coordinates) as is evident from Eq. (3.28) due to the standard velocity operator expectation value that is not zero; however, we can still define the electron's velocity without any need to modify the continuity-type Eq. (3.28).

(iii) For an assumed closed system, we can define the particle's local spin density as $\Psi^\dagger(\mathbf{r},t)\,\mathbf{S}\,\Psi(\mathbf{r},t)$ and the rate of change of the local spin density by $\frac{d}{dt}\Psi^\dagger(\mathbf{r},t)\,\mathbf{S}\,\Psi(\mathbf{r},t)$. Therefore, by replacing $\mathbf{G} = \mathbf{S}$ and according to Eq. (3.18) and Eq. (3.28), we can evaluate the particle's spin expectation value rate of change $\frac{d}{dt}\langle\Psi(t)|\,\mathbf{S}\,|\Psi(t)\rangle$ that has two explicit contributions, namely, a standard bulk one given from the expectation value of Eq. (3.5) and a boundary, non-Hermitian effect one, given from Eq. (3.13). It is worth pointing out that, the spin expectation value $\langle\Psi(t)|\,\mathbf{S}\,|\Psi(t)\rangle$ is not a conserved quantity with respect to space coordinates (in a similar manner as the particle's main position) according to Eq. (3.28) whenever the bulk source term is not zero, that is, the bulk torque operator $\frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{S}]$ expectation value is not zero.

3.2 Spin-accumulation rate of change operator

In Ref. [128], and without realizing the necessary presence of the non-Hermitian effect terms, the authors found out, by using a local continuity-like equation that, in order to completely describe the so-called spin transport $\frac{d}{dt}\Psi^\dagger(\mathbf{r},t)\,\mathbf{S}\,\Psi(\mathbf{r},t)$, one has to introduce the angular spin current apart from the linear spin current. The angular spin current, was attributed to the bulk source term that violates the conservation of spin in the local continuity equation. On the other hand, no inside observation about the unexpected emergence (within the standard theory of Hermitian operator's definition) of the linear spin current owing to the

non-Hermitian effect was ever made.

This spin transport or spin accumulation rate of change, can be studied as a special case of the general theoretical method that was presented in Sec.3.1, by defining a proper operator in an extended manner. This is made by replacing the abstract $\mathbf{G}$ operator in Eq. (3.18) with the spin (matrix) operator $\mathbf{S}$ that gives

$$\langle \boldsymbol{\tau} \rangle + \langle \boldsymbol{\tau}_b \rangle = \frac{d}{dt} \langle \mathbf{S} \rangle \,, \tag{3.30}$$

where we can rigorously define the bulk electron's spin-accumulation rate of change operator as

$$\boldsymbol{\tau} = \frac{i}{\hbar} \left[H(\mathbf{r}, t), \mathbf{S} \right], \tag{3.31}$$

and the boundary spin-accumulation rate of change operator as

$$\boldsymbol{\tau}_b = \frac{i}{\hbar} \big(H(\mathbf{r}, t)^+ - H(\mathbf{r}, t) \big) \mathbf{S}. \tag{3.32}$$

The above two operators, namely, $\boldsymbol{\tau}$ and $\boldsymbol{\tau}_b$ can also be interpreted as the bulk and the boundary torque operators respectively.

The bulk spin-accumulation rate of change operator expectation value $\langle \boldsymbol{\tau} \rangle$ can explicitly be evaluated by employing the specific Hamiltonian of the system and the quantum state under consideration. Therefore, for the Hamiltonian given either from Eq. (3.7) or by Eq. (3.14), and by using $[\sigma_i, \sigma_j] = 2i\, \epsilon_{ijk}\, \sigma_k$, giving $[\boldsymbol{\sigma} \cdot \mathbf{B}, \boldsymbol{\sigma}] = -2i\, \mathbf{B} \times \boldsymbol{\sigma}$ and $[(\boldsymbol{\sigma} \times \nabla V) \cdot \Pi, \boldsymbol{\sigma}] = -2i\, (\nabla V \times \Pi) \times \boldsymbol{\sigma}$, we find the explicit form of the bulk spin-accumulation rate of change (bulk spin torque) operator that is given by

$$\boldsymbol{\tau} = \left(-\frac{e}{mc} \mathbf{B}(\mathbf{r}, t) + \frac{1}{2m^2 c^2} \left(\nabla V(\mathbf{r}, t) \times \boldsymbol{\Pi}(\mathbf{r}, t) \right) \right) \times \mathbf{S}. \tag{3.33}$$

The expectation value of the boundary spin-accumulation rate of change (boundary spin torque) operator $\langle \boldsymbol{\tau}_b \rangle$, is also evaluated by employing the specific Hamiltonian of the system Eq. (3.7) and the state under consideration. In this respect, we replace $\mathbf{G} = \mathbf{S}$ in Eqs. (3.12) –(3.13) which leads to

$$\overleftrightarrow{\mathbf{J}}_{\mathbf{S}}(\mathbf{r}, t) = \frac{1}{2} \left((\mathbf{v} \Psi(\mathbf{r}, t))^\dagger + \Psi(\mathbf{r}, t)^\dagger \mathbf{v} \right) \mathbf{S} \Psi(\mathbf{r}, t) \tag{3.34}$$

and

$$\langle \boldsymbol{\tau}_b \rangle = - \oiint_S d\mathbf{s} \cdot \overleftrightarrow{\mathbf{J}}_{\mathbf{S}}(\mathbf{r}, t). \tag{3.35}$$

The expectation values $\langle \boldsymbol{\tau} \rangle$ and $\langle \boldsymbol{\tau}_b \rangle$, are the analogs of the angular spin current and the linear spin current given in Ref. [128], and according to our formulation, the expectation value of the boundary spin-accumulation rate of change operator $\langle \boldsymbol{\tau}_b \rangle$ is not zero only whenever the spin operator $\mathbf{S}$ becomes anomalous breaking the domain of definition D_H of the Hamiltonian.

Whenever the calculations are performed with respect to a stationary state, that is, the spin expectation value is constant $\frac{d}{dt}\langle\Psi_n(t)|\,\mathbf{S}\,|\Psi_n(t)\rangle = 0$, then according to Eq. (3.30) there exists a strict gain-loss balance relation between the standard (bulk) spin expectation value rate of change and the boundary spin accumulation rate of change given by

$$\langle\boldsymbol{\tau}\rangle_n = -\langle\boldsymbol{\tau}_b\rangle_n\,, \tag{3.36}$$

suggesting that, for stationary states, whenever the bulk of the system behaves as a spin source the boundaries operates as a spin sink and *vice versa*.

Furthermore, by defining the localized stationary states (in a macroscopic sense with respect to the system's boundaries) as the ones that satisfy $\langle\boldsymbol{\tau}_b\rangle_n = 0$, implying that the spin operator $\mathbf{S}$ behaves as a normal operator (in the sense that it does nor break the domain of definition of the Hamiltonian operator) and the boundary integral Eq. (3.35) is zero, we deduce from Eq. (3.36) that the standard, bulk spin-accumulation rate of change operator expectation value (with respect to such stationary and localized states) is also zero $\langle\boldsymbol{\tau}\rangle_n = 0$. In this framework, the spin expectation value $\langle\mathbf{S}\rangle_n$ can be assumed as separately constant, in the bulk as well as on the boundaries.

On the other hand, if we assume a spin Hall stationary state in which spins are created in the bulk and sink over the boundaries, then according to Eq. (3.36), $\langle\boldsymbol{\tau}_b\rangle_n = -\langle\boldsymbol{\tau}\rangle_n - \neq 0$ indicating that the spin $\mathbf{S}$ is behaving as an anomalous operator due to the non-Hermitian effect, that is, the spin polarization orientation over the opposite boundaries of the material is altered due to acquired $SU(2)$ phases induced by the bulk spin torques that influence the electron's spinor wavefunction.

Owing to the form of Eq. (3.33), it is evident that $\mathbf{S}\cdot\boldsymbol{\tau} = 0$ which implies that, in the bulk of any material, the spin is performing an involved precession motion around the direction of the vector $-\frac{e}{mc}\mathbf{B}(\mathbf{r},t) + \frac{1}{2m^2c^2}\left(\nabla V(\mathbf{r},t)\times\boldsymbol{\Pi}(\mathbf{r},t)\right)$. Actually, this is a generic feature of the spin in every closed system, that is, it makes an involved precession motion both in the bulk and at the boundaries of the material owing to the exerted local spin torques. This generic, bulk and boundary precession of the spin, can globally be explained due to $\sigma_i^2 = I$ and $\mathbf{S}^2 = 3\frac{\hbar}{2}I$, which leads to $\frac{d}{dt}\langle\Psi(t)|\,\mathbf{S}^2\,|\Psi(t)\rangle = 0$ for every closed system owing to $\frac{d}{dt}\langle\Psi(t)|\Psi(t)\rangle = 0$. Local analysis of this precession, for bulk and boundary regions, can be made by using Eq. (3.18) if we replace $\mathbf{G}\to\mathbf{S}\cdot\mathbf{S}$. In this respect, the rate of change of the modulus of the spin in the bulk is given by the expectation of the operator $\mathbf{S}\cdot\boldsymbol{\tau}$ which turns to zero due to the latter operator being locally zero. Similarly, the rate of change of the modulus of the spin over the boundaries turns also to zero (for an assumed closed system), as evident from Eq. (3.12) – (3.13) when we replace $\mathbf{G}\to\mathbf{S}\cdot\mathbf{S} = 3\frac{\hbar}{2}I$.

In the case we want to study the spin torque in a given direction, i.e. the z direction, we replace the abstract vector operator $\mathbf{G}$ in Eq. (3.18) with the scalar operator S_z and the tensor generalized current $\overleftrightarrow{\mathbf{J}}_{\mathbf{S}}(\mathbf{r},t)$ is simplified to a vector quantity, that is

$$\begin{aligned}\mathbf{J}_{S_z}(\mathbf{r},t) &= \frac{1}{2}\left((\mathbf{v}\Psi(\mathbf{r},t))^\dagger + \Psi(\mathbf{r},t)^\dagger\mathbf{v}\right) S_z\Psi(\mathbf{r},t) \\ &= \mathrm{Re}\left(\frac{1}{2}\Psi(\mathbf{r},t)^\dagger\left\{\mathbf{v},S_z\right\}\Psi(\mathbf{r},t)\right)\end{aligned} \tag{3.37}$$

where $\{,\}$ denotes the anticommutator, and the boundary torque is given respectively by

$$\left\langle \tau_{b(z)} \right\rangle = -\oiint_S d\mathbf{s}\cdot\mathbf{J}_{S_z}(\mathbf{r},t). \tag{3.38}$$

3.3 Defining extended current operators

In transport phenomena, flux is defined as the rate of flow of a property per unit area, which has the dimensions $[\text{quantity}].[\text{time}]^{-1}.[\text{area}]^{-1}$. In this respect, by assuming a single particle system and using the transport definition of flux, we can define a local micro-flux (for an assumed 3D system) of an observable as $\frac{d}{dt}\Psi^\dagger(\mathbf{r},t)\mathbf{r}\mathcal{Q}\Psi(\mathbf{r},t)$, that has the desirable dimensions, namely, $[\text{quantity}].[\text{time}]^{-1}.[\text{area}]^{-1}$ where, $\mathbf{r}$ is the position operator and $\mathcal{Q}$ is the magnitude of the assumed scalar property.

The coordinate integration (over the system's volume) of the micro-flux, gives the global value $\frac{d}{dt}\langle\Psi(t)|\,\mathbf{r}\mathcal{Q}\,|\Psi(t)\rangle$ that has dimensions $[\text{quantity}].[\text{time}]^{-1}.[\text{length}]$, representing therefore a global propagation (within the medium) of the quantity $\mathcal{Q}$ that is captured by the quantum mechanical operator $\mathbf{G}=\mathbf{r}\mathcal{Q}$.

In this fashion, and according to Sec. 3.1, we can define an extended current operator as

$$\mathbf{J}_{ext} = \mathbf{J} + \mathbf{J}_b \tag{3.39}$$

that has two explicit contributions, namely, the standard (bulk) one given by

$$\mathbf{J} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}\mathcal{Q}\right] + \mathbf{r}\frac{d\mathcal{Q}}{dt} \tag{3.40}$$

and a boundary one due to the non-Hermitian effect (owing to the anomalous action of the operator $\mathbf{r}\mathcal{Q}$) given by

$$\mathbf{J}_b = \frac{i}{\hbar}\left(H(\mathbf{r},t)^+ - H(\mathbf{r},t)\right)\mathbf{r}\mathcal{Q}. \tag{3.41}$$

The expectation value of the standard current operator $\langle\Psi(t)|\,\mathbf{J}\,|\Psi(t)\rangle$, represents the bulk propagation of the property $\mathcal{Q}$, and the expectation value of the boundary operator $\langle\Psi(t)|\,\mathbf{J}_b\,|\Psi(t)\rangle$ the boundary propagation respectively.

3.3.1 Extended charge current operator

It is useful to see a simple example of Eq. (3.40) and Eq. (3.41), by examining the charge e propagation in a closed system, that is, by assuming $\mathcal{Q}=e$ for the assumed single particle

system. In this fashion, the value of $\frac{d}{dt}\langle\Psi(t)|\, e\,\mathbf{r}\,|\Psi(t)\rangle$ represents the global propagation of the charge and has two explicit contributions. Specifically, the first one $\langle\Psi(t)|\,\mathbf{J}^{e}\,|\Psi(t)\rangle$, is given by the expectation value of Eq. (3.40) for $\mathcal{Q}=e$, and represents the bulk propagation that is given by the standard velocity operator expectation value times the electron charge e. The second one $\langle\Psi(t)|\,\mathbf{J}^{e}_{b}\,|\Psi(t)\rangle$, has a non-Hermitian origin, and is given by the expectation value of Eq. (3.41) which (in position representation and for real scalar and vector potentials) is always truncated to a boundary integral over the terminate boundaries of the system. It represents the transmission of electric charge through the boundaries and its expectation value is not zero whenever the position operator becomes anomalous. It is worth pointing out that the charge transport can be formalized by means of Eq. (3.40) and Eq. (3.41), even though no local conservation law is satisfied by the position weighted charge density $\Psi^{\dagger}(\mathbf{r},t)e\,\mathbf{r}\Psi(\mathbf{r},t)$. The conservation of the charge on the other hand, is captured by the local charge density $\Psi^{\dagger}(\mathbf{r},t)e\Psi(\mathbf{r},t)$ that satisfies a local conservation law.

3.3.2 Extended spin current operator

We now turn to the transport of the spin property and the method used in Ref. [121]. In order to resolve two critical flaws of the conventional spin current definition, that is, (i) spin is not a conserved quantity (does not satisfy a local conservation law) as well as (ii) it does not describe transport, they provided an improved spin current definition for spin-orbit coupled systems within an explicit restriction, namely, that no global spin generation in the bulk is made $\langle\Psi(t)|\,\tau_z\,|\Psi(t)\rangle = \left\langle \Psi(t)|\,\frac{i}{\hbar}[H(\mathbf{r},t),S_z]\,|\Psi(t)\right\rangle = 0$, due to symmetry reasons. By then working in the Heisenberg picture, they defined the spin current (of the z component of the spin) as the time derivative of the spin displacement operator $\mathbf{r}S_z$, that is, $\mathbf{J}^{sp(z)} = \frac{d(\mathbf{r}S_z)}{dt}$. In a recent work Ref. [147] they provided also the operator form of this spin current as $\mathbf{J}^{sp(z)} = \frac{i}{\hbar}[H(\mathbf{r},t),\mathbf{r}S_z]$.

Incorporating now our formalism (within Schrödinger picture), and without any constraint with respect to the spin density $\Psi(\mathbf{r},t)^{\dagger}S_z\Psi(\mathbf{r},t)$ conservation, the propagation of the spin S_z property (spin current), is formalized by means of Eq. (3.40) and Eq. (3.41) by replacing $\mathcal{Q}=S_z$. In this respect, the extended spin current operator is given by

$$\mathbf{J}^{sp(z)}_{ext} = \mathbf{J}^{sp(z)} + \mathbf{J}^{sp(z)}_{b}, \tag{3.42}$$

where the bulk propagation of the z component of the spin is given by the standard (bulk) spin current operator

$$\mathbf{J}^{sp(z)} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}S_z\right], \tag{3.43}$$

which is identical to the one given in Ref. [147] while the boundary spin propagation is given by the boundary operator

$$\mathbf{J}^{sp(z)}_{b} = \frac{i}{\hbar}\big(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\big)\mathbf{r}S_z. \tag{3.44}$$

By expanding the commutator of the right side of Eq. (3.43), the standard spin current operator is recast in the form

$$\mathbf{J}^{sp(z)} = \mathbf{v}\, S_z + \mathbf{r}\, \tau_z \tag{3.45}$$

where $\mathbf{v} = \frac{i}{\hbar}[H(\mathbf{r},t), \mathbf{r}]$ is the standard (bulk) velocity operator, and $\tau_z = \frac{i}{\hbar}[H(\mathbf{r},t), S_z]$ is the standard (bulk) z component of the spin torque operator. For the Hamiltonian of Eq. (3.7), the spin torque $\boldsymbol{\tau}$ is given by Eq. (3.33), and the z component of the spin torque by $\tau_z = \boldsymbol{\tau}\cdot\boldsymbol{e}_z$. Although not obvious, the right side of Eq. (3.45) is a properly symmetric operator. This is explicitly shown by using the expressions, $\mathbf{v}\, S_z = \frac{1}{2}(\mathbf{v}\, S_z + S_z\, \mathbf{v}) + \frac{1}{2}[\mathbf{v},\, S_z\,]$ and $\mathbf{r}\, \tau_z = \frac{1}{2}(\mathbf{r}\, \tau_z + \tau_z\, \mathbf{r}) + \frac{1}{2}[\mathbf{r},\, \tau_z\,]$, as well as the commutation relation identity $[\,\mathbf{r},\, \tau_z\,] = -[\,\mathbf{v},\, S_z\,]$. In this respect, the standard spin current operator can be recast in the form

$$\mathbf{J}^{sp(z)} = \frac{1}{2}(\mathbf{v}\, S_z + S_z\, \mathbf{v}) + \frac{1}{2}(\mathbf{r}\, \tau_z + \tau_z\, \mathbf{r}) \tag{3.46}$$

which obviously shows that it is a properly symmetric operator. The first term on the right side of Eq. (3.46) is the conventional spin current operator, while the second term is a contribution owing to the spin torque.

Due to the explicit (linear) dependence of the spin current operators Eq. (3.44) and Eq. (3.45) by the position operator $\mathbf{r}$, we have to examine their behavior with respect to periodic systems. This investigation shows that, both operators are generally ill defined operators with respect to periodic systems. Namely, each one of the spin current expectation values behaves as an extensive quantity for a periodic system because their values scale linearly with respect to the system's length, therefore they have an undefined value in the thermodynamic limit.

In order to show the above assertion, we assume a 3D cubic crystal and a spinor Bloch form wavefunction $\psi_{\mathbf{k}}(\mathbf{r},t) = \frac{1}{\sqrt{N}} e^{i\mathbf{k}.\mathbf{r}} u_{\mathbf{k}}(\mathbf{r},t)$ that satisfies Born-von Kármán periodic boundary conditions over the material's boundaries where $u_{\mathbf{k}}(\mathbf{r},t)$ are the cell periodic part of the wavefunction.

We adopt the normalization convention $\langle\psi_{\mathbf{k}}(t)|\psi_{\mathbf{k}}(t)\rangle = \langle u_{\mathbf{k}}(t)|u_{\mathbf{k}}(t)\rangle_{cell} = 1$, thus, N are the total number of primitive cells enclosed by the volume V the system. By now taking the expectation value of Eq. (3.45) with respect to the Bloch wavefunction $\psi(\mathbf{r},\mathbf{k},t)$ and at the same time exploiting the symmetry of the integrands, namely, taking into account that the spinor cell periodic wavefunction $u(\mathbf{r},\mathbf{k},t)$ as well as that the operators $\mathbf{v}(\mathbf{r},t)$ and $\tau_z(\mathbf{r},t)$ are cell periodic, we find that the standard (bulk) spin current expectation value is given by

$$\begin{aligned}\left\langle\psi_{\mathbf{k}}(t)\right|\mathbf{J}^{sp(z)}\left|\psi_{\mathbf{k}}(t)\right\rangle &= \left\langle u_{\mathbf{k}}(t)\right|\mathbf{J}^{sp(z)}\left|u_{\mathbf{k}}(t)\right\rangle_{cell} \\ &+ \left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x + \frac{(N_y-1)}{2}\boldsymbol{\alpha}_y + \frac{(N_z-1)}{2}\boldsymbol{\alpha}_z\right)\left\langle u_{\mathbf{k}}(t)\right|\tau_z\left|u_{\mathbf{k}}(t)\right\rangle_{cell}\end{aligned} \tag{3.47}$$

where the expectation value of the z component of the standard (bulk) spin torque $\tau_z = \boldsymbol{\tau}\cdot\boldsymbol{e}_z$,

evaluated with respect to a cell periodic state within one primitive cell, is related to the Bloch state expectation value by $\langle u_{\mathbf{k}}(t)|\,\tau_z\,|u_{\mathbf{k}}(t)\rangle_{cell} = \langle\psi_{\mathbf{k}}(t)|\,\tau_z\,|\psi_{\mathbf{k}}(t)\rangle$.

Similarly, the expectation value of Eq. (3.44) is recast in the form

$$\left\langle\psi_{\mathbf{k}}(t)|\,\mathbf{J}_b^{sp(z)}|\psi_{\mathbf{k}}(t)\right\rangle = \left\langle u_{\mathbf{k}}(t)|\,\mathbf{J}_b^{sp(z)}|u_{\mathbf{k}}(t)\right\rangle_{cell} + \left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x + \frac{(N_y-1)}{2}\boldsymbol{\alpha}_y + \frac{(N_z-1)}{2}\boldsymbol{\alpha}_z\right)\langle u_{\mathbf{k}}(t)|\,\tau_{b(z)}\,|u_{\mathbf{k}}(t)\rangle_{cell} \tag{3.48}$$

where the expectation value of the z component of the boundary spin torque operator $\tau_{b(z)} = \boldsymbol{\tau}_b\cdot\boldsymbol{e}_z$, is evaluated with respect to a Bloch state by $\langle u_{\mathbf{k}}(t)|\,\tau_{b(z)}\,|u_{\mathbf{k}}(t)\rangle_{cell} = \langle\psi_{\mathbf{k}}(t)|\,\tau_{b(z)}\,|\psi_{\mathbf{k}}(t)\rangle$. In deriving the latter equation that relates the boundary spin torques expectation values, we have used the bulk counterpart expression of Eq. (3.32) for the expectation value of the boundary spin torque, namely, $\langle\psi_{\mathbf{k}}(t)|\,\tau_{b(z)}\,|\psi_{\mathbf{k}}(t)\rangle = \frac{i}{\hbar}(\langle H(\mathbf{r},t)\psi_{\mathbf{k}}(t)|\,S_z\psi_{\mathbf{k}}(t)\rangle - \langle\psi_{\mathbf{k}}(t)|H(\mathbf{r},t)S_z\psi_{\mathbf{k}}(t)\rangle)$, and exploited the translation symmetry of the integrands. By summing now Eq. (3.47) and Eq. (3.48) we find the equation of motion of the spin displacement operator $\mathbf{r}S_z$ caused by the extended spin current operator $\mathbf{J}_{ext}^{sp(z)}$ expectation value, which is given by

$$\frac{d}{dt}\langle\psi_{\mathbf{k}}(t)|\,\mathbf{r}S_z\,|\psi_{\mathbf{k}}(t)\rangle = \left\langle\psi_{\mathbf{k}}(t)|\,\mathbf{J}_{ext}^{sp(z)}|\psi_{\mathbf{k}}(t)\right\rangle = \langle\psi_{\mathbf{k}}(t)|\,\mathbf{J}^{sp(z)}|\psi_{\mathbf{k}}(t)\rangle + \left\langle\psi_{\mathbf{k}}(t)|\,\mathbf{J}_b^{sp(z)}|\psi_{\mathbf{k}}(t)\right\rangle \tag{3.49}$$

that leads as to two conclusions:

First, in order for the spin current operators Eq. (3.43) and Eq. (3.44), to have a well defined and intensive value in periodic systems, the standard (bulk) spin torque expectation value $\langle\psi_{\mathbf{k}}(t)|\,\tau_z\,|\psi_{\mathbf{k}}(t)\rangle$ as well as the boundary (non-Hermitian effect) spin torque expectation value $\left\langle\psi_{\mathbf{k}}(t)|\,\tau_{b(z)}\,|\psi_{\mathbf{k}}(t)\right\rangle$ have to be simultaneously zero. We stress that, the zero boundary spin torque restriction, was not pointed out in this manner in Ref. [121], rather they assumed that the boundary spin torque density can be neglected. Moreover, by taking into account the boundary spin torque Eq. (3.38), we can deduce that, whenever is zero, then, the spin operator S_z behaves as a normal operator and no spin Hall effect is possible. In virtue of Eq. (3.30), the two restrictions of zero bulk and boundary spin torques, are satisfied whenever the z component of the spin is a constant of the motion $\frac{d}{dt}\langle S_z\rangle = 0$ (within bulk and over boundaries), which is fulfilled, either due to the above mentioned symmetry reasons, or more generally for any stationary state and without any symmetry considerations being involved, in which cases the right side of Eq. (3.49) has a well defined value.

Second, in order for the spin current to be rigorously given by the time derivative of the spin displacement operator Eq. (3.49), the non-Hermitian boundary contribution Eq. (3.48) has to be taken into account, which was also not noticed in Ref. [121].

The two restrictions with respect to the validity of this extended spin current operator, namely, the zero bulk and zero boundary spin torques, guarantees that its expectation value is

origin independent. This argument is verified by assuming a shift by $\mathbf{L}$ of the position origin, that is, $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{L}$. In this respect, the expectation value of Eq. (3.42) is transformed as $\frac{d}{dt}\langle \mathbf{r}S_z\rangle \rightarrow \frac{d}{dt}\langle \mathbf{r}S_z\rangle - \mathbf{L}\frac{d}{dt}\langle S_z\rangle$, from which it is clear that the extended spin current operator Eq. (3.42) is position origin independent whenever $\frac{d}{dt}\langle S_z\rangle = 0$.

3.4 Intrinsic spin current operator

Although the spin density is generally a non-conserved quantity with respect to materials that carry local spin-torques, the modulus of the spin is always a constant of the motion as long as the system is closed. In this respect, the electron's spin makes a precession motion around an involved direction (varying in space and time) in the bulk and over the boundaries of the material. In this framework we define the electron's extended intrinsic spin current as the time derivative of the correlation between electron's position and electron's spin. Whenever the two observables, spin and position, are uncorrelated, the extended spin current operator turns to zero value.

3.4.1 Extended intrinsic spin current operator

Based on the method developed in Sec.3.3, we define the local, intrinsic micro-flux of the z component of the spin as $\frac{d}{dt}\Psi^{\dagger}(\mathbf{r},t)\left(\mathbf{r}-\langle\mathbf{r}\rangle\right)S_z\Psi(\mathbf{r},t)$, which has the desirable dimensions, namely, $[\text{spin}].[\text{time}]^{-1}.[\text{area}]^{-1}$, where $(\mathbf{r}-\langle\mathbf{r}\rangle)$ is the electron's induced position displacement operator due to the action of the spin S_z operator on the quantum state under consideration. Similarly, the coordinate integration (over the system's volume) of this intrinsic micro-flux, gives the global value $\frac{d}{dt}\langle\Psi(t)|\left(\mathbf{r}-\langle\mathbf{r}\rangle\right)S_z|\Psi(t)\rangle$ that has dimensions $[\text{spin}].[\text{time}]^{-1}.[\text{length}]$, representing therefore the global intrinsic propagation of the z component of the spin that is captured by the quantum mechanical operator $\mathbf{G}$ defined as $\mathbf{G} = \left(\mathbf{r}-\langle\mathbf{r}\rangle\right)S_z$. By inserting this $\mathbf{G}$ operator in Eq. (3.5) and Eq. (3.6) we find the two operators of the observable, namely, the standard "bulk" intrinsic spin current operator given by

$$\boldsymbol{\mathcal{O}}_{int}^{sp(z)} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\left(\mathbf{r}-\langle\mathbf{r}\rangle\right)S_z\right] - \frac{d\langle\mathbf{r}\rangle}{dt}S_z \tag{3.50}$$

and the boundary intrinsic spin current operator given from

$$\boldsymbol{\mathcal{O}}_{int\ (b)}^{sp(z)} = \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\right)\left(\mathbf{r}-\langle\mathbf{r}\rangle\right)S_z. \tag{3.51}$$

We employ our extended velocity operator definition for the second term of the right hand side of Eq. (3.50). In this respect, the extended velocity operator is given by,

$$\mathbf{v}_{ext} = \mathbf{v} + \mathbf{v}_b \tag{3.52}$$

where,

$$\mathbf{v} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}\right] \tag{3.53}$$

is the standard (bulk) velocity operator and

$$\mathbf{v}_b = \frac{i}{\hbar}\big(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\big)\mathbf{r} \tag{3.54}$$

is the boundary velocity operator (see Eq. (2.3)).

By following the steps of derivation of Eq. (3.50) and Eq. (3.51) with the use of the Ehrenfest theorem, as well as using the identities $\langle\langle\mathbf{v}\rangle S_z\rangle = \langle\mathbf{v}\langle S_z\rangle\rangle$ and $\langle\langle\mathbf{v}_b\rangle S_z\rangle = \langle\mathbf{v}_b\langle S_z\rangle\rangle$ during the derivation, we find the final forms of the bulk and the boundary intrinsic spin current operators denoted as $\boldsymbol{\mathcal{J}}^{sp(z)}$ and $\boldsymbol{\mathcal{J}}_b^{sp(z)}$ respectively.

In this respect, the bulk intrinsic spin current operator $\boldsymbol{\mathcal{J}}^{sp(z)}$ is given by

$$\boldsymbol{\mathcal{J}}^{sp(z)} = (\mathbf{v} - \langle\mathbf{v}\rangle)S_z + (\mathbf{r} - \langle\mathbf{r}\rangle)\tau_z, \tag{3.55}$$

where we have expanded the commutator on the right side of Eq. (3.50) and use $\mathbf{v} = \frac{i}{\hbar}\left[H(\mathbf{r},t),\mathbf{r}\right]$ as well as $\tau_z = \frac{i}{\hbar}[H(\mathbf{r},t),S_z]$, while the boundary intrinsic spin current operator $\boldsymbol{\mathcal{J}}_b^{sp(z)}$ is given from

$$\boldsymbol{\mathcal{J}}_b^{sp(z)} = \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\right)(\mathbf{r} - \langle\mathbf{r}\rangle)S_z - \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\right)\mathbf{r}\langle S_z\rangle, \tag{3.56}$$

where the second term on the right side of Eq. (3.56) is attributed to the boundary velocity operator. The boundary intrinsic spin current operator $\boldsymbol{\mathcal{J}}_b^{sp(z)}$ can be recast in a more symmetrical form given by

$$\boldsymbol{\mathcal{J}}_b^{sp(z)} = \frac{i}{\hbar}\left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t)\right)(\mathbf{r}S_z - \langle\mathbf{r}\rangle S_z - \mathbf{r}\langle S_z\rangle). \tag{3.57}$$

The two terms of the bulk intrinsic spin current operator $\boldsymbol{\mathcal{J}}^{sp(z)}$ in Eq. (3.55) have a simple interpretation, namely: (i) the first one represents the spin current due to an induced velocity shift $(\mathbf{v} - \langle\mathbf{v}\rangle)$ produced by the action of the spin S_z operator on the quantum state under consideration, while (ii) the second term gives a spin current contribution due to an induced position displacement of the particle $(\mathbf{r} - \langle\mathbf{r}\rangle)$ produced by the action of the spin torque τ_z on the above mentioned quantum state.

By using Eq. (3.55) and Eq. (3.57), we find the extended intrinsic spin current operator that is given by

$$\boldsymbol{\mathcal{J}}_{ext}^{sp(z)} = \boldsymbol{\mathcal{J}}^{sp(z)} + \boldsymbol{\mathcal{J}}_b^{sp(z)}, \tag{3.58}$$

which is the necessary operator that causes the equation of motion of the operator $(\mathbf{r} - \langle\mathbf{r}\rangle)S_z$ by satisfying the equation

$$\frac{d}{dt}\langle\Psi(t)|(\mathbf{r} - \langle\mathbf{r}\rangle)S_z|\Psi(t)\rangle = \left\langle\Psi(t)|\boldsymbol{\mathcal{J}}_{ext}^{sp(z)}|\Psi(t)\right\rangle \tag{3.59}$$

without any constraints with respect to the expectation values of the bulk and the boundary spin torques being involved.

Based on Eq. (3.59), the expectation value of the extended spin current operator $\left\langle \Psi(t)\right| \boldsymbol{\mathcal{J}}^{sp(z)}_{ext} \left|\Psi(t)\right\rangle$, has the intuitive interpretation of the time derivative of the correlation between electron's spin and electron's position

$$\frac{d}{dt}\left\langle \Psi(t)\right| \left(\mathbf{r}-\left\langle \mathbf{r}\right\rangle\right) S_z \left|\Psi(t)\right\rangle = \frac{d}{dt}\left(\left\langle \mathbf{r}\, S_z\right\rangle - \left\langle \mathbf{r}\right\rangle\left\langle S_z\right\rangle\right),$$

measuring therefore of how spin projection along $\mathbf{e}_z$ direction and position co-vary with one another. In this framework, whenever the correlation between the electron's spin projection along $\mathbf{e}_z$ direction and position, is constant in time, then, the extended intrinsic spin current operator turns zero expectation value. In the simplest case, whenever spin's projection and position are uncorrelated, e.g. when spin S_z is constant of the motion, the extended spin current operator turns zero value.

By now using Eqs. (3.55) – (3.59) we can determine the basic properties of the bulk intrinsic spin current operator $\boldsymbol{\mathcal{J}}^{sp(z)}$ which are:
(i) For stationary states there exists a gain-loss detailed balance relation that explicitly relates the bulk expectation value with the corresponding boundary one given by

$$\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}\right\rangle_n = -\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}_b\right\rangle_n, \tag{3.60}$$

implying that, whenever the bulk of the system behaves as a source of spin current the boundaries operates as a sink and *vice versa*.
(ii) By defining the localized stationary states (in a macroscopic sense with respect to the system's boundaries) as the ones that satisfy $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}_b\right\rangle_n = 0$, implying that a boundary integral of the form Eq. (3.9) with $\mathbf{G} = \mathbf{r}S_z - \langle \mathbf{r}\rangle S_z - \mathbf{r}\langle S_z\rangle$ is zero, we can deduce from Eq. (3.60) that the standard, bulk intrinsic spin current expectation value (with respect to such stationary and localized state) is also zero.
(iii) For systems that do not exert spin torques in the z direction $\tau_z = 0$, the expectation value of the bulk intrinsic spin current operator Eq. (3.55) is zero $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}\right\rangle_n = 0$ provided that the Hamiltonian's stationary eigenstate is an eigenstate of the z component of the spin also. Accordingly, taking into account Eq. (3.57) as well as that the eigenstate belongs within the domain of definition of the Hamiltonian, that is, $\langle \Psi_n(t)|(H(\mathbf{r})^+ - H(\mathbf{r}))|\,\Psi_n(t)\rangle = 0$, the boundary intrinsic spin current expectation value turns also zero $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}_b\right\rangle_n = 0$.
(iv) The expectation values of, the extended intrinsic spin current Eq. (3.59), bulk intrinsic spin current Eq. (3.55) as well as of the boundary spin current Eq. (3.57), are separately position origin-independent quantities, which can be verified by assuming a shift by $\mathbf{L}$ of the position origin $\mathbf{r} \to \mathbf{r} - \mathbf{L}$.
(v) The expectation values, of the bulk and boundary intrinsic spin currents, $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}\right\rangle$ and $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}_b\right\rangle$ respectively, are always well defined quantities without any restrictions being involved, e.g. with respect to spin generation in the bulk or over the boundaries. In or-

der to prove this assertion, we calculate their expectation values with respect to a spinor Bloch wavefunction $\psi_{\mathbf{k}}(\mathbf{r},t)=\frac{1}{\sqrt{N}}e^{i\mathbf{k}.\mathbf{r}}u_{\mathbf{k}}(\mathbf{r},t)$ that satisfies Born-von Kármán periodic boundary conditions over the material's boundaries. The method of calculation is identical to the ones used in Sec.3.3 where we computed the expectation values of Eq. (3.44) and Eq. (3.45). Specifically, by exploiting the symmetry of the integrands, that is, taking into account that the spinor wavefunction $u_{\mathbf{k}}(\mathbf{r},t)$ as well as that the operators $\mathbf{v}(\mathbf{r},t)$ and $\tau_z(\mathbf{r},t)$ are cell periodic, we find that the standard (bulk) intrinsic spin current expectation value with respect to a periodic system is given by

$$\begin{aligned}\left\langle \psi_{\mathbf{k}}(t)\right|\boldsymbol{\mathcal{J}}^{sp(z)}\left|\psi_{\mathbf{k}}(t)\right\rangle &= \left\langle u_{\mathbf{k}}(t)\right|\left(\mathbf{r}-\left\langle u_{\mathbf{k}}(t)\right|\mathbf{r}\left|u_{\mathbf{k}}(t)\right\rangle_{cell}\right)\tau_z\left|u_{\mathbf{k}}(t)\right\rangle_{cell}\\ &+\left\langle u_{\mathbf{k}}(t)\right|\left(\mathbf{v}-\left\langle u_{\mathbf{k}}(t)\right|\mathbf{v}\left|u_{\mathbf{k}}(t)\right\rangle_{cell}\right)\tau_z\left|u(t)\right\rangle_{cell}.\end{aligned} \tag{3.61}$$

without any undefined quantities being involved.

Although the expectation value of the boundary intrinsic spin current is computed by a boundary integral over the terminated surface of the system, we use the bulk expression counterpart given by

$$\begin{aligned}\left\langle \psi_{\mathbf{k}}(t)\right|\boldsymbol{\mathcal{J}}_b^{sp(z)}\left|\psi_{\mathbf{k}}(t)\right\rangle &= \frac{i}{\hbar}\left\langle H_{\mathbf{k}}(\mathbf{r},t)u_{\mathbf{k}}(t)\right|\left(\mathbf{r}S_z-\langle\mathbf{r}\rangle S_z-\mathbf{r}\langle S_z\rangle\right)\left|u_{\mathbf{k}}(t)\right\rangle\\ &-\frac{i}{\hbar}\left\langle u_{\mathbf{k}}(t)\right|H_{\mathbf{k}}(\mathbf{r},t)\left(\mathbf{r}S_z-\langle\mathbf{r}\rangle S_z-\mathbf{r}\langle S_z\rangle\right)\left|u_{\mathbf{k}}(t)\right\rangle\end{aligned}$$

where $H_{\mathbf{k}}(\mathbf{r},t)=e^{-\mathbf{k}.\mathbf{r}}H(\mathbf{r},t)e^{\mathbf{k}.\mathbf{r}}$, in order to exploit the symmetry of the integrands. By doing so, we find that all undefined terms cancel each other and the boundary intrinsic spin current is given by

$$\begin{aligned}&\left\langle \psi_{\mathbf{k}}(t)\right|\boldsymbol{\mathcal{J}}_b^{sp(z)}\left|\psi_{\mathbf{k}}(t)\right\rangle\\ &\quad=\frac{i}{\hbar}\left\langle u_{\mathbf{k}}(t)\right|\left(H_{\mathbf{k}}(\mathbf{r},t)^{+}-H_{\mathbf{k}}(\mathbf{r},t)\right)\left(\mathbf{r}S_z-\langle\mathbf{r}\rangle_{cell}S_z-\mathbf{r}\langle S_z\rangle_{cell}\right)\left|u_{\mathbf{k}}(t)\right\rangle_{cell},\end{aligned} \tag{3.62}$$

without any undefined quantities being involved whatsoever. Moreover, the right side of Eq. (3.62) can be transformed and evaluated as a boundary integral over the unit cell. At this point, it is worth comparing our extended intrinsic bulk spin current Eq. (3.58), with the one defined in Ref. [121] and given by Eq. (3.46), as well as with the conventional spin current defined as $\frac{1}{2}(\mathbf{v}\,S_z+S_z\,\mathbf{v})$. The comparison shows that:
(i) The conventional spin current cannot be derived by means of a global quantum equation of motion, whenever the spin S_z is not conserved (e.g. in systems with non zero local spin torque τ_z) and the non-Hermitian boundary velocity of the electron $\langle\mathbf{v}_b\rangle$ is not zero. On the other hand, if we assume that, no local spin torques are exerted in the z direction $\tau_z=0$ and

the quantum state under consideration has a well-defined spin S_z eigenvalue $\pm\frac{\hbar}{2}$, as well as that the boundary velocity operator expectation value is zero $\langle \mathbf{v}_b \rangle = 0$, then, according to Eqs. (3.44), (3.46) and (3.49), the conventional spin current operator satisfies trivially the quantum equation of motion $\frac{d}{dt}\langle \mathbf{r} S_z \rangle = \frac{1}{2}\langle (\mathbf{v}\, S_z + S_z\, \mathbf{v}) \rangle$. In this framework we conclude that, the conventional spin current cannot be employed whenever spin dependent interactions and boundary non-Hermitian effects are present.

(ii) The Ref. [121] spin current $\left\langle \mathbf{J}^{sp(z)} \right\rangle$ given by Eq. (3.46), is an extension of the conventional spin current operator owing to explicitly taking into account the local spin torques that are exerted on the electron's spin S_z, but, on the other hand it has an undefined value in periodic systems. Only whenever no global spin generation in the bulk is made $\langle \tau_z \rangle = 0$, due to bulk symmetry reasons, its value Eq. (3.47) turns well defined. On the other hand, only the bulk symmetry is not adequate for this operator to satisfy the quantum equation of motion $\frac{d}{dt}\langle \mathbf{r} S_z \rangle = \left\langle \mathbf{J}^{sp(z)} \right\rangle$ assumed in Ref. [121]. In order for the latter equation to be satisfied, the boundary spin propagation expectation value Eq. (3.48) has to also be zero $\left\langle \mathbf{J}_b^{sp(z)} \right\rangle = 0$ meaning that, $\left\langle u_{\mathbf{k}}(t)\right| \mathbf{J}_b^{sp(z)} \left|u_{\mathbf{k}}(t)\right\rangle_{cell} = 0$ as well as $\left\langle \psi_{\mathbf{k}}(t)\right| \tau_{b(z)} \left|\psi_{\mathbf{k}}(t)\right\rangle = 0$, thus no spin Hall effect is possible. In summary, the Ref. [121] spin current expectation value cannot generally satisfy a quantum equation of motion, unless certain constraints are satisfied, thus the Ref. [121] spin current operator cannot be generally employed for arbitrary interactions (due to the above mentioned symmetry constraints being involved) to study coupled transport processes.

(iii) Our extended intrinsic spin current operator Eq. (3.58) always has a well defined value and satisfies a quantum equation of motion Eq. (3.59) without any constraints being involved, provided that the system is closed. In this respect, it can be used to study interactions that cause the time evolution of the extended spin current expectation value that is captured by the quantum equation of motion $\frac{d}{dt}\left\langle \Psi(t)\right| \boldsymbol{\mathcal{J}}_{ext}^{sp(z)} \left|\Psi(t)\right\rangle = \boldsymbol{\mathcal{F}}^{sp(z)}$ where $\boldsymbol{\mathcal{F}}^{sp(z)}$ denotes the spin force expectation value. The latter equation is in accordance with the quantum analogue of Newton's 2nd law, namely the quantum equation of motion $\frac{d}{dt}\langle \Psi(t)| \mathbf{J}_{ext}^{m} |\Psi(t)\rangle = \mathbf{F}$, where the extended particle's mass current $\mathbf{J}_{ext}^{m}$ expectation value is defined by $\langle \mathbf{J}_{ext}^{m} \rangle = m\langle \Psi(t)| \mathbf{v}_{ext} |\Psi(t)\rangle = \frac{d}{dt}\langle \Psi(t)| \mathbf{r} m |\Psi(t)\rangle$. In this framework, near the equilibrium stationary states that satisfy $\left\langle \Psi(t)\right| \boldsymbol{\mathcal{J}}_{ext}^{sp(z)} \left|\Psi(t)\right\rangle = 0$, one can use a linear dissipation approximation equation for an assumed irreversible process, that is use Eq. (3.21) applied to the extended intrinsic spin current and study the dissipation of the extended intrinsic spin current. This method gives the coupled first order differential equations

$$\begin{pmatrix} \mathcal{F}_x^{sp(z)} \\ \mathcal{F}_y^{sp(z)} \\ \mathcal{F}_z^{sp(z)} \end{pmatrix} = - \begin{pmatrix} k_{xx} & k_{xy} & k_{xz} \\ k_{yx} & k_{yy} & k_{yz} \\ k_{zx} & k_{zy} & k_{zz} \end{pmatrix} \begin{pmatrix} \left\langle \mathcal{J}_{ext\ x}^{sp(z)} \right\rangle \\ \left\langle \mathcal{J}_{ext\ y}^{sp(z)} \right\rangle \\ \left\langle \mathcal{J}_{ext\ z}^{sp(z)} \right\rangle \end{pmatrix}, \tag{3.63}$$

where the elements k_{ij} of the above matrix are all real quantities and satisfy $k_{ij} = k_{ji}$, in order that an exponential attenuating solution exist for each $\left\langle \mathcal{J}^{sp(z)}_{ext\ i} \right\rangle$. In the right side of Eq. (3.63) the extended intrinsic spin current is given by definition as $\left\langle \boldsymbol{\mathcal{J}}^{sp(z)}_{ext} \right\rangle = \dfrac{d}{dt} \langle (\mathbf{r} - \langle \mathbf{r} \rangle) S_z \rangle$.

The counterpart irreversible linear charge current dissipation equation is given by

$$\begin{pmatrix} F^{ch}_x \\ F^{ch}_y \\ F^{ch}_z \end{pmatrix} = - \begin{pmatrix} \mu_{xx} & \mu_{xy} & \mu_{xz} \\ \mu_{yx} & \mu_{yy} & \mu_{yz} \\ \mu_{zx} & \mu_{zy} & \mu_{zz} \end{pmatrix} \begin{pmatrix} \langle J^{ch}_{ext\ x} \rangle \\ \langle J^{ch}_{ext\ y} \rangle \\ \langle J^{ch}_{ext\ z} \rangle \end{pmatrix}, \tag{3.64}$$

where by definition, $\left\langle \mathbf{J}^{ch}_{ext} \right\rangle = \dfrac{d}{dt} \langle \mathbf{r} e \rangle$ and $\mathbf{F}^{ch} = \dfrac{d}{dt} \langle \mathbf{v}_{ext}\, e \rangle = \dfrac{e}{m} \mathbf{F}^{elec} = \dfrac{e^2}{m} \boldsymbol{\mathcal{E}}$, where $\boldsymbol{\mathcal{E}}$ is the electric field acting on the electron charge and m is its mass. Eq. (3.63) and Eq. (3.64) can be expressed in compact forms as $\mathcal{F}^{sp(z)}_i = k_{ij} \left\langle \mathcal{J}^{sp(z)}_{ext\ j} \right\rangle$ and $F^{ch}_i = \mu_{ij} \left\langle J^{ch}_{ext\ j} \right\rangle$ respectively. By having in mind that the spin dipole $\langle (\mathbf{r} - \langle \mathbf{r} \rangle) S_z \rangle$ will saturate to a constant value at the end of the irreversible process, we express the extended intrinsic spin current as a linear dissipation equation given by $\left\langle \mathcal{J}^{sp(z)}_{ext\ j} \right\rangle = h_{jn} \left(C_n - \langle (r_n - \langle r_n \rangle) S_z \rangle \right)$, where h_{jn} are phenomenological coefficients and C_n the (constant) value in which each $\langle (r_n - \langle r_n \rangle) S_z \rangle$ will saturate in equilibrium. Accordingly, having in mind that each $\langle \mathbf{r} e \rangle$ will also saturate to a constant value when equilibrium is reached, we express the extended charge current as $\left\langle J^{ch}_{ext\ j} \right\rangle = \nu_{jl} \left(R_l - \langle r_l\, e \rangle \right)$ where ν_{jl} are phenomenological coefficients and each R_l is the (constant) value in which $\langle r_l\, e \rangle$ will saturate. In this fashion, one can couple Eq. (3.63) with Eq. (3.64), and form Onsager relations that relate the extended intrinsic spin current generated by an electric force $\mathbf{F}^{ch}$ to the extended charge current generated by a spin-electric force $\boldsymbol{\mathcal{F}}^{sp(z)}$.

Chapter 4

Topology in transport processes: Extended Hellmann-Feynman theorem

We now proceed to some independent study with the purpose to extend an elementary quantum mechanical theorem so that it can become a tool for the investigation of transport properties in Solid State Physics. In spite of the independent nature of this study, we will witness an overlap with the viewpoint reflected in the previous two Chapters; the outcomes of the present Chapter will inherit the non-Hermitian effects of Chapters 2 and 3 in combination with nontrivial topology.

Collective robust patterns of behaviors such as the precise quantization of the transverse conductivity in the quantum Hall effect [77], are attributed to the so-called topology of the first (magnetic) Brillouin zone of the Hilbert space [135, 78]. These collective topological properties, in the simplest case, emerge when the Hamiltonian H of the system varies slowly with time, either due to explicit time-dependence or implicitly by a time-dependent parameter. With time, this kind of change, makes each electron's ground-state wavefunction to deviate infinitesimally from stationarity (the wavefunction is an instantaneous eigenfunction of H), resulting into an extra, geometrical type of phase for the wavefunction during the time-evolution. When the extra phase is non-integrable (cannot be expressed as a regular function of the parameter), it signals that the quantum system is set into a topological quantum process[1], which is stable against local perturbations and sometimes maintains quantum coherence even at high temperatures (i.e. it can exhibit robustness to environmental decoherence).

The topological quantum processes can roughly be separated into two general categories, the first one described by equilibrium quantum states (the quantum state is parallel to an instantaneous eigenstate of the Hamiltonian), and the second one described by non-equilibrium quantum states where the wavefunction is in a coherent superposition and occupies more than

[1] Since the seminal theoretical work of M.V. Berry [17], all of the scientific community was standing on the Fock's false observation, who unintentionally excluded all topological processes. He suggested that, during all processes that the wavefunction evolves in time adiabatically, one can always eliminate the extra phases by a proper adjustment of the wavefunction's phase with a regular function, that is, by performing a regular $U(1)$ gauge transformation.

one direction of the available Hilbert space. The study of equilibrium quantum processes is in a very mature state, while the study of the non-equilibrium is at an ongoing research stage (i.e some new topological invariants have been suggested based on the time-evolution operator [76, 83, 31, 116], as well as some dynamical order parameters have been used for the description of topological phase transitions [65, 26, 68, 138, 53, 117, 64]).

The equilibrium quantum processes, are mainly studied by three different methods:

In the first kind of methods, which resides on the route opened by M.V. Berry, one studies the phases that are accumulated by the wavefunctions during closed (cyclic) process when a time-dependent parameter undergoes a periodic evolution (when the accumulated phase is not zero, it indicates that the wavefunctions carry non-trivial topological charge). In this kind of methods, the local (on the path of integration) quantities involved are the Berry connections which are not gauge-invariant quantities.

In the second and third kind of methods, gauge-invariant topological quantities such as Berry curvatures, are explicitly engaged into observable formulas, therefore, one can directly study the impact of topology to collective transport properties. Specifically, in the second kind of methods, one employs a quantum mechanical framework and uses a first order (linear response) time-dependent perturbation theory (alternatively the adiabatic limit of Kubo formula), in order to calculate for example the electron's velocity expectation value. Within this method, an electron that is assumed to initially be in a non-degenerate ground state, acquires an extra velocity term (named anomalous velocity) besides its group velocity, that explicitly depends on a Berry curvature, which has topological origin. This extra velocity contribution, is responsible for the quantization of the transverse Hall conductivity [77, 135, 78], as well as, plays a crucial role in the theoretical explanation of the anomalous quantum Hall effect [73, 34, 94, 145, 59, 85, 18, 84, 62, 124]. As will be shown (based on a dynamic Hellmann-Feynman (HF) theorem that we have derived), there exist two other velocity contributions in general: the one is of topological origin and is attributed to another Berry curvature, and the other is of non-Hermitian boundary origin. These extra contributions will be explicitly used to study the (Thouless pump) particle transport [134, 97, 122, 89, 105, 156, 141], as well as the polarization current [75, 101, 109, 114, 111, 126, 139, 57] in a dielectric medium.

The third method is a semiclassical one, first derived by M. C. Chang, D. Sundaram and Q. Niu [35, 130]. In this method the electron's motion is described by a trial wave packet constructed from Bloch eigenstates (with small spread in crystal momentum space compared to the Brillouin zone). An effective Lagrangian of the motion, with generalized variables the electron's main position and the electron's main crystal momentum is defined, whereas the external (electric and magnetic) fields are taken into account as perturbations. Under the approximations that: (i) the external fields vary slowly over the spatial extension of the wave packet, as well as that (ii) the fields do not cause excitations (adiabatic approximation), by employing a time-dependent variational principle for the trial wave packet one finds the two equations of motion; one for the electron's main position and the other for the crystal momentum motion. Within this method, the velocity of the wave packet's center acquires an

extra contribution (besides the group velocity) which explicitly depends on a Berry curvature.

Having in mind all three above methods, a plausible theoretical question has motivated us: "Can one use a kind of a Hellmann-Feynman theorem to study such topological quantum processes?" The answer is affirmative yes, and up to date, to the best of our knowledge, there has not been any extension of the known static Hellmann-Feynman (HF) theorem [63, 50] that can be applied to dynamic topological transport processes and at the same time take into account boundary contributions as an emerging non-Hermitian effect. In this respect, a brief review of known forms of the Hellmann-Feynman theorem will be given followed by our derivation accompanied by interesting implications (i.e. equation of motion of the elementary parameter volume $\Delta V_R(t)$ that causes complications when one transforms a sum over states to a counterpart Riemann integration, and a Maxwell type of equation with monopoles for flux preserving motions), followed by certain applications (i.e. particle transport with boundaries explicitly taken into account, electronic polarization with boundary contributions explicitly included, quantum equations of motion as extension of the semiclassical counterparts, and modification of the density of states for spinfull motions with monopole sources included).

The known HF theorem is a very practical method for calculating expectation values of observables with respect to stationary eigenstates of static Hamiltonians by taking the derivative of the energy eigenvalue with respect to a static parameter that is assumed to take continuous values. After the first derivation of the HF theorem [63, 50], Epstein utilized it, and showed its direct relation to time-independent perturbation theory [46]. These two methods deal with static parameters and time-independent eigenstates of the Hamiltonian.

An extension that uses time-dependent parameters and relates the theorem to adiabatically evolving eigenstates of the Hamiltonian is hardly known and has only been noted in passing [10, 9]. Another extension was later made by us, a preliminary report of which has been given in [80]. All forms of the HF theorem mentioned above, have a common assumption: the states that are created by the action of the parameter's differential operator are assumed to belong within the domain of definition of the Hermitian Hamiltonian (thus belong within the given Hilbert space) which is hardly the case. This kind of anomaly leaves a residue in the HF theorem and was first noted in [49]. Based on this observation [49], they have generalized the static HF theorem (applied to static parameters and time-independent eigenstates of the Hamiltonian) in order to take into account these extra anomalous terms (differential operators that cause such non-Hermitian effect are sometimes called anomalous operator, and by definition create states that lie outside the given Hilbert space). These residue terms, are always transformed to a surface integral (assuming a 3D system) over the material boundaries, therefore giving an extra boundary contribution (that explicitly depends on the realistic boundary conditions of the wavefunctions).

4.1 Formulating the dynamical extension of the HF theorem

Dynamic vector parameter $\mathbf{R}(t)$:

We consider a real vector parameter $\mathbf{R}$ that has an arbitrary time-dependence (without any adiabatic approximation involved), namely, $\mathbf{R} = \boldsymbol{\mathcal{R}}(t, \mathbf{R_o})$ where $\mathbf{R_o}$ is the initial value of the parameter satisfying $\mathbf{R_o} = \boldsymbol{\mathcal{R}}(0, \mathbf{R_o})$. Therefore, the parameter satisfies the general equation of motion $\mathbf{R} = \mathbf{R_o} + \int_0^t \frac{\partial \mathbf{R}}{\partial t'} dt'$, and its time derivative is given by $\frac{\partial \mathbf{R}}{\partial t} = \frac{\partial \boldsymbol{\mathcal{R}}(t, \mathbf{R_o})}{\partial t}$. The theorem that we are to prove is for a continuous vector parameter $\mathbf{R}$, therefore the initial value $\mathbf{R_o}$ is assumed to have continuous values. The Hamiltonian of the system $H(t, \mathbf{R})$, apart from the implicit time-dependence (via the parameter) may also have an arbitrary explicit time-dependence. The derivation that is given owes its existence to the Hamiltonian being the generator of time evolution of quantum states. We provide the derivation for a single-particle state while the generalization to a many-particle system is straightforward. A particle's motion is generally encoded in its normalized time-dependent state $|\Psi(t, \mathbf{R})\rangle$ which evolves either by the time-dependent Schrödinger equation for non-relativistic and spinless particle, or by the time-dependent Dirac equation for spin-full particle. We assume for simplicity a one particle quantum system. The motion of the particle is described by a general state, not necessarily an eigenstate of the Hamiltonian nor a localized state (such as a narrow wave packet). The system is assumed to be closed $\langle \Psi(t, \mathbf{R}) | \Psi(t, \mathbf{R}) \rangle = 1$, and the quantum state time evolution is determined by the time-dependent equation

$$i\hbar \frac{d}{dt} |\Psi(t, \mathbf{R})\rangle = H(t, \mathbf{R}) |\Psi(t, \mathbf{R})\rangle , \tag{4.1}$$

where the Hamiltonian is either of Schrödinger or Dirac type. The time derivative in Eq. (4.1) is the total time derivative given by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{\partial \mathbf{R}}{\partial t} \cdot \boldsymbol{\nabla}_{\mathbf{R}} \tag{4.2}$$

where $\boldsymbol{\nabla}_{\mathbf{R}} = \sum_{i=1}^{3} \mathbf{e}_i \frac{\partial}{\partial_{\mathbf{R}_i}}$. The initial value of the parameter $\mathbf{R_o}$ that implicitly enters Eq. (4.1) can be used to label the quantum states $|\Psi(t, \mathbf{R})\rangle$. The expectation value of the Hamiltonian

$$\langle \Psi(t, \mathbf{R}) | H(t, \mathbf{R}) |\Psi(t, \mathbf{R})\rangle = E(t, \mathbf{R}) \tag{4.3}$$

can be seen as the instantaneous time-dependent "energy" of the particle $E(t, \mathbf{R})$. Differentiation with respect to the parameter $\mathbf{R}$ of both sides of Eq. (4.3) gives

$$\langle \Psi \,|\, \boldsymbol{\nabla}_{\mathbf{R}} H \,|\, \Psi \rangle = \boldsymbol{\nabla}_{\mathbf{R}} E - \langle \boldsymbol{\nabla}_{\mathbf{R}} \Psi \,|\, H\Psi \rangle - \langle \Psi | \, H \, \boldsymbol{\nabla}_{\mathbf{R}} \Psi \rangle . \tag{4.4}$$

Taking now into account that the parameter gradient operator $\boldsymbol{\nabla}_{\mathbf{R}}$ can generally be an anomalous operator, that is, the states $|\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle$ may not belong within the domain of the Hermitian Hamiltonian which is expressed by the non-trivial inequality $\langle H\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle = \langle\Psi\,|\,H^{+}\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle \neq \langle\Psi\,|\,H\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle$, we recast Eq. (4.4) in the form

$$\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E - \langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,|\,H\Psi\rangle - \langle H\Psi|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle + \left\langle\Psi\,\middle|\,\left(H^{+}-H\right)\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle. \quad (4.5)$$

By then using Eq. (4.1) in Eq. (4.5) we find

$$\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E + \left\langle\Psi\,\middle|\,\left(H^{+}-H\right)\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle - i\hbar\left(\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,\middle|\,\frac{d\Psi}{dt}\right\rangle - \left\langle\frac{d\Psi}{dt}\middle|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle\right). \quad (4.6)$$

Applying the total time derivative Eq. (4.2) on Eq. (4.6) we get

$$\begin{aligned}\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle \;=\; & \boldsymbol{\nabla}_{\mathbf{R}}E + \left\langle\Psi\,\middle|\,\left(H^{+}-H\right)\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle \\ & -i\hbar\left(\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,\middle|\,\frac{\partial\Psi}{\partial t}\right\rangle - \left\langle\frac{\partial\Psi}{\partial t}\middle|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle\right) \\ & -i\hbar\left(\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,\middle|\,\frac{\partial\mathbf{R}}{\partial t}\cdot\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle - \left\langle\frac{\partial\mathbf{R}}{\partial t}\cdot\boldsymbol{\nabla}_{\mathbf{R}}\Psi\middle|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle\right).\end{aligned} \quad (4.7)$$

Using then the vector identity, $\dfrac{\partial\mathbf{R}}{\partial t}\times(\mathbf{A}\times\mathbf{B}) = \mathbf{A}\left(\dfrac{\partial\mathbf{R}}{\partial t}\cdot\mathbf{B}\right) - \left(\dfrac{\partial\mathbf{R}}{\partial t}\cdot\mathbf{A}\right)\mathbf{B}$ in the last term on the right hand side of Eq. (4.7), we finally find

$$\langle\boldsymbol{O}(t,\mathbf{R})\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E(t,\mathbf{R}) + \boldsymbol{\mathcal{S}}(t,\mathbf{R}) - \hbar\,\boldsymbol{\mathcal{E}}(t,\mathbf{R}) - \hbar\,\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{B}}(t,\mathbf{R}), \quad (4.8)$$

where

$$\langle\boldsymbol{O}(t,\mathbf{R})\rangle = \langle\Psi(t,\mathbf{R})\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H(t,\mathbf{R})\,|\,\Psi(t,\mathbf{R})\rangle \quad (4.9)$$

is the observable in quest, whereas

$$\boldsymbol{\mathcal{B}}(t,\mathbf{R}) = i\,\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi(t,\mathbf{R})|\times|\boldsymbol{\nabla}_{\mathbf{R}}\Psi(t,\mathbf{R})\rangle \quad (4.10)$$

is a generalized Berry curvature in the $\mathbf{R}\times\mathbf{R}$ space and

$$\boldsymbol{\mathcal{E}}(t,\mathbf{R}) = i\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi(t,\mathbf{R})\,\middle|\,\frac{\partial\Psi(t,\mathbf{R})}{\partial t}\right\rangle - i\left\langle\frac{\partial\Psi(t,\mathbf{R})}{\partial t}\middle|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi(t,\mathbf{R})\right\rangle \quad (4.11)$$

is a second generalized Berry curvature in the $t\times\mathbf{R}$ space. The $\boldsymbol{\mathcal{S}}(t,\mathbf{R})$ term is a non-Hermitian boundary quantity which, by working in position representation and assuming real scalar and vector potentials, is always transformed to a boundary integral (due to symmetry

of the integrands) over the system's boundaries and is given (assuming a 3D system) by

$$\begin{aligned} \boldsymbol{\mathcal{S}}(t,\mathbf{R}) &= \left\langle \Psi(t,\mathbf{R}) \right| \left(H(t,\mathbf{R})^{+} - H(t,\mathbf{R}) \right) \boldsymbol{\nabla}_{\mathbf{R}} \Psi(t,\mathbf{R}) \Big\rangle \\ &= \frac{i\hbar}{2} \oiint_{S} \mathbf{n} \cdot \Big(\left(\mathbf{v}\, \Psi(t,\mathbf{R}) \right)^{+} + \Psi(t,\mathbf{R})^{+}\, \mathbf{v} \Big)\, \boldsymbol{\nabla}_{\mathbf{R}} \Psi(t,\mathbf{R})\, dS, \end{aligned} \tag{4.12}$$

where $\mathbf{v} = \frac{i}{\hbar}\left[H(t,\mathbf{R}), \mathbf{r}\right]$ is the standard velocity operator and $\mathbf{n}$ is the unit vector that is locally normal to the surface that encloses the system. The dynamical extension of the HF theorem given by Eq. (4.8) is the first major result of this chapter, and one of the major results of this dissertation.

As is evident from the structure of the dynamical HF Eq. (4.8), the observables $\langle \boldsymbol{O}(t,\mathbf{R}) \rangle$ that are given by this theorem always have a part that is transverse to the direction of the parameter variation $\partial\mathbf{R}$ which is given by

$$\langle \boldsymbol{O}(t,\mathbf{R}) \rangle_{tran} = -\hbar \frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{R}), \tag{4.13}$$

as easily confirmed by $\langle \boldsymbol{O}(t,\mathbf{R}) \rangle_{tran} \cdot \partial\mathbf{R} = 0$ (where we have used the vector identity $\partial\mathbf{R} \times \mathbf{A} \cdot \partial\mathbf{R} = \mathbf{A} \cdot \partial\mathbf{R} \times \partial\mathbf{R} = 0$), while the first three terms

$$\langle \boldsymbol{O}(t,\mathbf{R}) \rangle = \boldsymbol{\nabla}_{\mathbf{R}} E(t,\mathbf{R}) + \boldsymbol{\mathcal{S}}(t,\mathbf{R}) - \hbar\, \boldsymbol{\mathcal{E}}(t,\mathbf{R}) \tag{4.14}$$

may have longitudinal as well transverse part. It is interesting to note that, when the assumed parameter $\mathbf{R}$ is static, the transverse part turns to zero $\langle \boldsymbol{O}(t,\mathbf{R}) \rangle_{tran} = 0$ (the generalized curvature $\boldsymbol{\mathcal{B}}(t,\mathbf{R})$ need not be zero), while, when the quantum state does not have explicit time dependence, the generalized curvature $\boldsymbol{\mathcal{E}}(t,\mathbf{R})$ turns to zero by definition Eq. (4.11).

The general form of the theorem Eq. (4.8), has a very interesting property. Namely, when the assumed Hamiltonian H does not depend explicitly on the parameter $\mathbf{R}$, but on the other hand the quantum states explicitly depend on it (the parameter enters the wavefunction due to symmetry reasons as a constant of the motion, or in virtue of a large gauge transformation), then, by definition $\langle \boldsymbol{O}(t,\mathbf{R}) \rangle = 0$, one can clearly relate the boundary contribution $\boldsymbol{\mathcal{S}}(t,\mathbf{R})$ of an observable to bulk quantities such as, the gradient of the "energy" and the generalized curvatures (such examples are discussed in Sec.4.1.3 as well as in 4.3.1 and 4.3.2). Furthermore, if the boundary contribution is expressed by the expectation value of a boundary operator (such as the boundary velocity operator), then, there is a relatively simple way that one can relate boundary contributions of an observable to the bulk topology of the projective Hilbert space via the generalized Berry curvatures. We explicitly use this argument in applications of the theorem for the particle transport.

Static vector parameter:

Whenever the vector parameter is static $\mathbf{R}(t) = \mathbf{R_o}$, we use Eqs. (4.8) – (4.12) and substitute $\frac{\partial \mathbf{R}(t)}{\partial t} = 0$ as well as $\boldsymbol{\nabla}_{\mathbf{R}} = \boldsymbol{\nabla}_{\mathbf{R}_o}$.

Dynamic scalar parameter $\lambda(t)$:

For a real scalar dynamic parameter, we replace $\mathbf{R}(t) \mapsto \lambda(t)$ as well as $\boldsymbol{\nabla}_{\mathbf{R}} \mapsto \dfrac{\partial}{\partial \lambda}$ in Eq. (4.7) that results to

$$\langle O(t,\lambda)\rangle = \frac{\partial}{\partial \lambda} E(t,\lambda) \,+\, \mathcal{S}(t,\lambda) \,-\, \hbar\, \mathcal{E}(t,\lambda). \tag{4.15}$$

where the initial value λ_o of the parameter $\lambda = \lambda(t,\lambda_o)$ is assumed to take continuous values. The curvature $\mathcal{E}(t,\lambda)$ is given by

$$\mathcal{E}(t,\lambda) = i \left\langle \frac{\partial \Psi(t,\lambda)}{\partial \lambda} \,|\, \frac{\partial \Psi(t,\lambda}{\partial t} \right\rangle - i \left\langle \frac{\partial \Psi(t,\lambda)}{\partial t} | \, \frac{\partial \Psi(t,\lambda)}{\partial \lambda} \right\rangle, \tag{4.16}$$

and the boundary non-Hermitian term by

$$\begin{aligned} \mathcal{S}(t,\lambda) &= \left\langle \Psi(t,\lambda) \,|\, \left(H(t,\lambda)^{+} - H(t,\lambda)\right) \frac{\partial \Psi(t,\lambda)}{\partial \lambda} \right\rangle \\ &= \frac{i\hbar}{2} \oiint_S \mathbf{n}\cdot \Big(\left(\mathbf{v}\, \Psi(t,\lambda)\right)^{+} + \Psi(t,\lambda)^{+}\, \mathbf{v} \Big) \frac{\partial \Psi(t,\lambda)}{\partial \lambda}\, dS. \end{aligned} \tag{4.17}$$

We conclude that, for a scalar parameter and 3D system no transverse contribution can be defined.

4.1.1 Adiabatic limit of the extended HF theorem

It is instructive to derive the adiabatic limit of the extended HF theorem Eq. (4.8), because numerous quantum processes related to topological invariant properties, are studied within this limit. In this respect, we assume an adiabatic evolved quantum state with initially well defined energy, namely, $|\Psi(t,\mathbf{R})\rangle \equiv e^{i\Theta_n(t,\mathbf{R})}\, |n(t,\mathbf{R})\rangle$ where $|n(t,\mathbf{R})\rangle$ is the instantaneous eigenstate of the Hamiltonian satisfying the eigenvalue equation

$$H(t,\mathbf{R})\, |n(t,\mathbf{R})\rangle = E_n(t,\mathbf{R})\, |n(t,\mathbf{R})\rangle$$

and $\Theta_n(t,\mathbf{R})$ is the total (sum of dynamic and geometric) phase of the wavefunction satisfying the equation

$$-\hbar \frac{d\Theta_n(t,\mathbf{R})}{dt} = E_n(t,\mathbf{R}) - i\hbar \left\langle n(t,\mathbf{R})| \, \frac{dn(t,\mathbf{R})}{dt} \right\rangle.$$

By substituting $|\Psi(t,\mathbf{R})\rangle \equiv e^{i\Theta_n(t,\mathbf{R})}\, |n(t,\mathbf{R})\rangle$ in all members of Eq. (4.8), that is, by using

$$|\boldsymbol{\nabla}_{\mathbf{R}} \Psi(t,\mathbf{R})\rangle \equiv e^{i\Theta_n(t,\mathbf{R})}\, i\, \boldsymbol{\nabla}_{\mathbf{R}} \Theta_n(t,\mathbf{R})\, |n(t,\mathbf{R})\rangle + e^{i\Theta_n(t,\mathbf{R})}\, |\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\rangle\,,$$

as well as

$$\left|\frac{\partial\Psi(t,\mathbf{R})}{\partial t}\right\rangle \equiv e^{i\Theta_n(t,\mathbf{R})}\, i\,\frac{\partial\Theta_n(t,\mathbf{R})}{\partial t}\,|n(t,\mathbf{R})\rangle + e^{i\Theta_n(t,\mathbf{R})}\left|\frac{\partial n(t,\mathbf{R})}{\partial t}\right\rangle,$$

we find after straightforward calculation,

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_n = \boldsymbol{\nabla}_{\mathbf{R}} E_n(t,\mathbf{R}) \,+\, \boldsymbol{\mathcal{S}}_n(t,\mathbf{R}) - \hbar\,\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{B}}_n(t,\mathbf{R}) \,-\, \hbar\,\boldsymbol{\mathcal{E}}_n(t,\mathbf{R}), \tag{4.18}$$

where,

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_n = \langle n(t,\mathbf{R})\,|\,\boldsymbol{\nabla}_{\mathbf{R}} H(t,\mathbf{R})\,|\,n(t,\mathbf{R})\rangle \tag{4.19}$$

is the observable in quest, and

$$\boldsymbol{\mathcal{B}}_n(t,\mathbf{R}) = i\,\langle\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})|\times|\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\rangle \tag{4.20}$$

is the standard Berry curvature evaluated with respect to the Hamiltonian's instantaneous eigenstates. Accordingly

$$\boldsymbol{\mathcal{E}}_n(t,\mathbf{R}) = i\left\langle \boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\,|\,\frac{\partial n(t,\mathbf{R})}{\partial t}\right\rangle - i\left\langle\frac{\partial n(t,\mathbf{R})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\right\rangle \tag{4.21}$$

is a Berry curvature in $t\times\mathbf{R}$ space, while the non-Hermitian boundary term is given by

$$\begin{aligned}\boldsymbol{\mathcal{S}}_n(t,\mathbf{R}) &= \big\langle n(t,\mathbf{R})\,|\,\big(H(t,\mathbf{R})^+ - H(t,\mathbf{R})\big)\,\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\big\rangle \\ &= \frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\big(\,(\mathbf{v}\,\Phi_n)^+ + \Phi_n^+\,\mathbf{v}\,\big)\,\boldsymbol{\nabla}_{\mathbf{R}}\Phi_n\,dS,\end{aligned} \tag{4.22}$$

where $\Phi_n \equiv \Phi_n(t,\mathbf{R}) = \langle\,\mathbf{r}\,|\,n(t,\mathbf{R})\rangle$. In deriving Eqs. (4.20) and (4.21) we have used the normalization condition $\langle n(t,\mathbf{R})|n(t,\mathbf{R})\rangle = 1$, which upon differentiation gives the relations

$$\langle\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})|n(t,\mathbf{R})\rangle + \langle n(t,\mathbf{R})|\boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R})\rangle = 0$$

and

$$\left\langle\frac{\partial n(t,\mathbf{R})}{\partial t}|n(t,\mathbf{R})\right\rangle + \left\langle n(t,\mathbf{R})|\frac{\partial n(t,\mathbf{R})}{\partial t}\right\rangle = 0$$

that have been used. Furthermore, we have used that the states $|n(t,\mathbf{R})\rangle$ belong within the domain of definition of the Hamiltonian $H(t,\mathbf{R})$, that is

$$\big\langle n(t,\mathbf{R})\,|\,\big(H(t,\mathbf{R})^+ - H(t,\mathbf{R})\big)\,n(t,\mathbf{R})\big\rangle = 0.$$

4.1.2 Symmetry considerations

From the symmetries of the instantaneous eigenvalue equation

$$H(t,\mathbf{R})\,\psi_n(\mathbf{r},t,\mathbf{R}) = E_n(t,\mathbf{R})\,\psi_n(\mathbf{r},t,\mathbf{R}), \tag{4.23}$$

where $\psi_n(\mathbf{r}, t, \mathbf{R}) = \langle \mathbf{r} \,|\, n(t, \mathbf{R}) \rangle$, the symmetries of the curvatures themselves can sometimes be deduced, which gives valuable information about the topology of the projective Hilbert space of the energy band $E_n(t, \mathbf{R})$. In the latter eigenvalue equation, the time t and the parameter momentum $\mathbf{R}$ are assumed to be fixed parameters.

Continuous Symmetries

Whenever the Hamiltonian does not have explicit time dependence $\dfrac{\partial H}{\partial t} = 0$, then $H \equiv H(\mathbf{R})$, thus the instantaneous eigenstates $\psi_n(\mathbf{r}, t, \mathbf{R})$ do not have explicit time dependence owing to the eigenvalue equation $H(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R}) = E_n(\mathbf{R})\psi_n(\mathbf{r}, \mathbf{R})$. As a result, the Berry curvature given by Eq. (4.21) turns to zero $\boldsymbol{\mathcal{E}}_n(\mathbf{R}) = 0$ by definition.

Discrete Symmetries

This section is useful in band theory applications if we identify the parameter as the wave vector $\mathbf{R} \equiv \mathbf{k}$, where the instantaneous wavefunction has the ansatz form $\Psi_n(\mathbf{r}, t, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_n(\mathbf{r}, t, \mathbf{k})$. The states $u_n(\mathbf{r}, t, \mathbf{k})$ need not be cell periodic. For simplicity reasons we assume spinless motion, that is, the Hamiltonian is a scalar operator and the wavefunctions $u_n(\mathbf{r}, t, \mathbf{k})$ are scalar quantities. We further assume that the initial Hamiltonian does not have explicit wave vector (parameter) dependence, therefore the wavefunctions $\psi_n(\mathbf{r}, t, \mathbf{k})$ satisfies the eigenvalue equation

$$H(t)\, \psi_n(\mathbf{r}, t, \mathbf{k}) = E_n(t, \mathbf{k})\, \psi_n(\mathbf{r}, t, \mathbf{k}), \tag{4.24}$$

and accordingly, the wavefunction $u_n(\mathbf{r}, t, \mathbf{k})$ fulfills the equation

$$e^{-i\mathbf{k}\cdot\mathbf{r}} H(t)\, e^{i\mathbf{k}\cdot\mathbf{r}}\, u_n(\mathbf{r}, t, \mathbf{k}) = E_n(t, \mathbf{k})\, u_n(\mathbf{r}, t, \mathbf{k}). \tag{4.25}$$

Time reversal

In a time-reversal symmetric (spinless) Hamiltonian, under the action of the anti-unitary operator $\mathcal{O}$ that performs the inversions

$$(i, \mathbf{r}, t, \mathbf{k}) \longmapsto (-i, \mathbf{r}, -t, -\mathbf{k}),$$

the Hamiltonian remains invariant

$$\mathcal{O}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}\, H(t)\, e^{i\mathbf{k}\cdot\mathbf{r}}\right)\mathcal{O}^{-1} = e^{-i\mathbf{k}\cdot\mathbf{r}}\, H(t)\, e^{i\mathbf{k}\cdot\mathbf{r}}.$$

As a result, the eigenfunctions of a time-reversal invariant Hamiltonian satisfies the symmetries

$$\psi_n(\mathbf{r}, t, \mathbf{k}) = \psi_n(\mathbf{r}, -t, -\mathbf{k})^* \quad \text{and} \quad u_n(\mathbf{r}, t, \mathbf{k}) = u_n(\mathbf{r}, -t, -\mathbf{k})^*,$$

up to a $U(1)$ phase $e^{i\lambda}$ which is neglected for simplicity (the curvatures and the non-Hermitian boundary term are invariant with respect to such phases). In this respect, the curvatures satisfy the following symmetries

$$\begin{aligned}\boldsymbol{\mathcal{B}}_n(t,\mathbf{k}) &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right\rangle = i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k})^*\right| \times \left|\boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k})^*\right\rangle \\ &= -i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k})\right\rangle \\ &= -i\left\langle \boldsymbol{\nabla}_{(-\mathbf{k})} n(-t,-\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{(-\mathbf{k})} n(-t,-\mathbf{k})\right\rangle = -\boldsymbol{\mathcal{B}}_n(-t,-\mathbf{k}) \end{aligned} \tag{4.26}$$

and

$$\begin{aligned}\boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\,|\,\frac{\partial n(t,\mathbf{k})}{\partial t}\right\rangle - i\left\langle \frac{\partial n(t,\mathbf{k})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right\rangle \\ &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k}))^*\,|\,\frac{\partial n(-t,-\mathbf{k}))^*}{\partial t}\right\rangle - i\left\langle \frac{\partial n(-t,-\mathbf{k}))^*}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k}))^*\right\rangle \\ &= -\left(i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k}))\,|\,\frac{\partial n(-t,-\mathbf{k}))}{\partial t}\right\rangle - i\left\langle \frac{\partial n(-t,-\mathbf{k}))}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} n(-t,-\mathbf{k}))\right\rangle\right) \\ &= -\boldsymbol{\mathcal{E}}_n(-t,-\mathbf{k}). \end{aligned} \tag{4.27}$$

We note that the above time-reversal symmetry transformation rules remain the same in spinfull motions. That is, the curvature $\boldsymbol{\mathcal{B}}_n(t,\mathbf{k})$ is transformed according to Eq. (4.26) and $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ according to Eq. (4.27), although the wavefunction becomes a two-component spinor $u_n(\mathbf{r},t,\mathbf{k}) \equiv (a_n(\mathbf{r},t,\mathbf{k}),\ b_n(\mathbf{r},t,\mathbf{k}))^{\mathrm{T}}$ in the non-relativistic limit. In these spinfull motions, due to the spin-orbit coupling term in the Hamiltonian, the anti-unitary time-reversal operator $\mathcal{O}$ becomes a matrix quantity that also interchanges the components of the spinor wavefunction, resulting in a symmetry transformation

$$(a_n(\mathbf{r},t,\mathbf{k}),\ \ b_n(\mathbf{r},t,\mathbf{k}))^{\mathrm{T}} = \left(-b_n(\mathbf{r},-t,-\mathbf{k})^*,\ \ a_n(\mathbf{r},-t,-\mathbf{k})^*\right)^{\mathrm{T}},$$

that gives the symmetries of the curvatures.

Space inversion

In a space-inversion symmetric (spinless) Hamiltonian, under the action of the unitary operator $\mathcal{O}$ that performs the inversions

$$(i,\mathbf{r},t,\mathbf{k}) \longmapsto (i,-\mathbf{r},t,-\mathbf{k}),$$

the Hamiltonian remains invariant

$$\mathcal{O}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}\,H(t)\,e^{i\mathbf{k}\cdot\mathbf{r}}\right)\mathcal{O}^{-1} = e^{-i\mathbf{k}\cdot\mathbf{r}}\,H(t)\,e^{i\mathbf{k}\cdot\mathbf{r}}.$$

As a result, the eigenfunctions of this space-inversion symmetric Hamiltonian satisfy the symmetries

$$\psi_n(\mathbf{r},t,\mathbf{k}) = \psi_n(-\mathbf{r},t,-\mathbf{k}) \quad and \quad u_n(\mathbf{r},t,\mathbf{k}) = u_n(-\mathbf{r},t,-\mathbf{k}).$$

As a result, the curvatures satisfy the following symmetries

$$\begin{aligned} \boldsymbol{\mathcal{B}}_n(t,\mathbf{k}) &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right\rangle = i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,-\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{\mathbf{k}} n(t,-\mathbf{k})\right\rangle \\ &= i\left\langle \boldsymbol{\nabla}_{(-\mathbf{k})} n(t,-\mathbf{k})\right| \times \left|\boldsymbol{\nabla}_{(-\mathbf{k})} n(t,-\mathbf{k})\right\rangle = \boldsymbol{\mathcal{B}}_n(t,-\mathbf{k}) \end{aligned} \tag{4.28}$$

and

$$\begin{aligned} \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\,|\,\frac{\partial n(t,\mathbf{k})}{\partial t}\right\rangle - i\left\langle \frac{\partial n(t,\mathbf{k})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} n(t,\mathbf{k})\right\rangle \\ &= i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} n(t,-\mathbf{k}))\,|\,\frac{\partial n(t,-\mathbf{k}))}{\partial t}\right\rangle - i\left\langle \frac{\partial n(t,-\mathbf{k}))}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} n(t,-\mathbf{k}))\right\rangle \\ &= -\left(i\left\langle \boldsymbol{\nabla}_{(-\mathbf{k})} n(t,-\mathbf{k}))\,|\,\frac{\partial n(t,-\mathbf{k}))}{\partial t}\right\rangle - i\left\langle \frac{\partial n(t,-\mathbf{k}))}{\partial t}|\,\boldsymbol{\nabla}_{(-\mathbf{k})} n(t,-\mathbf{k}))\right\rangle\right) \\ &= -\boldsymbol{\mathcal{E}}_n(t,-\mathbf{k}). \end{aligned} \tag{4.29}$$

The symmetries Eq. (4.27) and Eq. (4.29) of the Berry curvature $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ are not frequently used in the literature. We believe that they are important in topological transport process, e.g. in Thouless pump, because they give a simple criterion to know when the collective pump charge will be zero. For example, in an adiabatic pump process of a fully occupied band (in a gapped insulator), the total transported charge in any one of the directions during the cycle will be zero provided that the space inversion-symmetry is unbroken.

Mirror inversion

Driven by the last conclusion, with respect to a zero Thouless pump by any inversion symmetric Hamiltonian, this lead us to examine the mirror inversion as a lower symmetry. Our aim is to indicate the symmetries of the curvature $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ in a given Cartesian direction. In this respect, we assume that the Hamiltonian is invariant under the action of the unitary operator $\mathcal{O}$

$$\mathcal{O}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}\,H(t)\,e^{i\mathbf{k}\cdot\mathbf{r}}\right)\mathcal{O}^{-1} = e^{-i\mathbf{k}\cdot\mathbf{r}}\,H(t)\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

that performs the mirror inversions over the plane $x=0$

$$(i,x,y,z,t,k_x,k_y,k_z) \longmapsto (i,-x,y,z,t,-k_x,k_y,k_z).$$

The eigenfunctions satisfy the symmetries

$$\psi_n(x,y,z,t,k_x,k_y,k_z) = \psi_n(-x,y,z,t,-k_x,k_y,k_z)$$

and

$$u_n(x,y,z,t,k_x,k_y,k_z) = u_n(-x,y,z,t,-k_x,k_y,k_z).$$

Therefore, the curvature $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ satisfies the following symmetry

$$\begin{aligned}\boldsymbol{\mathcal{E}}_n(t,k_x,k_y,k_z)\cdot\boldsymbol{e}_x &= \mathcal{E}_{n,x}(t,k_x,k_y,k_z)\\ &= i\left\langle\frac{\partial n(t,\mathbf{k})}{\partial k_x}\,|\,\frac{\partial n(t,\mathbf{k})}{\partial t}\right\rangle - i\left\langle\frac{\partial n(t,\mathbf{k})}{\partial t}|\,\frac{\partial n(t,\mathbf{k})}{\partial k_x}\right\rangle\\ &= -\mathcal{E}_{n,x}(t,-k_x,k_y,k_z).\end{aligned} \tag{4.30}$$

The latter equation implies that, in the directions that there exists a reflection symmetry, the collective pumped charge of a fully occupied band is expected to always be zero. This kind of mirror symmetry is for example broken by a homogeneous electric field $E_x(t)$ along the x direction, which results to the mirror symmetry-breaking Hamiltonian

$$H(\mathbf{r},t) = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x} + e\int_0^t E_x(t')dt'\right)^2 + \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial y}\right)^2 + \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial z}\right)^2 + V_{crys}(\mathbf{r}).$$

4.1.3 Static limit of the extended HF theorem

In the static limit of the dynamical HF theorem, we assume that the Hamiltonian as well as the parameter are static; that is, $\frac{\partial\mathbf{R}}{\partial t} = 0$ and $H = H(\mathbf{R})$. We apply the static limit of the HF theorem into an eigenstate of the Hamiltonian $|\Psi(t,\mathbf{R})\rangle \equiv e^{i\Theta_n(t,\mathbf{R})}\,|n(\mathbf{R})\rangle$, where $|n(\mathbf{R})\rangle$ is a Hamiltonian's eigenstate satisfying the eigenvalue equation $H(\mathbf{R})\,|n(\mathbf{R})\rangle = E_n(\mathbf{R})\,|n(\mathbf{R})\rangle$, and $\Theta_n(t,\mathbf{R})$ is the phase of the wavefunction satisfying the equation $-\hbar\frac{d\Theta_n(t,\mathbf{R})}{dt} = E_n(\mathbf{R})$. In this fashion, employing Eq. (4.18) we replace $\frac{\partial\mathbf{R}}{\partial t} = 0$ as well as $\boldsymbol{\mathcal{E}}_n(t,\mathbf{R}) = 0$ due to the considered eigenstate $|n(\mathbf{R})\rangle$ that does not have an explicit time dependence. In this respect, Eq. (4.18) is simplified into

$$\langle n(\mathbf{R})\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H(\mathbf{R})\,|\,n(\mathbf{R})\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E_n(\mathbf{R}) + \boldsymbol{\mathcal{S}}_n(\mathbf{R}) \tag{4.31}$$

which is the form of the generalized static HF theorem that was derived in Ref.[49]. The simplest example where one can ascertain the necessity of presence of the boundary non-Hermitian term $\boldsymbol{\mathcal{S}}_n(\mathbf{R})$, is a free electron motion in 1D. In this respect, we assume the Hamiltonian

$H=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$ which does not have any parameter dependence. We consider an electron's motion, described by an eigenstate of the Hamiltonian $\Phi_k=\frac{1}{\sqrt{L}}e^{ikx}$ with well defined energy given by $\frac{\hbar^2k^2}{2m}$, where $\hbar k$ is the momentum of the electron and L is the normalization constant. When one uses the electron's momentum $R\equiv k$ (assumed to take continuous values) as a parameter, by employing the standard static HF theorem without the non-Hermitian term (the 1D analogue of Eq. (4.31) without the boundary term $S(k)$), **will eventually lead to a paradox** since $\left\langle\frac{dH}{dk}\right\rangle=0$ while $\frac{dE(k)}{dk}=\frac{d}{dk}\frac{\hbar^2k^2}{2m}=\frac{\hbar^2k}{m}\neq 0$. The paradox is resolved whenever one takes into account the boundary non-Hermitian term $S(k)$. Specifically, the 1D analogue of Eq. (4.31) is given by

$$0=\frac{dE(k)}{dk}+S(k), \tag{4.32}$$

where $S(k)$ is truncated to a two point formula (*cf.* Eq. (4.22))

$$S(k)=\frac{i\hbar}{2}\left[\left(\left(\mathrm{v}\,\Phi_k\right)^*+\Phi_k^*\,\mathrm{v}\right)\frac{d\Phi_k}{dk}\right]_x^{x+L}. \tag{4.33}$$

We substitute in Eq. (4.33) the standard velocity operator $\mathrm{v}=-\frac{i\hbar}{m}\frac{\partial}{\partial x}$, as well as $\left(\mathrm{v}\,\Phi_k\right)=\frac{1}{\sqrt{L}}\frac{\hbar k}{m}e^{ikx}=\frac{\hbar k}{m}\Phi_k$ and $\frac{d\Phi_k}{dk}=\frac{1}{\sqrt{L}}i\,x\,e^{ikx}=i\,x\,\Phi_k$. In this respect, Eq. (4.33) takes the value

$$\begin{aligned}
S(k) &= \frac{i\hbar}{2}\left[\left(\frac{\hbar k}{m}\Phi_k^*-\frac{i\hbar}{m}\Phi_k^*\frac{\partial}{\partial x}\right)i\,x\,\Phi_k\right]_x^{x+L} \\
&= \frac{i\hbar}{2}\left[\frac{i\,\hbar\,k}{m}|\Phi_k|^2x+\frac{\hbar}{m}|\Phi_k|^2+i\,x\,\Phi_k^*\left(\mathrm{v}\,\Phi_k\right)\right]_x^{x+L} \\
&= \frac{i\hbar}{2}\left[2\frac{i\,\hbar\,k}{m}|\Phi_k|^2x+\frac{\hbar}{m}|\Phi_k|^2\right]_x^{x+L} \\
&= \frac{i\hbar^2}{2mL}\left[2\,i\,k\,x+1\right]_x^{x+L} \\
&= \frac{i\hbar^2}{2mL}(2\,i\,k\,L)=-\frac{\hbar^2k}{m},
\end{aligned} \tag{4.34}$$

which together with $\frac{dE(k)}{dk}=\frac{\hbar^2k}{m}$ verifies Eq. (4.32) and guarantees the validity of the static HF theorem. Therefore, whenever the momentum gradient operator $\frac{d}{dk}$ becomes anomalous, the boundary non-Hermitian effect term cannot be excluded from the HF theorem.

In this respect, one can draw a clear conclusion: whenever the initial Hamiltonian does not depend explicitly on the momentum $\boldsymbol{\nabla}_{\mathbf{k}}H(\mathbf{k})=0$, rather than involving the momentum only in the form of the considered state (i.e. whenever Bloch states are employed and the crystal momentum is assumed as the parameter), one must also use the non-Hermitian

boundary term $\boldsymbol{\mathcal{S}}_n(\mathbf{k})$ as a probe for detecting information about the dispersion relation with respect to the boundary behavior of the Bloch functions

$$\boldsymbol{\nabla}_{\mathbf{k}} E_n(\mathbf{k}) = -\boldsymbol{\mathcal{S}}_n(\mathbf{k}). \tag{4.35}$$

Consequently, by defining the bulk localized eigenstates of the Hamiltonian as the ones that their values and all of their derivatives are zero over the boundaries of the material, that is $\boldsymbol{\mathcal{S}}_n(\mathbf{k}) = 0$, it is evident from Eq. (4.35) that these states will have flat band dispersion relations $\boldsymbol{\nabla}_{\mathbf{k}} E_n(\mathbf{k}) = 0$.

We suggest that, by employing Eq. (4.35), one can theoretically explain the changing of the dispersion relation slope in relation to the localization of the involved states.

For example, in the Quantum Hall Effect, the bulk states are localized and described by flat bands (Landau levels) dispersion relations $E_n(\mathbf{k}) \equiv E_n = \textit{constant}$, while the states near the boundaries have dispersion relations with non-zero slopes that are approximately linear [60]. This kind of behavior, can most probably be theoretically explained when the non-Hermitian boundary term is taken into account (although this has to be worked out in detail).

Moreover, in Dirac and Weyl semimetals [6, 137, 151, 72, 28], linear dispersion relations are found near the vicinity of degenerate points in the Brillouin zone, which represent the bulk electrons' physics near these degeneracy points. Although the electrons' motions are not fully relativistic (apart from correction due to spin-orbit coupling), these are theoretically explained by employing various model Hamiltonians $H(\mathbf{k})$ which are effectively relativistic. We suggest that, these emerging relativistic linear dispersion relations that are accompanied by exotic boundary behaviors such as Fermi arcs, can alternatively be explained by employing the non-Hermitian boundary term. Specifically, by taking a Taylor expansion of the non-Hermitian boundary term $\boldsymbol{\mathcal{S}}_n(\mathbf{k})$ near a degenerate point $\mathbf{k}_o$ we find

$$\boldsymbol{\nabla}_{\mathbf{k}} E_n(\mathbf{k}) = -\boldsymbol{\mathcal{S}}_n(\mathbf{k}_o) - ((\mathbf{k}-\mathbf{k}_o)\cdot\boldsymbol{\nabla}_{\mathbf{k}})\,\boldsymbol{\mathcal{S}}_n(\mathbf{k})|_{\mathbf{k}=\mathbf{k}_o} + O(\mathbf{k}^2) + \dots. \tag{4.36}$$

Provided that the linear dispersion relation $E_n(\mathbf{k})$ profile is experimentally obtained, one can extract information about the boundary term $\boldsymbol{\mathcal{S}}_n(\mathbf{k})$ by keeping only up to first order terms in the Taylor expansion. By then, employing the Bloch functions $\Psi_n(\mathbf{r},\mathbf{k})$ in Eq. (4.22), further information about the behavior of the wavefunction at the boundary can be extracted.

4.1.4 Non-adiabatic motion: Floquet states

The dynamic extension Eq. (4.8) can in principle be employed to non-adiabatic quantum processes where the quest for topological invariants is still in an ongoing research state [76, 42, 83, 31, 116, 27, 98, 105, 141, 79]. In this framework, by assuming periodic in time Hamiltonian $H(t+T,\mathbf{R}(t+T)) = H(t,\mathbf{R}(t))$, where the time of T is the period of driving and a parameter that has the same time periodicity $\mathbf{R}(t+T) = \mathbf{R}(t)$, we apply a

Floquet state $|\Psi(t,\mathbf{R})\rangle \equiv e^{-\frac{i}{\hbar}\varepsilon_a t}\,|\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle$ into Eq. (4.8), where $|\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle$ are the Floquet modes that are periodic in time $|\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle = |\Phi_{\varepsilon_a}(t+T,\mathbf{R})\rangle$ and ε_a is the static quasienergy (restricted to the interval $\Delta\varepsilon_a = \dfrac{2\pi\hbar}{T}$ called first Floquet-zone which contains all the physically non-equivalent quantum states). After a straightforward calculation we find

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_a = \boldsymbol{\nabla}_{\mathbf{R}} E_a(t,\mathbf{R}) \,+\, \boldsymbol{\mathcal{S}}_a(t,\mathbf{R}) - \hbar\,\frac{\partial \mathbf{R}}{\partial t}\times \boldsymbol{\mathcal{B}}_a(t,\mathbf{R}) \,-\, \hbar\,\boldsymbol{\mathcal{E}}_a(t,\mathbf{R}), \tag{4.37}$$

where

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_a = \langle \Phi_{\varepsilon_a}(t,\mathbf{R})\,|\,\boldsymbol{\nabla}_{\mathbf{R}} H\,|\,\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle \tag{4.38}$$

and

$$E_a(t,\mathbf{R}) = \langle \Phi_{\varepsilon_a}(t,\mathbf{R})|\,H\,|\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle\,. \tag{4.39}$$

The curvatures are given by

$$\boldsymbol{\mathcal{B}}_a(t,\mathbf{R}) = i\,\langle \boldsymbol{\nabla}_{\mathbf{R}}\Phi_{\varepsilon_a}(t,\mathbf{R})|\times|\boldsymbol{\nabla}_{\mathbf{R}}\Phi_{\varepsilon_a}(t,\mathbf{R})\rangle \tag{4.40}$$

and

$$\boldsymbol{\mathcal{E}}_a(t,\mathbf{R}) = i\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Phi_{\varepsilon_a}(t,\mathbf{R})\,|\,\frac{\partial\Phi_{\varepsilon_a}(t,\mathbf{R})}{\partial t}\right\rangle - i\left\langle \frac{\partial\Phi_{\varepsilon_a}(t,\mathbf{R})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{R}}\Phi_{\varepsilon_a}(t,\mathbf{R})\right\rangle \tag{4.41}$$

while the non-Hermitian boundary term is given from

$$\begin{aligned}\boldsymbol{\mathcal{S}}_a(t,\mathbf{R}) &= \big\langle \Phi_{\varepsilon_a}(t,\mathbf{R})|\,\big(H^+ - H\big)\,\boldsymbol{\nabla}_{\mathbf{R}}\Phi_{\varepsilon_a}(t,\mathbf{R})\big\rangle \\ &= \frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\big(\,(\mathbf{v}\,\Phi_a)^+ + \Phi_a^+\,\mathbf{v}\,\big)\,\boldsymbol{\nabla}_{\mathbf{R}}\Phi_n\,dS,\end{aligned} \tag{4.42}$$

where $\Phi_a \equiv \Phi_{\varepsilon_a}(t,\mathbf{R})$ are the time periodic Floquet wavefunctions.

Discrete Symmetries

Our extended HF theorem applied to a Floquet state, is useful in band theory if we identify the parameter as the crystal momentum $\mathbf{R}\equiv\mathbf{k}$. We further assume an initial Hamiltonian that does not depend on the parameter, as well as take into account that the Floquet states satisfy the eigenvalue equation

$$H_F(t)\,\Phi_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}) = \varepsilon_a\,\Phi_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}), \tag{4.43}$$

where the Floquet operator is given by

$$H_F(t) = H(t) - i\hbar\frac{d}{dt}.$$

If we now express the Floquet state $\Phi_{\varepsilon_a}(\mathbf{r},t,\mathbf{k})$ as

$$\Phi_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\varepsilon_a}(\mathbf{r},t,\mathbf{k})$$

where $u_{\varepsilon_a}(\mathbf{r},t,\mathbf{k})$ is periodic in time $u_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}) = u_{\varepsilon_a}(\mathbf{r},t+T,\mathbf{k})$, then, from the symmetries of the eigenvalue equation

$$e^{-i\mathbf{k}\cdot\mathbf{r}} H_F(t)\, e^{i\mathbf{k}\cdot\mathbf{r}}\; u_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}) = \varepsilon_a\; u_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}) \tag{4.44}$$

we can deduce the symmetries of the curvatures themselves (which are evaluated with respect to the Floquet states), thus we can find valuable information about the topology of the projective Hilbert space of the Floquet band. We claim that, the implications of the discrete symmetries, namely, (i) time reversal, (ii) space inversion and (iii) mirror inversion symmetry, are completely analogous with the ones performed for the instantaneous eigenstates of the Hamiltonian, making therefore, the results given by Eqs. (4.26) – (4.30), straightforwardly mapped to the Floquet system, with the identification

$$\Psi_n(\mathbf{r},t,\mathbf{k}) \longmapsto \Phi_{\varepsilon_a}(\mathbf{r},t,\mathbf{k}).$$

4.2 Implications of the theorem

4.2.1 Lagrangian and Eulerian description of the parameter space

In the dynamic and extended HF theorem Eq. (4.8) that we have derived, the velocity of the parameter $\dfrac{\partial \mathbf{R}}{\partial t} = \dfrac{\partial \boldsymbol{\mathcal{R}}(t,\mathbf{R_o})}{\partial t}$ is assumed to be arbitrary, and the equation of motion of each quantum state is defined by $i\hbar\dfrac{d}{dt}\left|\Psi(t,\mathbf{R})\right\rangle = H(t,\mathbf{R})\left|\Psi(t,\mathbf{R})\right\rangle$. In this respect, one can use the initial value of the parameter $\mathbf{R_o}$ in order to label each inequivalent quantum state. Under certain boundary conditions for the wavefunctions (e.g. periodic) at an initial moment t_o, one can find an elementary parameter volume $\Delta V_o(t_o,\mathbf{R_o})$ that is "attached" to each inequivalent state. Furthermore, if the system has lowered translation symmetry over position coordinates (i.e. the distance between any two adjacent primitive cells within the crystal, or between two adjacent magnetic cells when there is magnetic field) than the large periodic boundary conditions, one can define a larger volume $\Delta V_{BZ}(t_o)$ (the first Brillouin zone or the first magnetic Brillouin zone) in which all inequivalent states are restricted. These labeled and countable quantum states, form a projective Hilbert space, the topology of which discriminates the conventional from the topological quantum processes. A subtle question that as far as we know hasn't been considered in a quantum mechanical framework[2], is what are the consequences of the time evolution of the (i) elementary parameter volume $\Delta V_t(t,\mathbf{R_o})$ per quantum state, as well as that (ii) of the larger volume $\Delta V_{BZ}(t)$ where all

[2] In a semiclassical framework the phase-space volume $\Delta V_k(t)V_r(t)$ time evolution has been studied [149] leading to an apparent modification of the density of states.

the elementary volumes are being enclosed. The method mentioned above is quite similar to the Lagrangian description of fluid mechanics as we will show. In this respect we review the basic ideas of the Lagrangian and Eulerian descriptions, and subsequently apply these ideas to quantum mechanics wavefunctions that depend on a parameter $\mathbf{R}$ that varies with time.

In the Lagrangian description of fluid mechanics, one uses the parcels picture for the fluid (the fluid is composed by countable and distinguishable parcels) with each parcel having a prescribed label and volume. Let us assume for a moment that the parameter $\mathbf{R}$ denotes the position of a labeled parcel. In the Lagrangian description in a given space $t\times\mathbf{R}$, the trajectory of each labeled parcel is defined by $\mathbf{R}=\boldsymbol{\mathcal{R}}(t,\mathbf{R_o})$, where time t and the initial position of the parcel $\mathbf{R_o}$ are independent variables (while the position $\mathbf{R}$ is a dependent one). In this framework, the velocity of each parcel is defined as

$$\boldsymbol{v_R}(t,\mathbf{R_o})=\frac{\partial\mathbf{R}}{\partial t}=\frac{\partial\boldsymbol{\mathcal{R}}(t,\mathbf{R_o})}{\partial t} \tag{4.45}$$

On the contrary, in the Eulerian, field description formalism, within a given space $t\times\mathbf{R}$ time t and position $\mathbf{R}$ are the independent variables, and *a priori* there does not exist a parameter path. A velocity in the Eulerian description $\mathbf{v_R}(t,\mathbf{R})$ is defined by using the inverse transformation $\mathbf{R_o}(t,\mathbf{R})$ in Eq. (4.45), and is defined by the equation

$$\mathbf{v_R}(t,\mathbf{R})=\boldsymbol{v_R}(t,\mathbf{R_o}(t,\mathbf{R}))=\frac{\partial\mathbf{R}}{\partial t}. \tag{4.46}$$

4.2.2 Time evolution of a volume in parameter space

As time evolves, each volume over parameter space (either the volume per quantum state or the collective volume) expands or dilates according to the equation

$$\Delta V_t(t)=\mathrm{Det}J(t,t_o)\,\Delta V_o, \tag{4.47}$$

where $\mathrm{Det}J(t,t_o)$ denotes the determinant of the Jacobian matrix of the transformation. The Jacobian matrix, captures the transformation of the initial value of the parameter (equivalently the initial position of a fluid parcel) $\mathbf{R}(t_o)=\boldsymbol{\mathcal{R}}(t_o,\mathbf{R_o})$ to a subsequent one $\mathbf{R}(t)=\boldsymbol{\mathcal{R}}(t,\mathbf{R_o})$. The latter transformation, as well as the Jacobian matrix, are completely arbitrary in our formulation because it is assumed that the velocity of the parameter is arbitrary. Therefore, the Jacobian matrix is solely determined by the way that one defines the velocity of the parameter. The time evolution of the Jacobian matrix is given by

$$\frac{d}{dt}\mathrm{Det}J(t,t_o)=\boldsymbol{\nabla}_{\mathbf{R}}\cdot\mathbf{v}_{\mathbf{R}}\,\mathrm{Det}J(t,t_o), \tag{4.48}$$

and by taking the total time derivative of Eq. (4.47) and then substituting in Eq. (4.48) one finds the time evolution of each quantum state's elementary parameter volume that is given

by

$$\frac{d}{dt} ln \Delta V_t(t) = \boldsymbol{\nabla}_{\mathbf{R}} \cdot \mathbf{v}_{\mathbf{R}} = \boldsymbol{\nabla}_{\mathbf{R}} \cdot \frac{\partial \mathbf{R}}{\partial t}. \tag{4.49}$$

The latter equation implies for our extended HF theorem formalism the following: Each volume in the parameter space $\Delta V_t(t)$, evolves in time according to the divergence of the assumed velocity of the parameter that one employs. As evidenced from Eq. (4.49), when the velocity of the parameter has zero divergence $\boldsymbol{\nabla}_{\mathbf{R}} \cdot \mathbf{v}_{\mathbf{R}} = 0$, each assumed volume in the parameter space remains constant and the $t \times \mathbf{R}$ space behaves as an incompressible fluid.

An alternative, and presumably the simplest way for one to see how each quantum state's elementary parameter volume $\Delta V(\mathbf{R})$ evolves in time, is by using the convection theorem

$$\frac{d}{dt} \iiint\limits_{V(t)} F \cdot dV(t) = \iiint\limits_{V(t)} \left(\frac{dF}{dt} + F \, \boldsymbol{\nabla}_{\mathbf{R}} \cdot \mathbf{v}_{\mathbf{R}} \right) dV(t)$$

where F is an arbitrary scalar function. By setting the arbitrary scalar function F equal to one $F = 1$, and by considering an infinitesimal volume over which $\boldsymbol{\nabla}_{\mathbf{R}} \cdot \mathbf{v}_{\mathbf{R}}$ can be assumed as constant, one can derive Eq. (4.49).

4.2.3 Band Theory: Sum of states when the volume in the (parameter) crystal momentum space changes with time

In band theory we label each single particle's state by its band index n and its corresponding crystal momentum $\mathbf{k}$ index. By further assuming that the crystal momentum is constant of the motion, we may equally replace $\mathbf{k} = \mathbf{k}_o$, where $\mathbf{k}_o$ is the initial value of the crystal momentum. In order to compute a collective non-interacting electrons' property, we use the above mentioned labels and sum over all available values of the indices, that is $\sum_{n} \sum_{\mathbf{k}_o}^{BZ}$. In the thermodynamic limit, the crystal momentum takes continuous values and each sum over crystal momenta is transformed into a Riemann integral according to the limit

$$\lim_{\Delta V_{\mathbf{k_o}} \to 0} \left(\sum_{\mathbf{k}_o}^{BZ} \Delta V_{\mathbf{k_o}} \right) \to \iiint\limits_{BZ} dV_{k_o}. \tag{4.50}$$

Each infinitesimal volume $\Delta V_{\mathbf{k}_o}$ is assumed to be determined once and for all by the initial coordinate boundary conditions of the wavefunctions, provided that that the boundary conditions do not change with time. For periodic boundary conditions for the wavefunctions and for a 3D system, this infinitesimal volume is the volume per quantum state in crystal momentum space and is equal to $\Delta V_{\mathbf{k}_o} = \frac{(2\pi)^3}{V}$ for spinless electrons, where V is the volume of the material. Therefore, the sum is transformed into the integral expression

$$\sum_{\mathbf{k}_o}^{BZ} \to \frac{V}{(2\pi)^3} \iiint\limits_{BZ} dV_{k_o}. \tag{4.51}$$

On the assumption that the crystal momentum is a parameter that is changing with time, then the infinitesimal volume $dV_k(t)$ at time t need not coincide with the initial counterpart dV_{k_o} at time t_o, that is, $dV_k(t) \neq dV_{k_o}$. Employing the Jacobian of the transformation namely, $dV_k(t) = \text{Det}J(t,t_o)dV_{k_o}$, we find

$$\sum_{\mathbf{k}_t}^{BZ} \rightarrow \frac{V}{(2\pi)^3} \iiint_{FBZ(t)} \frac{1}{\text{Det}J(t,t_o)} dV_k(t). \tag{4.52}$$

where $FBZ(t)$ denotes a time-dependent Brillouin zone.
We note that, in Eq. (4.52) the quantity $\frac{1}{\text{Det}J(t,t_o)}dV_k(t)$ is constant in time, and the limits of integration $FBZ(t)$ changes only due to external fields that can form an irreducible electric-magnetic translation group [7, 153, 25]. In time, these groups may create a zone $FBZ(t)$ (that depends on the fields) having a different volume than the initial Brillouin zone.

By using Eq. (4.48) and Eq. (4.49), we find that the time evolution of the Jacobian of the transformation is determined by

$$\frac{d}{dt} ln\text{Det}J(t,t_o) = \frac{d}{dt} ln\Delta V_k(t) = \boldsymbol{\nabla}_{\mathbf{k}} \cdot \mathbf{v}_{\mathbf{k}} = \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t}, \tag{4.53}$$

implying that the divergence of the crystal momentum velocity field $\mathbf{v}_{\mathbf{k}}$ is the quantity that determines the equation of motion of the Jacobian matrix of the transformation. Equations (4.52) and (4.53) constitute a transformation from the Lagrangian, labeled description of inequivalent quantum states, to a counterpart Eulerian field description, where *a priori* the quantum states cannot be labeled.

In the formulation of Eq. (4.52) we have silently made an assumption, namely, each infinitesimal volume $\Delta V_{\mathbf{k}_o}$ that is occupied by one particle does change size over time. On the other hand, the volume of the first Brillouin zone may change over time according to Eq. (4.53), thus, whenever $\boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} \neq 0$, the particles behave as a compressible fluid within the crystal momentum space. Solving now Eq. (4.53) for $\text{Det}J(t,t_o)$, and taking into account that $\text{Det}J(t_o,t_o) = 1$, the sum over the crystal momentum is transformed (in the thermodynamic limit) to an integration given by

$$\sum_{\mathbf{k}_t}^{BZ} \rightarrow \frac{V}{(2\pi)^3} \iiint_{BZ(t)} e^{-\int_{t_o}^{t} \left(\boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t'} \right) dt'} dV_k(t). \tag{4.54}$$

When the crystal momentum is a static parameter $\frac{\partial \mathbf{k}}{\partial t} = 0$, or when its velocity field $\mathbf{v}_{\mathbf{k}}(t,\mathbf{k}) = \frac{\partial \mathbf{k}}{\partial t}$ behaves as an incompressible fluid within the first Brillouin zone $\boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} = 0$, Eq. (4.54) is simplified to the standard one.

At this point is worth making an observation. A classical mechanical system behaves as

canonical whenever the phase-space volume is conserved

$$\frac{d}{dt} ln\left(\Delta V_k(t)\Delta V_p(t)\right) = \boldsymbol{\nabla}_{\mathbf{k}}\cdot\frac{\partial \mathbf{k}}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}}\cdot\frac{\partial \mathbf{r}}{\partial t} = 0$$

owing to the Hamilton's equation that couple the two canonical variables, that is, $\frac{\partial \mathbf{k}}{\partial t} = -\boldsymbol{\nabla}_{\mathbf{r}} H$ and $\frac{\partial \mathbf{r}}{\partial t} = \boldsymbol{\nabla}_{\mathbf{k}} H$, which always results into the conservation of the phase-space volume. On the quantum mechanical formalism that we have employed, where the observables become operators, *a priori* there does not exist such relation between two independent generalized quantities; we only have the equation of motion of parameters that can be defined arbitrarily. In this respect, in the semiclassical framework study made by [149], the phase-space volume $\Delta V_k(t)V_r(t)$ conservation was found to be violated, leading to an apparent modification of the density of states[3].

4.2.4 Maxwell type of equations in $t\times\mathbf{R}$ space generated by the dynamical HF theorem

By taking the curl of both sides of Eq. (4.8) and using the vector identity $\boldsymbol{\nabla}\times(\mathbf{A}\times\mathbf{B}) = \mathbf{A}(\boldsymbol{\nabla}\cdot\mathbf{B}) - \mathbf{B}(\boldsymbol{\nabla}\cdot\mathbf{A}) + (\mathbf{B}\cdot\boldsymbol{\nabla})\mathbf{A} - (\mathbf{A}\cdot\boldsymbol{\nabla})\mathbf{B}$, as well as $\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\nabla}_{\mathbf{R}}E(t,\mathbf{R}) = 0$, we find the relation

$$\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\mathcal{E}} = \mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{B}} + \boldsymbol{\mathcal{B}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\mathbf{v}_{\mathbf{R}} - \mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}} - \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{R}}\times(\langle\boldsymbol{O}\rangle - \boldsymbol{\mathcal{S}}) \tag{4.55}$$

where

$$\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{B}} = (\mathbf{v}_{\mathbf{R}}\cdot\boldsymbol{\nabla}_{\mathbf{R}})\,\boldsymbol{\mathcal{B}} - (\boldsymbol{\mathcal{B}}\cdot\boldsymbol{\nabla}_{\mathbf{R}})\,\mathbf{v}_{\mathbf{R}} \tag{4.56}$$

is the Lie derivative of the vector field $\boldsymbol{\mathcal{B}}(t,\mathbf{R})$ with respect to the parameter's velocity $\mathbf{v}_{\mathbf{R}}(t,\mathbf{R})$ vector field. Eq. (4.55) is a general Maxwell type of equation in $t\times\mathbf{R}$ space with monopole sources and without any conservation law being involved. The generalized curvature $\boldsymbol{\mathcal{E}}(t,\mathbf{R})$ behaves as an effective electric field, whereas the curvature $\boldsymbol{\mathcal{B}}(t,\mathbf{R})$ as an effective magnetic field in $\mathbf{R}$-space.

Flux preserving motion

Motivated by magnetohydrodynamics theories [144], we pursuit Lie drag invariants. By using the 2D analogue of the convection theorem for an arbitrary surface $S(t)$ that is moving with the flow (with velocity $\mathbf{v}_{\mathbf{R}} = \frac{\partial \mathbf{R}}{\partial t}$), the flux of the generalized Berry curvature $\boldsymbol{\mathcal{B}}(t,\mathbf{R})$

[3]This violation is justified according to [22, 45], due to the assumed generalized coordinates $(\mathbf{r}_c(t),\,\mathbf{k}_c(t))$ employed in the semiclassical treatment of the wavepacket motion [149, 130] that are not canonical variables.

is Lie dragged with the flow when

$$\frac{d}{dt}\iint\limits_{S(t)}\boldsymbol{\mathcal{B}}\cdot d\mathbf{S}=\iint\limits_{S(t)}\left(\frac{\partial\boldsymbol{\mathcal{B}}}{\partial t}-\boldsymbol{\nabla}_{\mathbf{R}}\times(\mathbf{v}_{\mathbf{R}}\times\boldsymbol{\mathcal{B}})+\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}\right)\cdot d\mathbf{S}=0, \tag{4.57}$$

where the surface $S(t)$ is arbitrary. By taking into account that the surface $S(t)$ is arbitrary, the generalized Berry curvature satisfies the local equation

$$\frac{\partial\boldsymbol{\mathcal{B}}}{\partial t}-\boldsymbol{\nabla}_{\mathbf{R}}\times(\mathbf{v}_{\mathbf{R}}\times\boldsymbol{\mathcal{B}})+\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}=0, \tag{4.58}$$

which by using the Lie derivative $\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{B}}$ is expressed as

$$\frac{\partial\boldsymbol{\mathcal{B}}}{\partial t}+\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{B}}+\boldsymbol{\mathcal{B}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\mathbf{v}_{\mathbf{R}}=0. \tag{4.59}$$

Substituting Eq. (4.59) into Eq. (4.55) we find a Maxwell type of equation

$$\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\mathcal{E}}=-\boldsymbol{J}_{\mathbf{R}}-\frac{\partial\boldsymbol{\mathcal{B}}}{\partial t} \tag{4.60}$$

for the advected flux motion, where

$$\boldsymbol{J}_{\mathbf{R}}=\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}+\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{R}}\times(\langle\boldsymbol{O}\rangle-\boldsymbol{\mathcal{S}}) \tag{4.61}$$

is the current that is entering into the Maxwell equation. Taking the divergence of both sides of Eq. (4.58) (which guarantees the Lie dragging) we find

$$\frac{\partial}{\partial t}\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}+\boldsymbol{\nabla}_{\mathbf{R}}\cdot\left(\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}\right)=0, \tag{4.62}$$

which with the aid of Eq. (4.61) is transformed into a continuity equation

$$\frac{\partial\rho_M}{\partial t}+\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{J}_{\mathbf{R}}=0 \tag{4.63}$$

where ρ_M is defined by

$$\rho_M=\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}} \tag{4.64}$$

and is the topological monopole charge density. Continuity equation Eq. (4.63) alongside with Eq. (4.57), implies that the total topological monopole charge is conserved

$$\frac{d}{dt}\oiint\limits_{S(t)}\boldsymbol{\mathcal{B}}\cdot d\mathbf{S}=\frac{d}{dt}\iiint\limits_{V(t)}\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{B}}\,dV=\frac{dQ_M}{dt}=0, \tag{4.65}$$

for flux preserving motions, meaning that, either no monopole charges are created (annihilated), or monopole and anti-monopole charges form into pairs.

By identifying the parameter as the wave vector of crystal momentum $\mathbf{R}\equiv\mathbf{k}$, then, the

Maxwell type of equations (4.60) and (4.55) are the generalization of the Maxwell type of equation that has been found over the past years in the study of Weyl semimetals [69, 70], which has arisen by heuristic analogy to the electromagnetic induction law and without any detailed derivation.

4.3 Particle transport

As a first application we study the Thouless charge pump [134] using the dynamical HF theorem that we have derived. The Thouless charge pump serves as a simple yet fundamental example of topology in quantum systems. The hallmark of this effect is the transport of a precisely quantized amount of charge during an adiabatic cycle in the parameter space. This remarkable phenomenon, has recently been demonstrated by experiments in a one-dimensional chains of ultra-cold atoms trapped in an optical lattice [88, 96, 87].

Our purpose is threefold, (i) first to reveal the practical aspect of evaluating an observable within the HF theorem, (ii) second to show the importance of the boundary non-Hermitian term in the HF theorem, and finally, (iii) to make use of the boundary velocity operator Eqs. (2.3) – (2.4) that we have already used in the orbital magnetization of the electrons.

4.3.1 Adiabatic process (Thouless pump)

The adiabatic particle transport was first studied by D. J. Thouless [134] using first order (linear response) time-dependent perturbation theory. In the introduction of his article he explicitly raises the theoretical question: "If the potential is changed slowly in such a way that it returns to its starting value in time T, is the integrated current across the boundary quantized?" He affirmatively found that the transported charge is quantized due to topological reasons, provided that the system is an insulator evolving in time adiabatically and the thermodynamic limit is taken. In his study, no explicit consideration of the boundaries of the system has been made. The Thouless pump shares the same topological origin as the quantized Hall conductivity [135, 78], and may thus be regarded as a dynamical version of the Integer Quantum Hall effect.

We will study the transport in a slightly different context. Instead of assuming a sliding potential $V(\mathbf{r} - \upsilon\, t\, \boldsymbol{e}_x)$ like in the original problem [134], we assume an electric field along $\boldsymbol{e}_x$ direction which is periodic in space (over x coordinates with period equal to the lattice constant) as well as over time t. Each electron's wavefunction evolves in time by the Hamiltonian

$$H(\mathbf{r}, t) = \frac{1}{2m}\mathbf{p}^2 + e\phi(x, t) + V_{crys}(\mathbf{r}) \tag{4.66}$$

where m and e are the mass and charge of the electron respectively, and $\mathbf{p}$ the canonical momentum operator. The time-dependent scalar potential is periodic in time $\phi(x, T) = \phi(x, 0)$, and produces the periodic in time electric field $\mathbf{E}(x, t) = -\boldsymbol{\nabla}\phi(x, t) = -\dfrac{d\phi(x, t)}{dx}\,\boldsymbol{e}_x$, with boundary condition $\mathbf{E}(x, 0) = \mathbf{E}(x, T) = 0$. Moreover, we assume that the scalar potential

is periodic over position coordinate x at every moment $\phi(x+na,t)=\phi(x,t)$, where n is an integer and a is the primitive cell length in x direction (hence ϕ has the same periodicity with V_{crys} in the x-direction), as well as $\frac{d\phi(x,t)}{dx}=\frac{d\phi(x+na,t)}{dx}$, which produces the periodic electric field $\mathbf{E}(x,t)=\mathbf{E}(x+na,t)$. Therefore, the Hamiltonian Eq. (4.66) is periodic in time $H(\mathbf{r},0)=H(\mathbf{r},T)$ and coordinates $H(\mathbf{r}+\mathbf{R},t)=H(\mathbf{r},t)$, where $\mathbf{R}$ is a Bravais lattice vector.

The crucial property that we assume, is that the scalar potential breaks the mirror symmetry along the x direction resulting to $\phi(x,t)\neq\phi(-x,t)$. This is analogous to the case of the Thouless sliding scalar potential $V(x-\upsilon\, t,y,z)\neq V(-x-\upsilon\, t,y,z)$ which also breaks the mirror symmetry over x direction. Each electron's state evolves in time according to the time-dependent Schrödinger equation (TDSE)

$$i\hbar\frac{d}{dt}\left|\Psi(t)\right\rangle=\left(\frac{1}{2m}\mathbf{p}^2+e\phi(x,t)+V_{crys}(\mathbf{r})\right)\left|\Psi(t)\right\rangle. \tag{4.67}$$

We assume that each electron is initially in a non-degenerate ground state, $|\Psi(t_o)\rangle\equiv|\psi_n(t_o)\rangle$, where n labels the energy. The ground state energy band is for all moments $0\leq t\leq T$ separated by a gap from the upper bands. Each electron's ground state wavefunction satisfies periodic boundary conditions over the material's boundaries

$$\psi_n(\mathbf{r}+\mathbf{L},t_o)=\psi_n(\mathbf{r},t_o),$$

where $\mathbf{L}$ denotes the (vector) length of the material in each direction. Assuming that the electric field $\mathbf{E}(x,t)$ is slowly changing with time, meaning $T\to\infty$, each ground state evolves in time adiabatically

$$\Psi_n(\mathbf{r},t)=e^{i\Theta_n(t)}\psi_n(\mathbf{r},t),$$

where $\Theta_n(t)$ is the total phase of the wavefunction (the sum of the dynamic and the geometric adiabatic phase). Each wavefunction $\psi_n(\mathbf{r},t)$ satisfies the instantaneous eigenvalue equation

$$\left(\frac{1}{2m}\mathbf{p}^2+e\phi(x,t)+V_{crys}(\mathbf{r})\right)\psi_n(\mathbf{r},t)=E_n(t)\,\psi_n(\mathbf{r},t). \tag{4.68}$$

By following [134], we assume that the electron's wavefunction has the form

$$\psi_n(\mathbf{r},t,\mathbf{k})=e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{r},t,\mathbf{k}), \tag{4.69}$$

and the $u_n(\mathbf{r},t,\mathbf{k})$ satisfies periodic boundary conditions $u_n(\mathbf{r}+\mathbf{L},t,\mathbf{k})=u_n(\mathbf{r},t,\mathbf{k})$, which constrains the allowed wave vector $\mathbf{k}$-values by the condition $e^{i\mathbf{k}\cdot\mathbf{L}}=1$. In order to apply the dynamic and extended HF theorem Eq. (4.8) we need to define a continuous parameter $\mathbf{R}$ and its corresponding velocity $\frac{\partial\mathbf{R}}{\partial t}$. The parameter definition is made by using the assumed form of the quantum state. Namely, we define the parameter $\mathbf{R}$ as the static wave

vector $\mathbf{R} \equiv \mathbf{k}$ which has zero corresponding velocity $\frac{\partial \mathbf{R}}{\partial t} \equiv \frac{\partial \mathbf{k}}{\partial t} = 0$. In order for the application of the theorem to be valid, the parameter $\mathbf{k}$ has to be a continuous one. Therefore, we assume that the length of the system $\mathbf{L}$ is infinite, which results to infinitesimal minimum spacing between the allowed values of the wave vectors $\Delta\mathbf{k} \to 0$. By noting that the Hamiltonian $H(\mathbf{r},t)$ does not depend on any parameter $\boldsymbol{\nabla}_{\mathbf{k}} H(\mathbf{r},t) = 0$, application of the adiabatic form of our extended HF theorem Eq. (4.18) with respect to the state $\psi_n(\mathbf{r},t,\mathbf{k})$ gives

$$0 = \boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) \; + \; \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) \; - \; \hbar\, \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}), \tag{4.70}$$

where

$$\boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) = i \left\langle \boldsymbol{\nabla}_{\mathbf{k}} \psi_n(t,\mathbf{k}) \,|\, \frac{\partial \psi_n(t,\mathbf{k})}{\partial t} \right\rangle - i \left\langle \frac{\partial \psi_n(t,\mathbf{k})}{\partial t} | \, \boldsymbol{\nabla}_{\mathbf{k}} \psi_n(t,\mathbf{R}) \right\rangle \tag{4.71}$$

and

$$\begin{aligned} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) &= \left\langle \psi_n(t,\mathbf{k}) \,|\, \left(H(\mathbf{r},t)^+ - H(\mathbf{r},t) \right) \boldsymbol{\nabla}_{\mathbf{k}} \psi_n(t,\mathbf{k}) \right\rangle \\ &= \frac{i\hbar}{2} \oiint_S \mathbf{n} \cdot \left(\left(\mathbf{v}\, \psi_n \right)^+ + \psi_n^+ \, \mathbf{v} \right) \boldsymbol{\nabla}_{\mathbf{k}} \psi_n \, dS. \end{aligned} \tag{4.72}$$

By now using Eq. (4.69) into Eq. (4.72), that is, taking into account that

$$\boldsymbol{\nabla}_{\mathbf{k}} \psi_n(\mathbf{r},t,\mathbf{k}) = i\, \mathbf{r}\, \psi_n(\mathbf{r},t,\mathbf{k}) \; + \; e^{i\mathbf{k}\cdot\mathbf{r}}\, \boldsymbol{\nabla}_{\mathbf{k}} u_n(\mathbf{r},t,\mathbf{k}),$$

the non-Hermitian boundary term is transformed into

$$\begin{aligned} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) &= i \left\langle \psi_n(t,\mathbf{k}) \,|\, \left(H(\mathbf{r},t)^+ - H(\mathbf{r},t) \right) \mathbf{r}\, \psi_n(t,\mathbf{k}) \right\rangle \\ &\quad + \left\langle u_n(t,\mathbf{k}) \,|\, \left(H_k(\mathbf{r},t,\mathbf{k})^+ - H_k(\mathbf{r},t,\mathbf{k}) \right) \boldsymbol{\nabla}_{\mathbf{k}} u_n(t,\mathbf{k}) \right\rangle \end{aligned} \tag{4.73}$$

where $H_k(\mathbf{r},t,\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} H(\mathbf{r},t) e^{i\mathbf{k}\cdot\mathbf{r}}$.
Because we have assumed periodic boundary conditions, $\psi_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = \psi_n(\mathbf{r},t,\mathbf{k})$ as well as $u_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = u_n(\mathbf{r},t,\mathbf{k})$, the quantum state $\boldsymbol{\nabla}_{\mathbf{k}} u_n(\mathbf{r},t,\mathbf{k})$ is periodic with respect to space coordinates $\boldsymbol{\nabla}_{\mathbf{k}} u_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = \boldsymbol{\nabla}_{\mathbf{k}} u_n(\mathbf{r},t,\mathbf{k})$, it therefore belongs within the domain of definition of the Hamiltonian $H_k(\mathbf{r},t,\mathbf{k})$ which results to

$$\left\langle u_n(t,\mathbf{k}) \,|\, \left(H_k(\mathbf{r},t,\mathbf{k})^+ - H_k(\mathbf{r},t,\mathbf{k}) \right) \boldsymbol{\nabla}_{\mathbf{k}} u_n(t,\mathbf{k}) \right\rangle = 0.$$

On the other hand, the quantum state $\mathbf{r}\, \psi_n(\mathbf{r},t,\mathbf{k})$ lies outside of the domain of definition of periodic wavefunctions, and leaves a residue on our extended and dynamical HF theorem. Employing our non-Hermitian boundary velocity defined by Eq. (2.4)

$$\left\langle \mathbf{v}_b(t,\mathbf{k}) \right\rangle_n = \frac{i}{\hbar} \left\langle \psi_n(t,\mathbf{k}) \,|\, \left(H(\mathbf{r},t)^+ - H(\mathbf{r},t) \right) \mathbf{r}\, \psi_n(t,\mathbf{k}) \right\rangle,$$

as well as Eq. (4.73), the HF theorem Eq. (4.70) that governs the adiabatic particle transport is recast in the form

$$\langle \mathbf{v}_b(t,\mathbf{k})\rangle_n = -\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) + \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}). \tag{4.74}$$

To the best of our knowledge, it is the first time that the particle transport is explicitly related with a non-Hermitian boundary velocity $\langle \mathbf{v}_b(t,\mathbf{k})\rangle_n$, together with an effective electric field $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ (an "electric curvature") that originates from the extended HF theorem. Having in mind Eq. (2.1) which gives $\frac{d}{dt}\langle \mathbf{r}\rangle_n = \langle \mathbf{v}\rangle_n + \langle \mathbf{v}_b\rangle_n$, the time integral $\int_0^T \langle \mathbf{v}_b(t,\mathbf{k})\rangle_n \, dt$ can be interpreted as the displacement of the electron through the boundaries of the material. We stress that, owing to the Bloch functions which are not cell periodic, the boundary velocity expectation value $\langle \mathbf{v}_b(t,\mathbf{k})\rangle_n$ cannot be simplified to a quantity that is evaluated over the boundaries of the unit cell in contrast to the example given in Eq. (2.7).

The electron's boundary velocity in x direction is therefore given by

$$\langle \mathrm{v}_b(t,\mathbf{k})\rangle_{n,x} = -\frac{1}{\hbar}\frac{\partial E_n(t,\mathbf{k})}{\partial k_x} + \mathcal{E}_{n,x}(t,\mathbf{k}) \tag{4.75}$$

where the electric curvature is given from

$$\mathcal{E}_{n,x}(t,\mathbf{k}) = i\left\langle \frac{\partial \psi_n(t,\mathbf{k})}{\partial k_x} \middle| \frac{\partial \psi_n(t,\mathbf{k})}{\partial t} \right\rangle - i\left\langle \frac{\partial \psi_n(t,\mathbf{k})}{\partial t} \middle| \frac{\partial \psi_n(t,\mathbf{k})}{\partial k_x} \right\rangle \tag{4.76}$$

Assuming now for simplicity a simple cubic crystal with lattice constant a, the collective electrons' displacement over the material's boundaries in the x direction, for a fully occupied band, is given by

$$\Delta x_{(Boundary)} = \sum_{\mathbf{k}} \int_0^T \left(\langle \mathrm{v}_b(t,\mathbf{k})\rangle_{n,x} \, dt \right) \rightarrow \frac{V}{(2\pi)^3} \iiint_{BZ} \left(\int_0^T \langle \mathrm{v}_b(t,\mathbf{k})\rangle_{n,x} \, dt \right) dk_x \, dk_y \, dk_z, \tag{4.77}$$

which gives

$$\begin{aligned} \Delta x_{(Boundary)} \;=\; & -\frac{1}{\hbar}\frac{V}{(2\pi)^3} \int_0^T dt \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_{-\pi/a}^{+\pi/a} \frac{\partial E_n(t,\mathbf{k})}{\partial k_x} \, dk_x \right) \\ & + \frac{V}{(2\pi)^3} \int_0^T dt \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_{-\pi/a}^{+\pi/a} \mathcal{E}_{n,x}(t,\mathbf{k}) \, dk_x \right). \end{aligned} \tag{4.78}$$

The first term is zero $\int_{-\pi/a}^{+\pi/a} \frac{\partial E_n(t,\mathbf{k})}{\partial k_x} \, dk_x = 0$ due to symmetry of the instantaneous "energy"

$E(t,\mathbf{k})$ over the edges of the Brillouin zone, and the collective displacement is given by

$$\Delta x_{(Boundary)} = \frac{V}{(2\pi)^3} \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_{0}^{T} \int_{-\pi/a}^{+\pi/a} \mathcal{E}_{n,\,x}(t,\mathbf{k})\, dt\, dk_x \right). \tag{4.79}$$

The integral over k_x is not zero (according to Eq. (4.30)) due to the mirror symmetry that is broken by the external electric field along the x direction. Moreover, the integration over the manifold spanned by $dk_x\, dt$ is quantized due to topological reasons and is given by

$$\left(\int_{0}^{T} \int_{-\pi/a}^{+\pi/a} \mathcal{E}_{n,\,x}(t,\mathbf{k})\, dt\, dk_x \right) = 2\pi\, C_1^{(n)}, \qquad C_1^{(n)} \in \mathbb{Z} \tag{4.80}$$

where $C_1^{(n)}$ is the first Chern number [95]. The first Chern number defines the mapping from the parameter space $(t,\mathbf{k})$ to the complex projective space of normalized Bloch states $\Psi_n(\mathbf{r},t,\mathbf{k})$. Non-zero Chern number indicates that the mapping is non-trivial. For example, because we have assumed periodic boundary conditions at every instant, $\psi_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = \psi_n(\mathbf{r},t,\mathbf{k})$ as well as $u_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = u_n(\mathbf{r},t,\mathbf{k})$, it implies that the Bloch states are generally periodic over the parameter $\mathbf{k}$ up to a phase $\psi_n(\mathbf{r},t,\mathbf{k}+\mathbf{G}) = e^{i\Theta_G}\,\psi_n(\mathbf{r},t,\mathbf{k})$ where $\mathbf{G}$ is a reciprocal lattice vector. Similarly, because we have assumed time-periodic Hamiltonian, the Bloch states are periodic over the parameter t up to a phase $\psi_n(\mathbf{r},t+T,\mathbf{k}) = e^{i\Theta_T}\,\psi_n(\mathbf{r},t,\mathbf{k})$. The last two equations imply that the Bloch states $\Psi_n(\mathbf{r},t,\mathbf{k})$ are not in general single-valued quantities in the parameter space $(t,\mathbf{k})$. Non-zero first Chern number $C_1^{(n)}$ indicates that the Bloch states $\Psi_n(\mathbf{r},t,\mathbf{k})$ cannot be everywhere single-valued in the parameter space domain $0 \le t \le T$ and $-\frac{\pi}{a} \le t \le \frac{\pi}{a}$.

Therefore, the collective electrons' displacement is equal to

$$\Delta x_{(Boundary)} = C_1^{(n)} \frac{V}{(2\pi)^2} \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z = C_1^{(n)} \frac{N\,\alpha^3}{(2\pi)^2} \left(\frac{2\pi}{\alpha}\right)^2, \tag{4.81}$$

where N is the total number of unit cells of the material. Eq. (4.81) implies that, after one period T of adiabatic driving, the displacement per particle in the x direction and over the boundaries of the material, or equivalently, the displacement of the center of mass of the electrons in the x direction and over the boundaries, is quantized in units of lattice constant a (along the x direction) given by

$$\frac{\Delta x_{(Boundary)}}{N} = C_1^{(n)}\,\alpha. \tag{4.82}$$

This implies that the center of mass of the electrons performs a quantized rigid displacement over the boundaries along the x direction, or equivalently the electrons behaves as an incompressible fluid in $\mathbf{k}$-space.

Accordingly, the collective electrons' displacement over y and z directions are zero

$$\Delta y_{(Boundary)} = \Delta z_{(Boundary)} = 0 \tag{4.83}$$

due to the mirror inversion symmetries

$$\mathcal{E}_{n,y}(t, k_x, k_y, k_z) = -\mathcal{E}_{n,y}(t, k_x, -k_y, k_z)$$

and

$$\mathcal{E}_{n,y}(t, k_x, k_y, k_z) = -\mathcal{E}_{n,y}(t, k_x, k_y, -k_z)$$

that are satisfied by the curvatures along those directions.

We conclude that, in the original problem of charge pumping [134] studied with a sliding potential $V(\mathbf{r} - \upsilon\, t\, \boldsymbol{e}_x)$ along the x direction, or in our study with periodic in time t and coordinate x electric field, the mirror symmetry must be broken along the x direction, which results to

$$\mathcal{E}_{n,y}(t, k_x, k_y, k_z) \neq -\mathcal{E}_{n,y}(t, -k_x, k_y, k_z),$$

and which, together with topology, provide the nontrivial (i.e. nonzero) quantization.

As an outcome, we argue that, in materials such as conventional metals which most probably show large internal screening (within adiabatic evolution) of the externally applied electric field, mirror inversion symmetry along the electric field will not be broken. As a result, the Berry curvature $\mathcal{E}_{n,x}(t, \mathbf{k})$ contribution to the longitudinal conductivity due to each pair of electrons with opposite crystal momentums $-k_x$ and k_x will sum to zero. Therefore, no considerable contribution by the curvature $\mathcal{E}_{n,x}(t, \mathbf{k})$ to the longitudinal collective conductivity is expected. On the other hand, in Weyl semimetals [6, 28, 151] where there is at least one direction where the mirror symmetry is broken, the curvature's $\boldsymbol{\mathcal{E}}_n(t, \mathbf{k})$ contribution to conductivity is expected to be significant.

4.3.2 Non-adiabatic process (periodic driving)

Non-adiabatic particle transport using the Floquet-Bloch bands ε_a and the counterpart periodic in time Floquet states, was first made in [122] where they showed that the quantization of the particle transport breaks down due to emergence of band gaps at the quasienergy bands. In a very recent study [105], by performing a careful Floquet analysis of a closed, clean, and non-interacting driven Rice-Mele model in the thermodynamic limit, they found that the pumped charge deviates from the topologically quantized value for a suddenly switched-on periodic driving.

In this respect and in an analogous manner to the one in Sec.4.3.1, we propose that one can use the Floquet-Bloch band ε_a and the counterpart Floquet states in order to study the non-equilibrium charge pump with the dynamical HF theorem. We assume the Hamiltonian Eq. (4.66) having the same potentials as in Sec.4.3.1, with the difference that the scalar potential is periodic over repeated cycles, and changes fast over time. The scalar potential

satisfies the boundary condition $\phi(x, nT) = \phi(x, T)$, where n is the integer number of the cycles. The Hamiltonian $H(\mathbf{r}, t)$ does not depend on any parameter $\boldsymbol{\nabla}_{\mathbf{k}} H(\mathbf{r}, t) = 0$, therefore we use the HF theorem Eq. (4.37) of Sec.4.1.4 by identifying the parameter as the static crystal momentum $\mathbf{R} \equiv \mathbf{k}$. Each electron's wavefunction evolves in time according to the TDSE

$$i\hbar \frac{d}{dt} \Psi(\mathbf{r}, t, \mathbf{k}) = H(\mathbf{r}, t)\, \Psi(\mathbf{r}, t, \mathbf{k}) \tag{4.84}$$

and the quantum state has the form $\Psi(\mathbf{r}, t, \mathbf{k}) \equiv e^{-\frac{i}{\hbar}\varepsilon_a t} \Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k})$. The Floquet states $\Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k})$ are periodic in time $\Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k}) = \Phi_{\varepsilon_a}(\mathbf{r}, t + T, \mathbf{k})$ and satisfy the eigenvalue equation

$$\left(H(\mathbf{r}, t) - i\hbar \frac{d}{dt} \right) \Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k}) = H_F(\mathbf{r}, t) \Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k}) = \varepsilon_a(\mathbf{k}) \Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k}) \tag{4.85}$$

where $\varepsilon_a(\mathbf{k})$ is the quasienergy.

We assume that each Floquet state is expressed with respect to the Floquet-Bloch state [55]

$$\Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_a(\mathbf{r}, t, \mathbf{k}), \tag{4.86}$$

where $u_a(\mathbf{r}, t, \mathbf{k})$ is periodic both in $\mathbf{r}$ and t. Application of the HF theorem Eq. (4.37) with respect to the Floquet state $\Phi_{\varepsilon_a}(\mathbf{r}, t, \mathbf{k})$ gives

$$0 = \boldsymbol{\nabla}_{\mathbf{k}} E_a(t, \mathbf{k}) + \boldsymbol{\mathcal{S}}_a(t, \mathbf{k}) - \hbar\, \boldsymbol{\mathcal{E}}_a(t, \mathbf{k}), \tag{4.87}$$

where the "energy" is given by

$$E_a(t, \mathbf{k}) = \langle \Phi_{\varepsilon_a}(t, \mathbf{k}) |\, H(t)\, | \Phi_{\varepsilon_a}(t, \mathbf{k}) \rangle = \varepsilon_a(\mathbf{k}) + i\hbar \left\langle \Phi_{\varepsilon_a}(t, \mathbf{k}) \,|\, \frac{d}{dt} \Phi_{\varepsilon_a}(t, \mathbf{k}) \right\rangle. \tag{4.88}$$

By assuming time-reversal symmetry in the eigenvalue equation Eq. (4.85), results to the symmetry $\varepsilon_a(\mathbf{k}) = \varepsilon_a(-\mathbf{k})$ for the quasienergy. Using the counterpart of Eq (4.78) for a single period and for a fully occupied quasienergy band gives

$$\begin{aligned} \Delta x_{(Boundary)} \;=\; & -\frac{1}{\hbar} \frac{V}{(2\pi)^3} \int_0^T dt \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_{-\pi/a}^{+\pi/a} \frac{\partial E_n(t, \mathbf{k})}{\partial k_x}\, dk_x \right) \\ & + \frac{V}{(2\pi)^3} \int_0^T dt' \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_{-\pi/a}^{+\pi/a} \mathcal{E}_{n,x}(t, \mathbf{k})\, dk_x \right). \end{aligned} \tag{4.89}$$

Taking into account Eq. (4.88) and the symmetry relation $\varepsilon_a(\mathbf{k}) = \varepsilon_a(-\mathbf{k})$ we find

$$\begin{aligned}\frac{\Delta x_{(Boundary)}}{N} &= -\frac{1}{(2\pi)^3}\frac{V}{N}\int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \\ &\times \int_{-\pi/a}^{+\pi/a} \frac{\partial}{\partial k_x}\left(\int_0^T i\left\langle \Phi_{\varepsilon_a}(t,\mathbf{k}) \,|\, \frac{d}{dt}\Phi_{\varepsilon_a}(t,\mathbf{k})\right\rangle dt\right) dk_x \\ &+ C_1^{(n)}\,\alpha. \end{aligned} \tag{4.90}$$

The first term on the right side of Eq. (4.90) captures the non-adiabatic deviation from the topologically quantized value $C_1^{(n)}\alpha$ due to a non-trivial (non-integrable) Aharonov-Anandan phase [1]. In the special case of parallel transport of the Floquet states

$$\left\langle \Phi_{\varepsilon_a}(t,\mathbf{k}) \,|\, \frac{d}{dt}\Phi_{\varepsilon_a}(t,\mathbf{k})\right\rangle = 0,$$

the quasienergy coincides with the expectation value of the Hamiltonian $\varepsilon_a(\mathbf{k}) \equiv E_a(t,\mathbf{k})$ according to Eq. (4.88), and the displacement of the center of mass of the electrons in the x direction over the boundaries is quantized in units of lattice constant a.

4.4 Electric polarization

Charge pumping has played a central role in the development of the Modern Theory of Polarization [75, 101, 109, 114, 111] in periodic and extended systems. It has theoretically been recognized that in an extended system, only the change in polarization has physical meaning, and it can be quantified by using the Berry phase of the electronic wave functions. The modern theory, in agreement with the experiment, avoids addressing the "absolute" polarization of a given equilibrium state, quite in agreement with the experiments, which invariably measure polarization differences.

We now give a short review of the subtle issues concerning the "absolute" polarization definition, and then use our extended velocity operator definition Eqs. (2.1) –(2.8), together with the dynamical extended HF theorem in order to give a formula that evaluates the polarization difference.

In a classical description, the dipole moment of a single point particle is defined as $\mathbf{p}_i = q_i\,\mathbf{r}_i$ where q_i is the charge of the particle. This "absolute" definition of the dipole moment is a position origin dependent quantity. For a collection of charge particles, the sums of all individual dipole moments $\mathbf{p} = \sum_i \mathbf{p}_i = \sum_i q_i\,\mathbf{r}_i$ gives the collective dipole moment $\mathbf{p}$ of the sample. This collective dipole moment is an origin independent quantity provided that the total charge of the sample is zero. The polarization $\mathbf{P}$ of a material is defined as the dipole moment density per volume of the material $\mathbf{P} = \frac{d\mathbf{p}}{dV}$, and it is known that is not a

gauge invariant quantity [67]. On the other hand, the polarization differences are well defined quantities without any ambiguity and are related to the polarization current $\mathbf{J}_p = \dfrac{d\mathbf{P}}{dt}$.

In a quantum mechanical description, for the bulk electronic polarization of a periodic insulator, a plausible analogy from the classical description, is to find the collective dipole moment of all electrons $\mathbf{p} = \sum_i \langle \mathbf{p}_i \rangle = \sum_i e \langle \psi_i(t) | \mathbf{r}_i | \psi_i(t) \rangle$, and then divide by the volume of the material to find the polarization itself. This however causes serious problems since, for periodic and extended systems, the expectation value of the position operator $\langle \psi_i(t) | \mathbf{r}_i | \psi_i(t) \rangle$ within Bloch representation and in the thermodynamic limit is an undefined quantity (besides being a position origin dependent quantity as well). This was a perplexing issue for some years until the development of the Modern Theory of Polarization [75, 101].

As we have shown in Appendix A, for a periodic and extended system in the thermodynamic limit, the electron's displacement

$$\Delta \langle \psi(t) | \mathbf{r} | \psi(t) \rangle$$

is a well defined quantity provided that one uses our extended velocity operator definition

$$\Delta \langle \psi(t) | \mathbf{r} | \psi(t) \rangle = \int_0^T \langle \psi(t) | \mathbf{v}_{ext} | \psi(t) \rangle \, dt.$$

In this respect, the collective induced polarization of non-interacting electrons is given by

$$\Delta \mathbf{P} = \frac{1}{V} \sum_i e \, \Delta \langle \psi_i(t) | \mathbf{r} | \psi_i(t) \rangle \tag{4.91}$$

where V is the volume of the material and e is the electron charge.

We assume the Hamiltonian Eq. (4.66) and the same potentials as in Sec.4.3.1, that is, a periodic crystal potential together with a time periodic scalar potential $\phi(x, T) = \phi(x, 0)$, which is also periodic over position coordinates. Our aim is to calculate the collective electrons' displacement that gives the collective induced dipole moment, which in turn provides the quantum electronic induced polarization. Each electron's state evolves in time according to the TDSE

$$i\hbar \frac{d}{dt} \Psi(\mathbf{r}, t) = \left(\frac{1}{2m} \mathbf{p}^2 + e\phi(x, t) + V_{crys}(\mathbf{r}) \right) \Psi(\mathbf{r}, t). \tag{4.92}$$

We use the ansatz wavefunction

$$\psi(\mathbf{r}, t, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}, t, \mathbf{k}), \tag{4.93}$$

where the static wave vector $\mathbf{k}$ is a continuous, static vector parameter. Substituting Eq. (4.93) in Eq. (4.92), gives

$$i\hbar \frac{d}{dt} u(\mathbf{r}, t, \mathbf{k}) = \left(\frac{1}{2m} (\mathbf{p} + \hbar\mathbf{k})^2 + e\phi(x, t) + V_{crys}(\mathbf{r}) \right) u(\mathbf{r}, t, \mathbf{k}), \tag{4.94}$$

where the quantum state $u(\mathbf{r},t,\mathbf{k})$ is evolved over time by the Hamiltonian

$$H_k(\mathbf{r},t,\mathbf{k}) = \frac{1}{2m}\left(\mathbf{p}+\hbar\mathbf{k}\right)^2 + e\phi(x,t) + V_{crys}(\mathbf{r}). \tag{4.95}$$

We assume that the electron is initially in the ground state. The scalar potential turns on and changes slowly over time $T\to\infty$, resulting in each ground state evolving in time adiabatically.

$$u(\mathbf{r},t,\mathbf{k}) \equiv e^{i\Theta_n(t,\mathbf{k})}u_n(\mathbf{r},t,\mathbf{k}),$$

where $\Theta_n(t,\mathbf{k})$ is the total phase of the wavefunction (the sum of the dynamic and the geometric adiabatic phase) and $u_n(\mathbf{r},t,\mathbf{k})$ is the instantaneous eigenstate of the Hamiltonian $H_k(\mathbf{r},t,\mathbf{k})$. We now apply the adiabatic form of the HF theorem Eqs. (4.18) – (4.22) on Eq. (4.94) for the Hamiltonian $H_k(\mathbf{r},t,\mathbf{k})$ and the static vector parameter $\mathbf{k}$. The gradient of the Hamiltonian with respect to the wave vector gives

$$\boldsymbol{\nabla}_{\mathbf{k}}H_k(\mathbf{r},t,\mathbf{k}) = \frac{i}{\hbar}[H_k(\mathbf{r},t,\mathbf{k}),\mathbf{r}] = \mathbf{v}$$

which is the (bulk) standard velocity operator. Therefore, we find

$$\langle\mathbf{v}\rangle_n = \boldsymbol{\nabla}_{\mathbf{R}}E_n(t,\mathbf{k}) + \boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k}) - \hbar\,\boldsymbol{\mathcal{E}}_n(t,\mathbf{k}), \tag{4.96}$$

where,

$$\boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) = i\left\langle \boldsymbol{\nabla}_{\mathbf{k}}u_n(t,\mathbf{k})\,|\,\frac{\partial u_n(t,\mathbf{k})}{\partial t}\right\rangle - i\left\langle\frac{\partial u_n(t,\mathbf{k})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}}u_n(t,\mathbf{k})\right\rangle \tag{4.97}$$

is the $t\times\mathbf{R}$ space corresponding Berry curvature, while the non-Hermitian boundary term is given by

$$\boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k}) = \left\langle u_n(t,\mathbf{k})\,|\,\left(H_k(t,\mathbf{k})^+ - H_k(t,\mathbf{k})\right)\boldsymbol{\nabla}_{\mathbf{k}}u_n(t,\mathbf{R})\right\rangle. \tag{4.98}$$

The crucial difference with respect to the theoretical approach that was made in the study of the topological particle transport (Thouless pump), is that, the states $u_n(\mathbf{r},t,\mathbf{k})$ are assumed to be cell periodic in the bulk of the material at every instant, but, need not satisfy periodic boundary conditions over the boundaries of the material. Therefore, except from the initial moment $t=0$, we do not assume periodic boundary condition for the Bloch and the cell periodic wavefunctions at every instant. In this respect, we employ the boundary conditions

$$u_n(\mathbf{r}+\mathbf{L},0,\mathbf{k}) = u_n(\mathbf{r},0,\mathbf{k}) \qquad \text{and} \qquad u_n(\mathbf{r}+\mathbf{L},T,\mathbf{k}) = e^{i\Theta}u_n(\mathbf{r},T,\mathbf{k}),$$

where Θ is a phase, while at intermediate times $0\le t\le T$ the modulus of the wavefunction may not be periodic

$$|u_n(\mathbf{r}+\mathbf{L},t,\mathbf{k})| \neq |u_n(\mathbf{r},t,\mathbf{k})|$$

(analogous boundary conditions are satisfied by the Bloch states).

This breaking of the periodicity over the material boundaries is due to an assumed imbalance of the electron accumulation over opposite boundaries during the time-periodic evolution of the Hamiltonian and can be attributed to a piezoelectric effect. In this framework $\boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k})$ is not zero and cannot be neglected. By taking into account Eq. (4.73) which relates the boundary velocity with the boundary terms of our extended HF theorem

$$\boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) = \hbar \left\langle \mathbf{v}_b \right\rangle_n + \boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k}), \tag{4.99}$$

where $\mathbf{v}_b$ is our non-Hermitian boundary velocity defined by Eq. (2.4) and

$$\boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) = \left\langle \Psi_n(t,\mathbf{k}) \right| \left(H(\mathbf{r},t)^+ - H(\mathbf{r},t) \right) \boldsymbol{\nabla}_{\mathbf{k}} \Psi_n(t,\mathbf{k}) \Big\rangle$$

then, Eq. (4.96) is transformed into

$$\left\langle \mathbf{v} \right\rangle_n + \left\langle \mathbf{v}_b \right\rangle_n = \frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}). \tag{4.100}$$

By using the extended velocity operator definition Eqs. (2.1) – (2.3) given by

$$\left\langle \mathbf{v}_{ext} \right\rangle_n = \left\langle \mathbf{v} \right\rangle_n + \left\langle \mathbf{v}_b \right\rangle_n = \frac{d}{dt} \left\langle \mathbf{r} \right\rangle_n ,$$

we find the electron's main position time derivative given from

$$\frac{d}{dt} \left\langle \mathbf{r} \right\rangle_n = \frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}). \tag{4.101}$$

Therefore, the adiabatic electron's displacement after the cyclic evolution of the Hamiltonian over a period of time T, is given by

$$\Delta \left\langle u_n(t,\mathbf{k}) \right| \mathbf{r} \left| u_n(t,\mathbf{k}) \right\rangle = \int_0^T \left(\frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) \right) dt \tag{4.102}$$

Next, by using Eq.(4.91), we calculate the induced electronic polarization for a single fully occupied band, which is now given by

$$\Delta \mathbf{P}_n = \frac{e}{V} \frac{V}{(2\pi)^3} \iiint_{BZ} \int_0^T \left(\frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E_n(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}_n(t,\mathbf{k}) \right) dt\, dk_x\, dk_y\, dk_z. \tag{4.103}$$

Due to time-reversal symmetry, the contributions from the group velocity cancel out resulting in

$$\Delta \mathbf{P}_n = \frac{e}{\hbar(2\pi)^3} \int_0^T dt \iiint_{BZ} \boldsymbol{\mathcal{S}}_n(t,\mathbf{k})\, d^3k - \frac{e}{(2\pi)^3} \int_0^T dt \iiint_{BZ} \boldsymbol{\mathcal{E}}_n(t,\mathbf{k})\, d^3k. \tag{4.104}$$

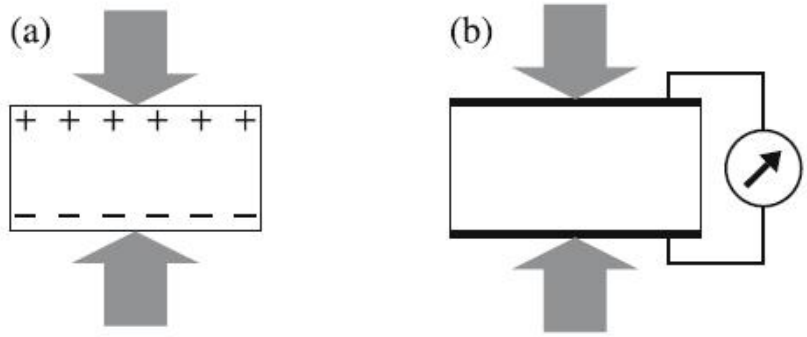

Figure 4.1: Two possible realizations of the piezoelectric effect in a crystal strained along a piezoelectric axis. In (a) the crystal is not shorted, and induced charges pile up at its surfaces. In (b) the crystal is inserted into a shorted capacitor; the surface charges are then removed by the electrodes, and the induced polarization is measured by the current flowing through the shorting wire. Adapted from [114].

Comparing Eq. (4.104) to the Modern Theory of Polarization [75, 101, 139], we have found an extra non-Hermitian boundary contribution to the electronic polarization captured by $\boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k})$, that most probably captures the piezoelectric effect as shown in (a) of Figure 4.1 (although this needs to be investigated further). In the special case that the states $u_n(\mathbf{r},t,\mathbf{k})$ satisfy periodic boundary conditions at every instant, the boundary non-Hermitian contribution turns to zero $\boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k})=0$. This can be shown by expanding the cell periodic functions in a Fourier series over all reciprocal lattice vectors $\mathbf{G}$, namely, $u_n(\mathbf{r},t,\mathbf{k})=\sum_{\mathbf{G}} C_n(t,\mathbf{k},\mathbf{G})e^{-i\mathbf{G}\cdot\mathbf{r}}$. This shows that $\boldsymbol{\nabla}_{\mathbf{k}}u_n(\mathbf{r},t,\mathbf{k})$ as well as $u_n(\mathbf{r},t,\mathbf{k})$, are periodic over position coordinates, which by employing Eq. (4.22) results to $\boldsymbol{\mathcal{S}}_{k,n}(t,\mathbf{k})=0$ due to symmetry [4].

4.5 Quantum equations of motion for a spinless electron

In this section we derive a set of quantum equations of motion with respect to an assumed closed system that conserves the particle number $\langle\Psi(t,\mathbf{R})|\Psi(t,\mathbf{R})\rangle=1$. The first equation gives the velocity of the electron and is derived by means of our extended and dynamical HF theorem Eq. (4.7). The second one gives the equation of motion of the parameter and is derived by means of an extended Ehrenfest theorem [47, 48] that takes into account the boundary non-Hermitian contributions. In the derivation we do not use: (i) specific orthonormal basis set, (ii) semiclassical localization approximation, and (iii) adiabatic time-evolution (in contrast to the common practice that is used in the semiclassical derivations [35, 130, 41, 148, 36, 39] where: (i) they employ as basis states the time-independent Bloch states, (ii) they assume localization in both momentum and space coordinates, and (iii) adiabatic time-evolution is used).

[4] Provided that the electrons are spinless and no spin-Hall effect is present.

4.5.1 Theoretical framework of the method

The basic idea is to use an initial Hamiltonian $H(\mathbf{r},t)$ that does not depend on any parameter, and insert a time dependent parameter with a large gauge transformation. Namely, we assume a time dependent wave vector as the parameter $\mathbf{R}(t) \equiv \mathbf{k}(t)$ and the ansatz

$$|\Psi(t,\mathbf{k})\rangle = e^{i\Lambda(\mathbf{r},t,\mathbf{k}(t))}\,|u(t,\mathbf{k})\rangle\,, \tag{4.105}$$

where the phase $\Lambda(\mathbf{r},t,\mathbf{k}(t))$ explicitly depends on space coordinates $\mathbf{r}$, time t, as well as on the time-dependent parameter $\mathbf{k}(t)$.

The quantum state $|\Psi(t,\mathbf{k})\rangle$ evolves in time by the time-dependent equation

$$i\hbar\frac{d}{dt}\,|\Psi(t,\mathbf{k})\rangle = H(\mathbf{r},t)\,|\Psi(t,\mathbf{k})\rangle\,, \tag{4.106}$$

while $|u(t,\mathbf{k})\rangle$ evolves by

$$i\hbar\frac{d}{dt}\,|u(t,\mathbf{k})\rangle = H_k(\mathbf{r},t,\mathbf{k})\,|u(t,\mathbf{k})\rangle\,, \tag{4.107}$$

where

$$H_k(\mathbf{r},t,\mathbf{k}) = e^{-i\Lambda(\mathbf{r},t,\mathbf{k})}H(\mathbf{r},t)\,e^{i\Lambda(\mathbf{r},t,\mathbf{k})} + \hbar\,\frac{d\Lambda(\mathbf{r},t,\mathbf{k})}{dt} \tag{4.108}$$

is the gauge-transformed Hamiltonian that is explicitly dependent on the parameter. We then apply our dynamical and extended HF theorem to the Hamiltonian Eq. (4.108) in order to evaluate the electron's velocity. In order to explicitly involve the standard velocity operator $\mathbf{v} = \frac{i}{\hbar}\,[H(\mathbf{r},t),\mathbf{r}]$ into the theorem, we assume that the phase has the form

$$\Lambda(\mathbf{r},t,\mathbf{k}(t)) = \mathbf{k}(t)\cdot\mathbf{r} + \lambda(\mathbf{k}(t)), \tag{4.109}$$

thus Eq. (4.108) is given by

$$H_k(\mathbf{r},t,\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}}H(\mathbf{r},t)\,e^{i\mathbf{k}\cdot\mathbf{r}} + \hbar\left(\frac{\partial\mathbf{k}}{\partial t}\cdot\mathbf{r} + \frac{d\lambda(\mathbf{k})}{dt}\right). \tag{4.110}$$

We now act with the momentum gradient operator $\boldsymbol{\nabla}_{\mathbf{k}}$ on both sides of the above equation which gives

$$\boldsymbol{\nabla}_{\mathbf{k}}H_k(\mathbf{r},t,\mathbf{k}) = \boldsymbol{\nabla}_{\mathbf{k}}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}H(\mathbf{r},t)\,e^{i\mathbf{k}\cdot\mathbf{r}}\right) + \hbar\left(\boldsymbol{\nabla}_{\mathbf{k}}\left(\frac{\partial\mathbf{k}}{\partial t}\cdot\mathbf{r}\right) + \boldsymbol{\nabla}_{\mathbf{k}}\left(\frac{d\lambda(\mathbf{k})}{dt}\right)\right). \tag{4.111}$$

The first term on the right side of Eq. (4.111) is equal to

$$\boldsymbol{\nabla}_{\mathbf{k}}\left(e^{-i\mathbf{k}\cdot\mathbf{r}}H(\mathbf{r},t)\,e^{i\mathbf{k}\cdot\mathbf{r}}\right) = [\,H_k(\mathbf{r},t,\mathbf{k})\,,\,i\,\mathbf{r}\,] = \hbar\left(\frac{i}{\hbar}\,[\,H_k(\mathbf{r},t,\mathbf{k})\,,\,\mathbf{r}\,]\right) = \hbar\,\mathbf{v}_k, \tag{4.112}$$

where $\mathbf{v}_k$ is the standard velocity operator.

In our formulation, the wave vector $\mathbf{k}(t)$ is an arbitrary time-dependent parameter. Depending on its definition, it may not have zero $\mathbf{k}$-space derivatives, that is $\boldsymbol{\nabla}_{\mathbf{k}} \frac{\partial k_i}{\partial t} \neq 0$, thus the second term on the right side of Eq. (4.111) is not generally zero. In this respect we define the phase $\lambda(\mathbf{k})$ in such a way that

$$\left\langle u(t,\mathbf{k}) \,|\, \left(\boldsymbol{\nabla}_{\mathbf{k}} \frac{d\Lambda(\mathbf{r},t,\mathbf{k})}{dt} \right) \,|\, u(t,\mathbf{k}) \right\rangle = 0, \tag{4.113}$$

resulting to

$$\langle u(t,\mathbf{k}) \,|\boldsymbol{\nabla}_{\mathbf{k}} H_k(\mathbf{r},t,\mathbf{k})\, |u(t,\mathbf{k})\rangle = \hbar\, \langle u(t,\mathbf{k})|\, \mathbf{v}_k\, |u(t,\mathbf{k})\rangle\,. \tag{4.114}$$

Eq. (4.113) and (4.114) will be directly used in what follows.

4.5.2 Velocity of the spinless electron

We assume that the electron moves within a crystal environment, subject to arbitrary electric and magnetic fields. Therefore, the initial Hamiltonian is

$$H(\mathbf{r},t) = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + e\,\phi(\mathbf{r},t) + V_{crys}(\mathbf{r}), \tag{4.115}$$

where e is the electron charge $(e<0)$, m is the bare electron mass and c the speed of light. The electron interacts with the electric field

$$\mathbf{E}(\mathbf{r},t) = -\boldsymbol{\nabla}_{\mathbf{r}}\left(\phi(\mathbf{r},t) + \frac{1}{e}V_{crys}(\mathbf{r})\right) - \frac{1}{c}\frac{d\mathbf{A}(\mathbf{r},t)}{dt}$$

as well as with the magnetic field

$$\mathbf{B}(\mathbf{r},t) = \boldsymbol{\nabla}_{\mathbf{r}} \times \mathbf{A}(\mathbf{r},t),$$

which results to the classical Lorentz force given by the second Newton's law

$$\frac{d\boldsymbol{\Pi}}{dt} = e\mathbf{E}(\mathbf{r},t) + \frac{e}{c}\frac{d\mathbf{r}}{dt} \times \mathbf{B}(\mathbf{r},t),$$

where $\boldsymbol{\Pi}$ is the classical kinematic momentum of the electron.

With the ansatz $|\Psi(t,\mathbf{k})\rangle = e^{i\,(\mathbf{k}\cdot\mathbf{r}\,+\,\lambda(\mathbf{k}))}\,|u(t,\mathbf{k})\rangle$, the Hamiltonian Eq. (4.115) takes the explicit gauge transformed form

$$H_k(\mathbf{r},t,\mathbf{k}) = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t) + \hbar\mathbf{k}\right)^2 + e\,\phi(\mathbf{r},t) + V_{crys}(\mathbf{r}) \,+\, \hbar\left(\frac{\partial\mathbf{k}}{\partial t}\cdot\mathbf{r} \,+\, \frac{d\lambda(\mathbf{k})}{dt}\right). \tag{4.116}$$

Using now Eqs. (4.113) – (4.114), as well as our extended HF theorem Eq. (4.8) for parameter $\mathbf{R}(t) \equiv \mathbf{k}(t)$, we find the standard velocity expectation value of the electron which is given by

$$\langle\, \mathbf{v} \,\rangle = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_k(t,\mathbf{k}) \,+\, \frac{1}{\hbar}\boldsymbol{\mathcal{S}}_k(t,\mathbf{k}) \,-\, \boldsymbol{\mathcal{E}}(t,\mathbf{k}) - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}), \tag{4.117}$$

where all involved quantities are evaluated with respect to the quantum state $|u(t,\mathbf{k})\rangle$. The electron's velocity expectation value

$$\langle\, \mathbf{v} \,\rangle \equiv \langle u(t,\mathbf{k})|\, \mathbf{v}_k \,|u(t,\mathbf{k})\rangle = \langle \Psi(t,\mathbf{k})|\, \mathbf{v} \,|\Psi(t,\mathbf{k})\rangle$$

where $\mathbf{v} = \frac{i}{\hbar}\,[\, H(\mathbf{r},t)\,,\,\mathbf{r}\,]$, is invariant with respect to the large gauge transformation Eq. (4.109) that has been performed. The generalized curvatures are given by

$$\boldsymbol{\mathcal{B}}(t,\mathbf{k}) = i\,\langle \boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k})| \times |\boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k})\rangle \tag{4.118}$$

and

$$\boldsymbol{\mathcal{E}}(t,\mathbf{k}) = i\left\langle \boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{R})\,|\,\frac{\partial u(t,\mathbf{k})}{\partial t}\right\rangle - i\left\langle \frac{\partial u(t,\mathbf{k})}{\partial t}|\,\boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k})\right\rangle \tag{4.119}$$

respectively, whereas the non-Hermitian boundary term is given by

$$\begin{aligned} \boldsymbol{\mathcal{S}}_k(t,\mathbf{k}) &= \left\langle u(t,\mathbf{k})\,|\,\left(H_k(t,\mathbf{k})^{+} - H_k(t,\mathbf{k})\right)\boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k})\right\rangle \\ &= \frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\left(\,(\mathbf{v}_k\, u(t,\mathbf{k}))^{+} + u(t,\mathbf{k})^{+}\,\mathbf{v}_k\,\right)\boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k})\, dS. \end{aligned} \tag{4.120}$$

We stress that, each of the generalized curvatures $\boldsymbol{\mathcal{B}}(t,\mathbf{k})$ and $\boldsymbol{\mathcal{E}}(t,\mathbf{k})$, as well as the boundary non-Hermitian term $\boldsymbol{\mathcal{S}}_k(t,\mathbf{k})$, are gauge-invariant quantities with respect to $U(1)$ transformation of the form $|u(t,\mathbf{k})\rangle \to e^{i\lambda(\mathbf{k})}\,|u(t,\mathbf{k})\rangle$. Therefore, the part of the velocity that is attributed to the curvatures and the non-Hermitian boundary term, does not depend on the specific choice of $\lambda(\mathbf{k})$ that was made in Eq. (4.113). On the other hand, the "energy"

$$E_k(t,\mathbf{k}) = \langle u(t,\mathbf{k})|\, H_k(t,\mathbf{k})\,|u(t,\mathbf{k})\rangle \tag{4.121}$$

is shifted by the time-derivative of the phase $\hbar\left(\frac{\partial \mathbf{k}}{\partial t}\cdot\mathbf{r} + \frac{d\lambda(\mathbf{k})}{dt}\right)$ as evident from (4.116), which is the typical case of large gauge transformations with gauge functions that explicitly depend on time, and changes the part of the electron's velocity that is attributed to the gradient of the "energy". Due to Eq. (4.113), the part of the group velocity $\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_k(t,\mathbf{k})$ that is attributed to the phase $\lambda(\mathbf{k})$ is given by

$$\frac{1}{\hbar}\,\boldsymbol{\nabla}_{\mathbf{k}}\left\langle \hbar\frac{d\lambda(\mathbf{k})}{dt}\right\rangle = \hbar\,\boldsymbol{\nabla}_{\mathbf{k}}\frac{d\lambda(\mathbf{k})}{dt} = -\left\langle \boldsymbol{\nabla}_{\mathbf{k}}\left(\frac{\partial \mathbf{k}}{\partial t}\cdot\mathbf{r}\right)\right\rangle,$$

indicating that the group velocity does also not have any gauge ambiguity with respect to the phase $\lambda(\mathbf{k})$.

The electron's standard velocity expectation value Eq. (4.117) is one of our major applications of the extended HF theorem, and we argue that it generalizes the semiclassical

electrons' velocity [35, 130, 41, 148, 36, 39].

Taking into account Eq. (4.73) which relates the boundary velocity with the boundary terms of the HF theorem

$$\boldsymbol{\mathcal{S}}(t,\mathbf{k}) = \hbar \langle\, \mathbf{v}_b \,\rangle + \boldsymbol{\mathcal{S}}_k(t,\mathbf{k}), \tag{4.122}$$

where $\mathbf{v}_b$ is the non-Hermitian boundary velocity defined by Eq. (2.4), and the boundary terms of the HF theorem are given by

$$\boldsymbol{\mathcal{S}}(t,\mathbf{k}) = \big\langle \Psi(t,\mathbf{k}) \,|\, \big(H(\mathbf{r},t)^+ - H(\mathbf{r},t)\big)\, \boldsymbol{\nabla}_{\mathbf{k}} \Psi(t,\mathbf{k}) \big\rangle$$

and

$$\boldsymbol{\mathcal{S}}_k(t,\mathbf{k}) = \big\langle u(t,\mathbf{k}) \,|\, \big(H_k(\mathbf{r},t,\mathbf{k})^+ - H_k(\mathbf{r},t,\mathbf{k})\big)\, \boldsymbol{\nabla}_{\mathbf{k}} u(t,\mathbf{k}) \big\rangle$$

respectively, then, Eq. (4.117) is transformed into

$$\langle\, \mathbf{v} \,\rangle + \langle\, \mathbf{v}_b \,\rangle = \frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}(t,\mathbf{k}) - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}). \tag{4.123}$$

By using the extended velocity operator definition Eqs. (2.1) – (2.3) that is defined as

$$\langle\, \mathbf{v}_{ext} \,\rangle = \langle\, \mathbf{v} \,\rangle + \langle\, \mathbf{v}_b \,\rangle = \frac{d}{dt} \langle\, \mathbf{r} \,\rangle,$$

we rigorously find the electron's main position equation of motion

$$\frac{d}{dt} \langle\, \mathbf{r} \,\rangle = \frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E(t,\mathbf{k}) + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}(t,\mathbf{k}) - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}), \tag{4.124}$$

without any semiclassical or localization approximation being involved.

4.5.3 Equation of motion of the parameter-wavevector

The electron's velocity in Eq. (4.117) depends explicitly on the time derivative of the wavevector $\frac{\partial \mathbf{k}}{\partial t}$, which for the moment is an arbitrary parameter. We now define the equation of motion of the wavevector in a physically plausible manner. Namely, we demand that, for a free electron motion the parameter becomes a static quantity. In this framework, we define the time derivative of the wavevector $\mathbf{k}$ (times $\hbar$) to be equal with the time derivative of the electron's kinematic momentum expectation value

$$\hbar \frac{\partial \mathbf{k}}{\partial t} = \frac{d}{dt} \langle\, \boldsymbol{\Pi} \,\rangle. \tag{4.125}$$

The time derivative of the kinematic momentum expectation value $\frac{d}{dt} \langle\, \boldsymbol{\Pi} \,\rangle$ is calculated by the Ehrenfest theorem with the non-Hermitian boundary terms taken into account [47, 48].

Due to the kinematic momentum which is a gauge invariant quantity

$$\langle \Psi(t,\mathbf{k})| \, \mathbf{\Pi} \, |\Psi(t,\mathbf{k})\rangle = \langle u(t,\mathbf{k})| \, \mathbf{\Pi}_k \, |u(t,\mathbf{k})\rangle \, ,$$

$\dfrac{d}{dt} \langle \, \mathbf{\Pi} \, \rangle$ is equally calculated either by using

$$\mathbf{\Pi} = -i\hbar \boldsymbol{\nabla}_{\mathbf{r}} - \frac{e}{c}\mathbf{A}(\mathbf{r},t) \tag{4.126}$$

and the Hamiltonian Eq. (4.115), or by using

$$\mathbf{\Pi}_k = -i\hbar \boldsymbol{\nabla}_{\mathbf{r}} - \frac{e}{c}\mathbf{A}(\mathbf{r},t) + \hbar\mathbf{k} \tag{4.127}$$

and the gauge-transformed Hamiltonian Eq. (4.116).

For simplicity reasons, we choose to work with the Hamiltonian $H(\mathbf{r},t)$ that is given by Eq. (4.115). Therefore, according to the Ehrenfest theorem

$$\frac{d}{dt} \langle \Psi(t,\mathbf{k})| \, \mathbf{\Pi} \, |\Psi(t,\mathbf{k})\rangle = \langle \Psi(t,\mathbf{k})| \, \boldsymbol{\mathcal{F}} \, |\Psi(t,\mathbf{k})\rangle + \langle \Psi(t,\mathbf{k})| \, \boldsymbol{\mathcal{F}}_b \, |\Psi(t,\mathbf{k})\rangle \tag{4.128}$$

where

$$\boldsymbol{\mathcal{F}} = \frac{i}{\hbar} \left[H(\mathbf{r},t), \mathbf{\Pi} \right] + \frac{d\mathbf{\Pi}}{dt} \tag{4.129}$$

is the standard (bulk) operator which gives the bulk quantum force that is exerted on the electron, whereas

$$\boldsymbol{\mathcal{F}}_b = \frac{i}{\hbar} \left(H(\mathbf{r},t)^+ - H(\mathbf{r},t) \right) \mathbf{\Pi} \tag{4.130}$$

is the non-Hermitian effect operator, which gives the boundary counterpart force.

Using the Hamiltonian Eq. (4.115) and the kinematic momentum Eq. (4.126), by straightforward calculation, we find the bulk force operator $\boldsymbol{\mathcal{F}}$ which is given by

$$\boldsymbol{\mathcal{F}} = e\mathbf{E}(\mathbf{r},t) - \boldsymbol{\nabla}_{\mathbf{r}} V_{crys}(\mathbf{r}) + \frac{e}{2c} \Big(\, \mathbf{v} \times \mathbf{B}(\mathbf{r},t) - \mathbf{B}(\mathbf{r},t) \times \mathbf{v} \, \Big) \, . \tag{4.131}$$

The first two terms give the forces that are exerted on the electron by the externally applied electric field and the internal electric field of the crystal. The last term gives the velocity-dependent force due to the externally applied magnetic field, where $\mathbf{v}$ is the standard velocity operator which does not commute with the magnetic field $\mathbf{B}(\mathbf{r},t)$ when the field is not homogeneous. In this respect, the bulk force that is exerted on the electron is given by

$$\langle \, \boldsymbol{\mathcal{F}} \, \rangle = e \, \langle \, \mathbf{E} \, \rangle - \langle \, \boldsymbol{\nabla}_{\mathbf{r}} V_{crys} \, \rangle + \frac{e}{2c} \langle \, \mathbf{v} \times \mathbf{B} \, \rangle - \frac{e}{2c} \langle \, \mathbf{B} \times \mathbf{v} \, \rangle \, . \tag{4.132}$$

For purposes of later application, when the spin-orbit interaction is included (which behaves as an effective inhomogeneous internal magnetic field), it is helpful to express the

operator of the local external magnetic field $\mathbf{B}(\mathbf{r},t)$ as

$$\mathbf{B}(\mathbf{r},t) = \mathbf{B}(\mathbf{r},t) - \langle \mathbf{B}(\mathbf{r},t) \rangle + \langle \mathbf{B}(\mathbf{r},t) \rangle \,, \tag{4.133}$$

where $\langle \mathbf{B}(\mathbf{r},t) \rangle \equiv \langle \Psi(t,\mathbf{k}) | \, \mathbf{B}(\mathbf{r},t) | \, \Psi(t,\mathbf{k}) \rangle$. Therefore, the expectation value of the bulk force Eq. (4.132) is equivalently expressed as

$$\begin{aligned} \langle \boldsymbol{\mathcal{F}} \rangle &= e \langle \mathbf{E} \rangle - \langle \boldsymbol{\nabla}_{\mathbf{r}} V_{crys} \rangle + \frac{e}{c} \langle \mathbf{v} \rangle \times \langle \mathbf{B} \rangle \\ &\quad + \frac{e}{2c} \langle \mathbf{v} \times (\mathbf{B} - \langle \mathbf{B} \rangle) \rangle - \frac{e}{2c} \langle (\mathbf{B} - \langle \mathbf{B} \rangle) \times \mathbf{v} \rangle \end{aligned} \tag{4.134}$$

where the second line captures the part of the magnetic force due to deviation of the external magnetic field from homogeneity, which turns to zero whenever the external magnetic field is homogeneous $\mathbf{B}(\mathbf{r},t) \equiv \mathbf{B}(t)$.

The expectation value of the boundary force $\langle \boldsymbol{\mathcal{F}}_b \rangle$ is calculated by assuming $\mathbf{G} \equiv \boldsymbol{\Pi}$ in Eqs. (3.9) – (3.10) of Chap.3, that gives

$$\begin{aligned} \langle \boldsymbol{\mathcal{F}}_b \rangle &= \left\langle \Psi(t,\mathbf{k}) \, | \, \left(H(\mathbf{r},t)^{+} - H(\mathbf{r},t) \right) \boldsymbol{\Pi} \Psi(t,\mathbf{k}) \right\rangle \\ &= -\frac{1}{2} \oiint_S \mathbf{n} \cdot \left(\left(\mathbf{v} \, \Psi(\mathbf{r},t,\mathbf{k}) \right)^{*} + \Psi(\mathbf{r},t,\mathbf{k})^{*} \, \mathbf{v} \right) \boldsymbol{\Pi} \Psi(\mathbf{r},t,\mathbf{k}) \, dS, \end{aligned} \tag{4.135}$$

where S is the boundary surface that encloses the material and $\mathbf{n}$ is the unit vector that is locally normal to the surface. In general, whenever the wavefunction is not zero at the boundaries of the material, the boundary force may not be zero. For the special case of zero external fields $\mathbf{E} = 0$ and $\mathbf{B} = 0$, the boundary force is definitely zero with respect to a Bloch eigenstate whenever the boundaries do not break the periodicity of the cell periodic states. In order to prove this claim, we calculate the 1D analogue of Eq. (4.135) (which truncates to a two point formula) with respect to Bloch eigenstate $\Psi_n(x,k) = e^{ikx} u_n(k,x)$ which gives

$$\langle \mathcal{F}_b \rangle = -\frac{\hbar^2}{2m} \left[\frac{\partial \Psi_n(x,k)}{\partial x}^{*} \frac{\partial \Psi_n(x,k)}{\partial x} - \Psi_n(x,k)^{*} \frac{\partial^2 \Psi_n(x,k)}{\partial x^2} \right]_{x=0}^{x=L}$$

where L is the length of the system over which we assume periodic boundary conditions $\Psi_n(x+L,k) = \Psi_n(x,k)$. Taking then into account that

$$\frac{\partial \Psi_n(x,k)}{\partial x} = ik \Psi_n(x,k) + e^{ikx} \frac{\partial u_n(x,k)}{\partial x},$$

and expanding the cell periodic functions in a Fourier series over all reciprocal lattice vectors G, namely, $u_n(x,k) = \sum_G C_n(k,G) e^{-iGx}$, it is evident that all terms within the boundary force expression $\langle \mathcal{F}_b \rangle$ are periodic, resulting to zero boundary force $\langle \mathcal{F}_b \rangle = 0$ for Bloch states that satisfy periodic boundary conditions. Similarly, the bulk force is also zero within

Table 4.1: Quantum equations of motion for a spinless electron.

Quantity	**Equation**
$\langle \mathbf{r} \rangle$	$\frac{d}{dt}\langle \mathbf{r} \rangle = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E(t,\mathbf{k}) + \frac{1}{\hbar}\boldsymbol{\mathcal{S}}(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}(t,\mathbf{k}) - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k})$
$\langle \mathbf{\Pi} \rangle$	$\frac{d}{dt}\langle \mathbf{\Pi} \rangle = -\langle \boldsymbol{\nabla}_{\mathbf{r}} V_{crys} \rangle + \langle \boldsymbol{\mathcal{F}}_b \rangle + e\langle \mathbf{E} \rangle + \frac{e}{2c}\langle \mathbf{v} \times \mathbf{B} \rangle - \frac{e}{2c}\langle \mathbf{B} \times \mathbf{v} \rangle$
$\mathbf{k}(t)$	$\hbar \frac{\partial \mathbf{k}}{\partial t} = \frac{d}{dt}\langle \mathbf{\Pi} \rangle$

this approximation

$$\begin{aligned} \langle \mathcal{F} \rangle &= -\int_0^L |\Psi_n(x,k)|^2 \frac{\partial V_{cryst}(x)}{\partial x} dx = -\int_{-L/2}^{L/2} |\Psi_n(x-\frac{L}{2},k)|^2 \frac{\partial V_{cryst}(x-\frac{L}{2})}{\partial x} dx \\ &= -\int_{-L/2}^{L/2} |\Psi_n(x,k)|^2 \frac{\partial V_{cryst}(x)}{\partial x} dx = 0, \end{aligned}$$

because the integrand $|\Psi_n(x,k)|^2 \frac{\partial V_{cryst}(x)}{\partial x}$ is an antisymmetric quantity. In this respect, whenever the bulk and the boundary forces are zero, our parameter k is identical with the static crystal momentum of band theory.

In conclusion, for a spinless electron that moves within a crystal and is subject to external fields, we have derived two equations of motion, one for the electron's main position derived by our extended HF theorem, and the other for the main kinematic momentum derived by the Ehrenfest theorem, which are all presented in Table 4.1. The two equations are coupled to each other owing to the definition of the velocity of the parameter $\hbar \frac{\partial \mathbf{k}}{\partial t} = \frac{d}{dt}\langle \mathbf{\Pi} \rangle$. We stress that, the states that we have assumed are generally extended ones, with no semiclassical wavepacket localization involved. In this manner, our equations can be thought as the quantum mechanical generalization of the semiclassical counterpart equations of motion [35, 130, 41, 148, 36, 39]. Moreover, the electrons velocity $\frac{d}{dt}\langle \mathbf{r} \rangle$ that we give in Table 4.1, can rigorously be employed in topological quantum processes such as in quantum Hall effects which are attributed to delocalized and extended states.

In this framework, one can identify the part of the electron's velocity

$$\left(\frac{d}{dt}\langle \mathbf{r} \rangle\right)_{trans} = -\frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}) = -\frac{1}{\hbar}\frac{d}{dt}\langle \mathbf{\Pi} \rangle \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}) = -\frac{1}{\hbar}\langle \boldsymbol{\mathcal{F}} \rangle \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}), \quad (4.136)$$

as the one that is always transverse to the bulk quantum force $\langle \boldsymbol{\mathcal{F}} \rangle$ that is exerted on the

electron. Furthermore, by defining an effective electric field $\mathbf{E}_{\text{eff}}$ withing the material as

$$\langle \boldsymbol{\mathcal{F}} \rangle = e\, \mathbf{E}_{\text{eff}}, \tag{4.137}$$

one can employ a simplified relation

$$\left(\frac{d}{dt}\langle \mathbf{r} \rangle\right)_{trans} = -\frac{e}{\hbar}\, \mathbf{E}_{\text{eff}} \times \boldsymbol{\mathcal{B}}(t, \mathbf{k}), \tag{4.138}$$

in order to model the transverse response (with respect to the quantum force) of the electron.

4.5.4 Maxwell type of equation

Assuming a flux preserving motion, we now use Eq. (4.60) which gives the Maxwell type of equation

$$\boldsymbol{\nabla}_{\mathbf{k}} \times \boldsymbol{\mathcal{E}}(t, \mathbf{k}) = -\boldsymbol{J}_{\mathbf{k}} - \frac{\partial \boldsymbol{\mathcal{B}}(t, \mathbf{k})}{\partial t} \tag{4.139}$$

where the current is defined by

$$\boldsymbol{J}_{\mathbf{k}} = \frac{\partial \mathbf{k}}{\partial t}\, \boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}(t, \mathbf{k}) + \boldsymbol{\nabla}_{\mathbf{k}} \times \left(\langle \mathbf{v} \rangle - \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_k(t, \mathbf{k}) \right). \tag{4.140}$$

The current satisfies the continuity equation

$$\frac{\partial \rho_M}{\partial t} + \boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{J}_{\mathbf{k}} = 0 \tag{4.141}$$

where ρ_M is the magnetic monopole charge density given from

$$\rho_M = \boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}(t, \mathbf{k}) \tag{4.142}$$

in accordance with Eqs. (4.63) – (4.64), and the above equations are precisely the generalization of the semiclassical Maxwell type of equations that have been heuristically found in the study of Weyl semimetals [69, 70] in the last few years.

4.5.5 Relation to the semiclassical equations of motion

We are now making a comparison between our quantum mechanical equations of motion with the semiclassical [35, 130, 148, 41] counterpart. In this respect, we use the closure relation of the static Bloch states

$$I = \sum_{n}^{\text{HS}} \iiint_{BZ} d^3 k_o \, |\psi_n(\boldsymbol{k}_o)\rangle \, \langle \psi_n(\boldsymbol{k}_o)| \,,$$

where $\boldsymbol{k}_o$ is the static crystal momentum, and expand the quantum state $|\Psi(t,\mathbf{k}(t))\rangle$ in the basis of the static Bloch states resulting to

$$|\Psi(t,\mathbf{k}(t))\rangle = \sum_{n}^{\text{HS}} \iiint_{BZ} C_n(t,\boldsymbol{k}_o,\mathbf{k}(t))\,|\psi_n(\boldsymbol{k}_o)\rangle\,d^3k_o. \tag{4.143}$$

The time-dependent expansion coefficients $C_n(t,\boldsymbol{k}_o,\mathbf{k}(t)) = \langle\psi_n(\boldsymbol{k}_o)|\Psi(t,\mathbf{k}(t))\rangle$ evolve in time in a way that is determined by the time-dependent Schrödinger equation. Expressing each static Bloch eigenstate as $|\Psi_n(\boldsymbol{k}_o)\rangle = e^{i\boldsymbol{k}_o\cdot\mathbf{r}}\,|u_n(\boldsymbol{k}_o)\rangle$, where $|u_n(\boldsymbol{k}_o)\rangle$ are the cell periodic states, the quantum state takes the form

$$|\Psi(t,\mathbf{k}(t))\rangle = \sum_{n}^{\text{HS}} \iiint_{BZ} C_n(t,\boldsymbol{k}_o,\mathbf{k}(t))\,e^{i\boldsymbol{k}_o\cdot\mathbf{r}}\,|u_n(\boldsymbol{k}_o)\rangle\,d^3k_o. \tag{4.144}$$

Multiplying the right side of Eq. (4.144) by $e^{i\mathbf{k}(t)\cdot\mathbf{r}}\,e^{-i\mathbf{k}(t)\cdot\mathbf{r}}$, where $\mathbf{k}(t)$ is a time-dependent arbitrary parameter, the assumed quantum state finally takes the form

$$|\Psi(t,\mathbf{k}(t))\rangle = e^{i\mathbf{k}(t)\cdot\mathbf{r}}\left(\sum_{n}^{\text{HS}} \iiint_{BZ} C_n(t,\boldsymbol{k}_o,\mathbf{k}(t))\,e^{i\,(\boldsymbol{k}_o-\mathbf{k}(t))\cdot\mathbf{r}}\,|u_n(\boldsymbol{k}_o)\rangle\,d^3k_o\right). \tag{4.145}$$

If we now identify

$$\sum_{n}^{\text{HS}} \iiint_{BZ} C_n(t,\boldsymbol{k}_o,\mathbf{k}(t))\,e^{i\,(\boldsymbol{k}_o-\mathbf{k}(t))\cdot\mathbf{r}}\,|u_n(\boldsymbol{k}_o)\rangle\,d^3k_o = |u(t,\mathbf{k}(t))\rangle\,, \tag{4.146}$$

we end up with the assumed general ansatz

$$|u(t,\mathbf{k}(t))\rangle = e^{i\mathbf{k}(t)\cdot\mathbf{r}}\;|u(t,\mathbf{k}(t))\rangle$$

that we have already used. Having in mind that, in our Eq. (4.124) that determines the equation of motion of the electron's position expectation value, the generalized curvatures, as well as the "energy" are evaluated with respect to the state $|u(t,\mathbf{k}(t))\rangle$, whereas the boundary non-Hermitian term $\boldsymbol{\mathcal{S}}(t,\mathbf{k})$ is evaluated with respect to the $|\Psi(t,\mathbf{k}(t))\rangle$ state, we are now in position to make a comparison with the semiclassical counterpart equations of motion [130, 148, 41].

We assume an electron that initially moves within a crystal without the external fields. Its initial state is a single band (ground state) narrow wavepacket, that is, it has sharp distribution in the Brillouin zone, as well as it is narrowly localized around its center of mass in real space. We identify the initial value of the parameter as the initial value of the main wave vector (center) of the wave packet $\mathbf{k}(0) \equiv \mathbf{k}_c(0)$. We turn on the static electric and magnetic fields, and assume that the length scale of perturbations (the length scale of the externally applied potentials) are much larger than the spatial spread of the wavepacket, therefore the

electric and magnetic fields can be approximated as homogeneous vector fields over the extend of the wavepacket in real space. We further assume adiabatic evolution, that is, the external fields do not cause transitions to higher energy bands. We identify our parameter wave vector $\mathbf{k}(t)$ as the time-dependent main wave vector of the wavepacket $\mathbf{k}(t) \equiv \mathbf{k}_c(t)$, which results to

$$|u_n(t, \mathbf{k}_c(t))\rangle = \iiint_{BZ} C_n(t, \boldsymbol{k}_o, \mathbf{k}_c(t))\, e^{i\,(\boldsymbol{k}_o - \mathbf{k}_c(t))\cdot \mathbf{r}}\, |u_n(\boldsymbol{k}_o)\rangle\, d^3k_o. \tag{4.147}$$

By using the identification

$$\hbar \frac{\partial \mathbf{k}(t)}{\partial t} \equiv \hbar \frac{\partial \mathbf{k}_c(t)}{\partial t} = \frac{d}{dt} \langle\, \boldsymbol{\Pi} \,\rangle\,,$$

as well as the equation of motion of the kinematic momentum given in Table 4.1, we find the equation of motion of the main wave vector that is given by

$$\hbar \frac{\partial \mathbf{k}_c(t)}{\partial t} = e\mathbf{E}(\mathbf{r}_c(t)) \,+\, \frac{e}{c} \langle\, \mathbf{v} \rangle \times \mathbf{B}(\mathbf{r}_c(t)), \tag{4.148}$$

where the non-Hermitian boundary force is assumed to be zero

$$\langle\, \boldsymbol{\mathcal{F}}_b \,\rangle = 0$$

due to the spatial localization of the wavepacket.

Again, in deriving Eq. (4.148) we have assumed that the wavepacket is narrowly localized around its center of its mass $\mathbf{r}_c(t)$, as well as that the external fields are approximately homogeneous over the extend of the wavepacket, thus we have replaced

$$\langle\, \mathbf{E} \,\rangle = \langle\, u(t, \mathbf{k}_c(t))|\, \mathbf{E}(\mathbf{r})\, |u(t, \mathbf{k}_c(t))\,\rangle \approx \mathbf{E}(\mathbf{r}_c(t)),$$

as well as

$$\begin{aligned} \frac{1}{2} \langle\, \mathbf{v} \times \mathbf{B} - \mathbf{B} \times \mathbf{v} \,\rangle &= \frac{1}{2} \langle\, u(t, \mathbf{k}_c(t))|\, \mathbf{v} \times \mathbf{B}(\mathbf{r}) - \mathbf{B}(\mathbf{r}) \times \mathbf{v}\, |u(t, \mathbf{k}_c(t))\,\rangle \\ &\approx \frac{1}{2} \langle\, \mathbf{v} \,\rangle \times \mathbf{B}(\mathbf{r}_c(t)) \,-\, \mathbf{B}(\mathbf{r}_c(t)) \times \langle\, \mathbf{v} \,\rangle \\ &= \langle\, \mathbf{v} \,\rangle \times \mathbf{B}(\mathbf{r}_c(t)). \end{aligned}$$

Furthermore, because of the assumed localization, the non-Hermitian boundary terms and the boundary velocity turns to zero

$$\boldsymbol{\mathcal{S}}_k(t, \mathbf{k}) = \boldsymbol{\mathcal{S}}(t, \mathbf{k}) = 0,$$

$$\langle \mathbf{v}_b \rangle = 0.$$

Within this approximation we can replace

$$\langle \mathbf{v} \rangle = \frac{d}{dt}\langle \mathbf{r} \rangle = \frac{d\mathbf{r}_c(t)}{dt}$$

in Eq. (4.148) resulting to

$$\hbar\frac{\partial \mathbf{k}_c(t)}{\partial t} = e\mathbf{E}(\mathbf{r}_c(t)) + \frac{e}{c}\frac{d\mathbf{r}_c(t)}{dt} \times \mathbf{B}(\mathbf{r}_c(t)). \tag{4.149}$$

For the electron's velocity expectation value Eq. (4.117), we take into account the following approximation. The localized quantum state $|u_n(t, \mathbf{k}_c(t))\rangle$ given by Eq. (4.146), is assumed to be non-degenerate and to evolve in time adiabatically. Due to this kind of time evolution, the time-evolved quantum state has the form

$$|u_n(t, \mathbf{k}_c(t))\rangle = e^{i\Theta_n(t,\, \mathbf{k}_c)}\, |u_n(\mathbf{k}_c(t))\rangle\,,$$

where $\Theta_n(t, \mathbf{k}_c)$ is the total (dynamic plus geometric) phase of the wavefunction, and the quantum state $|u_n(\mathbf{k}_c(t))\rangle$ satisfies the instantaneous eigenvalue equation

$$H_k(\mathbf{k}_c(t))\, |u_n(\mathbf{k}_c(t))\rangle = E_n(\mathbf{k}_c(t))\, |u_n(\mathbf{k}_c(t))\rangle\,,$$

where the Hamiltonian is given by Eq. (4.116) and the electromagnetic potentials $\mathbf{A}(\mathbf{r})$ and $\phi(\mathbf{r})$ are constant in time. In this framework, the instantaneous (localized) eigenstate $|u_n(\mathbf{k}_c(t))\rangle$ does not have explicit time dependence, which results to

$$\begin{aligned} |u_n(t, \mathbf{k}_c(t))\rangle &= \iiint_{BZ} C_n(\boldsymbol{k}_o, \mathbf{k}_c(t))\, e^{i\,(\boldsymbol{k}_o\, -\, \mathbf{k}_c(t))\cdot \mathbf{r}}\, |u_n(\boldsymbol{k}_o)\rangle\, d^3k_o \\ &\equiv e^{i\Theta_n(t,\, \mathbf{k}_c)}\, |u_n(\mathbf{k}_c(t))\rangle\,. \end{aligned} \tag{4.150}$$

Using the above equation for the form of the localized quantum state $|u_n(t, \mathbf{k}_c(t))\rangle$ we deduce that

$$\boldsymbol{\mathcal{E}}(t, \mathbf{k}_c(t)) = 0, \tag{4.151}$$

because the curvature $\boldsymbol{\mathcal{E}}(t, \mathbf{k}_c(t))$ is evaluated with respect to $|u_n(\mathbf{k}_c(t))\rangle$ that does not have explicit time-dependence. Therefore, the electron's main position equation of motion is given by

$$\frac{d\mathbf{r}_c(t)}{dt} = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k_c}} E_n(\mathbf{k}_c(t)) - \frac{\partial \mathbf{k}_c(t)}{\partial t} \times \boldsymbol{\mathcal{B}}(\mathbf{k}_c(t)), \tag{4.152}$$

where the curvature $\boldsymbol{\mathcal{B}}(t, \mathbf{k}_c(t))$ is calculated with respect to $|u_n(\mathbf{k}_c(t))\rangle$ in agreement with the one given by [35, 130, 148].

4.5.6 Solution of the coupled quantum equations of motion

Taking now into account Eq. (4.117), as well as Eqs. (4.125), (4.128), (4.131) and (4.135), we solve the coupled equations

$$\langle \mathbf{v} \rangle = \boldsymbol{v}_k - \boldsymbol{\mathcal{E}} - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}} \tag{4.153}$$

$$\hbar \frac{\partial \mathbf{k}}{\partial t} = \langle \boldsymbol{F}_{total} \rangle + e \langle \mathbf{E} \rangle + \frac{e}{c} \langle \mathbf{v} \rangle \times \langle \mathbf{B} \rangle \tag{4.154}$$

where

$$\boldsymbol{v}_k = \frac{1}{\hbar} \boldsymbol{\nabla}_{\mathbf{k}} E_k + \frac{1}{\hbar} \boldsymbol{\mathcal{S}}_k \tag{4.155}$$

is the sum of the group velocity and a contribution due to the non-Hermitian boundary effect, whereas

$$\langle \boldsymbol{F}_{total} \rangle = - \langle \boldsymbol{\nabla}_{\mathbf{r}} V_{crys} \rangle + \frac{e}{2c} \langle \mathbf{v} \times (\mathbf{B} - \langle \mathbf{B} \rangle) \rangle - \frac{e}{2c} \langle (\mathbf{B} - \langle \mathbf{B} \rangle) \times \mathbf{v} \rangle + \langle \boldsymbol{\mathcal{F}}_b \rangle \tag{4.156}$$

is the composition of forces due to crystal environment, inhomogeneous magnetic field and the boundaries. Solving then Eqs. (4.153) – (4.154) for $\langle \mathbf{v} \rangle$ and $\frac{\partial \mathbf{k}}{\partial t}$, we find

$$\mathcal{D} \langle \mathbf{v} \rangle = \boldsymbol{v}_k - \boldsymbol{\mathcal{E}} - \frac{1}{\hbar} \Big(\langle \boldsymbol{F}_{total} \rangle + e \langle \mathbf{E} \rangle \Big) \times \boldsymbol{\mathcal{B}} - \frac{e}{\hbar c} \Big(\boldsymbol{v}_k \cdot \boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{B}} \Big) \langle \mathbf{B} \rangle \tag{4.157}$$

and

$$\begin{aligned} \mathcal{D} \hbar \frac{\partial \mathbf{k}}{\partial t} &= \langle \boldsymbol{F}_{total} \rangle + e \langle \mathbf{E} \rangle + \frac{e}{c} \Big(\boldsymbol{v}_k - \boldsymbol{\mathcal{E}} \Big) \times \langle \mathbf{B} \rangle \\ &- \frac{e}{\hbar c} \Big(\langle \boldsymbol{F}_{total} \rangle \cdot \langle \mathbf{B} \rangle + e \langle \mathbf{E} \rangle \cdot \langle \mathbf{B} \rangle \Big) \boldsymbol{\mathcal{B}}, \end{aligned} \tag{4.158}$$

where

$$\mathcal{D} = 1 - \frac{e}{\hbar c} \langle \mathbf{B} \rangle \cdot \boldsymbol{\mathcal{B}}. \tag{4.159}$$

From Eq. (4.157) we see that the electron's standard velocity has roughly three contributions which are:
(i) the first one given by

$$\boldsymbol{v} - \boldsymbol{\mathcal{E}}$$

which contributes mainly to the longitudinal conductivity,
(ii) the second one

$$-\frac{1}{\hbar} \Big(\langle \boldsymbol{F}_{total} \rangle + e \langle \mathbf{E} \rangle \Big) \times \boldsymbol{\mathcal{B}}$$

which is responsible for the quantization of the transverse Hall conductivity, and
(iii) the last one

$$-\frac{e}{\hbar c} \Big(\boldsymbol{v} \cdot \boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{B}} \Big) \langle \mathbf{B} \rangle$$

which is in the direction of the main value of the externally applied magnetic field.

4.5.7 Sum of states when the crystal momentum k changes with time

We now use Eqs. (4.157) – (4.159) in order to demonstrate how the sum over time-dependent crystal momentums $\mathbf{k}$ can be converted to an integration (in the thermodynamic limit). Our aim is to explicitly find the Jacobian of the transformation $dV_k(t) = \mathrm{Det}J(t,t_o)dV_{k_o}$ in Eq. (4.52). The Jacobian of the transformation evolves in time according to the equation

$$\frac{d}{dt} ln \mathrm{Det}J(t,t_o) = \frac{d}{dt} ln \Delta V_k(t) = \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t}.$$

Because the semiclassical counterpart modified density of states for the phase space volume $\Delta V_k(t) V_r(t)$ was derived, (i) by using the semiclassical equations of motion [130, 148], as well as (ii) by means of a number of approximations such as the absence of monopoles [149], we now give a quantum mechanical derivation without the need of the semiclassical position-momentum phase space, and show explicitly the approximations involved with the aim to possibly find an exact closed result. We start the calculation by taking the divergence $\boldsymbol{\nabla}_{\mathbf{k}}$ of both sides of Eq. (4.158) and then apply the following approximations:

1st approximation

We assume that all involved expectation values $\langle \dots \rangle$ do not depend on the crystal momentum $\mathbf{k}$. Therefore, we find

$$\begin{aligned} \hbar \left(\boldsymbol{\nabla}_{\mathbf{k}} \mathcal{D}\right) \cdot \frac{\partial \mathbf{k}}{\partial t} + \hbar \mathcal{D}\, \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} = & \frac{e}{c} \langle \mathbf{B} \rangle \cdot \boldsymbol{\nabla}_{\mathbf{k}} \times \left(\boldsymbol{v}_k - \boldsymbol{\mathcal{E}} \right) \\ & - \frac{e}{\hbar c} \left(\langle \boldsymbol{F}_{total} \rangle \cdot \langle \mathbf{B} \rangle + e \langle \mathbf{E} \rangle \cdot \langle \mathbf{B} \rangle \right) \boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}} \end{aligned}$$

2nd approximation

We assume adiabatic time evolution, whereas the electron's motion is described by a non-degenerate state that is at every instant an eigenstate of the Hamiltonian. Therefore, all expectation values are assumed to be taken with respect to instantaneous eigenstates of the Hamiltonian $\langle \dots \rangle \equiv \langle \dots \rangle_n$.

3rd approximation

We assume that the Hamiltonian of motion Eq. (4.116) does not have explicit time dependence $H_k \equiv H_k(\mathbf{r}, \mathbf{k})$. Thus the instantaneous eigenstates $|u_n\rangle \equiv |u_n(\mathbf{k})\rangle$ do not have explicit time dependence, which results to zero Berry curvature $\boldsymbol{\mathcal{E}}_n$ by definition

$$\boldsymbol{\mathcal{E}}_n = i \left\langle \boldsymbol{\nabla}_{\mathbf{R}} u_n(\mathbf{k}) \,|\, \frac{\partial u_n(\mathbf{k})}{\partial t} \right\rangle - i \left\langle \frac{\partial u_n(\mathbf{k})}{\partial t} | \, \boldsymbol{\nabla}_{\mathbf{k}} u_n(\mathbf{k}) \right\rangle = 0.$$

Due to the latter approximation, the Berry curvature $\boldsymbol{\mathcal{B}}_n(\mathbf{k})$ has not gotten any time dependence, which in turn results to $\mathcal{D} \equiv \mathcal{D}_n(\mathbf{k})$. In this framework, the total time derivative of $\mathcal{D}_n(\mathbf{k})$ is given by $\boldsymbol{\nabla}_{\mathbf{k}}\mathcal{D}_n(\mathbf{k}) \cdot \dfrac{\partial \mathbf{k}}{\partial t} = \dfrac{d\mathcal{D}_n(\mathbf{k})}{dt}$.

4th approximation

We assume that the curl of the boundary non-Hermitian term is zero

$$\boldsymbol{\nabla}_{\mathbf{k}} \times \boldsymbol{\mathcal{S}}_{nk}(\mathbf{k}) = 0.$$

Result

With the above four approximations we find

$$\hbar \frac{d\mathcal{D}_n(\mathbf{k})}{dt} + \hbar \mathcal{D}_n(\mathbf{k})\, \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} = -\frac{e}{\hbar c}\Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big)\, \boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k}),$$

which gives

$$\frac{dln\mathcal{D}_n(\mathbf{k})}{dt} + \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} = -\frac{e}{\hbar^2 c}\Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big)\, \frac{\boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k})}{\mathcal{D}_n(\mathbf{k})}, \tag{4.160}$$

that leads to the equation of motion of the Jacobian of the transformation

$$\frac{d}{dt} ln\mathrm{Det}J(t,t_o) = -\frac{dln\mathcal{D}_n(\mathbf{k})}{dt} - \frac{e}{\hbar^2 c}\Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big)\, \frac{\boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k})}{\mathcal{D}_n(\mathbf{k})}. \tag{4.161}$$

The Jacobian satisfies $\mathrm{Det}J(t_o,t_o) = 1$, and by assuming the boundary condition $\mathcal{D}_n(\mathbf{k}(t_o)) = 1$, then, by time integration of Eq. (4.161) we find

$$ln\mathrm{Det}J(t,t_o) = -ln\mathcal{D}_n(\mathbf{k}) - \frac{e}{\hbar^2 c}\int_{t_o}^{t} \Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big)\, \frac{\boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k})}{\mathcal{D}_n(\mathbf{k})}\, dt'. \tag{4.162}$$

By exponentiating the above equation we finally get

$$\frac{1}{\mathrm{Det}J(t,t_o)} = \mathcal{D}_n(\mathbf{k})\, \mathrm{e}^{\frac{e}{\hbar^2 c}\int_{t_o}^{t} \Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big)\, \frac{\boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k})}{\mathcal{D}_n(\mathbf{k})}\, dt'}, \tag{4.163}$$

that has to be substituted in Eq. (4.52) within the approximations (1–4). Our Eq. (4.163) provides a quantum derivation of the semiclassical counterpart presented in Ref. [149], that however also takes into account the monopoles of the projective Hilbert space. In the absence of monopoles, $\boldsymbol{\nabla}_{\mathbf{k}} \cdot \boldsymbol{\mathcal{B}}_n(\mathbf{k}) = 0$, or when $\Big(\langle\, \boldsymbol{F}_{total}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle + e\, \langle\, \mathbf{E}\,\rangle \cdot \langle\, \mathbf{B}\,\rangle \Big) = 0$, one recovers the semiclassical counterpart formula. We re-emphasize that Eq. (4.163) is valid only within the assumed approximations (1 –4) and for a spinless electron motion.

4.6 Quantum equations of motion for a spinfull electron

In this section we extend the quantm equations of motion derived in Section4.5 in order to take into account the electron's spin (or pseudospin) degree of freedom which take part in most topological materials with high atomic numbers. For such motions we use the non-relativistic limit of the Dirac equation with the Zeeman and spin-orbit coupling terms taken into account. The theoretical framework of the method is analogous to that of Sec.4.5.1, but with the difference that the assumed quantum state is now a two-component spinor. Therefore, we use the $U(1)$ ansatz form

$$|\Psi(t,\mathbf{k})\rangle = e^{i\Lambda(\mathbf{r},t,\mathbf{k}(t))}\,|u(t,\mathbf{k})\rangle\,, \tag{4.164}$$

where the quantum state $|u(t,\mathbf{k})\rangle$ is a two component spinor

$$|u(t,\mathbf{k})\rangle \equiv (\,|u_a(t,\mathbf{k})\rangle\,,\ |u_b(t,\mathbf{k})\rangle\,)^T\,.$$

The initial Hamiltonian is now

$$H(\mathbf{r},t) = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + e\,\phi(\mathbf{r},t) + V_{crys}(\mathbf{r}) + H_{\rm z}(\mathbf{r},t) + H_{\rm s.o}(\mathbf{r},t) \tag{4.165}$$

where e is the electron charge $(e<0)$, m is the bare mass of electron and c the speed of light, while

$$H_{\rm z}(\mathbf{r},t) = -\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t) \tag{4.166}$$

is the Zeeman term, and

$$H_{\rm s.o}(\mathbf{r},t) = \frac{\hbar}{4m^2c^2}\Big(\,\boldsymbol{\sigma}\times(e\nabla\phi(\mathbf{r},t) + \nabla V_{crys}(\mathbf{r}))\Big)\cdot\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right) \tag{4.167}$$

is the spin-orbit coupling term.

4.6.1 Velocity of the spinfull electron

Using similar arguments as in Eqs. (4.106) – (4.114), the bulk velocity operator is now given by

$$\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}}H_k(\mathbf{r},t,\mathbf{k}) = \frac{i}{\hbar}\,[\,H_k(\mathbf{r},t,\mathbf{k})\,,\ \mathbf{r}\,] = \frac{1}{m}\left(\mathbf{p} + \hbar\mathbf{k} - \frac{e}{c}\Big(\,\mathbf{A}(\mathbf{r},t) + \mathbf{A}^{\rm eff}(\mathbf{r},t)\Big)\right) \equiv \mathbf{v}_k \tag{4.168}$$

where

$$\mathbf{A}^{\rm eff}(\mathbf{r},t) = -\frac{\hbar}{4emc}\boldsymbol{\sigma}\times\Big(\,e\nabla\phi(\mathbf{r},t) + \nabla V_{crys}(\mathbf{r})\Big) \tag{4.169}$$

comes from the spin-orbit coupling and plays the role of an $SU(2)$ effective gauge vector potential. Therefore, we identify as kinematic momentum operator the quantity

$$\mathbf{\Pi}_k = \mathbf{p} + \hbar\mathbf{k}(t) - \frac{e}{c}\Big(\,\mathbf{A}(\mathbf{r},t) + \mathbf{A}^{\rm eff}(\mathbf{r},t)\Big)\,. \tag{4.170}$$

According then to our extended HF theorem Eq. (4.8) for parameter $\mathbf{R}(t) \equiv \mathbf{k}(t)$, the velocity operator expectation value is given by

$$\langle \mathbf{v}_k \rangle = \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}} E_k(t,\mathbf{k}) + \frac{1}{\hbar}\boldsymbol{\mathcal{S}}_k(t,\mathbf{k}) - \boldsymbol{\mathcal{E}}(t,\mathbf{k}) - \frac{\partial \mathbf{k}}{\partial t} \times \boldsymbol{\mathcal{B}}(t,\mathbf{k}). \tag{4.171}$$

4.6.2 Equation of motion of the parameter-wavevector

In an analogous manner to that of Sec.4.5.3 we use the initial (before the $U(1)$ transformation) kinematic momentum operator

$$\boldsymbol{\Pi} = \mathbf{p} - \frac{e}{c}\Big(\mathbf{A}(\mathbf{r},t) + \mathbf{A}^{\text{eff}}(\mathbf{r},t)\Big), \tag{4.172}$$

as well as the initial Hamiltonian Eq. (4.165) and define the time derivative of the wavevector $\mathbf{k}$ (times $\hbar$) to be equal with the time derivative of the electron's kinematic momentum expectation value

$$\hbar\frac{\partial \mathbf{k}}{\partial t} = \frac{d}{dt}\langle \boldsymbol{\Pi} \rangle . \tag{4.173}$$

The time derivative of the kinematic momentum expectation value $\frac{d}{dt}\langle \boldsymbol{\Pi} \rangle$ is calculated by the Ehrenfest theorem with the non-Hermitian boundary terms taken into account [47, 48]. According to Ref. [119], the kinematic momentum Eq. (4.172) satisfies the commutation relation $[\Pi_\alpha\,,\,\Pi_\beta] = i\frac{\hbar e}{m^2 c}\epsilon_{\alpha\beta\gamma}B^{\text{total}} + \frac{e^2}{m^2c^2}[A^{\text{eff}}_\alpha\,,\,A^{\text{eff}}_\beta]$ where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol whereas

$$\mathbf{B}^{\text{total}}(\mathbf{r},t) = \mathbf{B}(\mathbf{r},t) + \mathbf{B}^{\text{eff}}(\mathbf{r},t) \tag{4.174}$$

is the total magnetic field. The effective magnetic field

$$\mathbf{B}^{\text{eff}}(\mathbf{r},t) = \nabla \times \mathbf{A}^{\text{eff}}(\mathbf{r},t) \tag{4.175}$$

is present due to strong spin-orbit coupling, whereas the standard magnetic field is given by $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r},t)$.

By only keeping terms up to $\frac{1}{c^2}$ (in agreement with the accuracy of the Hamiltonian Eq. (4.165)) the bulk force operator $\boldsymbol{\mathcal{F}}$ is given by

$$\begin{aligned}\boldsymbol{\mathcal{F}} &= \frac{i}{\hbar}[\,H(\mathbf{r},t),\,\boldsymbol{\Pi}\,] - \frac{e}{c}\left(\frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t} + \frac{\partial \mathbf{A}_{\text{eff}}(\mathbf{r},t)}{\partial t}\right)\\ &\approx e\,\mathbf{E}^{\text{total}}(\mathbf{r},t) - \boldsymbol{\nabla}_{\mathbf{r}} V_{crys}(\mathbf{r}) + \frac{e}{2c}\Big(\,\mathbf{v}\times\mathbf{B}_{\text{total}}(\mathbf{r},t) - \mathbf{B}_{\text{total}}(\mathbf{r},t)\times\mathbf{v}\,\Big),\end{aligned}$$

where the total electric field is given by

$$\mathbf{E}^{\text{total}}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t) + \mathbf{E}^{\text{eff}}(\mathbf{r},t), \tag{4.176}$$

with the effective electric field

$$\mathbf{E}^{\text{eff}}(\mathbf{r},t)=\frac{\hbar}{2mc}\nabla\left(\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r},t)\right) \tag{4.177}$$

being a Stern-Gerlach type of electric field.

Accordingly, the non-Hermitian boundary force operator is given from

$$\boldsymbol{\mathcal{F}}_b=\frac{i}{\hbar}\left(H(\mathbf{r},t)^{+}-H(\mathbf{r},t)\right)\boldsymbol{\Pi}. \tag{4.178}$$

In an analogous manner as in Eq. (4.133), we express the total magnetic field in the form

$$\mathbf{B}^{\text{total}}(\mathbf{r},t)=\mathbf{B}^{\text{total}}(\mathbf{r},t)-\left\langle\mathbf{B}^{\text{total}}(\mathbf{r},t)\right\rangle+\left\langle\mathbf{B}^{\text{total}}(\mathbf{r},t)\right\rangle, \tag{4.179}$$

therefore, the time derivative of the kinematic momentum expectation value is given by

$$\begin{aligned}\frac{d}{dt}\langle\,\boldsymbol{\Pi}\,\rangle=\langle\,\boldsymbol{\mathcal{F}}\,\rangle\;\approx\;& e\left\langle\,\mathbf{E}^{\text{total}}\,\right\rangle-\langle\,\boldsymbol{\nabla}_{\mathbf{r}}V_{crys}\,\rangle+\frac{e}{c}\langle\,\mathbf{v}\,\rangle\times\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle\\&+\frac{e}{2c}\left\langle\,\mathbf{v}\times\left(\mathbf{B}^{\text{total}}-\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle\right)\right\rangle-\frac{e}{2c}\left\langle\left(\mathbf{B}^{\text{total}}-\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle\right)\times\mathbf{v}\,\right\rangle\\&+\langle\,\boldsymbol{\mathcal{F}}_b\,\rangle\,.\end{aligned} \tag{4.180}$$

4.6.3 Solution of the coupled spinfull quantum equations of motion

In an analogous manner as in the spinless motion Eqs. (4.153) – (4.154), the two coupled equations of motion are expressed as

$$\langle\,\mathbf{v}\,\rangle\;=\;\boldsymbol{v}_k\;-\;\boldsymbol{\mathcal{E}}-\frac{\partial\mathbf{k}}{\partial t}\times\boldsymbol{\mathcal{B}} \tag{4.181}$$

$$\hbar\frac{\partial\mathbf{k}}{\partial t}\;=\;\langle\,\boldsymbol{F}\,\rangle\;+\;e\left\langle\,\mathbf{E}^{\text{total}}\,\right\rangle\;+\;\frac{e}{c}\langle\,\mathbf{v}\,\rangle\times\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle \tag{4.182}$$

where

$$\boldsymbol{v}_k=\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{k}}E_k\;+\;\frac{1}{\hbar}\boldsymbol{\mathcal{S}}_k \tag{4.183}$$

is the sum of the group velocity and a contribution due to the non-Hermitian boundary effect, whereas

$$\begin{aligned}\langle\,\boldsymbol{F}\,\rangle\;=\;&-\langle\,\boldsymbol{\nabla}_{\mathbf{r}}V_{crys}\,\rangle+\langle\,\boldsymbol{\mathcal{F}}_b\,\rangle\\&+\frac{e}{2c}\left\langle\,\mathbf{v}\times\left(\mathbf{B}^{\text{total}}-\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle\right)\right\rangle-\frac{e}{2c}\left\langle\left(\mathbf{B}^{\text{total}}-\left\langle\,\mathbf{B}^{\text{total}}\,\right\rangle\right)\times\mathbf{v}\,\right\rangle.\end{aligned} \tag{4.184}$$

Solving then Eq. (4.181) – (4.182) for $\langle\,\mathbf{v}\,\rangle$ and $\frac{\partial\mathbf{k}}{\partial t}$, we find the two spinfull quantum

equations

$$\mathcal{C}\left\langle \mathbf{v}\right\rangle = \boldsymbol{v}_k \;-\; \boldsymbol{\mathcal{E}} \;-\; \frac{1}{\hbar}\left(\left\langle \boldsymbol{F}\right\rangle + e\left\langle \mathbf{E}^{\text{total}}\right\rangle\right)\times\boldsymbol{\mathcal{B}} \;-\; \frac{e}{\hbar c}\left(\boldsymbol{v}_k\cdot\boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{B}}\right)\left\langle \mathbf{B}^{\text{total}}\right\rangle \tag{4.185}$$

and

$$\begin{aligned}\mathcal{C}\,\hbar\frac{\partial\mathbf{k}}{\partial t} \;&=\; \left\langle \boldsymbol{F}\right\rangle + e\left\langle \mathbf{E}^{\text{total}}\right\rangle + \frac{e}{c}\left(\boldsymbol{v}_k \;-\; \boldsymbol{\mathcal{E}}\right)\times\left\langle \mathbf{B}^{\text{total}}\right\rangle \\ &\quad -\frac{e}{\hbar c}\left(\left\langle \boldsymbol{F}\right\rangle\cdot\left\langle \mathbf{B}^{\text{total}}\right\rangle + e\left\langle \mathbf{E}^{\text{total}}\right\rangle\cdot\left\langle \mathbf{B}^{\text{total}}\right\rangle\right)\boldsymbol{\mathcal{B}},\end{aligned} \tag{4.186}$$

where

$$\mathcal{C} = 1 - \frac{e}{\hbar c}\left\langle \mathbf{B}^{\text{total}}\right\rangle\cdot\boldsymbol{\mathcal{B}} \tag{4.187}$$

with

$$\left\langle \mathbf{B}^{\text{total}}\right\rangle = \left\langle \mathbf{B}\right\rangle + \left\langle \mathbf{B}^{\text{eff}}\right\rangle.$$

Eqs. (4.185) – (4.187) are the generalization of the spinless quantum equations of motion that we derived in Sec. 4.5, and we believe that, due the explicit spin dependence, they can be applied to quite general non-interacting topological quantum processes. The spinfull electron has three velocity contributions, namely, the first one $\boldsymbol{v} - \boldsymbol{\mathcal{E}}$ that contributes mainly to the longitudinal conductivity, the second one $-\frac{1}{\hbar}\left(\left\langle \boldsymbol{F}\right\rangle + e\left\langle \mathbf{E}^{\text{total}}\right\rangle\right)\times\boldsymbol{\mathcal{B}}$ that is in a direction normal to the quantum force (which can presumably be used to model the transverse quantum anomalous Hall conductivity), and the last one $-\frac{e}{\hbar c}\left(\boldsymbol{v}\cdot\boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{B}}\right)\left\langle \mathbf{B}^{\text{total}}\right\rangle$ which is in the direction of the main total magnetic field. (In all of them, the extra non-Hermitian effect has been incorporated.)

4.6.4 Sum of states in spinfull motions when the crystal momentum k changes with time

Assuming the same approximations (1 – 4) of Sec.4.5.7, we can straightforwardly map the spinless result Eq. (4.163) to the spinfull one by substituting

$$\begin{aligned}\mathbf{E} &\mapsto \mathbf{E}^{\text{total}}\\ \mathbf{B} &\mapsto \mathbf{B}^{\text{total}}\\ \boldsymbol{F}_{total} &\mapsto \boldsymbol{F}\\ \mathcal{D}_n(\mathbf{k}) &\mapsto \mathcal{C}_n(\mathbf{k})\end{aligned}$$

in Eqs. (4.157) – (4.159). This gives a closed result of the Jacobian of the transformation

$$\frac{1}{\mathrm{Det}J(t,t_o)} = \mathcal{C}_n(\mathbf{k})\, \mathrm{e}^{\frac{e}{\hbar^2 c}\int_{t_o}^{t}\left(\langle\, \boldsymbol{F}\,\rangle\cdot\langle\, \mathbf{B}^{\mathrm{total}}\,\rangle + e\,\langle\, \mathbf{E}^{\mathrm{total}}\,\rangle\cdot\langle\, \mathbf{B}^{\mathrm{total}}\,\rangle\right)\frac{\boldsymbol{\nabla}_{\mathbf{k}}\cdot\boldsymbol{\mathcal{B}}_n(\mathbf{k})}{\mathcal{C}_n(\mathbf{k})}\,dt'}, \tag{4.188}$$

which is a new result and extends the semiclassical modification of density of states [150, 22, 45] to topological spinfull motions provided that the approximations (1 – 4) are satisfied.

A simplified model for the Quantum Anomalous Hall Effect

As a final application, and always within the non-interacting electron approximation, we assume that each electron is confined in a thin film of, either a magnetically doped or magnetic proximity topological insulator [34, 18, 62, 85], without any externally applied magnetic field.

In order to apply our quantum equations of motion, we assume the Hamiltonian

$$H(\mathbf{r},t) = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + V_{crys}(\mathbf{r}) + H_{\mathrm{z}}(\mathbf{r}) + H_{\mathrm{s.o}}(\mathbf{r},\mathbf{t}) \tag{4.189}$$

and use a phenomenological inhomogeneous magnetic field $\mathbf{B}(\mathbf{r})$ in the Zeeman term

$$H_{\mathrm{z}}(\mathbf{r},t) = -\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r}), \tag{4.190}$$

in order to break the time-reversal symmetry. This microscopic magnetic field is assumed to be of Haldane's type, that is, it is periodic over space coordinates and averages to zero $\langle\, \mathbf{B}(\mathbf{r})\,\rangle = 0$, therefore no net macroscopic magnetic field is present. Moreover, this type of inhomogeneous microscopic magnetic field is coupled to the electron's spin $\boldsymbol{\sigma}$, thus it can be thought of as a term that probes the local ordered magnetic moments of the electron. We assume that this kind of microscopic magnetic field depends on the magnetic doping (or magnetic proximity) and for undoped material is zero.

The spin-orbit coupling term that has no effect on the time-reversal symmetry is given by

$$H_{\mathrm{s.o}}(\mathbf{r},t) = \frac{\hbar}{4m^2c^2}\left(\boldsymbol{\sigma}\times\nabla V_{crys}(\mathbf{r})\right)\cdot\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r},t)\right),$$

where $-\frac{1}{c}\frac{d\mathbf{A}(\mathbf{r},t)}{dt} = \mathbf{E}(\mathbf{r})$ is the externally applied electric field.

Each electron's (standard) velocity (see Eq. (4.185)) is given by

$$\mathcal{C}\,\langle\, \mathbf{v}\,\rangle = \boldsymbol{v}_k - \boldsymbol{\mathcal{E}} - \frac{1}{\hbar}\left(\langle\, \boldsymbol{F}\,\rangle + e\,\langle\, \mathbf{E}^{\mathrm{total}}\,\rangle\right)\times\boldsymbol{\mathcal{B}} - \frac{e}{\hbar c}\left(\boldsymbol{v}_k\cdot\boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{B}}\right)\langle\, \mathbf{B}^{\mathrm{eff}}\,\rangle \tag{4.191}$$

where

$$\mathcal{C} = 1 - \frac{e}{\hbar c} \left\langle \mathbf{B}^{\text{eff}} \right\rangle \cdot \boldsymbol{\mathcal{B}}. \tag{4.192}$$

If we assume a 2D material, then, the Berry curvature $\boldsymbol{\mathcal{B}}$ is in the direction normal to the material, let's say $\boldsymbol{e}_z$ direction, which results to

$$\Big(\boldsymbol{v}_k \cdot \boldsymbol{\mathcal{B}} - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{B}}\Big) = \Big(\boldsymbol{v}_k - \boldsymbol{\mathcal{E}}\Big) \cdot \boldsymbol{e}_z \;\; \mathcal{B} = 0$$

because each one of $\boldsymbol{v}_k$ and $\boldsymbol{\mathcal{E}}$ has in-plane direction as evident by their definition (the momentum gradient operator $\boldsymbol{\nabla}_{\mathbf{k}}$ having in-plane direction for 2D materials).

All the quantities involved in Eq. (4.191) are evaluated with respect to the time-dependent state $|u(t, \mathbf{k})\rangle$ which evolves in time by the Hamiltonian

$$H_k(\mathbf{r}, t, \mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}} H(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} \; + \; \hbar \left(\frac{\partial \mathbf{k}}{\partial t} \cdot \mathbf{r} \; + \; \frac{d\lambda(\mathbf{k})}{dt} \right), \tag{4.193}$$

where $H(\mathbf{r})$ is given by Eq. (4.189). This Hamiltonian is generally time-dependent, thus it is difficult to analytically find the time-dependent states. On the other hand, if there exists a steady-state limit where the quantum force that is exerted on the electron is approximatively zero

$$\hbar \frac{\partial \mathbf{k}}{\partial t} \to 0,$$

then, the latter Hamiltonian is translation invariant and we can study these steady-state limit quantum processes in a topological band theory framework. In this framework, we assume a homogeneous and static externally applied electric field, with the vector potential given by $\mathbf{A}(t) = -ct\mathbf{E}$. Assuming that the electron is initially in a (non-degenerate) ground state, and considering the steady state limit, then, we may assume adiabatic evolution (provided that the external electric field is sufficiently low) of each ground state.

The electron's velocity is then given by

$$\mathcal{C}_n \left\langle \mathbf{v} \right\rangle_n = \boldsymbol{v}_{k,n}(t, \mathbf{k}) \; - \; \boldsymbol{\mathcal{E}}_n(t, \mathbf{k}) \; - \; \frac{1}{\hbar} \left(\left\langle \boldsymbol{F} \right\rangle_n + e \left\langle \mathbf{E}^{\text{total}} \right\rangle_n \right) \times \boldsymbol{\mathcal{B}}_n(t, \mathbf{k}), \tag{4.194}$$

where the total electric field is given by

$$\left\langle \mathbf{E}^{\text{total}} \right\rangle_n = \mathbf{E} + \frac{\hbar}{2mc} \left\langle \nabla \left(\boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{r}) \right) \right\rangle_n .$$

We then define as collective electric field the quantity

$$\mathbf{E}_{\text{col}} = \left(\frac{1}{e} \left\langle \boldsymbol{F} \right\rangle_n + \left\langle \mathbf{E}^{\text{total}} \right\rangle_n \right), \tag{4.195}$$

which by definition has four contributions coming from: (i) the externally applied electric field $\mathbf{E}$, (ii) the Stern-Gerlach type of electric field due to the inhomogeneous microscopic magnetic field $\mathbf{B}(\mathbf{r})$, (iii) the electric field created by the crystal environment, and (v) an

effective electric field due to the boundary non-Hermitian force.

The electron's velocity component in x direction is given by

$$\langle \mathrm{v}_x \rangle_n = \frac{1}{\mathcal{C}_n} \Big(v_x(t,\mathbf{k}) \; - \; \mathcal{E}_x(t,\mathbf{k}) \; - \; \frac{e}{\hbar} E_{y,\mathrm{col}} \, \mathcal{B}_z(t,\mathbf{k}) \Big) \,, \tag{4.196}$$

where $-\frac{e}{\hbar} E_{y,\mathrm{col}} \, \mathcal{B}_z(t,\mathbf{k})$ is a velocity contribution due to the collective electric field in the y direction. We assume that the electric field of the (perfect) crystal averages to zero, as well as that the externally applied electric field is in the x direction $\mathbf{E} = E\boldsymbol{e}_x$. In this respect, the collective electric field $E_{y,\mathrm{col}}$ is created solely due to boundary forces and the bulk Stern-Gerlach type of force in the y direction. Now one can sum Eq. (4.196) over all single particle sates of the fully occupied bands, in order to find the collective electrons' velocity. It should be noted that, in order to convert the sum to an integration in the thermodynamic limit, we cannot use Eq. (4.188) because the Berry curvature $\boldsymbol{\mathcal{E}}_n(t,\mathbf{k})$ is not zero. Instead we make a different kind of approximation, namely, the incompressible fluid one,

$$\frac{d}{dt} ln \mathrm{Det} J(t,t_o) = \boldsymbol{\nabla}_{\mathbf{k}} \cdot \frac{\partial \mathbf{k}}{\partial t} = 0$$

which results to $\mathrm{Det} J(t,t_o) = \mathrm{Det} J(t_o,t_o) = 1$. By using now Eq. (4.52), we find that the transverse conductivity of fully occupied bands is given by

$$\sigma_{xy} = \sum_{n,\mathbf{k}} \frac{1}{E_{y,\mathrm{col}}} \frac{e}{S} \langle \mathrm{v}_x \rangle_n \;\; \rightarrow \;\; \frac{e}{(2\pi)^2} \iint\limits_{BZ} \frac{1}{E_{y,\mathrm{col}}} \frac{1}{\mathcal{C}_n} \Big(v_x(t,\mathbf{k}) \; - \; \mathcal{E}_x(t,\mathbf{k}) \Big) \, dk_x dk_y$$
$$- \frac{e^2}{h} \frac{1}{2\pi} \iint\limits_{BZ} \frac{1}{\mathcal{C}_n} \mathcal{B}_z(t,\mathbf{k}) dk_x dk_y \tag{4.197}$$

where S is the sample area.

The above result can be used to model the various contributions to the Quantum Anomalous Hall effect such as the skew scattering[5] contribution. This contribution can be encoded for example in the effective magnetic field $\langle \mathbf{B}^{\mathrm{eff}} \rangle_n$ that is attributed to the spin-orbit coupling, as well as in the effective Stern-Gerlach type of electric field $\langle \mathbf{E}^{\mathrm{eff}} \rangle_n$ which is in turn encoded in the collective electric field $E_{y,\mathrm{col}}$. In this framework, for a "pure" transverse motion of the electron we may assume

$$\Big(v_x(t,\mathbf{k}) \; - \; \mathcal{E}_x(t,\mathbf{k}) \Big) \rightarrow 0$$

in accordance to Eq. (4.191), and together with a limit of zero effective magnetic field $\langle \mathbf{B}^{\mathrm{eff}} \rangle_n \rightarrow 0$ which (by expanding Eq. (4.192)) leads to

$$\frac{1}{\mathcal{C}_n} \approx 1 \; + \; \frac{e}{\hbar c} \langle \mathbf{B}^{\mathrm{eff}} \rangle_n \cdot \boldsymbol{\mathcal{B}}_n \; + \; \Big(\frac{e}{\hbar c} \langle \mathbf{B}^{\mathrm{eff}} \rangle_n \cdot \boldsymbol{\mathcal{B}}_n \Big)^2 \tag{4.198}$$

[5]The asymmetric scattering of the electrons in the presence of spin-orbit coupling and Ferromagnetism which leads to unbalanced transverse motion.

in accordance to Eq. (4.192), we conclude that the transverse conductivity is given by

$$\sigma_{xy} \approx -\frac{e^2}{h}\frac{1}{2\pi}\iint\limits_{BZ}\left(1 + \frac{e}{\hbar c}\left\langle \mathbf{B}^{\text{eff}}\right\rangle_n \cdot \boldsymbol{\mathcal{B}}_n + \left(\frac{e}{\hbar c}\left\langle \mathbf{B}^{\text{eff}}\right\rangle_n \cdot \boldsymbol{\mathcal{B}}_n\right)^2\right)\mathcal{B}_z(t,\mathbf{k})\,dk_x dk_y. \tag{4.199}$$

The first term in the integrand gives a quantized value for topological reasons (first Chern number), while the other two terms gives corrections due to the non-zero effective magnetic field. We hope that this result may shed some light upon the controversy resulting from the difficulty to interpret experimental results in this area [145].

Chapter 5

Topological stabilization in dynamic transport processes

The topological characterization of equilibrium quantum systems[1] undergoing linear response or adiabatic evolutions as a result of perturbations, seems to have been studied in considerable depth and is nowadays in a mature state. These states are characterized either by their abelian geometric phases, or by the explicit calculation of expectation values within linear response methods. The topological equilibrium states of matter display many striking features, ranging from the precise quantization of macroscopic properties (such as the transverse Hall conductivity in the Quantum Hall Effect), to the emergence of fractional excitations and gapless edge states. A fundamental characteristic of an observable that is quantized due to topology, is that its value is immune against local perturbations such as local sample defects.

On the other hand, in systems that are out of equilibrium and occupy more than one dimensions of the available Hilbert space, that is, the quantum state is made of coherent superposition of different eigenstates, much less is known about the topological behavior. In the point of view of geometrical phases, these non-equilibrium topological quantum processes can be characterized by means of non-Abelian geometric phases [146, 82, 5].

As a general rule, the inductions of quantum phases by global perturbations are inherently nonequilibrium phenomena, and thus their understanding is quite challenging. Even some basic questions such as the physical signatures of the induced phases and how such phases can be stabilized in a steady state do not yet have satisfactory answers. In this framework, much theoretical [30, 143, 29, 140, 83, 136, 76, 27, 118, 156, 122, 105, 42, 55] and experimental [89, 115] work, has being carried out the last few years in the quest to find patterns of behaviors that emerge due to the combination of dynamics and the topology of the projective Hilbert space that is instantaneously occupied. In this theoretical quest, some new topological invariants have been proposed based on the time-evolution operator [76, 83, 31, 116], as well as some dynamical order parameters for topological phase tran-

[1] By equilibrium it is meant that the quantum states occupy one dimension of the available Hilbert space for all times.

sitions [65, 26, 68, 138, 53, 117, 64]. Most of the above mentioned theoretical studies, are performed either by using the orthonormal basis of the instantaneous eigenstates of the Hamiltonian within linear-response time-dependent perturbation theory, or within Floquet theory for time periodic systems by using the complete set of the periodic Floquet modes.

With this in mind, we derive in this Chapter a dynamical extension of the Hellmann-Feynman theorem for closed systems (the total number of the particles being conserved) by using a complete and orthonormal basis. Our motivation is to find the simplest possible theoretical method which gives a formula for an observable's expectation value that (i) incorporates the real time dynamics as well as (ii) takes into account the instantaneous topology of the Hilbert space. The theorem that we derive is valid for any complete orthonormal basis state set, therefore it can be applied either to the instantaneous eigenstates of the Hamiltonian or to the time periodic Floquet modes. We will witness the appearance of interesting generalizations of non-Abelian curvatures, of both magnetic and electric type, intertwined with the non-Hermitian effect discussed in the previous Chapters.

5.1 Derivation of the theorem

We consider a real vector parameter $\mathbf{R}$ that has an arbitrary time-dependence (without any adiabatic approximation involved), namely, $\mathbf{R} = \boldsymbol{\mathcal{R}}(t, \mathbf{R_o})$ where $\mathbf{R_o}$ is the initial value of the parameter satisfying $\mathbf{R_o} = \boldsymbol{\mathcal{R}}(0, \mathbf{R_o})$. Therefore, the parameter satisfies the general equation of motion $\mathbf{R} = \mathbf{R_o} + \int_0^t \frac{\partial \mathbf{R}}{\partial t'} dt'$, and its time derivative is given by $\frac{\partial \mathbf{R}}{\partial t} = \frac{\partial \boldsymbol{\mathcal{R}}(t, \mathbf{R_o})}{\partial t}$. The theorem that we are about to prove is for a continuous vector parameter $\mathbf{R}$, therefore the initial value of the parameter $\mathbf{R_o}$ is assumed to have continuous values. The Hamiltonian of the system $H(t, \mathbf{R})$, apart from the implicit time dependence (via the parameter), may also have an arbitrary explicit time-dependence. The derivation that is given owes its existence to the Hamiltonian being the generator of time evolution of quantum states. We provide the derivation for a single particle state while the generalization to a many-particle system is straightforward. Particle's motion is generally encoded in its normalized time-dependent state $|\Psi(t, \mathbf{R})\rangle$ which evolves either by the time-dependent Schrödinger equation for non-relativistic and spinless particle, or by the time-dependent Dirac equation for spinfull particle. Specifically, the wavefunction can in general be, either a scalar complex number $\Psi(\mathbf{r}, t, \mathbf{R})$ for spinless electron, or a complex vector, namely, a two component spinor $\Psi(\mathbf{r}, t, \mathbf{R}) = (\Psi_1(\mathbf{r}, t, \mathbf{R}),\ \Psi_2(\mathbf{r}, t, \mathbf{R}))^{\mathrm{T}}$ for the non-relativistic limit of Dirac's equation, or a relativistic four component spinor for a Dirac fermion $\Psi(\mathbf{r}, t, \mathbf{R}) = (\Psi_1(\mathbf{r}, t, \mathbf{R}),\ \Psi_2(\mathbf{r}, t, \mathbf{R}),\ \Psi_3(\mathbf{r}, t, \mathbf{R}),\ \Psi_4(\mathbf{r}, t, \mathbf{R}))^{\mathrm{T}}$.

We assume for simplicity a one particle quantum system. The motion of the particle is described by a general state, not necessarily an eigenstate of the Hamiltonian nor a localized state (such as a narrow wave packet). The system is assumed to be closed $\langle \Psi(t, \mathbf{R}) | \Psi(t, \mathbf{R}) \rangle = 1$, and the quantum state time evolution is determined by the time-

dependent equation

$$i\hbar\frac{d}{dt}\left|\Psi(t,\mathbf{R})\right\rangle = H(t,\mathbf{R})\left|\Psi(t,\mathbf{R})\right\rangle, \tag{5.1}$$

where the Hamiltonian is either of Schrödinger or Dirac type. The time derivative in Eq. (5.1) is the total time derivative given by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{\partial \mathbf{R}}{\partial t}\cdot\boldsymbol{\nabla}_{\mathbf{R}} \tag{5.2}$$

where $\boldsymbol{\nabla}_{\mathbf{R}} = \sum_{i=1}^{3} \mathbf{e}_i \frac{\partial}{\partial_{\mathbf{R}_i}}$. The initial value of the parameter $\mathbf{R_o}$ that implicitly enters Eq. (5.1) can be used to label the quantum states $|\Psi(t,\mathbf{R})\rangle$. The expectation value of the Hamiltonian

$$\langle\Psi(t,\mathbf{R})|\, H(t,\mathbf{R})\,|\Psi(t,\mathbf{R})\rangle = E(t,\mathbf{R}) \tag{5.3}$$

can be seen as the instantaneous time-dependent "energy" of the particle $E(t,\mathbf{R})$. Differentiation with respect to the parameter $\mathbf{R}$ of both sides of Eq. (5.3) gives

$$\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E - \langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,|\,H\Psi\rangle - \langle\Psi|\,H\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle\,. \tag{5.4}$$

Taking now into account that the parameter gradient operator $\boldsymbol{\nabla}_{\mathbf{R}}$ can generally be an anomalous operator, that is, the states $|\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle$ may not belong within the domain of the Hermitian Hamiltonian, which is expressed by the non-trivial inequality $\langle H\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle = \langle\Psi\,|\,H^{+}\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle \neq \langle\Psi\,|\,H\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle$, we recast Eq. (5.4) in the form

$$\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E - \langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,|\,H\Psi\rangle - \langle H\Psi|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\rangle + \left\langle\Psi\,\middle|\,\left(H^{+}-H\right)\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle. \tag{5.5}$$

By using Eq. (5.1) in Eq. (5.5) we find

$$\langle\Psi\,|\,\boldsymbol{\nabla}_{\mathbf{R}}H\,|\,\Psi\rangle = \boldsymbol{\nabla}_{\mathbf{R}}E + \left\langle\Psi\,\middle|\,\left(H^{+}-H\right)\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle - \left(\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,\middle|\,i\hbar\frac{d\Psi}{dt}\right\rangle + \left\langle i\hbar\frac{d\Psi}{dt}\middle|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle\right). \tag{5.6}$$

We then consider an orthonormal basis $\langle m(t,\mathbf{R})|n(t,\mathbf{R})\rangle = \delta_{mn}$, where the basis states $|n(t,\mathbf{R})\rangle$ need not be the instantaneous eigenstates of the Hamiltonian $H(t,\mathbf{R})$ of the system, rather they only depend explicitly on the same parameter $\mathbf{R}$, and we project the assumed time-dependent state $|\Psi(t,\mathbf{R})\rangle$ on this basis

$$|\Psi(t,\mathbf{R})\rangle = \sum_{n}^{\mathrm{HS}} C_n(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle\,, \tag{5.7}$$

where the sum runs over all Hilbert space (since the upper limit of the sum does not depend on time) and only the $N_{\mathrm{occ}}(t)$ occupied states (with $C_n(t,\mathbf{R}) \neq 0$) contribute to the sum,

namely

$$C_n(t,\mathbf{R})\begin{cases} \neq 0 & \text{for } n \leq N_{\text{occ}}(t), \\ = 0 & \text{for } n > N_{\text{occ}}(t). \end{cases} \tag{5.8}$$

By using Eq. (5.8) one can express the sum of Eq. (5.7) as

$$|\Psi(t,\mathbf{R})\rangle = \sum_{n}^{N_{\text{occ}}(t)} C_n(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle\,,$$

but this causes difficulties for taking the total time derivative of $|\Psi(t,\mathbf{R})\rangle$, since the upper limit of the sum is an integer number that depends on time. Therefore, we use Eq. (5.7) and after taking the total time derivatives we turn into Eq. (5.8).

We assume that one uses the same orthonormal basis set $|n(t,\mathbf{R})\rangle$ for all times, and that the number $N_{\text{occ}}(t)$ of basis states that are occupied is defined at first by the initial quantum state $|\Psi(t_o,\mathbf{R}_o)\rangle$ in combination with the orthonormal basis states, but, in subsequent times this number is governed by the dynamics of the system (generated by the Hamiltonian operator). Because the considered system is assumed closed

$$\frac{d}{dt}\langle\Psi(t,\mathbf{R})|\Psi(t,\mathbf{R})\rangle = 0, \tag{5.9}$$

the basis states $|n(t,\mathbf{R})\rangle$ that one may use, are constrained to belong within the domain of definition of the Hamiltonian $H(t,\mathbf{R})$ owing to

$$\frac{d}{dt}\langle\Psi|\Psi\rangle = \frac{i}{\hbar}\left(\langle H\Psi|\Psi\rangle - \langle\Psi|H\Psi\rangle\right) = \sum_{m}^{\text{HS}}\sum_{n}^{\text{HS}} C_m^* C_n \left\langle m\middle|\big(H^+ - H\big)n\right\rangle = 0, \tag{5.10}$$

which implies the constraint $\langle Hm|n\rangle = \langle m|Hn\rangle$. The superposition of $|\Psi(t,\mathbf{R})\rangle$ is considered in a general framework in order to (i) capture the dynamics that drives the system as encoded by the expansion coefficients $C_n(t,\mathbf{R})$, and to, (ii) take into account possible symmetries of the system (either over position coordinates or over time) which create degeneracies that are generally taken into account within the sum of Eq. (5.7); thus the indices n are assumed to run also within the degeneration subspace. In this respect, the indices n of Eq. (5.7) are taken into account in the most general sense and can label all above mentioned combinations. For example, when one considers a periodic in time Hamiltonian $H(t+T,\mathbf{R}(t+T)) = H(t,\mathbf{R}(t))$, where the time of T is the period of driving, and also a parameter that has the same time periodicity $\mathbf{R}(t+T) = \mathbf{R}(t)$, one can use as an orthonormal basis the complete set of the Floquet modes $I = \sum_{a}^{\text{HS}} |\Phi_a(t,\mathbf{R})\rangle\langle\Phi_a(t,\mathbf{R})|$ which are periodic in time $|\Phi_a(t+T,\mathbf{R})\rangle = |\Phi_a(t,\mathbf{R})\rangle$. The Floquet modes satisfies the eigenvalue equation $H_F(t,\mathbf{R})\,|\Phi_a(t,\mathbf{R})\rangle = \varepsilon_a(\mathbf{R})\,|\Phi_a(t,\mathbf{R})\rangle$, where $\varepsilon_a(\mathbf{R})$ is the quasienergy (restricted into the interval $\Delta\varepsilon_a = \dfrac{2\pi\hbar}{T}$ called first Floquet-zone, that contains all the physically non-equivalent quantum states) and $H_F(t,\mathbf{R})$ is the Floquet operator defined by

$H_F(t,\mathbf{R}) = H(t,\mathbf{R}) - i\hbar\frac{d}{dt}$. In this framework, on can take advantage of the discrete time symmetry of the Hamiltonian, and the quantum state Eq. (5.7) can be expanded in the Floquet modes $|\Psi(t,\mathbf{R})\rangle = \sum_a^{\text{HS}} C_a(t,\mathbf{R})\,|\Phi_a(t,\mathbf{R})\rangle$. A single Floquet mode $|\Psi(t,\mathbf{R})\rangle \equiv C_a(t,\mathbf{R})\,|\Phi_a(t,\mathbf{R})\rangle$, when inserted in Eq. (5.1) gives the time-dependent state of the system which is given by $|\Psi_a(t,\mathbf{R})\rangle = e^{-\frac{i}{h}\int_0^t \varepsilon_a(\mathbf{R})dt'}|\Phi_a(t,\mathbf{R})\rangle$. On the other hand, the use as an orthonormal basis of the instantaneous eigenstates of the Hamiltonian $H(t,\mathbf{R})$ allows one to keep track of the real time occupation of the Hilbert space as produced by the interaction of the system with the (externally) applied potentials, which is captured by the expansion coefficients $C_n(t,\mathbf{R})$ dynamics, as well as to take into account the space symmetries of the Hamiltonian and the topology of the instantaneous eigenstates. For example, if we consider a state $|\Psi(t,\mathbf{R})\rangle$ that is for all times the ground state of a degenerate system, that is, for every index n in the expansion of Eq. (5.7) the instantaneous eigenvalue equation $H(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle = E_g(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle$ is satisfied (with $E_g(t,\mathbf{R})$ being the ground state energy of the system) we have

$$\begin{aligned} i\hbar\frac{d}{dt}|\Psi(t,\mathbf{R})\rangle &= H(t,\mathbf{R})\,|\Psi_g(t,\mathbf{R})\rangle = H(t,\mathbf{R})\sum_{n\in S} C_n(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle \\ &= E_g(t,\mathbf{R})\,|\Psi_g(t,\mathbf{R})\rangle\,, \end{aligned} \tag{5.11}$$

where the index n labels each different orthonormal eigenstate within the degeneration subspace denoted by S, and then the method that we will develop can give valuable information on the observable in quest, with respect to the embedded degenerate Hilbert subspace of the system and the topology of the degenerate eigenstates.

Substituting now Eq. (5.7) into Eq. (5.1) and exploiting the orthonormality of the basis states $\langle m(t,\mathbf{R})|n(t,\mathbf{R})\rangle = \delta_{mn}$ we find the equation of motion for each coefficient that is given by

$$i\hbar\frac{dC_n}{dt} = \sum_l^{\text{HS}} C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right), \tag{5.12}$$

where the sum runs over all Hilbert space. By using Eq. (5.8), the above equation of motion of the expansion coefficients is equally expressed as

$$i\hbar\frac{dC_n}{dt} = \sum_l^{\text{occ}} C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right). \tag{5.13}$$

where the sum runs now only within occupied states.

The purpose now is to use the equation of motion of the expansion coefficients Eq. (5.12) (that incorporates the dynamics) together with Eqs. (5.7) – (5.8), in order to express each term of Eq. (5.6) as a function of the expansion coefficients and the assumed orthonormal basis states. At the end of the calculation, this will result into the dynamical and extended Hellmann-Feynman theorem projected on an orthonormal basis.

In this framework, we start our calculation with the gradient of the "energy" $\boldsymbol{\nabla}_{\boldsymbol{R}} E$ of the first term on the right side of Eq. (5.6) which takes the form

$$\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{R}} E &= \boldsymbol{\nabla}_{\boldsymbol{R}} \left(\sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C_m^* C_n \langle m|Hn\rangle \right) \\
&= \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} \boldsymbol{\nabla}_{\boldsymbol{R}} \left(C_m^* C_n \right) \langle m|Hn\rangle + \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C_m^* C_n \, \boldsymbol{\nabla}_{\boldsymbol{R}} \langle m|Hn\rangle \\
&\equiv \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} \boldsymbol{\nabla}_{\boldsymbol{R}} \left(C_m^* C_n \right) \langle m|Hn\rangle + \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \, \boldsymbol{\nabla}_{\boldsymbol{R}} \langle m|Hn\rangle \, . \qquad (5.14)
\end{aligned}$$

Analogously, the second non-Hermitian term on the right side of Eq. (5.6) is transformed into

$$\begin{aligned}
\left\langle \Psi \left| \left(H^+ - H \right) \boldsymbol{\nabla}_{\mathbf{R}} \Psi \right\rangle \right. &= \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C_m^* C_n \left\langle m \right| \left(H^+ - H \right) \boldsymbol{\nabla}_{\boldsymbol{R}} n \right\rangle \\
&= \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \left\langle m \right| \left(H^+ - H \right) \boldsymbol{\nabla}_{\boldsymbol{R}} n \right\rangle . \qquad (5.15)
\end{aligned}$$

where we have made use of $C_m^* \, \boldsymbol{\nabla}_{\boldsymbol{R}} C_n \left\langle m \right| \left(H^+ - H \right) n \rangle = 0$.

We proceed now into the calculation of the third and fourth terms right side of Eq. (5.6). By taking into account the superposition expansion Eq. (5.7), the total time derivative of $|\Psi(t, \mathbf{R})\rangle$ is given from

$$\left| \frac{d\Psi}{dt} \right\rangle = \sum_{n}^{\text{HS}} \left(\frac{dC_n}{dt} |n\rangle + C_n \left| \frac{dn}{dt} \right\rangle \right) . \qquad (5.16)$$

By then using the equation of motion $\dfrac{dC_n}{dt}$ of the expansion coefficients Eq. (5.12) the above equation takes the form

$$\left| i\hbar \frac{d\Psi}{dt} \right\rangle = \sum_{n}^{\text{HS}} \sum_{l}^{\text{HS}} C_l \left(\langle n|Hl\rangle - i\hbar \left\langle n \right| \frac{dl}{dt} \right\rangle \right) |n\rangle + \sum_{n=1}^{N} i\hbar C_n \left| \frac{dn}{dt} \right\rangle , \qquad (5.17)$$

which by using Eq. (5.8) is expressed as

$$\left| i\hbar \frac{d\Psi}{dt} \right\rangle = \sum_{n}^{\text{occ}} \sum_{l}^{\text{occ}} C_l \left(\langle n|Hl\rangle - i\hbar \left\langle n \right| \frac{dl}{dt} \right\rangle \right) |n\rangle + \sum_{n=1}^{N} i\hbar C_n \left| \frac{dn}{dt} \right\rangle , \qquad (5.18)$$

Similarly, the action of the parameter gradient operator on $|\Psi(t, \mathbf{R})\rangle$, when one takes into account the superposition expansion Eq. (5.7), gives

$$|\boldsymbol{\nabla}_{\boldsymbol{R}} \Psi\rangle = \sum_{n}^{\text{occ}} \left(\left(\boldsymbol{\nabla}_{\boldsymbol{R}} C_n \right) |n\rangle + C_n \left| \boldsymbol{\nabla}_{\boldsymbol{R}} n \right\rangle \right) . \qquad (5.19)$$

Accordingly, the dagger form of Eq. (5.17) and Eq. (5.19) are given by

$$\left\langle i\hbar\frac{d\Psi}{dt}\right| = \sum_{m}^{\text{occ}}\sum_{l}^{\text{occ}} C_l^*\left(\langle l|Hm\rangle - i\hbar\left\langle l|\frac{dm}{dt}\right\rangle\right)\langle m| - \sum_{m}^{\text{occ}} i\hbar C_m^*\left\langle\frac{dm}{dt}\right|, \tag{5.20}$$

where we have use $\left\langle\frac{dl}{dt}|m\right\rangle = -\left\langle l|\frac{dm}{dt}\right\rangle$, and

$$\langle\boldsymbol{\nabla}_{\boldsymbol{R}}\Psi| = \sum_{m}^{\text{occ}}\left(\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)\langle m| + C_m^*\langle\boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\right) \tag{5.21}$$

Taking now the inner product of Eq. (5.21) with Eq. (5.17) we find

$$\begin{aligned}\left\langle\boldsymbol{\nabla}_{\mathbf{R}}\Psi\,|\,i\hbar\frac{d\Psi}{dt}\right\rangle \;=\; & \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right)\delta_{mn}\\ & + \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}} C_m^*C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right)\langle\boldsymbol{\nabla}_{\mathbf{R}}m|n\rangle\\ & + \sum_{m}^{\text{HS}}\sum_{n}^{\text{HS}} i\hbar\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_n\left\langle m|\frac{dn}{dt}\right\rangle\\ & + \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} i\hbar C_m^*C_n\left\langle\boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{dn}{dt}\right\rangle.\end{aligned} \tag{5.22}$$

The first term on the right side of the above equation is simplified to

$$\begin{aligned}&\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right)\delta_{mn}\\ &\qquad = \sum_{m}^{\text{occ}}\sum_{l}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_l\left(\langle m|Hl\rangle - i\hbar\left\langle m|\frac{dl}{dt}\right\rangle\right),\end{aligned}$$

which by interchanging the dummy variables l and n is recast in the form

$$\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_n\left(\langle m|Hn\rangle - i\hbar\left\langle m|\frac{dn}{dt}\right\rangle\right).$$

Taking into account the above expression as well as by using $\langle\boldsymbol{\nabla}_{\mathbf{R}}m|n\rangle = -\langle m|\boldsymbol{\nabla}_{\mathbf{R}}n\rangle$ in

the second term on the right side of Eq. (5.22), we find

$$\begin{aligned}\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Psi \,|\, i\hbar\frac{d\Psi}{dt}\right\rangle &= \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_n\,\langle m|Hn\rangle \\ &\quad -\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}C_m^*C_l\left(\langle n|Hl\rangle - i\hbar\left\langle n|\frac{dl}{dt}\right\rangle\right)\langle m|\boldsymbol{\nabla}_{\mathbf{R}}n\rangle \\ &\quad +\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}i\hbar\,C_m^*C_n\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\,m|\frac{dn}{dt}\right\rangle. \end{aligned} \tag{5.23}$$

By interchanging the dummy variables l and n in the second term on the right side of Eq. (5.23), the $\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Psi \,|\, i\hbar\frac{d\Psi}{dt}\right\rangle$ term is finally rearranged into

$$\begin{aligned}\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Psi \,|\, i\hbar\frac{d\Psi}{dt}\right\rangle &= \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_m^*\right)C_n\,\langle m|Hn\rangle \\ &\quad -\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}C_m^*C_n\,\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\,\langle l|Hn\rangle \\ &\quad +\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}i\hbar\,C_m^*C_n\,\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\left\langle l\,|\frac{dn}{dt}\right\rangle \\ &\quad +\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}i\hbar\,C_m^*C_n\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\,m|\frac{dn}{dt}\right\rangle. \end{aligned} \tag{5.24}$$

Similarly, by using Eqs. (5.20) – (5.21) and performing analogous calculations, or equivalently by taking the complex conjugate of Eq. (5.23) and then interchanging the dummy variables n with m, we evaluate the $\left\langle i\hbar\frac{d\Psi}{dt}|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle$ term which is found to be

$$\begin{aligned}\left\langle i\hbar\frac{d\Psi}{dt}\,|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle &= \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^*\left(\boldsymbol{\nabla}_{\boldsymbol{R}}C_n\right)\langle m|Hn\rangle \\ &\quad +\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}C_m^*C_n\,\langle m|Hl\rangle\,\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle \\ &\quad -\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\sum_{l}^{\text{occ}}i\hbar\,C_m^*C_n\left\langle m|\frac{dl}{dt}\right\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle \\ &\quad -\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}i\hbar\,C_m^*C_n\left\langle \frac{dm}{dt}|\boldsymbol{\nabla}_{\boldsymbol{R}}\,n\right\rangle. \end{aligned} \tag{5.25}$$

By adding then Eq. (5.24) with Eq. (5.25) we get

$$\begin{aligned}\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Psi \,|\, i\hbar\frac{d\Psi}{dt}\right\rangle \;+\; \left\langle i\hbar\frac{d\Psi}{dt}|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle &= \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\boldsymbol{\nabla}_{\boldsymbol{R}}\big(C_m^* C_n\big)\,\langle m|Hn\rangle \\ &-\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^*C_n\left(\sum_{l}^{\text{occ}}\left(\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\,\langle l|Hn\rangle - \langle m|Hl\rangle\,\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle\right)\right) \\ &+i\hbar\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^*C_n\left(\sum_{l}^{\text{occ}}\left(\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\left\langle\, l\,|\frac{dn}{dt}\right\rangle - \left\langle m|\frac{dl}{dt}\right\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle\right)\right) \\ &+i\hbar\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^*C_n\left(\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\,m|\frac{dn}{dt}\right\rangle - \left\langle\frac{dm}{dt}|\boldsymbol{\nabla}_{\boldsymbol{R}}\,n\right\rangle\right). \end{aligned} \tag{5.26}$$

We will now take into account the action of the total time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \frac{\partial\mathbf{R}}{\partial t}\cdot\boldsymbol{\nabla}_{\mathbf{R}}$$

on the basis states $|\,n\,\rangle$, as well as use the vector identity

$$\frac{\partial\mathbf{R}}{\partial t}\times(\mathbf{A}\times\mathbf{B}) = \mathbf{A}\left(\frac{\partial\mathbf{R}}{\partial t}\cdot\mathbf{B}\right) - \left(\frac{\partial\mathbf{R}}{\partial t}\cdot\mathbf{A}\right)\mathbf{B}.$$

In this respect, the term

$$\left(\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\left\langle\, l\,|\frac{dn}{dt}\right\rangle - \left\langle m|\frac{dl}{dt}\right\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle\right)$$

within the sum of Eq. (5.26) takes the form

$$\begin{aligned}\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\left\langle\, l\,|\frac{dn}{dt}\right\rangle - \left\langle m|\frac{dl}{dt}\right\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle \;&=\; \frac{\partial\mathbf{R}}{\partial t}\times\left(\,\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\times\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle\,\right) \\ &+\langle m|\boldsymbol{\nabla}_{\mathbf{R}}l\,\rangle\left\langle\, l\,|\frac{\partial n}{\partial t}\right\rangle - \left\langle m|\frac{\partial l}{\partial t}\right\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}}n\rangle\,. \end{aligned} \tag{5.27}$$

By then defining the non-Abelian Berry connection

$$\mathbf{A}_{mn}(t,\mathbf{R}) = i\,\langle m|\boldsymbol{\nabla}_{\mathbf{R}}n\,\rangle\,, \tag{5.28}$$

as well as the the non-Abelian Berry potential

$$\Phi_{mn}(t,\mathbf{R}) = i\left\langle m|\frac{\partial n}{\partial t}\right\rangle, \tag{5.29}$$

Eq. (5.27) is recast in the form

$$\langle m|\boldsymbol{\nabla}_{\mathbf{R}} l\,\rangle\Big\langle\, l\,|\frac{dn}{dt}\Big\rangle-\Big\langle m|\frac{dl}{dt}\Big\rangle\langle\, l\,|\,\boldsymbol{\nabla}_{\mathbf{R}} n\rangle = -\,\frac{\partial\mathbf{R}}{\partial t}\times(\,\mathbf{A}_{ml}\times\mathbf{A}_{ln}\,)-(\,\mathbf{A}_{ml}\,\Phi_{ln}-\Phi_{ml}\,\mathbf{A}_{ln}\,)\,.$$

In an analogous manner, the term $\left(\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{dn}{dt}\right\rangle-\left\langle\frac{dm}{dt}|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\right\rangle\right)$ that enters the sum in Eq. (5.26) takes the form

$$\begin{aligned}\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{dn}{dt}\right\rangle-\left\langle\frac{dm}{dt}|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\right\rangle \;&=\; \frac{\partial\mathbf{R}}{\partial t}\times\langle\boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\times|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle\\ &\quad+\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{\partial n}{\partial t}\right\rangle-\left\langle\frac{\partial m}{\partial t}|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\right\rangle,\end{aligned}$$

which by defining the Berry curvatures

$$\boldsymbol{\mathcal{B}}_{mn}(t,\mathbf{R}) = i\,\langle\boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\times|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \tag{5.30}$$

and

$$\boldsymbol{\mathcal{E}}_{mn}(t,\mathbf{R}) = i\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{\partial n}{\partial t}\right\rangle-i\left\langle\frac{\partial m}{\partial t}|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\right\rangle, \tag{5.31}$$

is recast in the form

$$\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, m|\frac{dn}{dt}\right\rangle-\left\langle\frac{dm}{dt}|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\right\rangle = -i\,\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{B}}_{mn}\;-i\,\boldsymbol{\mathcal{E}}_{mn}. \tag{5.32}$$

Finally, by introducing the matrix elements of the Hamiltonian

$$E_{mn}(t,\mathbf{R}) = \langle m|Hn\rangle \tag{5.33}$$

we recast Eq. (5.26) in the form

$$\begin{aligned}\left\langle \boldsymbol{\nabla}_{\mathbf{R}}\Psi\,|\,i\hbar\frac{d\Psi}{dt}\right\rangle\;+\;\left\langle i\hbar\frac{d\Psi}{dt}|\,\boldsymbol{\nabla}_{\mathbf{R}}\Psi\right\rangle\;&=\;\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}\boldsymbol{\nabla}_{\boldsymbol{R}}\big(C_m^{*}C_n\big)\,E_{mn}\\ &\quad+i\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^{*}C_n\sum_{l}^{\text{occ}}\left(\mathbf{A}_{ml}\,E_{ln}-E_{ml}\,\mathbf{A}_{ln}\right)\\ &\quad-i\hbar\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^{*}C_n\sum_{l}^{\text{occ}}\left(\frac{\partial\mathbf{R}}{\partial t}\times(\,\mathbf{A}_{ml}\times\mathbf{A}_{ln}\,)\;+\;(\,\mathbf{A}_{ml}\,\Phi_{ln}-\Phi_{ml}\,\mathbf{A}_{ln}\,)\right)\\ &\quad\hbar\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}}C_m^{*}C_n\left(\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{B}}_{mn}\;+\;\boldsymbol{\mathcal{E}}_{mn}\right)\end{aligned} \tag{5.34}$$

Substituting then Eq. (5.34) and Eqs. (5.14) – (5.15) into Eq. (5.6) we find

$$\begin{aligned}\langle \boldsymbol{O}(t,\mathbf{R})\rangle \;=\; & \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n\, \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} \;+\; \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n\, \boldsymbol{\mathcal{S}}_{mn} \\ & - i \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \sum_{l}^{\text{occ}} \left(\mathbf{A}_{ml}\, E_{ln} - E_{ml}\, \mathbf{A}_{ln} \right) \\ & - \hbar \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \left(\boldsymbol{\mathcal{E}}_{mn} - i \sum_{l}^{\text{occ}} \left(\mathbf{A}_{ml}\, \Phi_{ln} - \Phi_{ml}\, \mathbf{A}_{ln} \right) \right) \\ & - \hbar \frac{\partial \mathbf{R}}{\partial t} \times \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \left(\boldsymbol{\mathcal{B}}_{mn} - i \sum_{l}^{\text{occ}} \mathbf{A}_{ml} \times \mathbf{A}_{ln} \right)\end{aligned}$$

where

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle = \langle \Psi(t,\mathbf{R}) \,|\, \boldsymbol{\nabla}_{\mathbf{R}} H(t,\mathbf{R}) \,|\, \Psi(t,\mathbf{R})\rangle \tag{5.35}$$

is the observable in quest, that can be related to a "generalized force" given by

$$\begin{aligned}\langle \boldsymbol{F}(t,\mathbf{R})\rangle \;&=\; -\langle \Psi(t,\mathbf{R}) \,|\, \boldsymbol{\nabla}_{\mathbf{R}} H(t,\mathbf{R}) \,|\, \Psi(t,\mathbf{R})\rangle \\ &=\; -\langle \boldsymbol{O}(t,\mathbf{R})\rangle\,. \end{aligned} \tag{5.36}$$

Eq. (5.35) is our generalized extended dynamical HF theorem.

The non-Hermitian term $\boldsymbol{\mathcal{S}}_{mn}(t,\mathbf{R})$, by working in position representation and assuming real scalar and vector potentials, is always transformed to a boundary integral (due to symmetry of the integrands) over the system's boundaries and is given (assuming a 3D system) by

$$\begin{aligned}\boldsymbol{\mathcal{S}}_{mn}(t,\mathbf{R}) \;&=\; \left\langle m(t,\mathbf{R}) \,\middle|\, \left(H(t,\mathbf{R})^{+} - H(t,\mathbf{R}) \right) \boldsymbol{\nabla}_{\mathbf{R}} n(t,\mathbf{R}) \right\rangle \\ &= \frac{i\hbar}{2} \oiint_{S} \mathbf{n} \cdot \left(\left(\mathbf{v}\, \Phi_m^{+} + \Phi_m^{+}\, \mathbf{v} \right) \boldsymbol{\nabla}_{\mathbf{R}} \Phi_n \right) dS, \end{aligned} \tag{5.37}$$

where $\mathbf{v} = \dfrac{i}{\hbar}\,[H(t,\mathbf{R}), \mathbf{r}]$ is the standard velocity operator, $\mathbf{n}$ is the unit vector that is locally normal to the surface that encloses the system and $\Phi_m \equiv \Phi_m(t,\mathbf{R}) = \langle\, \mathbf{r} \,|\, m(t,\mathbf{R}) \,\rangle$.

The form of the dynamical extended HF theorem Eq. (5.35) is the first major result of this theoretical analysis. It is applicable to dynamic quantum processes of closed systems, and it is based on the dynamics as encoded in the expansion coefficients equation of motion, as well as in the topology of the projective Hilbert space that is spanned by the basis states that are occupied; this way one can extract patterns of behaviors that come up owing to the dynamics and the topology.

Due to the emerging gauge structure of the observable's $\langle \boldsymbol{O}(t,\mathbf{R})\rangle$ expectation value formula Eq. (5.35), we are surprisingly led to define three different non-Abelian Berry curvatures, quantities that are explicitly involved into the dynamical extension of the HF

theorem that we have derived.

Namely, we define the non-Abelian curvature

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} = \boldsymbol{\mathcal{B}}_{mn} - i \sum_{l}^{\text{occ}} \mathbf{A}_{ml} \times \mathbf{A}_{ln}, \tag{5.38}$$

that involves the Berry "magnetic field" $\boldsymbol{\mathcal{B}}_{mn}$, a second one that involves the Berry "electric field" $\boldsymbol{\mathcal{E}}_{mn}$ and is given from

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} = \boldsymbol{\mathcal{E}}_{mn} - i \sum_{l}^{\text{occ}} \left(\mathbf{A}_{ml}\, \Phi_{ln} - \Phi_{ml}\, \mathbf{A}_{ln} \right), \tag{5.39}$$

with connections $\mathbf{A}_{mn}$ and Φ_{ml} given by Eq. (5.28) and Eq. (5.29), and the last one that involves the Hamiltonian's matrix elements and is given by

$$\boldsymbol{\mathcal{F}}^{(E)}_{mn} = i \sum_{l}^{\text{occ}} \left(\mathbf{A}_{ml}\, E_{ln} - E_{ml}\, \mathbf{A}_{ln} \right). \tag{5.40}$$

In this fashion, the dynamical and extended HF theorem is compactly recast in the form

$$\begin{aligned} \langle \boldsymbol{O}(t, \mathbf{R}) \rangle \;\; = \;\; & \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^{*}_{m} C_{n}\, \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} \; + \; \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{S}}_{mn} \\ & - \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{F}}^{(E)}_{mn} \; - \; \hbar \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} \\ & - \hbar \frac{\partial \mathbf{R}}{\partial t} \times \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}. \end{aligned} \tag{5.41}$$

The non-Abelian Berry curvatures $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ are emerging quantities with inherited non-Abelian gauge structure. These curvatures come up irrespectively of the energy scale of the quantum system, that is, they are independent of the character of the local probability amplitude field $\Psi(\mathbf{r}, t, \mathbf{R})$. They appear, either when the wavefunction is a scalar complex number (thus describing a spinless low energy quantum motion) or for a complex spinor wavefunction that describes a relativistic high energy spinfull motion. It is remarkable that the form of the non-Abelian curvatures that results from our derivation has similar structure to the ones of the field strength tensors of Yang-Mills theory [152]. The origin of these non-Abelian curvatures that we have found is attributed to the occupation of the available Hilbert space[2]. Specifically, whenever the quantum state under consideration $|\Psi(t, \mathbf{R})\rangle$ spans more than one dimension of the available Hilbert space, that is, the state is at any instant made

[2]Whenever the basis states $|\, n \,\rangle$ do not have explicit time-dependence, the non-Abelian curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ becomes zero by definition.

up by a coherent superposition of orthonormal basis states, the non-Abelian structure of the observable in quest comes up. On the other hand, whenever the assumed quantum state is at all times aligned in only one direction of the available Hilbert space (therefore the state is parallel to a single basis state), the non-Abelian Berry curvatures are truncated into Abelian quantities and the observable in quest $\langle \boldsymbol{O}(t,\mathbf{R})\rangle$ looses its internal non-Abelian gauge structure. A quantum process described by a coherent superposition may appear for example: (i) due to an adiabatic time evolution of a degenerate ground state, or (ii) due to a quantum quench that sets the system into a non-equilibrium state (after the quench) where the expansion coefficients evolve in time adiabatically, uncoupled to each other, with no optical transitions taking place, or finally, (iii) due to time-dependent driving where certain coupling between the expansion coefficients is expected. In addition, the observable in quest has an inherited non-Hermitian boundary contribution $\boldsymbol{\mathcal{S}}_{mn}$ that do not depend on the dynamics, rather they depend only on the spatial boundary conditions of the wavefunctions.

The observables $\langle \boldsymbol{O}(t,\mathbf{R})\rangle$ that are given by Eq. (5.41) always have a part that is transverse to the direction of the parameter variation $\partial\mathbf{R}$ which is given by

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_{tran} = -\hbar\,\frac{\partial\mathbf{R}}{\partial t}\times\sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}, \tag{5.42}$$

as easily confirmed by $\langle \boldsymbol{O}(t,\mathbf{R})\rangle_{tran}\cdot\partial\mathbf{R}=0$ (where we have used the vector identity $\partial\mathbf{R}\times\mathbf{A}\cdot\partial\mathbf{R}=\mathbf{A}\cdot\partial\mathbf{R}\times\partial\mathbf{R}=0$), while the first four terms on the right side of Eq. (5.41) may have longitudinal as well transverse part.

Due to the structure of the observable Eq. (5.41) one intuitively expects that, in virtue of this dynamical extended HF theorem, in dynamic quantum processes where only the diagonal non-Abelian curvatures survive, that is the only nonzero curvatures are

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn} = \boldsymbol{\mathcal{B}}_{nn} - i\sum_{l}^{\text{occ}}\mathbf{A}_{nl}\times\mathbf{A}_{ln}$$

and

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{nn} = \boldsymbol{\mathcal{E}}_{nn} - i\sum_{l}^{\text{occ}}\left(\,\mathbf{A}_{nl}\,\Phi_{ln} - \Phi_{nl}\,\mathbf{A}_{ln}\,\right),$$

which are real and gauge invariant quantities by definition, then the standard topology (1st Chern class) of the systems (that is defined by the fluxes of the Abelian curvatures $\boldsymbol{\mathcal{B}}_{nn}$ and $\boldsymbol{\mathcal{E}}_{nn}$) must be extended in order to include the fluxes of the extra terms in the above equations. These circumstances are analyzed further in Sec.5.2.

5.1.1 Emerging many-band covariant derivatives

Due to the structure of the non-Abelian Berry curvatures $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$, these can be transformed and equally expressed by the occupied-band covariant derivatives that we define below. Specifically, we define the (parameter) gradient occupied-band covariant derivative

as

$$\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} = \left(1 - \sum_{l}^{\text{occ}} |\, l \,\rangle \langle\, l \,|\right) \boldsymbol{\nabla}_{\boldsymbol{R}}, \tag{5.43}$$

and the time occupied-band covariant derivative as

$$\widetilde{\frac{\partial}{\partial t}} = \left(1 - \sum_{l}^{\text{occ}} |\, l \,\rangle \langle\, l \,|\right) \frac{\partial}{\partial t} \tag{5.44}$$

respectively. When each one of the above abstract occupied-band covariant derivatives acts on a state $|n\rangle$ gives

$$\left|\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} n\right\rangle = |\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle - \sum_{l}^{\text{occ}} \langle\, l \,|\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle \,|\, l \,\rangle \tag{5.45}$$

and

$$\left|\widetilde{\frac{\partial n}{\partial t}}\right\rangle = \left|\frac{\partial n}{\partial t}\right\rangle - \sum_{l}^{\text{occ}} \left\langle\, l \,|\frac{\partial n}{\partial t}\right\rangle |\, l \,\rangle \tag{5.46}$$

respectively.

By now using Eq. (5.45) as well as Eq. (5.28) and Eq. (5.30), and by exploiting the orthogonality of the basis states $\langle m|n\rangle = \delta_{mn}$, a straightforward calculation shows that the non-Abelian Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ of Eq. (5.38) is equally expressed as

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} = i \left\langle \widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} m| \times |\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} n \right\rangle. \tag{5.47}$$

Similarly, by using Eqs. (5.45) – (5.46) as well as Eq. (5.29) and Eq. (5.31), and the orthogonality of the basis states, straightforward calculation shows that the non-Abelian Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ of Eq. (5.39) is equally given by

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} = i \left\langle \widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} m|\widetilde{\frac{\partial n}{\partial t}} \right\rangle - i \left\langle \widetilde{\frac{\partial m}{\partial t}}|\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} n \right\rangle. \tag{5.48}$$

These two covariant derivatives are useful for two reasons.

First, by using them one can easily show the gauge invariance in the time-parameter space $t \times \mathbf{R}$ with respect to a large global gauge transformation that transforms each one of the basis states $|n\rangle \to e^{i\Lambda(t,\mathbf{R})}\,|n\rangle$, where $\Lambda(t,\mathbf{R})$ is real scalar function. Under this global gauge transformation, Eqs. (5.45) – (5.46) transforms (covariantly) like $\left|\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} n\right\rangle \to e^{i\Lambda(t,\mathbf{R})} \left|\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} n\right\rangle$ and $\left|\widetilde{\frac{\partial n}{\partial t}}\right\rangle \to e^{i\Lambda(t,\mathbf{R})} \left|\widetilde{\frac{\partial n}{\partial t}}\right\rangle$ respectively, which shows that the non-Abelian Berry curvatures $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ evaluated by Eqs. (5.47) – (5.48) are gauge-invariant with respect to this kind of global time-parameter gauge transformations, therefore they can carry a topological charge.

Second, whenever all the dimensions of the available Hilbert space are occupied due to the dynamics, that is, all expansion coefficients evolve in time coupled to each other,

we replace $\sum_{l}^{\text{occ}} \rightarrow \sum_{l}^{\text{HS}}$, which leads to $\widetilde{\boldsymbol{\nabla}_{\boldsymbol{R}}} = 0$ and $\widetilde{\frac{\partial}{\partial t}} = 0$, that gives $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} = 0$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} = 0$.

5.1.2 One basis state formula

In the adiabatic and non-degenerate limit, and whenever the time-dependent state $|\Psi(t,\mathbf{R})\rangle$ is aligned to a single basis state at all times

$$|\Psi(t,\mathbf{R})\rangle \equiv C_\nu(t,\mathbf{R})\,|\nu(t,\mathbf{R})\rangle\,, \tag{5.49}$$

therefore the occupied Hilbert space behaves as an effective one-dimension space, then, each sum in Eq. (5.41) is truncated into a single index ν term $\sum_{i}^{\text{occ}} \rightarrow \delta_{i\nu}$ without any summation taking place. In this one basis-state limit the non-Abelian curvatures truncates to

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} \rightarrow \boldsymbol{\mathcal{B}}_{\nu\nu} \qquad \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} \rightarrow \boldsymbol{\mathcal{E}}_{\nu\nu} \qquad \boldsymbol{\mathcal{F}}^{(E)}_{mn} \rightarrow 0, \tag{5.50}$$

as evidenced from Eqs. (5.38) – (5.40), and each one curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{\nu\nu} \equiv \boldsymbol{\mathcal{B}}_{\nu\nu}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{\nu\nu} = \boldsymbol{\mathcal{E}}_{\nu\nu}$ is evaluated with respect to the state $|\nu(t,\mathbf{R})\rangle$ in virtue of Eqs. (5.30) – (5.31). By taking into account the normalization condition, that is, replacing $|C_\nu(t,\mathbf{R})|^2 = 1$ within Eq. (5.41), one finds the observable's expectation value in this one-basis state approximation, which is evaluated as an Abelian quantity by

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle = \boldsymbol{\nabla}_{\boldsymbol{R}} E_{\nu\nu} + \boldsymbol{\mathcal{S}}_{\nu\nu} - \hbar\,\boldsymbol{\mathcal{E}}_{\nu\nu} - \hbar\,\frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{B}}_{\nu\nu}. \tag{5.51}$$

5.1.3 Matrix formulation

By combining Eq. (5.7) and Eq. (5.35) which gives

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle = \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C^*_m C_n\, \langle m|\, \boldsymbol{\nabla}_{\boldsymbol{R}} H(t,\mathbf{R})\,|n\rangle\,, \tag{5.52}$$

and then taking into account Eq. (5.41), each component

$$\boldsymbol{\mathcal{O}}(t,\mathbf{R})_{mn} = \langle m(t,\mathbf{R})\,|\,\boldsymbol{\nabla}_{\mathbf{R}} H(t,\mathbf{R})\,|\,m(t,\mathbf{R})\rangle$$

of the observable in quest is given by

$$\boldsymbol{\mathcal{O}}(t,\mathbf{R})_{mn} = \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} + \boldsymbol{\mathcal{S}}_{mn} - \boldsymbol{\mathcal{F}}^{(E)}_{mn} - \hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} - \hbar\,\frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}. \tag{5.53}$$

By using the Eq. (5.53) terms as matrix elements, we construct a vector-valued matrix equation (with the entries being vectors) for the observable in quest given by

$$\boldsymbol{\mathcal{O}}(t,\mathbf{R}) = \boldsymbol{\nabla}_{\boldsymbol{R}} E + \boldsymbol{\mathcal{S}} - \boldsymbol{\mathcal{F}}^{(E)} - \hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})} - \hbar\,\frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}. \tag{5.54}$$

In this equation, E is a scalar-valued matrix constructed from the elements E_{mn}, while all other bold and calligraphic letters, $\boldsymbol{\mathcal{S}}$, $\boldsymbol{\mathcal{F}}^{(E)}$, $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}$ as well as $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}$, denote the respective matrices (which do not generally commute with each other, thus, they satisfy non-Abelian algebra). In this fashion, the observables' expectation value $\langle \boldsymbol{O}(t,\mathbf{R})\rangle$ is given by the matrix product

$$\begin{aligned}
\langle \boldsymbol{O}(t,\mathbf{R})\rangle &= \mathcal{C}(t,\mathbf{R})^{\dagger}\,\boldsymbol{\mathcal{O}}(t,\mathbf{R})\,\mathcal{C}(t,\mathbf{R}) \\
&= \mathcal{C}(t,\mathbf{R})^{\dagger}\left(\boldsymbol{\nabla}_{\boldsymbol{R}} E + \boldsymbol{\mathcal{S}} - \boldsymbol{\mathcal{F}}^{(E)} - \hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})} - \hbar\,\frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)\mathcal{C}(t,\mathbf{R})
\end{aligned} \tag{5.55}$$

where

$$\mathcal{C}(t,\mathbf{R}) = \begin{pmatrix} C_1(t,\mathbf{R}) \\ C_2(t,\mathbf{R}) \\ C_3(t,\mathbf{R}) \\ \vdots \\ C_N(t,\mathbf{R}) \end{pmatrix} \tag{5.56}$$

is the column vector of the expansion coefficients. By using Eqs. (5.38) – (5.40) and Eqs. (5.28) – (5.31), as well as $\langle \boldsymbol{\nabla}_{\mathbf{R}} n|m\rangle = -\langle n|\boldsymbol{\nabla}_{\mathbf{R}} m\rangle$ and $\left\langle \frac{\partial n}{\partial t}|m \right\rangle = -\left\langle n|\frac{\partial m}{\partial t}\right\rangle$, by straightforward calculation one can show the following relations

$$\begin{aligned}
(E_{mn})^{*} &= E_{nm} \\
\left(\boldsymbol{\mathcal{F}}^{(E)}_{mn}\right)^{*} &= \boldsymbol{\mathcal{F}}^{(E)}_{nm} \\
\left(\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}\right)^{*} &= \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{nm} \\
\left(\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}\right)^{*} &= \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nm},
\end{aligned} \tag{5.57}$$

giving therefore that the respective matrices

$$\begin{aligned}
E^{\dagger} &= E \\
\left(\boldsymbol{\mathcal{F}}^{(E)}\right)^{\dagger} &= \boldsymbol{\mathcal{F}}^{(E)} \\
\left(\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}\right)^{\dagger} &= \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})} \\
\left(\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)^{\dagger} &= \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}
\end{aligned} \tag{5.58}$$

are Hermitian. On the other hand, taking into account the domain of definition of the Hamiltonian $\langle n\,|\,(H^+ - H)\,m\rangle = 0,$ by deriving both of its members with respect to the parameter $\boldsymbol{\nabla_R}$, we find

$$\left\langle \boldsymbol{\nabla_R} n\,|\,\left(H^+ - H\right) m\right\rangle + \langle (\boldsymbol{\nabla_R} H)\,n\,|m\rangle - \langle n\,|\,(\boldsymbol{\nabla_R} H)\,m\rangle + \left\langle n\,|\,\left(H^+ - H\right)\boldsymbol{\nabla_R} m\right\rangle = 0.$$

The first term of the left side of this equation is expressed as

$$\begin{aligned}\left\langle \boldsymbol{\nabla_R} n\,|\,\left(H^+ - H\right) m\right\rangle &= -\left\langle \left(H^+ - H\right)\boldsymbol{\nabla_R} n\,|m\right\rangle \\ &= -\left\langle m\,|\,\left(H^+ - H\right)\boldsymbol{\nabla_R} n\right\rangle^*\end{aligned}$$

By then using the definition $\boldsymbol{\mathcal{S}}_{mn} = \langle m\,|\,(H^+ - H)\,\boldsymbol{\nabla_R} n\rangle$ we find the relation

$$-(\boldsymbol{\mathcal{S}}_{mn})^* + \langle (\boldsymbol{\nabla_R} H)\,n\,|m\rangle - \langle n\,|\,(\boldsymbol{\nabla_R} H)\,m\rangle + \boldsymbol{\mathcal{S}}_{nm} = 0$$

which results into

$$(\boldsymbol{\mathcal{S}}_{mn})^* = \boldsymbol{\mathcal{S}}_{nm} + \langle (\boldsymbol{\nabla_R} H)\,n\,|m\rangle - \langle n\,|\,(\boldsymbol{\nabla_R} H)\,m\rangle\,, \tag{5.59}$$

that implies that the matrix $\boldsymbol{\mathcal{S}}$ is Hermitian whenever the operator $\boldsymbol{\nabla_R} H(t, \mathbf{R})$ belongs within the domain of definition of the Hamiltonian. Having in mind that each matrix can always be separated into a Hermitian and an anti-Hermitian part, then Eq. (5.59) provides the anti-Hermitian part of the matrix $\boldsymbol{\mathcal{S}}$ which cancels the corresponding anti-Hermitian part of the observable's matrix $\boldsymbol{\mathcal{O}}$. We remind that the matrix $\boldsymbol{\mathcal{S}}$ is not zero only whenever the parameter gradient operator $\boldsymbol{\nabla_R}$ gives states that do not belong within the domain of definition of the Hamiltonian.

5.1.4 Unitary transformations

The time evolution of the expansion coefficients given from

$$\begin{aligned}i\hbar\frac{dC_n}{dt} &= \sum_l^{\text{occ}} \left\langle n\right| \left(H(t,\mathbf{R}) - i\hbar\frac{d}{dt}\right) l \left.\right\rangle C_l \\ &= \sum_l^{\text{occ}} \langle n|\; H_F(t,\mathbf{R})\, l\,\rangle\, C_l,\end{aligned} \tag{5.60}$$

where

$$H_F(t,\mathbf{R}) = H(t,\mathbf{R}) - i\hbar\frac{d}{dt}, \tag{5.61}$$

can equally be expressed as a matrix equation given by

$$i\hbar\frac{d\mathcal{C}(t,\mathbf{R})}{dt} = \mathcal{H}_F(t,\mathbf{R})\,\mathcal{C}(t,\mathbf{R}), \tag{5.62}$$

where $\mathcal{C}(t,\mathbf{R})$ is the column vector given from Eq. (5.56) and $\mathcal{H}_F(t,\mathbf{R})$ is the Hermitian matrix given by

$$\mathcal{H}_F(t,\mathbf{R}) = \begin{pmatrix} \langle 1\,|H_F\,1\,\rangle & \langle 1\,|H_F\,2\,\rangle & \dots & \langle 1\,|H_F\,N\,\rangle \\ \langle 2\,|H_F\,1\,\rangle & \langle 2\,|H_F\,2\,\rangle & \dots & \langle 2\,|H_F\,N\,\rangle \\ \vdots & \vdots & \dots & \vdots \\ \langle N\,|H_F\,1\,\rangle & \langle N\,|H_F\,2\,\rangle & \dots & \langle N\,|H_F\,N\,\rangle \end{pmatrix}. \tag{5.63}$$

The above Hermitian matrix $\mathcal{H}_F(t,\mathbf{R})$ captures the real time coupling between the expansion coefficients due to the dynamics that are encoded by the potentials within the Hamiltonian operator $H(t,\mathbf{R})$ and the orthonormal basis states $|\,n\,\rangle$ that are being used. Whenever the time-dependent quantum state $|\Psi(t,\mathbf{R})\rangle$ is in a superposition and it occupies more than one dimension of the available Hilbert space, then, we can assume a unitary transformation of the expansion coefficients given by

$$\mathcal{C}(t,\mathbf{R}) = \mathcal{U}(t,\mathbf{R})\,\mathcal{C}'(t,\mathbf{R}). \tag{5.64}$$

The unitary matrix $\mathcal{U}(t,\mathbf{R})$ is an $N\times N$ matrix (where N is the instantaneous number of the dimensions of the Hilbert space that are occupied) satisfying

$$\mathcal{U}(t,\mathbf{R})^{\dagger}\,\mathcal{U}(t,\mathbf{R}) = \mathcal{U}(t,\mathbf{R})^{-1}\,\mathcal{U}(t,\mathbf{R}) = I$$

while $\mathcal{C}'(t,\mathbf{R})$ is the new column vector. In other words, Eq. (5.64) denotes a linear transformation of the expansion coefficients given by

$$C_m(t,\mathbf{R}) = \sum_{l}^{occ} U_{ml}(t,\mathbf{R})\,C'_l(t,\mathbf{R}). \tag{5.65}$$

Owing to Eq. (5.64), the expansion coefficients satisfy

$$\mathcal{C}(t,\mathbf{R})^{\dagger}\,\mathcal{C}(t,\mathbf{R}) = \mathcal{C}'(t,\mathbf{R})^{\dagger}\,\mathcal{C}'(t,\mathbf{R}),$$

which means that this kind of unitary transformation preserves the normalization

$$\langle\Psi(t,\mathbf{R})|\Psi(t,\mathbf{R})\rangle = \sum_{m}^{occ}|C_m(t,\mathbf{R})|^2 = \sum_{n}^{occ}|C'_n(t,\mathbf{R})|^2 = 1 \tag{5.66}$$

without affecting the basis states $|\,n\,\rangle$. Therefore, the action of any complex unitary matrix $\mathcal{U}(t,\mathbf{R})$ conserves the norm of the state-vector $|\Psi(t,\mathbf{R})\rangle$, which implies that they generate rotations in the Hilbert space over a unit sphere, resulting into the formation of a (generally non-Abelian) $U(N)$ group with elements the complex unitary matrices. The complex unitary matrix transformation Eq. (5.64) together with Eq. (5.62), implies that the equation of

motion of the new expansion coefficients is given by

$$i\hbar\frac{d\mathcal{C}'(t,\mathbf{R})}{dt}=\left(\mathcal{U}(t,\mathbf{R})^{-1}\mathcal{H}_F(t,\mathbf{R})\mathcal{U}(t,\mathbf{R})-i\hbar\mathcal{U}(t,\mathbf{R})^{-1}\frac{d\mathcal{U}(t,\mathbf{R})}{dt}\right)\mathcal{C}'(t,\mathbf{R}). \quad (5.67)$$

The (complex) unitary matrix transformation Eq. (5.64) together with Eq. (5.67), indicates that this kind of unitary transformation changes the coupling between the expansion coefficients without increasing the total number of dimensions of the Hilbert space that are occupied. For example, assume an initial basis state set where the matrix $\mathcal{H}_F(t,\mathbf{R})$ is diagonal and the expansion coefficients $\mathcal{C}(t,\mathbf{R})$ evolve uncoupled to each other, then, a unitary transformation with a constant matrix $\mathcal{U}$ results to new expansion coefficients $\mathcal{C}'(t,\mathbf{R})$ that will evolve by the matrix $\mathcal{U}^{-1}\mathcal{H}_F(t,\mathbf{R})\mathcal{U}$ which is not anymore diagonal, but, the total number of occupied dimensions is the same.

By now using the gauge freedom of the expansion coefficients column vectors $\mathcal{C}(t,\mathbf{R})$, we perform a unitary transformation and substitute Eq. (5.64) into Eq. (5.55) which gives

$$\langle\boldsymbol{O}\rangle=\mathcal{C}'^{\dagger}\ \mathcal{U}^{-1}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}E+\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{F}}^{(E)}-\hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)\mathcal{U}\ \mathcal{C}'$$

The above equation, together with the gauge freedom of choosing any appropriate unitary matrix $\mathcal{U}(t,\mathbf{R})$, has far reaching consequences. Specifically, having in mind that the matrix in the following parenthesis

$$\left(\boldsymbol{\nabla}_{\boldsymbol{R}}E+\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{F}}^{(E)}-\hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)$$

is a Hermitian matrix, then, by means of a unitary similarity transformation, one can always choose such a unitary matrix $\mathcal{U}(t,\mathbf{R})$ that transforms the quantity

$$\mathcal{U}(t,\mathbf{R})^{-1}\left(\boldsymbol{\nabla}_{\boldsymbol{R}}E+\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{F}}^{(E)}-\hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)\mathcal{U}(t,\mathbf{R})$$

into a diagonal matrix

$$\begin{aligned}\mathcal{U}(t,\mathbf{R})^{-1}&\left(\boldsymbol{\nabla}_{\boldsymbol{R}}E+\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{F}}^{(E)}-\hbar\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)\mathcal{U}(t,\mathbf{R})\\&=\left(\boldsymbol{\nabla}_{\boldsymbol{R}}\widetilde{E}+\widetilde{\boldsymbol{\mathcal{S}}}-\widetilde{\boldsymbol{\mathcal{F}}}^{(E)}-\hbar\,\widetilde{\boldsymbol{\mathcal{F}}}^{(\boldsymbol{\mathcal{E}})}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\widetilde{\boldsymbol{\mathcal{F}}}^{(\boldsymbol{\mathcal{B}})}\right)_{diagonal}\end{aligned} \quad (5.68)$$

In this framework, by choosing a convenient unitary matrix $\mathcal{U}(t,\mathbf{R})$, the expectation value of the observable $\langle\boldsymbol{O}(t,\mathbf{R})\rangle$ given by Eq. (5.41), can equally be calculated by a unitary similar diagonal form given from

$$\langle\boldsymbol{O}(t,\mathbf{R})\rangle=\sum_{n}^{\text{occ}}|C'_n|^2\left(\boldsymbol{\nabla}_{\boldsymbol{R}}\widetilde{E}_{nn}+\widetilde{\boldsymbol{\mathcal{S}}}_{nn}-\widetilde{\boldsymbol{\mathcal{F}}}^{(E)}_{nn}-\hbar\widetilde{\boldsymbol{\mathcal{F}}}^{(\boldsymbol{\mathcal{E}})}_{nn}-\hbar\frac{\partial\mathbf{R}}{\partial t}\times\widetilde{\boldsymbol{\mathcal{F}}}^{(\boldsymbol{\mathcal{B}})}_{nn}\right). \quad (5.69)$$

It is now wort pointing out the origin of the above mentioned unitary transformations. These are attributed to local gauge transformations of the wavefunctions

$$\Psi(\mathbf{r},t,\mathbf{R}) = e^{i\Lambda(\mathbf{r},t,\mathbf{R})}\Phi(\mathbf{r},t,\mathbf{R}) \tag{5.70}$$

where $\Psi(\mathbf{r},t,\mathbf{R}) = \sum_{m}^{occ} C_m(t,\mathbf{R})\,\psi_m(\mathbf{r},t,\mathbf{R})$ and $\Phi(\mathbf{r},t,\mathbf{R}) = \sum_{l}^{occ} C'_l(t,\mathbf{R})\,\psi_l(\mathbf{r},t,\mathbf{R})$. The wavefunctions $\psi_n(\mathbf{r},t,\mathbf{R})$ are the orthonormal basis state wavefunctions, which are assumed to be the same before and after the gauge transformation, whereas $C_n(t,\mathbf{R})$ and $C'_l(t,\mathbf{R})$ are the respective expansion coefficients. $\Lambda(\mathbf{r},t,\mathbf{R})$ is a real scalar function for scalar wavefunctions and a Hermitian matrix for spinor wavefunctions. The gauge transformation Eq. (5.70) gives

$$\sum_{m}^{occ} C_m(t,\mathbf{R})\,\psi_m(\mathbf{r},t,\mathbf{R}) = \sum_{l}^{occ} C'_l(t,\mathbf{R})\,e^{i\Lambda(\mathbf{r},t,\mathbf{R})}\psi_l(\mathbf{r},t,\mathbf{R}), \tag{5.71}$$

which by exploiting the orthogonality of the basis states results to

$$C_m(t,\mathbf{R}) = \sum_{l}^{occ} \left\langle \psi_m \left| e^{i\Lambda(\mathbf{r},t,\mathbf{R})} \right| \psi_l \right\rangle C'_l(t,\mathbf{R}), \tag{5.72}$$

that has the same structure as Eq. (5.65). We note that, for spinless electrons, if one assumes a gauge function $\Lambda(t,\mathbf{R})$ that does not depend on the position coordinates, then, $C_m(t,\mathbf{R}) = \sum_{l}^{occ} e^{i\Lambda(t,\mathbf{R})} \langle \psi_m \,|\, \psi_l \rangle\, C'_l(t,\mathbf{R}) = e^{i\Lambda(t,\mathbf{R})} C'_m(t,\mathbf{R})$, indicating that the gauge function must have coordinates dependence, in order to give a linear transformation that changes the expansion coefficients column vectors by a unitary matrix $\mathcal{U}(t,\mathbf{R})$ that is not diagonal.

5.1.5 Maxwell type of equation

By taking the curl of both sides of Eq. (5.54) and using the vector identity $\boldsymbol{\nabla}\times(\mathbf{A}\times\mathbf{B}) = \mathbf{A}\,(\boldsymbol{\nabla}\cdot\mathbf{B}) - \mathbf{B}\,(\boldsymbol{\nabla}\cdot\mathbf{A}) + (\mathbf{B}\cdot\boldsymbol{\nabla})\,\mathbf{A} - (\mathbf{A}\cdot\boldsymbol{\nabla})\,\mathbf{B}$ we find

$$\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})} = \mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})} + \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\mathbf{v}_{\mathbf{R}} - \mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})} - \frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{R}}\times\left(\boldsymbol{\mathcal{O}} - \boldsymbol{\mathcal{S}} - \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}\right)$$

where

$$\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})} = (\mathbf{v}_{\mathbf{R}}\cdot\boldsymbol{\nabla}_{\mathbf{R}})\,\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})} - \left(\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\cdot\boldsymbol{\nabla}_{\mathbf{R}}\right)\mathbf{v}_{\mathbf{R}} \tag{5.73}$$

is the Lie derivative of the curvature matrix $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}(t,\mathbf{R})$ with respect to the vector field $\mathbf{v}_{\mathbf{R}}(t,\mathbf{R})$. Eq. (5.73) is a general Maxwell type of equation in $t\times\mathbf{R}$ space without any conservation law being involved.

In the modern magnetohydrodynamics theories, one can formulate geometrical objects (i.e. vectors or tensors) that are Lie dragged and advected with the flow. In this framework,

by working (compactly) with the vector-valued matrix Eq. (5.54) (rather than working with each one equation of the matrix vector elements Eq. (5.53)), if one assumes that the flux

$$\iint_{S(t)} \boldsymbol{\mathcal{F}}(t,\mathbf{R})^{(\boldsymbol{\mathcal{B}})}\cdot d^2\mathbf{S}$$

is advected with the flow, one can derive a local Maxwell type of equation where the topological charges are conserved. By using the 2D analogue of the convection theorem for arbitrary surface $S(t)$ that is moving with the flow with velocity $\mathbf{v}_{\mathbf{R}}=\dfrac{d\mathbf{R}}{dt}$, then, the curvature matrix $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}(t,\mathbf{R})$ flux is Lie dragged with the flow when

$$\frac{d}{dt}\iint\limits_{S(t)}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\cdot d\mathbf{S}=\iint\limits_{S(t)}\left(\frac{\partial\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}}{\partial t}-\boldsymbol{\nabla}_{\mathbf{R}}\times\left(\mathbf{v}_{\mathbf{R}}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)+\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)\cdot d\mathbf{S}=0. \tag{5.74}$$

Because the surface $S(t)$ is arbitrary, the curvature matrix $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}(t,\mathbf{R})$ satisfies the local equation

$$\frac{\partial\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}}{\partial t}-\boldsymbol{\nabla}_{\mathbf{R}}\times\left(\mathbf{v}_{\mathbf{R}}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)+\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}=0, \tag{5.75}$$

which guarantees the Lie dragging. By using the Lie derivative $\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}$, the local Eq. (5.75) is expressed as

$$\frac{\partial\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}}{\partial t}+\mathcal{L}_{\mathbf{v}}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}+\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\mathbf{v}_{\mathbf{R}}=0. \tag{5.76}$$

Substituting Eq. (5.76) into Eq. (5.73) we find a (vector-valued matrix) Maxwell type of equation

$$\boldsymbol{\nabla}_{\mathbf{R}}\times\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}=-\boldsymbol{J}_{\mathbf{R}}-\frac{\partial\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}}{\partial t} \tag{5.77}$$

where

$$\boldsymbol{J}_{\mathbf{R}}=\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}+\frac{1}{\hbar}\boldsymbol{\nabla}_{\mathbf{R}}\times\left(\boldsymbol{\mathcal{O}}-\boldsymbol{\mathcal{S}}-\boldsymbol{\mathcal{F}}^{\boldsymbol{E}}\right) \tag{5.78}$$

is the vector-valued matrix of the current that is entering into the Maxwell equation. Taking the divergence of both sides of Eq. (5.75) (which guarantees the Lie drag) we find

$$\frac{\partial}{\partial t}\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}+\boldsymbol{\nabla}_{\mathbf{R}}\cdot\left(\mathbf{v}_{\mathbf{R}}\,\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}\right)=0, \tag{5.79}$$

which with the aid of Eq. (5.78) is transformed into a continuity equation

$$\frac{\partial\rho_M}{\partial t}+\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{J}_{\mathbf{R}}=0 \tag{5.80}$$

where ρ_M is defined by

$$\rho_M=\boldsymbol{\nabla}_{\mathbf{R}}\cdot\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})} \tag{5.81}$$

and is the scalar matrix of the topological monopole charge density. Note that, whenever all the dimensions of the available Hilbert space are occupied due to the dynamics, then each one entry of the matrix $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}=0$ is separately zero, which results to $\rho_M=0$, implying that

no topological monopole charges can be found. Hence, if no constraints in Hilbert space occupancies, the nontrivial topology is lost.

5.2 Topological Invariants

5.2.1 Single dimension of the available Hilbert space occupied: Chern class

When only one dimension of the available Hilbert space is occupied, the non-Abelian Berry curvature is simplified into the diagonal Abelian Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}(t,\mathbf{R}) \to \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})$ which is a real quantity $\boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})^* = \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})$. The flux of $\boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})$ over a closed manifold is a topological invariant

$$\frac{1}{2\pi}\oiint_S \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})\cdot d\mathbf{S} = C_1^{(n)} \quad \in \mathbb{Z} \tag{5.82}$$

called the first Chern number. This topological invariant is due to an obstruction to single-valuedness (integrability) of the wavefunction, with respect to the parameter coordinates $\mathbf{R}$, which is more easily shown within the Dirac string method.

Dirac string method

We use the vector identity $\boldsymbol{\nabla}_{\boldsymbol{R}} \times (f\boldsymbol{V}) = \boldsymbol{\nabla}_{\boldsymbol{R}} f \times \boldsymbol{V} + f\,\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{V}$ into the integrand of Eq. (5.82) which gives

$$\begin{aligned} \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R}) &= i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, n| \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\ &= i\,\boldsymbol{\nabla}_{\boldsymbol{R}} \times \langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \;-\; i\,\langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle\,, \end{aligned} \tag{5.83}$$

where the last term $i\,\langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle$ is a singular term that is not zero due to a Dirac string formation. If the assumed wavefunction $\Psi_n = \langle\, \mathbf{r}|\, n\rangle$ is everywhere single-valued (integrable) over the manifold, then, for any closed tangent line on the manifold it must satisfy $\oint_C \boldsymbol{\nabla}_{\boldsymbol{R}}\Psi_n \cdot d\mathbf{R} = 0$, which by using the Stokes theorem implies the local relation $\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\Psi_n = \langle\, \mathbf{r}|\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle = 0$, that is precisely the integrability condition. Therefore, by assuming that the wavefunction is integrable all over the manifold $\langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle = 0$, and by employing Eq. (5.83) in Eq. (5.82) we find

$$\frac{1}{2\pi}\oiint_S \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})\cdot d\mathbf{S} = \frac{i}{2\pi}\oiint_S \boldsymbol{\nabla}_{\boldsymbol{R}} \times \langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \cdot d\mathbf{S} = 0$$

for a closed manifold. Thus a zero Chern number indicates that there does not exist a Dirac string in parameter space.

Assuming a scalar wavefunction $\Psi_n = |\Psi_n| e^{iS_n}$, where $|\Psi_n|$ is its modulus and S_n its

phase, we define as Dirac string (or dislocation line), in parameter space, the segment of a line where the phase S_n is undetermined (with respect to parameter coordinates) and non-integrable $\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} S_n \neq 0$, but the modulus of the wavefunction $|\Psi_n|$ is not zero. By assuming that the modulus of the wavefunction is integrable quantity $\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} |\Psi_n| = 0$ (in order that the wavefunction to be normalized $\iiint_V |\Psi_n|^2 d^3r = 1$), this kind of Dirac string in parameter space exists on the lines where $\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} \Psi_n = i\,|\Psi_n| e^{iS_n}\, \boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} S_n \neq 0$. Because the phase factor e^{iS_n} is single-valued, the phase satisfies $\oint_C \boldsymbol{\nabla}_{\boldsymbol{R}} S_n \cdot d\mathbf{R} = \iint_S \boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} S_n \cdot d\mathbf{S} = 2\pi n$ where n is an integer. Then, for a single Dirac string penetrating once the manifold we may define

$$\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} S_n = 2\pi n\, \boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}})$$

where $\boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}})$ is the $2D$ vector Dirac delta function with direction parallel to the dislocation line. Then, the singular contribution of the Berry curvature is given by

$$\begin{aligned} -i\,\langle\, n|\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \;&\equiv\; -i^2 \iiint_V |\Psi_n|^2\, \boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} S_n\, d^3r \\ &=\; 2\pi n\, \boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}}) \iiint_V |\Psi_n|^2\, d^3r \\ &=\; 2\pi n\, \boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}}). \end{aligned} \tag{5.84}$$

By using Eq. (5.83) and Eq. (5.84) we find

$$-\,n\,\boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}}) = \frac{1}{2\pi}\Big(\,\boldsymbol{\nabla}_{\boldsymbol{R}} \times \mathbf{A}_{nn}(t, \mathbf{R}) \;-\; \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R})\Big)\,, \tag{5.85}$$

which is precisely the integrand that is used for the calculation of the Z_2 invariant [51, 52] that probes the obstruction to single-valuedness over the half Brillouin zone in the quantum spin Hall effect.

Therefore, within this kind of Dirac string formulation one finds

$$\frac{1}{2\pi} \oiint_S \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \cdot d\mathbf{S} = \frac{2\pi n}{2\pi} \oiint_S \boldsymbol{\delta}^2(\mathbf{R} - \mathbf{R}_{\mathbf{string}}) \cdot d\mathbf{S} = n$$

where n is an integer. The integer n is a topological invariant (called topological charge), which is a gauge invariant property with respect to any global gauge transformation in parameter space $|\,n\,\rangle \rightarrow e^{i\Lambda(\mathbf{R})}\,|\,n\,\rangle$, even if the assumed gauge function $\Lambda(\mathbf{R})$ is a function that has singularities $\boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}} \Lambda(\mathbf{R}) \neq 0$. This global topological invariant property, is guaranteed due to the definition of the diagonal Berry curvature Eq. (5.83), which guarantees local gauge invariance in $t \times \mathbf{R}$ space. Namely, by assuming the local (in $t \times \mathbf{R}$ space) gauge transformation $|\,n\,\rangle \rightarrow e^{i\Lambda(\mathbf{R})}\,|\,n\,\rangle$ in $\boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) = i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, n| \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle$, after a straightforward calculation one finds $\boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \rightarrow \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R})$.

Fiber bundle method

If one assumes that the basis states $|\, n \,\rangle$ are everywhere single-valued in $t \times \mathbf{R}$ space and neglects the singular term in Eq. (5.83), the diagonal Berry curvature in use is given by

$$\boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \equiv i\, \boldsymbol{\nabla}_{\boldsymbol{R}} \times \langle\, n | \boldsymbol{\nabla}_{\boldsymbol{R}}\, n \rangle = i\, \boldsymbol{\nabla}_{\boldsymbol{R}} \times \mathbf{A}_{nn}, \tag{5.86}$$

which is a gauge-dependent quantity with respect to a singular gauge transformation. As is evident from Eq. (5.86), in topologically non-trivial systems satisfying $\frac{1}{2\pi} \oiint_S \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \cdot d\mathbf{S} \neq 0$, the diagonal Berry connection $\mathbf{A}_{nn}$ must have singularities, namely, there is at least one point on the closed manifold where the Berry connection is undefined. It is a fact that, for topologically non-trivial systems, the Berry connection calculated with respect to a basis state $|\, n \,\rangle$ cannot be regular function of $\mathbf{R}$ all over the manifold without at least one singularity. In fiber bundle theory, one avoids the singularity problem by employing more than one Berry connections. In this fashion, one separates the closed manifold into two regions (patches), the north (N) one having a regular Berry connection $\mathbf{A}_N(t, \mathbf{R}) = i\, \langle\, n | \boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, n \rangle$ and the south one (S) that also has a regular Berry connection $\mathbf{A}_S(t, \mathbf{R}) = i\, \langle\, \widetilde{n} | \boldsymbol{\nabla}_{\boldsymbol{R}} \times \boldsymbol{\nabla}_{\boldsymbol{R}}\, \widetilde{n} \rangle$ evaluated with respect to a gauge transformed basis state $|\, \widetilde{n} \,\rangle = e^{i\Lambda(\mathbf{R})}\, |\, n \,\rangle$. In the overlapping region, this two connections are related by a singular gauge transformation given by $\mathbf{A}_S(t, \mathbf{R}) = \mathbf{A}_N(t, \mathbf{R}) - \boldsymbol{\nabla}_{\mathbf{R}} \Lambda(\mathbf{R})$, where $\Lambda(\mathbf{R})$ is called transition function and accounts for the singular gauge transformation. In this respect, by separating the closed manifold into two open manifolds, the north (N) part and the respective south part (S), the flux of the diagonal Berry curvature over the closed manifold is given by

$$\begin{aligned}
\frac{1}{2\pi} \oiint_S \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \cdot d\mathbf{S} &= \frac{1}{2\pi} \oiint_{S_N} \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \cdot d\mathbf{S} + \frac{1}{2\pi} \oiint_{S_S} \boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) \cdot d\mathbf{S} \\
&= \frac{1}{2\pi} \oint_C \left(\mathbf{A}_N(t, \mathbf{R}) - \mathbf{A}_S(t, \mathbf{R}) \right) \cdot d\mathbf{R} \\
&= \frac{1}{2\pi} \oint_C \boldsymbol{\nabla}_{\mathbf{R}} \Lambda(\mathbf{R}) \cdot d\mathbf{R} = n
\end{aligned} \tag{5.87}$$

where n is an integer.

Elementary consideration

It is interesting to note the connection of the diagonal Berry curvature $\boldsymbol{\mathcal{B}}_{nn}(t, \mathbf{R}) = i\, \langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, n | \times | \boldsymbol{\nabla}_{\boldsymbol{R}}\, n \rangle$ with respect to obstructions to analyticity in an elementary manner. We assume that the basis states $|\, n \,\rangle$ are the (instantaneous) eigenstates of the (Hermitian) Hamiltonian $H(t, \mathbf{R})$, therefore they satisfy the eigenvalue equation $H(t, \mathbf{R})\, |\, n \,\rangle = E_n\, |\, n \,\rangle$ for each value of the parameter $\mathbf{R}$. The latter equation implies that the quantum states $|\, n \,\rangle$ are functions of the energy E_n while the energy E_n can be a function of the parameter $\mathbf{R}$. Therefore, a one to one map can exist that, for each value of the parameter $\mathbf{R}$

one can define one analytic function of the energy $E_n(\mathbf{R})$ as well as one quantum state $|\, n \,\rangle$, which is symbolically indicated by the map $\mathbf{R} \mapsto E_n(\mathbf{R}) \mapsto |\, n \,\rangle$. In this respect, the action of the parameter gradient operator $\boldsymbol{\nabla}_{\boldsymbol{R}}$ on the quantum state can be evaluated by the chain rule

$$|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\,\rangle = \boldsymbol{\nabla}_{\boldsymbol{R}} E_n(\mathbf{R}) \left| \frac{\partial\, n}{\partial E_n} \right\rangle,$$

that gives

$$\begin{aligned} \boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R}) &= i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\, n| \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\ &= i \left\langle \frac{\partial\, n}{\partial E_n} \,|\, \frac{\partial\, n}{\partial E_n} \right\rangle \boldsymbol{\nabla}_{\boldsymbol{R}} E_n(\mathbf{R})^* \times \boldsymbol{\nabla}_{\boldsymbol{R}} E_n(\mathbf{R}), \end{aligned} \tag{5.88}$$

indicating that the Berry curvature curvature $\boldsymbol{\mathcal{B}}_{nn}(t,\mathbf{R})$ is always zero whenever the analyticity is not broken. The analytic behavior is broken at those values of the parameter $\mathbf{R}$, where the real energy $E_n(\mathbf{R})$ becomes a singular function of the parameter due to degeneracy which makes it locally a multiply-valued quantity, thus the derivative $\boldsymbol{\nabla}_{\boldsymbol{R}} E_n(\mathbf{R})$ cannot be defined. Similarly, at the degeneracy points the Hamiltonian's eigenfunction $\Psi_n(t,\mathbf{r},\mathbf{R})$ is not analytic function of the energy E_n and the derivative $\dfrac{\partial \Psi_n(t,\mathbf{r},\mathbf{R})}{\partial En}$ cannot be defined either.

5.2.2 Multiple dimensions of the available Hilbert space occupied: Chern class and Stiefel-Whitney class

Whenever more than one dimensions of the Hilbert space are occupied and the system is in a superposition of orthonormal basis states, one has to evaluate the flux of the diagonal non-Abelian Berry curvature

$$\frac{1}{2\pi} \oiint_S \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}(t,\mathbf{R}) \cdot d\mathbf{S}, \tag{5.89}$$

where $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}$ is a purely real quantity as seen by Eq. (5.57). The non-Abelian Berry curvature is given according to Eq. (5.38) from

$$\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn} = \boldsymbol{\mathcal{B}}_{nn} - i \sum_{l}^{\text{occ}} \mathbf{A}_{nl} \times \mathbf{A}_{ln},$$

where each term is separately a real quantity

$$\boldsymbol{\mathcal{B}}^*_{nn} = \boldsymbol{\mathcal{B}}_{nn} \quad \text{and} \quad (i\,\mathbf{A}_{nl} \times \mathbf{A}_{ln})^* = (i\,\mathbf{A}_{nl} \times \mathbf{A}_{ln})$$

where we have made use of $\mathbf{A}_{ln} = \mathbf{A}^{*}_{nl}$. Taking into account that $\mathbf{A}_{nn} \times \mathbf{A}_{nn} = 0$, as well as that $\mathbf{A}_{ln} = \mathbf{A}^{*}_{nl}$, we express Eq. (5.89) in the form

$$\frac{1}{2\pi} \oiint_{s} \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn} \cdot d\mathbf{S} = \frac{1}{2\pi} \oiint_{S} \boldsymbol{\mathcal{B}}_{nn} \cdot d\mathbf{S} \; + \; \frac{1}{2\pi} \sum_{l \neq n}^{\text{occ}} \oiint_{S} i \left(\mathbf{A}^{*}_{nl} \times \mathbf{A}_{nl} \right) \cdot d\mathbf{S}. \tag{5.90}$$

The first term on the right side of Eq. (5.90) is the first Chern number, while the value of the second term is for the moment unknown. When only the diagonal non-Abelian Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}$ is taken into account, each one cross product $\mathbf{A}_{nl} \times \mathbf{A}_{ln}$ that enters into the above sum is a gauge invariant quantity (with respect to gauge transformations of the form $|\, n \,\rangle \rightarrow e^{i\Lambda(\mathbf{R})} \,|\, n \,\rangle$, which results to $\mathbf{A}_{nl} \times \mathbf{A}_{ln} \rightarrow \mathbf{A}_{nl} \times \mathbf{A}_{ln}$). On the other hand, when one takes into account the off-diagonal Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$, then, it is the sum of all cross products which is the quantity that is gauge invariant $\sum_{l}^{\text{occ}} i \left(\mathbf{A}_{ml} \times \mathbf{A}_{ln} \right) \rightarrow \sum_{l}^{\text{occ}} i \left(\mathbf{A}_{ml} \times \mathbf{A}_{ln} \right)$. The latter considerations suggest that, each cross product $i \left(\mathbf{A}_{nl} \times \mathbf{A}_{ln} \right)$ that enters in the diagonal non-Abelian Berry curvature $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}$ can be linked separately to the topology of a given manifold.

Elementary consideration

By using similar arguments as in the Abelian consideration Eq. (5.88), namely, employing the definition of the non-Abelian Berry connection $\mathbf{A}_{nl}(t, \mathbf{R}) = i \, \langle n | \boldsymbol{\nabla}_{\mathbf{R}} l \, \rangle$ as well as taking into account the eigenvalue equation $H(t, \mathbf{R}) \,|\, l \,\rangle = E_l \,|\, l \,\rangle$ we find

$$i \left(\mathbf{A}^{*}_{nl} \times \mathbf{A}_{nl} \right) = i \left| \left\langle n | \frac{\partial \, l}{\partial E_l} \right\rangle \right|^2 \boldsymbol{\nabla}_{\boldsymbol{R}} E_l(\mathbf{R})^{*} \times \boldsymbol{\nabla}_{\boldsymbol{R}} E_l(\mathbf{R}) \tag{5.91}$$

indicating that the cross product $i \left(\mathbf{A}_{nl} \times \mathbf{A}_{ln} \right)$ is always zero

$$i \left(\mathbf{A}_{nl} \times \mathbf{A}_{ln} \right) = 0,$$

provided that the bands $E_l(\mathbf{R})$ that takes place into the superposition are analytic functions of the parameter. The analytic behavior is broken in those occupied bands (denoted by l) and at those values of the parameter $\mathbf{R}$, where the real energy $E_l(\mathbf{R})$ becomes a singular function of the parameter due to degeneracy (which makes it locally a multiple value quantity, thus the derivative $\boldsymbol{\nabla}_{\boldsymbol{R}} E_l(\mathbf{R})$ cannot be defined). Similarly, at the degeneracy points the Hamiltonian's eigenfunction $\Psi_l(t, \mathbf{r}, \mathbf{R})$ is not analytic function of the energy E_l and the derivative $\dfrac{\partial \Psi_n(t, \mathbf{r}, \mathbf{R})}{\partial E_l}$ cannot be defined either. In general, whenever the off-diagonal Berry connection $\mathbf{A}_{nl}(t, \mathbf{R})$ is (for any occupied band l and every value of the parameter $\mathbf{R}$) either a purely real or a purely imaginary quantity, then, the vectors $\mathbf{A}_{nl}(t, \mathbf{R})$ and $\mathbf{A}_{ln}(t, \mathbf{R})$ are parallel to each other resulting to $\mathbf{A}_{nl}(t, \mathbf{R}) \times \mathbf{A}_{ln}(t, \mathbf{R}) = 0$.

Stiefel-Whitney class

The first Stiefel-Whitney class [95] is an obstruction to the orientability of a manifold while the second Stiefel-Whitney class is an obstruction to linear dependence. In contrast to the rest of the characteristic classes, the Stiefel-Whitney class cannot be expressed in terms of the curvature of the bundle. It is very interesting that in a recent theoretical study, concerning the band topology and linking structure of nodal line semimetals with Z_2 monopoles charges [3], it was found that the non-trivial band topology is characterized by the second Stiefel-Whitney class, although the study was made for an equilibrium quantum processes.

We are now going to study the

$$\frac{1}{2\pi}\sum_{l\neq n}^{\text{occ}} \oiint_S i\left(\mathbf{A}_{nl}^{*}\times\mathbf{A}_{nl}\right)\cdot d\mathbf{S} \tag{5.92}$$

term that enters in Eq. (5.90). By expressing the manifold's elementary surface in Eq. (5.92) as

$$d\mathbf{S} = d\mathbf{R}_a \times d\mathbf{R}_b$$

where $d\mathbf{R}_a$ and $d\mathbf{R}_b$ are tangent vectors on the manifold, then, the integrand of Eq. (5.92) can equally be expressed as

$$i\left(\mathbf{A}_{nl}^{*}\times\mathbf{A}_{nl}\right)\cdot(d\mathbf{R}_a\times d\mathbf{R}_b) = i(\mathbf{A}_{nl}^{*}\cdot d\mathbf{R}_a)(\mathbf{A}_{nl}\cdot d\mathbf{R}_b) - i(\mathbf{A}_{nl}^{*}\cdot d\mathbf{R}_b)(\mathbf{A}_{nl}\cdot d\mathbf{R}_a). \tag{5.93}$$

Alternatively, by using

$$\mathbf{A}_{nl}^{*}\times\mathbf{A}_{nl} = 2i\,\text{Real}[\mathbf{A}_{nl}]\times\text{Im}[\mathbf{A}_{nl}]$$

the integrand can equally be expressed by

$$\begin{aligned} &i\left(\mathbf{A}_{nl}^{*}\times\mathbf{A}_{nl}\right)\cdot(d\mathbf{R}_a\times d\mathbf{R}_b) \\ &\quad = -2\Big(\Big(\text{Real}[\mathbf{A}_{nl}]\cdot d\mathbf{R}_a\Big)\Big(\text{Im}[\mathbf{A}_{nl}]\cdot d\mathbf{R}_b\Big) - \Big(\text{Real}[\mathbf{A}_{nl}]\cdot d\mathbf{R}_b\Big)\Big(\text{Im}[\mathbf{A}_{nl}]\cdot d\mathbf{R}_a\Big)\Big) \end{aligned} \tag{5.94}$$

Torus manifold

When the manifold of integration is a torus Eq. (5.92) can be evaluated by

$$\begin{aligned} &\frac{1}{2\pi}\sum_{l\neq n}^{\text{occ}} \oiint_S i\left(\mathbf{A}_{nl}^{*}\times\mathbf{A}_{nl}\right)\cdot d\mathbf{S} \\ &\quad = -\frac{1}{\pi}\sum_{l\neq n}^{\text{occ}}\left(\oint_{S_1}\text{Real}[\mathbf{A}_{nl}]\cdot d\mathbf{R}\oint_{S_2}\text{Im}[\mathbf{A}_{nl}]\cdot d\mathbf{R} - \oint_{S_2}\text{Real}[\mathbf{A}_{nl}]\cdot d\mathbf{R}\oint_{S_1}\text{Im}[\mathbf{A}_{nl}]\cdot d\mathbf{R}\right), \end{aligned} \tag{5.95}$$

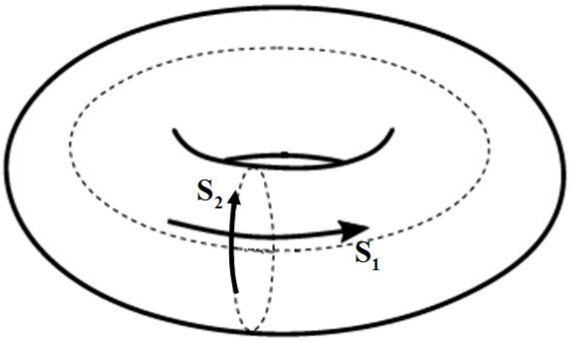

Figure 5.1: Relative magnetic helicity over a torus evaluated by the differences of the off-diagonal Berry's phases over the toroidal and poloidal directions.

which is given by the differences of the off-diagonal Berry's phases over the toroidal direction S_1 (with the major radius) and over the poloidal S_2 direction (with the minor radius) illustrated in Fig. 5.1, and has the form of a generalized relative **magnetic helicity** over toroidal and poloidal, directions which is a topological invariant.

Arbitrary closed manifold

For arbitrary closed manifold embedded in 3D parameter space, by using the divergence theorem we transform the surface (flux) integration of Eq. (5.92) to a bulk volume integration, which by using the vector identity $\boldsymbol{\nabla}_{\boldsymbol{R}}\cdot(\mathbf{A}\times\mathbf{B}) = \mathbf{B}\cdot\boldsymbol{\nabla}_{\boldsymbol{R}}\times\mathbf{A} - \mathbf{A}\cdot\boldsymbol{\nabla}_{\boldsymbol{R}}\times\mathbf{B}$ takes the form

$$\frac{1}{2\pi}\sum_{l\neq n}^{\text{occ}}\oiint_S i\left(\mathbf{A}^*_{nl}\times\mathbf{A}_{nl}\right)\cdot d\mathbf{S}$$
$$= \frac{1}{\pi}\sum_{l\neq n}^{\text{occ}}\iiint_V\Big(\text{Real}[\mathbf{A}_{nl}]\cdot\boldsymbol{\nabla}_{\boldsymbol{R}}\times\text{Im}[\mathbf{A}_{nl}] - \text{Im}[\mathbf{A}_{nl}]\cdot\boldsymbol{\nabla}_{\boldsymbol{R}}\times\text{Real}[\mathbf{A}_{nl}]\Big)\,dV \tag{5.96}$$

where V is the volume that is enclosed by the surface S. The latter integral has the form of a generalized relative helicity [144] which is a topological quantity. It describes the topology of the "magnetic" field lines of $\boldsymbol{\nabla}_{\boldsymbol{R}}\times\text{Real}[\mathbf{A}_{nl}]$ with respect to the field lines of $\boldsymbol{\nabla}_{\boldsymbol{R}}\times\text{Im}[\mathbf{A}_{nl}]$, and without having analytical proof, we suspect that it captures the linking between these field lines as illustrated in Fig. 5.2.

5.3 Dynamic topological processes

In what follows we describe certain dynamic processes where the observable in quest $\langle\boldsymbol{O}(t,\mathbf{R})\rangle$ is assumed to be evaluated with the HF theorem that we have derive. The purpose is to indicate in the simplest manner, how and when the topology of the Hilbert space is expected to play an important role in the quantization and robustness of observables.

Figure 5.2: Generalized helicity as the linking between the real and imaginary part of the off-diagonal Berry curvature. (Recall that the magnetic helicity is directly connected to the Gauss linking number, see i.e. [154], p. 327.)

5.3.1 Degenerate eigenstate of the Hamiltonian evolving adiabatically

We assume that the considered state $|\Psi_g(t,\mathbf{R})\rangle = \sum_{n\in S} C_n(t,\mathbf{R})\ |n(t,\mathbf{R})\rangle$ is a time-dependent, degenerate ground state with well defined instantaneous "energy" $E_g(t,\mathbf{R})$ satisfying the eigenvalue equation

$$\begin{aligned} H(t,\mathbf{R})\,|\Psi_g(t,\mathbf{R})\rangle &= \sum_{n\in S} C_n(t,\mathbf{R})\,H(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle \\ &= E_g(t,\mathbf{R})\,|\Psi_g(t,\mathbf{R})\rangle\,. \end{aligned} \tag{5.97}$$

Each orthonormal state $|n(t,\mathbf{R})\rangle$ has the same "energy" given by $H(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle = E_g(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle$, and the sum in Eq. (5.97) runs over all different orthonormal eigenstates within the degeneracy subspace S. We assume a degenerate adiabatic approximation, that is, no excitation to higher energy levels than the ground state E_g is possible, thus all the sums entering Eq. (5.41) are truncated into $\sum_{i}^{\text{occ}} \to \sum_{i\in S}$. Using Eq. (5.33) and the orthogonality condition of the degenerate states $E_{ln} = E_{nn}\,\delta_{ln} = E_g\,\delta_{ln}$, the non-Abelian curvature $\boldsymbol{\mathcal{F}}^{(E)}_{mn}$ turns up to be zero

$$\begin{aligned} \boldsymbol{\mathcal{F}}^{(E)}_{mn} &= i\sum_{l\in S}\left(\,\mathbf{A}_{ml}\,E_g\,\delta_{ln} - E_g\,\delta_{ml}\,\mathbf{A}_{ln}\,\right) \\ &= i\,\mathbf{A}_{mn}\,\left(\,E_g - E_g\,\right) = 0, \end{aligned} \tag{5.98}$$

while no simplification occurs for $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$. Similarly, the first term on the right side of Eq. (5.41) turns into

$$\begin{aligned}\sum_{m\in S}\sum_{n\in S} C^*_m C_n\, \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} &= \sum_{m\in S}\sum_{n\in S} C^*_m C_n\, \delta_{mn}\, \boldsymbol{\nabla}_{\boldsymbol{R}} E_g \\ &= \boldsymbol{\nabla}_{\boldsymbol{R}} E_g \sum_{m\in S} |C_m|^2 \\ &= \boldsymbol{\nabla}_{\boldsymbol{R}} E_g \end{aligned} \tag{5.99}$$

where we have used the normalization condition $\langle \psi_g(t,\mathbf{R})|\psi_g(t,\mathbf{R})\rangle = \sum\limits_{m\in S} |C_m|^2 = 1$. Therefore, Eq. (5.41) takes the form

$$\begin{aligned}\langle \boldsymbol{O}(t,\mathbf{R})\rangle_g &= \boldsymbol{\nabla}_{\boldsymbol{R}} E_g + \sum_{m\in S}\sum_{n\in S} C^*_m C_n\, \boldsymbol{\mathcal{S}}_{mn} \\ &\quad - \hbar \sum_{m\in S}\sum_{n\in S} C^*_m C_n\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} \\ &\quad - \hbar \frac{\partial \mathbf{R}}{\partial t} \times \sum_{m\in S}\sum_{n\in S} C^*_m C_n\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}, \end{aligned} \tag{5.100}$$

which by making a unitary transformation of the expansion coefficients

$$\mathcal{C}(t,\mathbf{R}) = \mathcal{U}(t,\mathbf{R})\, \mathcal{C}'(t,\mathbf{R}),$$

where $\mathcal{U}(t,\mathbf{R})$ is a unitary matrix, turns into the diagonal form

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle_g = \boldsymbol{\nabla}_{\boldsymbol{R}} E_g + \sum_{n\in S} |C'_n|^2\, \boldsymbol{\mathcal{S}}_{nn} - \hbar \sum_{n\in S} |C'_n|^2\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{nn} - \hbar \frac{\partial \mathbf{R}}{\partial t} \times \sum_{n\in S} |C'_n|^2\, \boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}. \tag{5.101}$$

Equal probability amplitude approximation

We now employ an "ergodic" approximation for the degenerate ground state E_g, that is, we assume that each one degenerate state $|n(t,\mathbf{R})\rangle$ with energy E_g in the superposition $|\Psi_g(t,\mathbf{R})\rangle = \sum\limits_{n\in S} C_n(t,\mathbf{R})\, |n(t,\mathbf{R})\rangle$, has the same probability to come out in a measurement.

$$|C_1(t,\mathbf{R})|^2 = |C_2(t,\mathbf{R})|^2 = |C_3(t,\mathbf{R})|^2 = \cdots = |C_N(t,\mathbf{R})|^2\,,$$

which by using the normalization condition gives,

$$\langle\, \psi_g(t,\mathbf{R})\,|\,\psi_g(t,\mathbf{R})\,\rangle = \sum_{m\in S} |C_m(t,\mathbf{R})|^2 = |C_g(t,\mathbf{R})|^2 \sum_{m\in S} = |C_g(t,\mathbf{R})|^2\, d(S) = 1, \tag{5.102}$$

where $d(S)$ denotes the degree of degeneracy of the subspace, thus each expansion coefficient is given by

$$C_g(t,\mathbf{R}) = \frac{1}{\sqrt{d(S)}}. \tag{5.103}$$

Using then the unitary (matrix) transformation freedom, together with the ergodic approximation Eq. (5.103), we find the dynamic HF theorem, that can be applied to such a degenerate state, which has the form

$$\boldsymbol{\mathcal{O}}_g(t,\mathbf{R}) = \boldsymbol{\nabla}_{\boldsymbol{R}} E_g + \frac{1}{d(S)}\sum_{n\in S}\boldsymbol{\mathcal{S}}_{nn} - \frac{\hbar}{d(S)}\sum_{n\in S}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{nn} - \frac{\hbar}{d(S)}\frac{\partial \mathbf{R}}{\partial t}\times\sum_{n\in S}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{nn}. \quad (5.104)$$

5.3.2 Non-topological limit: fully occupied Hilbert space due to dynamics

We now assume that each expansion coefficient $C_n(t,\mathbf{R})$ evolves in time according to Eq. (5.60) coupled to all other coefficients due to dynamical driving of the system. Specifically, we assume that the Hilbert space is at every instant fully occupied, irrespectively of the initial occupation of the Hilbert space; that is, we assume in Eq. (5.60) that

$$\left\langle n\right| \left(H(t,\mathbf{R}) - i\hbar\frac{d}{dt}\right) \left| l\right\rangle \neq 0 \quad \forall \quad n\neq l. \quad (5.105)$$

In this limit we replace $\sum_{l}^{\text{occ}} \rightarrow \sum_{l}^{\text{HS}}$ in all formulas, and with the aid of the closure relation $I = \sum_{l}^{\text{HS}} |\, l(t,\mathbf{R})\rangle\, \langle\, l(t,\mathbf{R})|$ we surprisingly find that the non-Abelian curvatures $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ turn to zero, that is

$$\begin{aligned}
\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} &= \boldsymbol{\mathcal{B}}_{mn} - i\sum_{l}^{\text{HS}} \mathbf{A}_{ml}\times\mathbf{A}_{ln} \\
&= \boldsymbol{\mathcal{B}}_{mn} + i\sum_{l}^{\text{HS}} \langle\, m|\boldsymbol{\nabla}_{\boldsymbol{R}} l\,\rangle \times \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\
&= \boldsymbol{\mathcal{B}}_{mn} - i\sum_{l}^{\text{HS}} \langle \boldsymbol{\nabla}_{\boldsymbol{R}} m|\, l\,\rangle \times \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\
&= \boldsymbol{\mathcal{B}}_{mn} - i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m| \left(\sum_{l}^{\text{HS}} |\, l\,\rangle\, \langle\, l\,| \right) \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\
&= \boldsymbol{\mathcal{B}}_{mn} - i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m| \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\, n\rangle \\
&= 0, \qquad (5.106)
\end{aligned}$$

as well as

$$\begin{aligned}
\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} &= \boldsymbol{\mathcal{E}}_{mn} - i\sum_{l}^{\text{HS}} (\, \mathbf{A}_{ml}\, \Phi_{ln} - \Phi_{ml}\, \mathbf{A}_{ln}\,) \\
&= \boldsymbol{\mathcal{E}}_{mn} + i\sum_{l}^{\text{HS}} \left(\langle m|\boldsymbol{\nabla}_{\boldsymbol{R}} l\,\rangle \left\langle l\,|\frac{\partial n}{\partial t}\right\rangle - \left\langle m\,|\frac{\partial l}{\partial t}\right\rangle \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}} n\,\rangle \right) \\
&= \boldsymbol{\mathcal{E}}_{mn} - i\sum_{l}^{\text{HS}} \left(\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m|\, l\,\rangle \left\langle l\,|\frac{\partial n}{\partial t}\right\rangle - \left\langle \frac{\partial m}{\partial t}|\, l\right\rangle \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}} n\,\rangle \right) \\
&= \boldsymbol{\mathcal{E}}_{mn} - i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m| \left(\sum_{l}^{\text{HS}} |\, l\,\rangle\, \langle\, l\,| \right) \left| \frac{\partial n}{\partial t} \right\rangle \\
&\quad + i \left\langle \frac{\partial m}{\partial t} \right| \left(\sum_{l}^{\text{HS}} |\, l\,\rangle\, \langle\, l\,| \right) |\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle \\
&= \boldsymbol{\mathcal{E}}_{mn} - i \left(\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m|\frac{\partial n}{\partial t}\right\rangle - \left\langle \frac{\partial m}{\partial t}|\boldsymbol{\nabla}_{\boldsymbol{R}} n\right\rangle \right) \\
&= 0. \qquad (5.107)
\end{aligned}$$

In an analogous manner, the non-Abelian curvatures $\boldsymbol{\mathcal{F}}^{(E)}_{mn}$ truncate into

$$\begin{aligned}
\boldsymbol{\mathcal{F}}^{(E)}_{mn} &= i\sum_{l}^{\text{HS}} (\mathbf{A}_{ml}\, E_{ln} - E_{ml}\, \mathbf{A}_{ln}) \\
&= -\sum_{l}^{\text{HS}} (\langle\, m|\boldsymbol{\nabla}_{\boldsymbol{R}} l\,\rangle\, \langle\, l\,|Hn\rangle - \langle\, m\,|Hl\rangle\, \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle) \\
&= -\sum_{l}^{\text{HS}} (-\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m|\, l\,\rangle\, \langle\, l\,|Hn\rangle - \langle Hm\,|\, l\rangle\, \langle\, l\,|\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle) \\
&= +\langle \boldsymbol{\nabla}_{\boldsymbol{R}} m| \left(\sum_{l}^{\text{HS}} |\, l\,\rangle\, \langle\, l\,| \right) |Hn\rangle \\
&\quad + \langle Hm\,| \left(\sum_{l}^{\text{HS}} |\, l\,\rangle\, \langle\, l\,| \right) |\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle \\
&\quad = \langle \boldsymbol{\nabla}_{\boldsymbol{R}} m|Hn\rangle + \langle Hm|\boldsymbol{\nabla}_{\boldsymbol{R}} n\rangle\,, \qquad (5.108)
\end{aligned}$$

and as result the observable $\boldsymbol{\mathcal{O}}(t, \mathbf{R})$ expectation value, in this fully occupied Hilbert space due to the dynamics, is given by

$$\begin{aligned}
\boldsymbol{\mathcal{O}}(t, \mathbf{R}) &= \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C^{*}_{m} C_{n}\, \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} + \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{S}}_{mn} \\
&\quad - \sum_{m}^{\text{HS}} \sum_{n}^{\text{HS}} C^{*}_{m} C_{n}\, \boldsymbol{\mathcal{F}}^{(E)}_{mn},
\end{aligned}$$

showing that the non-Abelian curvatures $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn}$ that carry the topology of the projective Hilbert have been eliminated due to the dynamics.

5.3.3 Topological limit in non-adiabatic processes: Separable Hilbert space

Guided by the previous subsection we assume a quantum state

$$|\Psi(t,\mathbf{R})\rangle = \sum_{n}^{\text{HS}} C_n\,(t,\mathbf{R})\,|n(t,\mathbf{R})\rangle, \tag{5.109}$$

that evolves in a non-adiabatic manner by a time-dependent Hamiltonian but is subject to one constraint, namely, there is a domain of the Hilbert space that remains unoccupied in all times. In this framework Eq. (5.109) is expressed as

$$|\Psi(t,\mathbf{R})\rangle = \sum_{n\in S_a} C_n\,|\,n\,\rangle + \sum_{n\in S_b} C_n\,|\,n\,\rangle$$

where the Hilbert space $\mathcal{H}$ is the union of the two domains $\mathcal{H} := S_a \cup S_b$, and the quantum state takes the form

$$|\Psi(t,\mathbf{R})\rangle = C_a\,|\Phi_a\,\rangle + C_b\,|\Phi_b\,\rangle\,, \tag{5.110}$$

where

$$\sum_{n\in S_a} C_n\,|\,n\,\rangle = C_a\,|\Phi_a\,\rangle \tag{5.111}$$

and

$$\sum_{n\in S_b} C_n\,|\,n\,\rangle = C_b\,|\Phi_b\,\rangle\,. \tag{5.112}$$

Assuming that the state $|\Phi_a\rangle$ is normalized, then $|C_a|^2 = \sum_{n\in S_a} |C_n|^2$ gives the probability of the system to be found in the domain S_a of the Hilbert space, and analogously, taking into account that the state $|\Phi_b\rangle$ is normalized, then $|C_b|^2 = \sum_{n\in S_b} |C_n|^2$ gives the probability of the system to be found in the S_b counterpart domain of the Hilbert space. In this respect, the Hilbert space is transformed into an effective two-dimension space with states $|\Phi_a\rangle$ and $|\Phi_b\rangle$, that are orthonormal $\langle\Phi_a|\Phi_b\rangle = \delta_{ab}$. By assuming now that the quantum state remains within the domain S_a for all times, that is $|C_a|^2 = \sum_{n\in S_a} |C_n|^2 = 1$ and $|C_b|^2 = 0$, the quantum state acquires the form

$$|\Psi(t,\mathbf{R})\rangle = C_a\,|\Phi_a\,\rangle\,, \tag{5.113}$$

where C_a is clearly a phase factor and the Hilbert space of the system is truncated into an effective one-dimensional space.

Single state expression

In an analogous manner as in the single-state approximation Eqs. (5.49) – (5.51), the observable's expectation value $\boldsymbol{\mathcal{O}}(t,\mathbf{R})$ takes the form

$$\boldsymbol{\mathcal{O}}(t,\mathbf{R}) = \boldsymbol{\nabla}_{\boldsymbol{R}} E_{aa} + \boldsymbol{\mathcal{S}}_{aa} - \hbar\,\boldsymbol{\mathcal{E}}_{aa} - \hbar\,\frac{\partial \mathbf{R}}{\partial t} \times \boldsymbol{\mathcal{B}}_{aa}. \tag{5.114}$$

where $\boldsymbol{\mathcal{E}}_{aa}$ and $\boldsymbol{\mathcal{B}}_{aa}$ are generalized non-adiabatic Berry curvatures given by

$$\boldsymbol{\mathcal{B}}_{aa}(t,\mathbf{R}) = i\,\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\Phi_a| \times |\boldsymbol{\nabla}_{\boldsymbol{R}}\Phi_a\rangle \tag{5.115}$$

and

$$\boldsymbol{\mathcal{E}}_{aa}(t,\mathbf{R}) = i\left\langle \boldsymbol{\nabla}_{\boldsymbol{R}}\Phi_a|\frac{\partial \Phi_a}{\partial t}\right\rangle - i\left\langle \frac{\partial \Phi_a}{\partial t}|\boldsymbol{\nabla}_{\boldsymbol{R}}\Phi_a\right\rangle, \tag{5.116}$$

while the non-Hermitian boundary term is given by

$$\boldsymbol{\mathcal{S}}_{aa}(t,\mathbf{R}) = \left\langle \Phi_a\right|\left(H(t,\mathbf{R})^{+} - H(t,\mathbf{R})\right)\boldsymbol{\nabla}_{\mathbf{R}}\Phi_a\rangle \tag{5.117}$$

and the gradient of the "energy" from

$$\boldsymbol{\nabla}_{\boldsymbol{R}} E_{aa} = \boldsymbol{\nabla}_{\boldsymbol{R}}\langle \Phi_a|\,H(t,\mathbf{R})\,|\Phi_a\rangle\,. \tag{5.118}$$

Eqs. (5.114) – (5.118) are essentially the counterparts of Eqs. (4.8) – (4.12) derived in the dynamic extension of the HF in Chapter 4.

Time periodic system: single Floquet state

Assuming that, (i) the parameter $\mathbf{R}$ is periodic in time $\mathbf{R}(t) = \mathbf{R}(t+T)$, as well as that (ii) the Hamiltonian is also periodic $H(t+T,\mathbf{R}(t+T)) = H(t,\mathbf{R}(t))$, then we can choose the phase factor C_a of the state $|\Psi(t,\mathbf{R})\rangle$ of Eq. (5.113), that lies within the effective one-dimensional Hilbert space, in such a manner that $|\Phi_a(t,\mathbf{R})\rangle$ is periodic in time, that is $|\Phi_a(t,\mathbf{R})\rangle = |\Phi_a(t+T,\mathbf{R})\rangle$, while $|\Psi_a(t+T,\mathbf{R})\rangle = (C_a(t+T,\mathbf{R})/C_a(t,\mathbf{R}))\,|\Psi_a(t,\mathbf{R})\rangle$. By inserting Eq. (5.113) into Eq. (5.1), we find the equation of motion of the phase factor $C_a(t,\mathbf{R})$ that is given by

$$i\hbar\frac{d}{dt}lnC_a(t,\mathbf{R}) = \langle \Phi_a(t,\mathbf{R})|\,H(t,\mathbf{R}) - i\hbar\frac{d}{dt}\,|\Phi_a(t,\mathbf{R})\rangle\,, \tag{5.119}$$

where by definition the right hand side of Eq. (5.119) is periodic in time. In this respect, the phase factor is given by

$$C_a(t,\mathbf{R}) = C_a(0,\mathbf{R_o})\;\; e^{-\frac{i}{\hbar}\int_0^t \langle \Phi_a|\,H(t',\mathbf{R}) - i\hbar\frac{d}{dt'}|\Phi_a\rangle\,dt'}, \tag{5.120}$$

which gives the dynamic phase together with the Aharonov-Anandan phase. If one further assumes that the state $|\Psi_a(t,\mathbf{R})\rangle$ is a Floquet state, that is, it satisfies the eigenvalue equation, $\left(H(t,\mathbf{R})-i\hbar\frac{d}{dt}\right)|\Phi_a(t,\mathbf{R})\rangle=\varepsilon_a\,|\Phi_a(t,\mathbf{R})\rangle$, where ε_a is the static quasienergy, then, the phase factor is simply given by $e^{-\frac{i}{\hbar}\varepsilon_a\,t}$, and the effective one-dimensional Hilbert space state is given by $|\Psi(t,\mathbf{R})\rangle\equiv e^{-\frac{i}{\hbar}\varepsilon_a\,t}\,|\Phi_a(t,\mathbf{R})\rangle$. In this fashion, Eqs. (5.114) – (5.118) are evaluated with respect to a single time periodic Floquet state $|\Phi_a(t,\mathbf{R})\rangle$.

Time periodic system: coherent superposition of Floquet states

Assuming now that the states $|\,n\,\rangle$ in Eq. (5.111)

$$\sum_{n\in S_a} C_n\,|\,n\,\rangle = C_a\,|\Phi_a\,\rangle\,,$$

are the Floquet states, then, the matrix $\mathcal{H}_F(t,\mathbf{R})$ given by Eq. (5.63) is diagonal, thus each expansion coefficient $C_n(t,\mathbf{R})$ evolves over time uncoupled to any other and has the form $C_n(t,\mathbf{R})=C_n(0,\mathbf{R})e^{-\frac{i}{\hbar}\varepsilon_n\,t}$ where ε_n is the quasienergy. Therefore, the observable in quest is given by Eq. (5.41) where the sums will run over all occupied Floquet eigenstates and the expansion coefficients are uncoupled to each other.

5.3.4 Topological limit in adiabatic and non-equilibrium systems

We now assume a quantum state that is made of a coherent quantum superposition of different eigenstates individually undergoing quantum adiabatic evolution. Therefore, each expansion coefficient $C_n(t,\mathbf{R})$ evolves in time according to

$$\left\langle n\right|\left(H(t,\mathbf{R})-i\hbar\frac{d}{dt}\right)\left|\,l\,\right\rangle=0\quad\forall\quad n\neq l \tag{5.121}$$

which prohibits any kind of transitions, either within the degeneracy subspace or optical transitions. In this limit, the occupation of the available Hilbert space is constant due to $\frac{d}{dt}|C_n(t,\mathbf{R})|=0$ (the Hermitian matrix $\mathcal{H}_F(t,\mathbf{R})$ of Eq. (5.63) is diagonal), but on the other hand, the non-equilibrium quantum state can occupy the whole Hilbert space, therefore, the quantum state that is encountered in this approximation can be thought as a dark quantum state. Using the total time derivative Eq. (5.2), as well as the definition of the non-Abelian Berry connection Eq. (5.28) and Berry potential Eq. (5.29), the non-excitation constraint Eq. (5.121), evaluated with respect to the states $\langle\,m\,|$ and $|\,l\,\rangle$, is expressed as

$$E_{ml}-\hbar\frac{\partial\mathbf{R}}{\partial t}\cdot\mathbf{A}_{ml}-\hbar\,\Phi_{ml}=0\quad\forall\quad l\neq m. \tag{5.122}$$

Multiplying both sides of Eq. (5.122) with $\mathbf{A}_{ln}$ we find the constraint

$$E_{ml}\mathbf{A}_{ln} - \hbar\left(\frac{\partial \mathbf{R}}{\partial t}\cdot\mathbf{A}_{ml}\right)\mathbf{A}_{ln} - \hbar\,\Phi_{ml}\mathbf{A}_{ln} = 0 \quad \forall \quad l \neq m. \tag{5.123}$$

Similarly, the non-excitation constraint Eq. (5.121), evaluated with respect to the states $\langle\, l\,|$ and $|\, n\,\rangle$, is expressed as

$$E_{ln} - \hbar\frac{\partial \mathbf{R}}{\partial t}\cdot\mathbf{A}_{ln} - \hbar\,\Phi_{ln} = 0 \quad \forall \quad l \neq n. \tag{5.124}$$

Multiplying both sides of Eq. (5.124) with $\mathbf{A}_{ml}$ we find the constraint

$$\mathbf{A}_{ml}E_{ln} - \hbar\mathbf{A}_{ml}\left(\frac{\partial \mathbf{R}}{\partial t}\cdot\mathbf{A}_{ln}\right) - \hbar\,\mathbf{A}_{ml}\Phi_{ln} = 0 \quad \forall \quad l \neq n. \tag{5.125}$$

Subtracting now Eq. (5.123) from Eq. (5.125) we find the constraint

$$(\mathbf{A}_{ml}E_{ln} - E_{ml}\mathbf{A}_{ln}) - \hbar\frac{\partial \mathbf{R}}{\partial t}\times(\mathbf{A}_{ml}\times\mathbf{A}_{ln}) - \hbar\,(\mathbf{A}_{ml}\Phi_{ln} - \Phi_{mi}\mathbf{A}_{ln}) = 0 \tag{5.126}$$

for $l \neq m$ and $l \neq n$.

Therefore, by using Eq. (5.126) constraint into the observable's $\langle \boldsymbol{O}(t,\mathbf{R})\rangle$ formula Eq. (5.35), leads into the apparent truncation of the sums

$$\sum_{l}^{\text{occ}} \rightarrow \sum_{l}^{\text{occ}} \delta_{lm}\delta_{ln}$$

involved in the formulas of $\boldsymbol{\mathcal{F}}^{(E)}$, $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}$ and $\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}$. In this respect, in the adiabatic limit, the curvatures are now given by

$$\boldsymbol{\mathcal{F}}^{(E)}_{mn} = i\sum_{l}^{HS}\delta_{lm}\delta_{ln}\,(\,\mathbf{A}_{ml}\,E_{ln} - E_{ml}\,\mathbf{A}_{ln}\,) = 0, \tag{5.127}$$

as well as

$$\begin{aligned}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{E}})}_{mn} &= \boldsymbol{\mathcal{E}}_{mn} - i\sum_{l}^{HS}\delta_{lm}\delta_{ln}\,(\,\mathbf{A}_{ml}\,\Phi_{ln} - \Phi_{ml}\,\mathbf{A}_{ln}\,)\\ &= \boldsymbol{\mathcal{E}}_{mn}\end{aligned} \tag{5.128}$$

end

$$\begin{aligned}\boldsymbol{\mathcal{F}}^{(\boldsymbol{\mathcal{B}})}_{mn} &= \boldsymbol{\mathcal{B}}_{mn} - i\sum_{l}^{HS}\delta_{lm}\delta_{ln}\,\mathbf{A}_{ml}\times\mathbf{A}_{ln}\\ &= \boldsymbol{\mathcal{B}}_{mn},\end{aligned} \tag{5.129}$$

while the observable in quest is given by

$$\langle \boldsymbol{O}(t,\mathbf{R})\rangle = \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \, \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} + \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \, \boldsymbol{\mathcal{S}}_{mn} - \hbar \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \, \boldsymbol{\mathcal{E}}_{mn} - \hbar \frac{\partial \mathbf{R}}{\partial t} \times \sum_{m}^{\text{occ}}\sum_{n}^{\text{occ}} C_m^* C_n \, \boldsymbol{\mathcal{B}}_{mn}. \tag{5.130}$$

We point out that, Eq. (5.130) cannot be simplified any further by means of a unitary transformation of the expansion coefficients

$$\mathcal{C}(t,\mathbf{R}) = \mathcal{U}\ \mathcal{C}'(t,\mathbf{R})$$

(with $\mathcal{U}$ a constant unitary matrix) into a diagonal form, because this kind of transformation would induce coupling between the expansion coefficients which are assumed to evolve in time uncoupled one to each other.

5.4 Particle transport in non-adiabatic and time-periodic system

As a final application we study the particle transport in manner analogous to the one of Sec.4.3.2 of Chapter 4. Thus we assume the same Hamiltonian and potentials, but, with the essential difference that each electron's quantum state is a coherent superposition of different Floquet states. Each electron's wavefunction evolves in time according to

$$i\hbar\frac{d}{dt}\Psi(\mathbf{r},t,\mathbf{k}) = H(\mathbf{r},t)\,\Psi(\mathbf{r},t,\mathbf{k}) \tag{5.131}$$

and the quantum state has the form

$$\Psi(\mathbf{r},t,\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r},t,\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{n}^{\text{S}_a} C_n(t,\mathbf{k})\Phi_n(\mathbf{r},t,\mathbf{k}) \tag{5.132}$$

where $\Phi_n(\mathbf{r},t,\mathbf{k})$ are the Floquet eigenstates and the sum runs over all occupied Floquet states. The Floquet operator $H_F(\mathbf{r},t) = H(\mathbf{r},t) - i\hbar\frac{d}{dt}$ is diagonal with respect to the states $\Phi_n(\mathbf{r},t,\mathbf{k})$. The Hamiltonian $H(\mathbf{r},t)$ is periodic over time and space coordinates, and does not depend on any parameter. We assume periodic boundary conditions over space coordinates thus $\psi(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = \psi(\mathbf{r},t,\mathbf{k})$ as well as, $u(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = u(\mathbf{r},t,\mathbf{k})$ and $\Phi_n(\mathbf{r}+\mathbf{L},t,\mathbf{k}) = \Phi_n(\mathbf{r},t,\mathbf{k})$. Using the Hamiltonian $H(\mathbf{r},t)$ and the Floquet states as basis states, as well as by using the static crystal momentum $\mathbf{k}$ as the parameter, thus

$\mathbf{k} = \mathbf{R}$, the dynamical extension of the HF theorem in Eq. (5.41) gives

$$0 = \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \left(\boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} \, + \, \boldsymbol{\mathcal{S}}_{mn} \, - \, \boldsymbol{\mathcal{F}}_{mn}^{(E)} \, - \, \hbar \boldsymbol{\mathcal{F}}_{mn}^{(\boldsymbol{\varepsilon})} \right), \tag{5.133}$$

where all quantities are evaluated with respect to the Floquet eigenstates, and the "energy" is given by

$$E_{mn}(t, \mathbf{k}) = \langle \Phi_m(t, \mathbf{k}) | \, H(\mathbf{r}, t) \, | \Phi_n(t, \mathbf{k}) \rangle = \varepsilon_n(\mathbf{k}) \delta_{mn} \, + \, i\hbar \left\langle \Phi_m(t, \mathbf{k}) \, | \, \frac{d}{dt} \Phi_n(t, \mathbf{k}) \right\rangle .$$

The matrix elements of the boundary velocity and the counterpart boundary terms of the HF theorem are related by

$$\boldsymbol{\mathcal{S}}_{mn}(t, \mathbf{k}) = \hbar \, \langle \, \mathbf{v}_b \, \rangle_{mn} \, + \, \boldsymbol{\mathcal{S}}_{k,mn}(t, \mathbf{k}), \tag{5.134}$$

where $\mathbf{v}_b$ is the non-Hermitian boundary velocity defined by Eq. (2.4), and the matrix elements of the non-Hermitian boundary terms $\boldsymbol{\mathcal{S}}_{k,mn}(t, \mathbf{k})$ are assumed to be zero in accordance to Sec. 4.3.2. Therefore, by applying Eq. (5.134) into Eq. (5.133) we find

$$\begin{aligned} \langle \, \mathbf{v}_b \, \rangle \; &= \; \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \, \langle \, \mathbf{v}_b \, \rangle_{mn} \\ &= \; \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \left(\frac{1}{\hbar} \boldsymbol{\nabla}_{\boldsymbol{R}} E_{mn} \, - \, \frac{1}{\hbar} \boldsymbol{\mathcal{F}}_{mn}^{(E)} \, - \, \boldsymbol{\mathcal{F}}_{mn}^{(\boldsymbol{\varepsilon})} \right), \end{aligned} \tag{5.135}$$

which is the generalization of Eq. (4.74) of Chapter 4. In this framework, the extension of Eqs. (4.89) – (4.90) is given by

$$\begin{aligned} \Delta x_{(Boundary)} \; = & - \frac{V}{(2\pi)^3} \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \int_{-\pi/a}^{+\pi/a} \frac{\partial}{\partial k_x} \left(\int_0^T i \left\langle \phi_m | \frac{d\phi_n}{dt} \right\rangle dt \right) dk_x \\ & + \frac{1}{\hbar} \frac{V}{(2\pi)^3} \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_0^T \int_{-\pi/a}^{+\pi/a} \mathcal{F}_{x\,mn}^{(E)} \, dt \, dk_x \right) \\ & + \frac{V}{(2\pi)^3} \sum_{m}^{\text{occ}} \sum_{n}^{\text{occ}} C_m^* C_n \int_{-\pi/a}^{+\pi/a} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \left(\int_0^T \int_{-\pi/a}^{+\pi/a} \mathcal{F}_{x\,mn}^{(\boldsymbol{\varepsilon})} \, dt \, dk_x \right) \end{aligned} \tag{5.136}$$

from which it is evident that the particle transport is given in terms of the non-Abelian curvatures $\mathcal{F}_{x\,mn}^{(E)}$ and $\mathcal{F}_{x\,mn}^{(\boldsymbol{\varepsilon})}$ weighted by the occupation numbers. We hope that, theoretical investigations in non-equilibrium and closed quantum systems [141, 105, 89, 42, 29, 136, 143], could take advantage of the general dynamical extension of the HF theorem Eq. (5.41) that

we have derived, and that even the special cases that we have worked out above can provide useful insights for future investigations.

Chapter 6

Conclusions

This dissertation was motivated by the inadequacy of existing formulations of adiabatic and non-adiabatic transport theory to capture non-Hermitian boundary effects, as well as by the need to find a formula for the observables that takes into account at the same time the dynamics and the topology of the instantaneous occupied Hilbert space in the simplest manner possible. In this respect, the dissertation was dedicated to the reformulation and extension of some fundamental concepts and theorems which resolve the above mentioned inadequacies. The results are summarized further below.

We have reconsidered the Modern Theory of Orbital Magnetization through careful definition of additional quantities that rigorously and analytically take into account the boundary contributions to the orbital magnetization. These contributions are shown to originate from non-Hermitian effects that emerge whenever the position operator $\mathbf{r}$ and the momentum gradient operator $\partial_{\mathbf{k}}$ (that enter the Ehrenfest and the Hellmann-Feynman theorems respectively) become anomalous, in the sense that they break the domain of definition of the Hamiltonian operator. In this theoretical framework, we have first extended the standard velocity operator definition in order to incorporate the anomaly of the position operator that is inherited in band theory, and this results in an explicit boundary velocity contribution. Using the extended velocity, we have defined the electrons' intrinsic orbital circulation within Bloch representation which we have shown that is an intensive and well defined quantity of periodic solids that properly counts the circulating micro-currents embodied in the wavefunctions' bulk and boundary structure. Using the defined electrons' intrinsic circulation, we have made a rigorous connection between the nth band electrons' collective intrinsic circulation and the local (LC) and itinerant circulation (IC) contributions, that are used within Wannier-localization and periodic gauge approximation in the Modern Theory of Orbital Magnetization [133, 33, 132]. With these concepts in hand, we have been able to rigorously reconsider the theory and derive quantum mechanical expressions for the orbital magnetization of non-interacting electrons that move within extended and topological solids (insulators or semimetals), without any Wannier-localization approximation [133, 132] or heuristic extension [33] been made. We have rigorously shown that, in the one-band approximation $\mathbf{k}$-space formula, a one-band covariant derivative enters the magnetization formula

as an emerging operator due to the non-Hermitian effect that is attributed to the anomaly of the momentum gradient operator $\partial_{\mathbf{k}}$; the one-band covariant derivative can be replaced by the normal derivative only whenever PBCs are satisfied. In the many-band and unrestricted $\mathbf{k}$-space formula of the orbital magnetization, the non-Hermitian effect has been shown to contribute an additional boundary term that originates from the anomalies of the position operator $\mathbf{r}$ and the momentum gradient operator $\partial_{\mathbf{k}}$. This additional boundary term is expected to give local gigantic orbital magnetization contributions in the vicinity of band crossings in topological materials (insulators or semimetals) whenever band crossings occur along with Hall voltage due to imbalance of electron accumulation at the opposite boundaries of the material under study. These local gigantic orbital magnetization contributions are encoded in the emerging non-Hermitian effect of the momentum gradient operator $\partial_{\mathbf{k}}$ that becomes anomalous whenever the PBCs for the electrons' wavefunctions are broken. On the contrary, whenever Hall voltage is zero and the electrons' wavefunctions satisfy PBCs, the momentum gradient operator $\partial_{\mathbf{k}}$ has a well defined behavior and, as a consequence, gigantic boundary contributions are not possible. By making a comparison between our derived formula and the one that had heuristically been given (in order to model the orbital magnetization of Chern insulators and metals) in Ref. [33], we have shown the (previously unnoticed) property that, within periodic boundary conditions, the orbital magnetization has explicit boundary contributions encoded in the off-diagonal matrix elements of the boundary velocity operator (which are not zero due to the emerging non-Hermitian effect of the position operator that becomes anomalous within PBCs). Finally, we point out that, all boundary contributions that emerge due to non-Hermitian effects can equally be calculated as bulk properties whenever the integrations by parts are not performed.

We have shown how one can set up a global quantum equation of motion within Schrödinger picture and study transport processes without any local conservation law being necessary in contrast to the established practice. This is achieved whenever additional, non-Hermitian effect boundary operators, are taken into account. By using the global quantum equation of motion we have shown how one can define an operator in an extended manner without any subtleties involved. This extended operator definition, leads into a bulk-boundary detailed balance relation for any stationary state, relating therefore the boundaries' rate of change of an observable with the corresponding bulk one. Moreover, it provides a way for defining linear approximation dissipation equations near equilibrium, therefore, one can derive Onsager reciprocal relations within a quantum mechanical framework. Our extended theoretical framework of studying transport processes, has then been applied in spin physics in order to resolve the controversies and ambiguities with respect to the coherent spin accumulation and spin transport. Specifically, there does not exist up to now a generally accepted agreement on the correct definition of the corresponding operators, namely, the spin-accumulation rate of change operator and the spin-current operator [108, 40, 128, 121, 125, 24, 44, 4, 23]. The reason for this controversy is that in any closed system that lacks spin-rotation invariance there is no given direction in the material along

which the spin is conserved; therefore, no local spin magnetization conservation law can be derived in a form of a continuity equation, and as a consequence it is said that, no quantum mechanical spin-current operator can unambiguously be well-defined. In this framework, by employing our extended operator definition and without any local conservation law being necessary, we had reviewed the Ref. [121] spin current definition (which is presumably the most widely accepted definition) and shown the limitation of its validity in comparison to our theoretical framework. Namely, in addition to the bulk spin generation, spin generation over the boundaries has to also be zero in order that their spin current operator definition to have a well defined value (in the thermodynamic limit); this spin generation over the boundaries although attributed to a non-Hermitian boundary operator in the present work, has not been so far recognized as such. We then defined the intrinsic spin current operator as the time derivative of the correlation between electron's position and electron's spin. The intrinsic spin current has two parts, a bulk one and a boundary one that is attributed to the non-Hermitian effect. Our definition of the spin current has always a well defined value without any constraints being involved whatsoever. For any stationary state there exist a gain-loss detailed balance relation that explicitly relates the bulk intrinsic spin current with the corresponding boundary one. For systems that lack local spin-torques in a given direction, both the bulk and the boundary intrinsic spin current turn zero value each (provided that the state under consideration has a well-defined spin in that specific direction) due to the position and spin being uncorrelated.

By just using quantum dynamics in an appropriate way, we have derived an extended and dynamical Hellmann-Feynman theorem for general non-adiabatic processes. The resulting formula for the dynamics of the observables is found to have profound connections to generalized Berry curvatures as well as to boundary contributions due to an emerging non-Hermitian effect. A complication when dealing with states that are labeled by time-dependent parameters has been resolved. Specifically, we have shown how the standard (in band theory) way of transformation between the discrete sum over static parameters (such as crystal momentum) to a counterpart Riemann integral over continuous variables can be modified when dealing with time-dependent parameters. This complication is overcome when the arbitrary Jacobian of transformation between the initial value of a parameter and the time-evolved one is taken into account. This way of transformation engages measurable consequences when the parameter velocity-field behaves as a compressible fluid field. This complication is precisely the "paradox" that appears in the semiclassical modification of density of states [149], which has not been realized or identified in this manner. Several applications of the theorem showing its usefulness have been made: (i) For flux preserving motions we have derived a Maxwell type of equation (in parameter space) with monopole sources which is a generalization of the counterpart Maxwell type of equation that has been found in the last few years [70] in the study of Weyl semimetals, and which has arisen by heuristic analogy to the electromagnetic induction law and without any detailed derivation. (ii) A study of the particle transport in the non-adiabatic limit [105] has been made, showing that

the adiabatic quantization breaks down due to a non-trivial Aharonov-Anandan phase. (iii) Similarly, a study of the electric polarization has also been performed indicating that there is a boundary non-Hermitian contribution that has been so far overlooked in the so called Modern Theory of Polarization [75, 101, 109, 114, 111]. (iv) Two sets of quantum equations of motion for the electron have been derived without any localization or adiabatic approximation involved. One is for spinless motion and the other for spinfull one. These quantum equations of motion are extensions of the semiclassical ones [130] that had been derived by means of a time-dependent variational principle applied to a trial localized wavepacket under the adiabatic approximation. The electron's velocity that we found depends explicitly on two generalized Berry curvatures as well as on a non-Hermitian boundary term. We have applied the spinfull quantum equations of motion to the Quantum Anomalous Hall Effect in a magnetically doped topological insulator [34, 18, 62, 85] and we have given a formula for the transverse Hall conductivity that, besides the topologically quantized values, acquires two other correction terms which emerge due to the non-zero effective magnetic field that is created by the strong spin-orbit coupling.

By using an orthonormal basis we have analyzed further the dynamical extension of the Hellmann-Feynman theorem. We have found a formula for the observables that depends on the dynamics through the expansion coefficients together with the topology of the instantaneous occupied Hilbert space. Interestingly, the observables turned out to have dependence on non-Abelian Berry curvatures when the quantum state occupies more than one dimensions in Hilbert space. The form of these non-Abelian Berry curvatures resembles the Yang-Mills field strength tensors [152]. The extension to multiple bands, allows the generalization of the invariants that come from the Abelian curvatures to the counterpart invariants that originate from the non-Abelian curvatures within the many bands. These new topological invariants have the form of generalized relative helicities [144]. In the fully dynamical limit, when all expansion coefficients evolve in time coupled to each other, these non-Abelian Berry curvatures turn to zero. By way of application of this extension we have studied the particle transport in the strong non-adiabatic limit where the quantum state is in a coherent superposition of different Floquet states. The particle transport was found to be given in terms non-Abelian curvatures weighted by the occupation numbers. We believe that the theoretical investigations in non-equilibrium and closed quantum systems [141, 105, 89, 42, 29, 136, 143] which are performed in the last few years by means of the time-dependent perturbation theory or the Kubo formula (both being more laborious and complicated methods than ours), could take advantage of the general dynamical extension of the HF theorem Eq. (5.41) that we have derived. By straightforward application one can easily find formulas for observables' expectation values that incorporate in a combined way both the topology of the instantaneous occupied Hilbert space and the dynamics in arbitrary time-dependent systems.

In summary, our dissertation gives a new perspective for a single theoretical formulation that is appropriate in describing a coexistence of boundary non-Hermitian effects together with non-trivial dynamical topological contributions in general quantum Condensed Matter

systems. It is hoped that the methods and results presented here will be relevant to future investigations where the above combination of factors plays the central role.

Appendices

Appendix A

Calculations of: Position expectation value $\langle \mathrm{r} \rangle_n$, displacement $\Delta \langle \mathrm{r} \rangle$, orbital circulation $\langle \mathrm{C} \rangle_n$, and intrinsic orbital circulation $\langle \mathrm{C}_{intr} \rangle_n$

In the following all calculations are performed for one electron states within Bloch representation.

A.1 Explicit calculation of $\langle \mathrm{r} \rangle_n$

For simplicity and without loss of generality we assume 1D configuration (while the generalization to 3D is straightforward). We assume a closed system $\langle \Psi(t) | \Psi(t) \rangle = 1$ of length L_x with PBSs for the wavefunction over the edges. We calculate the electrons position expectation value $\langle \Psi(t) | \, x \, | \Psi(t) \rangle$ with respect to a Bloch eigenstate

$$|\Psi_n(t,k)\rangle = \frac{1}{\sqrt{N_x}} e^{-\frac{i}{\hbar} E_n(k) t} e^{ikx} \, |u_n(k)\rangle \, .$$

The length L_x of the system is equal to $L_x = N_x \alpha_x$, where α_x is the primitive cell length and N_x the number of the primitive cells of the system. The Bloch state $|\Psi_n(t,k)\rangle$ is normalized within the length L_x of the system, thus $\langle \Psi_n(k) | \Psi_n(k) \rangle = \langle u_n(k) | u_n(k) \rangle_{cell} = 1$, where $\langle u_n(k) | u_n(k) \rangle_{cell}$ is calculated within one primitive cell and a normalization constant is assumed to be absorbed in the cell periodic state $|u_n(k)\rangle$. The electrons' position expectation value is a quantity that is position origin-dependent and is given by

$$\langle \psi_n(k) | \, x \, | \psi_n(k) \rangle = \frac{1}{N_x} \int_0^{L_x} x \, |u_n(x,k)|^2 \, dx \tag{A.1}$$

where the lower limit of the space integration is the starting point of the 1D system that coincides with the position-origin. Using the periodicity of the cell periodic states $u_n(x,k)$ we "transfer" all (N_x-1) primitives cells in the position of the 1$^{\text{st}}$ primitive cell (adjacent to the position origin), which gives

$$\begin{aligned}\langle\psi_n(k)|\,x\,|\psi_n(k)\rangle &= \int_0^{\alpha_x}|u_n(x,k)|^2\,x\,dx \qquad (A.2)\\ &\quad+\frac{1}{N_x}\,\alpha_x\,(1+2+3+...+(N_x-1))\int_0^{\alpha_x}|u_n(x,k)|^2\,dx\\ &= \langle u_n(k)|\,x\,|u_n(k)\rangle_{cell}+\frac{1}{N_x}\alpha_x N_x\frac{(N_x-1)}{2}\langle u_n(k)|u_n(k)\rangle_{cell} \qquad (A.3)\end{aligned}$$

where the *cell* subscript denotes that the space integrals are evaluated within the primitive cell located at the systems edge. Using the normalization condition Eq. (A.2) takes the form

$$\langle\psi_n(k)|\,x\,|\psi_n(k)\rangle=\frac{\alpha_x N_x}{2}+\left(\langle u_n(k)|\,x\,|u_n(k)\rangle_{cell}-\frac{\alpha_x}{2}\right). \qquad (A.4)$$

Performing analogous calculation as that in Eq. (A.2), we evaluate the off-diagonal matrix elements of the position operator for $n\neq m$ which gives

$$\langle\psi_n(k)|\,x\,|\psi_m(k)\rangle=\langle u_n(k)|\,x\,|u_m(k)\rangle_{cell}+\alpha_x\frac{(N_x-1)}{2}\langle u_n(k)|u_m(k)\rangle_{cell},$$

where using $\langle\psi_n(k)|\psi_m(k)\rangle=\langle u_n(k)|u_m(k)\rangle_{cell}=\delta_{nm}$, we finally find that the off-diagonal matrix elements are given by

$$\langle\psi_n(k)|\,x\,|\psi_m(k)\rangle=\langle u_n(k)|\,x\,|u_m(k)\rangle_{cell}. \qquad (A.5)$$

Therefore, in the system's infinite length limit $L_x\to\infty$, the number of primitive cells enclosed within the system also becomes infinite $N_x\to\infty$, and as a result, the electrons' position expectation value Eq. (A.4) takes an undefined value (due to the first term of the right hand side), in contrast to the off-diagonal position matrix elements Eq. (A.5) which they return a well defined value.

A.2 Explicit calculation of $\Delta\langle\mathbf{r}\rangle$

We assume a position periodic and closed system of length L_x. We will calculate the electrons' displacement after a finite time interval T in the limit of infinite length $L_x\to\infty$ and show that is a well-defined quantity. We assume that the electron is in an extended and

time-dependent Bloch type state at every instant, that is,

$$|\Psi(t,k(t))\rangle = \frac{1}{\sqrt{N_x}} e^{ik(t)x} |u(t,k(t))\rangle ,$$

where the state $|u(t,k(t))\rangle$ has arbitrary time-dependence and is cell-periodic at every instant, as well as $|\Psi(t,k(t))\rangle$ is normalized to unity at every instant

$$\langle\Psi(t,k(t))|\Psi(t,k(t))\rangle = \langle u(t,k(t))|u(t,k(t))\rangle_{cell} = 1.$$

Using similar reasoning as in Eq. (A.4) we find that the electrons' displacement is given by

$$\begin{aligned}
\Delta\langle x\rangle &= \Delta\langle\Psi(t,k(t))|\, x\,|\Psi(t,k(t))\rangle \\
&= \frac{1}{N_x}\langle u(t+T,k(t+T))|\, x\,|u(t+T,k(t+T))\rangle - \frac{1}{N_x}\langle u(t,k)|\, x\,|u(t,k)\rangle \\
&= \langle u(t+T,k(t+T))|\, x\,|u(t+T,k(t+T))\rangle_{cell} - \langle u(t,k(t))|\, x\,|u(t,k(t))\rangle_{cell}
\end{aligned} \tag{A.6}$$

where the undefined terms $\frac{\alpha_x N_x}{2}$ canceled each one another. In this fashion, Eq.(A.6) takes the form

$$\Delta\langle x\rangle = \int_t^{t+T} \frac{d}{dt'}\langle u(t',k(t'))|\, x\,|u(t',k(t'))\rangle_{cell}\, dt', \tag{A.7}$$

where, by using the extended velocity operator v_{ext} defined in Eq. (2.9) in the main text, it turns out that the electron displacement in a position periodic system has to be evaluated as

$$\Delta\langle x\rangle = \int_t^{t+T} \langle u(t',k(t'))|\, \mathrm{v}_{ext}\,|u(t',k(t'))\rangle_{cell}\, dt'. \tag{A.8}$$

A.3 Explicit calculation of $\langle \mathrm{C}\rangle_n$

We calculate the electrons' circulation operator expectation value $\langle\mathrm{C}\rangle$ given by Eq. (2.15) of the main text with respect to a Bloch eigenstate $|\Psi_n(t,\mathbf{k})\rangle = \frac{1}{\sqrt{N}} e^{-\frac{i}{\hbar}E_n(\mathbf{k})t} e^{i\mathbf{k}.\mathbf{r}} |u_n(\mathbf{k})\rangle$ that satisfies PBSs over the edges. For simplicity we assume a 2D system while the generalization to 3D is straightforward. The system has length $L_x = N_x\alpha_x$ in the x direction and $L_y = N_y\alpha_y$ in the normal y direction, where $N = N_xN_y$ is the total number of primitive cells within the system and $\alpha_x\alpha_y$ is the area of the primitive cell. The Bloch eigenstate is normalized within the area L_xL_y, therefore a normalization constant is assumed to be absorbed within the cell periodic states, $\langle\Psi_n(\mathbf{k})|\Psi_n(\mathbf{k})\rangle = \langle u_n(\mathbf{k})|u_n(\mathbf{k})\rangle_{cell} = 1$. The electrons' circulation is given by

$$\langle\Psi_n(\mathbf{k})|\,\mathbf{C}\,|\Psi_n(\mathbf{k})\rangle = \frac{1}{N_xN_y}\int_0^{N_x\alpha_x}\int_0^{N_y\alpha_y} \mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dxdy \tag{A.9}$$

where the local probability current density, is evaluated with respect to the cell periodic eigenstate $u_n(\mathbf{r},\mathbf{k})$ and is a cell-periodic quantity. We first carry out the integral $\frac{1}{N_y}\int_0^{N_y\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy$, where we exploit the periodicity of the local probability current density and "transfer" (N_y-1) primitives cells along the y direction on the $y=0$ line which gives

$$\begin{aligned}
&\frac{1}{N_y}\int_0^{N_y\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy \\
&\quad=\int_0^{\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy+\frac{1}{N_y}\left(1+2+...+(N_y-1)\right)\boldsymbol{\alpha}_y\times\int_0^{\alpha_y}\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy \\
&\quad=\int_0^{\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy+\frac{1}{N_y}N_y\frac{(N_y-1)}{2}\boldsymbol{\alpha}_y\times\int_0^{\alpha_y}\mathbf{J}_{pr(n)}(x,y,\mathbf{k})dy.
\end{aligned}$$

Exploiting the periodicity of the local probability current, we perform analogous calculation for the integral along the x direction which gives

$$\begin{aligned}
\frac{1}{N_xN_y}\int_0^{N_x\alpha_x}dx\left(\int_0^{N_\psi\alpha_\psi}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,\psi,\mathbf{k})dy\right)&=\int_0^{\alpha_x}\int_0^{\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(x,y,\mathbf{k})\,dxdy \\
&+\left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x+\frac{(N_y-1)}{2}\boldsymbol{\alpha}_y\right)\times\int_0^{\alpha_x}\int_0^{\alpha_y}\mathbf{J}_{pr(n)}(x,y,\mathbf{k})\,dxdy.
\end{aligned}\tag{A.10}$$

Eq. (A.9) with the aid of Eq. (A.10) finally takes the form

$$\begin{aligned}
\langle\Psi_n(\mathbf{k})|\,\mathbf{C}\,|\Psi_n(\mathbf{k})\rangle&=\int_0^{\alpha_x}\int_0^{\alpha_y}\mathbf{r}\times\mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})dxdy \\
&+\left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x+\frac{(N_y-1)}{2}\boldsymbol{\alpha}_y\right)\times\int_0^{\alpha_x}\int_0^{\alpha_y}\mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})dxdy
\end{aligned}\tag{A.11}$$

where all space integrals are taken within one primitive cell adjacent to a system's edge and located at the position origin. The first term on the right hand side of Eq. (A.11) is always a well-defined quantity even in the thermodynamic limit. Therefore, in the thermodynamic limit the electrons' circulation becomes infinite due to the second term of the right hand side of Eq. (A.11.)

A.4 Explicit calculation of $\langle\mathbf{C}_{intr}\rangle_n$

We calculate the electrons' intrinsic circulation $\langle\mathbf{C}_{intr}\rangle$ given by Eq. (2.16) of the main text with respect to a Bloch eigenstate $|\Psi_n(t,\mathbf{k})\rangle=\frac{1}{\sqrt{N}}e^{-\frac{i}{\hbar}E_n(\mathbf{k})t}e^{i\mathbf{k}.\mathbf{r}}|u_n(\mathbf{k})\rangle$ in a 2D

system identical to the one of the previous subsection. Therefore, we have to calculate

$$\langle \Psi_n(\mathbf{k})| \mathbf{C}_{intr} |\Psi_n(\mathbf{k})\rangle_n = \frac{1}{N_x N_y}\int_0^{N_x\alpha_x}\int_0^{N_y\alpha_y} \mathbf{r}\times \mathbf{J}_{pr(n)}(x,y,\mathbf{k})dxdy - \langle \mathbf{r}\rangle_n \times \frac{1}{N_x N_y}\int_0^{N_x\alpha_x}\int_0^{N_y\alpha_y} \mathbf{J}_{pr(n)}(x,y,\mathbf{k})dxdy.$$

The first term of the right hand side of Eq. (A.12) is given by Eq. (A.11). The electrons' position expectation value $\langle \mathbf{r}\rangle_n$ is given by the 2D generalization of Eq. (A.2), that is,

$$\langle \mathbf{r}\rangle_n = \left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x + \frac{(N_y-1)}{2}\boldsymbol{\alpha}_y\right) + \langle u_n(\mathbf{k})| \mathbf{r} |u_n(\mathbf{k})\rangle_{cell} \tag{A.12}$$

and the space integral of the local probability current density is easily truncated within one primitive cell adjacent to a system's edge (located at the position origin) due to the cell periodicity of the probability current, thus giving

$$\frac{1}{N_x N_y}\int_0^{N_x\alpha_x}\int_0^{N_y\alpha_y} \mathbf{J}_{pr(n)}(x,y,\mathbf{k})\, dxdy = \int_0^{\alpha_x}\int_0^{\alpha_y} \mathbf{J}_{pr(n)}(x,y,\mathbf{k})\, dxdy$$

Substituting Eq. (A.11) and Eq. (A.12) – (A.13) into Eq. (A.12) we finally obtain

$$\langle \Psi_n(\mathbf{k})| \mathbf{C}_{intr} |\Psi_n(\mathbf{k})\rangle = \int_0^{\alpha_x}\int_0^{\alpha_y} (\mathbf{r} - \langle u_n(\mathbf{k})| \mathbf{r} |u_n(\mathbf{k})\rangle_{cell}) \times \mathbf{J}_{pr(n)}(x,y,\mathbf{k})dxdy \tag{A.13}$$

where the two terms $\pm\left(\frac{(N_x-1)}{2}\boldsymbol{\alpha}_x + \frac{(N_y-1)}{2}\boldsymbol{\alpha}_y\right) \times \int_0^{\alpha_x}\int_0^{\alpha_y} \mathbf{J}_{pr(n)}(\mathbf{r},\mathbf{k})dxdy$, each one undefined in the thermodynamic limit,have canceled each other.

Appendix B

Action of the velocity operator $\mathbf{v}$ on a Bloch eigenstate, and of the operator $\left(\mathbf{r} - \langle \mathbf{r} \rangle_n\right)$ on a cell periodic state

B.1 Action of $\mathbf{v}$ on a Bloch eigenstate $|\Psi_n(t,\mathbf{k})\rangle$

At first we derive a general $\mathbf{k}$-derivative formula that gives the action of the standard velocity operator Eq. (2.2) on a Bloch type state of the form $|\Psi(t,\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\,|\Phi(t,\mathbf{k})\rangle$, where $\mathbf{k}$ is a static wave vector (assumed to take continuous values). This is accomplished by taking into account the specific Bloch type form of the state $|\Psi(t,\mathbf{k})\rangle$ as well as the time evolution of the state by $i\hbar\dfrac{d}{dt}\,|\Psi(t,\mathbf{k})\rangle = H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle$, that is governed by a static Hamiltonian $H(\mathbf{r})$.

Under these conditions, the action of the position operator on the state $|\Psi(t,\mathbf{k})\rangle$ can be expressed as

$$\mathbf{r}\,|\Psi(t,\mathbf{k})\rangle = -i\,|\partial_{\mathbf{k}}\Psi(t,\mathbf{k})\rangle + ie^{i\mathbf{k}.\mathbf{r}}\,|\partial_{\mathbf{k}}\Phi(t,\mathbf{k})\rangle\,. \tag{B.1}$$

Acting on both sides of Eq. (B.1) with the Hamiltonian $H(\mathbf{r})$ of the system, and taking into account that the Hamiltonian does not depended on the wavevector, that is $[H(\mathbf{r}),\partial_{\mathbf{k}}] = 0$, we find

$$H(\mathbf{r})\mathbf{r}\,|\Psi(t,\mathbf{k})\rangle = -i\partial_{\mathbf{k}}\left(H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle\right) + ie^{i\mathbf{k}.\mathbf{r}}H_k(\mathbf{r},\mathbf{k})\,|\partial_{\mathbf{k}}\Phi(t,\mathbf{k})\rangle \tag{B.2}$$

where the Hamiltonian $H_k(\mathbf{r},\mathbf{k})$ is defined by $H_k(\mathbf{r},\mathbf{k}) = e^{-i\mathbf{k}.\mathbf{r}}H(\mathbf{r})e^{i\mathbf{k}.\mathbf{r}}$. The term $\partial_{\mathbf{k}}\left(H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle\right)$ of the right hand side of Eq. (B.2) can be recast in the form

$$\partial_{\mathbf{k}}\left(H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle\right) = i\,\mathbf{r}\,H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle + e^{i\mathbf{k}.\mathbf{r}}\,i\hbar\frac{d}{dt}\,|\partial_{\mathbf{k}}\Phi(t,\mathbf{k})\rangle \tag{B.3}$$

where we have used

$$H(\mathbf{r})\,|\Psi(t,\mathbf{k})\rangle = i\hbar\frac{d}{dt}\,|\Psi(t,\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\,i\hbar\frac{d}{dt}\,|\Phi(t,\mathbf{k})\rangle\,,$$

as well as

$$\partial_{\mathbf{k}}\left(e^{i\mathbf{k}.\mathbf{r}}\, i\hbar\frac{d}{dt}\left|\Phi(t,\mathbf{k})\right\rangle\right) = -\hbar\, e^{i\mathbf{k}.\mathbf{r}}\mathbf{r}\frac{d}{dt}\left|\Phi(t,\mathbf{k})\right\rangle + e^{i\mathbf{k}.\mathbf{r}}\, i\hbar\frac{d}{dt}\left|\partial_{\mathbf{k}}\Phi(t,\mathbf{k})\right\rangle$$

and

$$-\hbar e^{i\mathbf{k}.\mathbf{r}}\mathbf{r}\frac{d}{dt}\left|\Phi(t,\mathbf{k})\right\rangle = \mathbf{r}\, i^2\hbar\frac{d}{dt}\left(e^{i\mathbf{k}.\mathbf{r}}\left|\Phi(t,\mathbf{k})\right\rangle\right) = i\,\mathbf{r}\,H(\mathbf{r})\left|\Psi(t,\mathbf{k})\right\rangle.$$

Substituting Eq. (B.3) into Eq. (B.2) we find that the action of commutator $[H(\mathbf{r}),\mathbf{r}]$ on the Bloch type state $|\Psi(t,\mathbf{k})\rangle$ is given by

$$[H(\mathbf{r}),\mathbf{r}]\left|\Psi(t,\mathbf{k})\right\rangle = i\, e^{i\mathbf{k}.\mathbf{r}}\left(H_k(\mathbf{r},\mathbf{k}) - i\hbar\frac{d}{dt}\right)\left|\partial_{\mathbf{k}}\Phi(t,\mathbf{k})\right\rangle. \tag{B.4}$$

The action of the commutator on a stationary Bloch type state of the form $|\Psi_n(t,\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\, e^{i\Theta_n(t,\mathbf{k})}\left|u_n(\mathbf{k})\right\rangle$ where $\Theta_n(t,\mathbf{k})$ is the dynamical phase with an additional k-dependent gauge phase, that is, $\Theta_n(t,\mathbf{k}) = -\frac{1}{\hbar}E_n(\mathbf{k})t + \Lambda_n(\mathbf{k})$ can be calculated by replacing $|\Phi(t,\mathbf{k})\rangle = e^{i\Theta_n(t,\mathbf{k})}\left|u_n(\mathbf{k})\right\rangle$ within Eq. (B.4). This gives

$$\begin{aligned}[H(\mathbf{r}),\mathbf{r}]\left|\Psi_n(t,\mathbf{k})\right\rangle &= i\, e^{i\mathbf{k}.\mathbf{r}}e^{i\Theta_n(t,\mathbf{k})}\left(H_k(\mathbf{r},\mathbf{k}) + \hbar\frac{d}{dt}\Theta_n(t,\mathbf{k})\right)\left|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle \\ &\quad + i\hbar\left(\partial_{\mathbf{k}}\frac{d}{dt}\Theta_n(t,\mathbf{k})\right)\left|\Psi_n(t,\mathbf{k})\right\rangle \end{aligned}\tag{B.5}$$

where we have used that $\frac{d}{dt}\left|u_n(\mathbf{k})\right\rangle = 0$, as well as $\left(H_k(\mathbf{r},\mathbf{k}) + \hbar\frac{d}{dt}\Theta_n(t,\mathbf{k})\right)\left|u_n(\mathbf{k})\right\rangle = 0$. From Eq. (B.5) we can deduce that the action of the standard velocity operator $\mathbf{v}$ on a stationary Bloch type state is given from

$$\mathbf{v}\left|\Psi_n(t,\mathbf{k})\right\rangle = -\frac{1}{\hbar}\, e^{i\mathbf{k}.\mathbf{r}}e^{i\Theta_n(t,\mathbf{k})}\left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\right)\left|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle + \frac{1}{\hbar}\partial_{\mathbf{k}}E_n(\mathbf{k})\left|\Psi_n(t,\mathbf{k})\right\rangle. \tag{B.6}$$

B.2 Action of $(\mathbf{r} - \langle\mathbf{r}\rangle)$ on a cell-periodic eigenstate $|u_n(\mathbf{k})\rangle$

We assume a Bloch type eigenstate in the form $|\Psi_n(t,\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\, e^{i\Theta_n(t,\mathbf{k})}\left|u_n(\mathbf{k})\right\rangle$ where $\Theta_n(t,\mathbf{k})$ is the dynamical phase with an additional k-dependent gauge phase, that is, $\Theta_n(t,\mathbf{k}) = -\frac{1}{\hbar}E_n(\mathbf{k})t + \Lambda(\mathbf{k})$. The time-independent eigenstate $|u_n(\mathbf{k})\rangle$ can be recast in the form

$$\left|u_n(\mathbf{k})\right\rangle = e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\left|\Psi_n(\mathbf{k})\right\rangle \tag{B.7}$$

where the time-dependence has been eliminated as expected.

In the position representation and by using Eq. (B.7), the action of the position operator on the eigenstate $|u_n(\mathbf{k})\rangle$ can be transformed to a k-derivative identity given by

$$\mathbf{r}\left|u_n(\mathbf{k})\right\rangle = i\left|\partial_{\mathbf{k}}u_n(\mathbf{k})\right\rangle - \partial_{\mathbf{k}}\Lambda(\mathbf{k})\left|u_n(\mathbf{k})\right\rangle - i\, e^{-i\mathbf{k}.\mathbf{r}}\, e^{-i\Lambda(\mathbf{k})}\left|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\right\rangle. \tag{B.8}$$

Accordingly, the expectation value of the position operator $\mathbf{r}$ with respect to the eigenstate $|u_n(\mathbf{k})\rangle$ takes with the aid of Eq. (B.8) the form

$$\langle u_n(\mathbf{k})|\,\mathbf{r}\,|u_n(\mathbf{k})\rangle = \mathbf{A}_{nn}(\mathbf{k}) - \partial_{\mathbf{k}}\Lambda_n(\mathbf{k}) - i\,\langle \Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,, \tag{B.9}$$

where $\mathbf{A}_{nn}(\mathbf{k}) = i\,\langle u_n(\mathbf{k})|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle$ is the Abelian Berry connection. By acting with Eq. (B.9) on $|u_n(\mathbf{k})\rangle$ and then subtracting the product from Eq. (B.8) we find the identity

$$\begin{aligned}(\,\mathbf{r} - \langle\mathbf{r}\rangle_n)\,|u_n(\mathbf{k})\rangle \;\;=\;\; & (\,i\partial_{\mathbf{k}} - \mathbf{A}_{nn}(\mathbf{k}))\,|u_n(\mathbf{k})\rangle \\ & - i\,e^{-i\mathbf{k}.\mathbf{r}}\,e^{-i\Lambda(\mathbf{k})}\,(\,|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle - \langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,|\Psi_n(\mathbf{k})\rangle\,)\,.\end{aligned} \tag{B.10}$$

By then using the one-band covariant derivative definition, that is,

$$i\widetilde{\partial}_{\mathbf{k}}\,|u_n(\mathbf{k})\rangle = (\,i\partial_{\mathbf{k}} - \mathbf{A}_{nn}(\mathbf{k}))|u_n(\mathbf{k})\rangle\,,$$

where $\widetilde{\partial}_{\mathbf{k}}$ is given by $\widetilde{\partial}_{\mathbf{k}} = (\,1 - |u_n(\mathbf{k})\rangle\langle u_n(\mathbf{k})|\,)\,\partial_{\mathbf{k}}$, Eq. (B.10) takes the form

$$(\,\mathbf{r} - \langle\mathbf{r}\rangle_n)\,|u_n(\mathbf{k})\rangle = i\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle - ie^{-i\mathbf{k}.\mathbf{r}}\,e^{-i\Lambda(\mathbf{k})}\,|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle + i\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,|u_n(\mathbf{k})\rangle\,. \tag{B.11}$$

We then expand the state $|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle$ on the complete basis of the Bloch eigenstates $|\psi_m(\mathbf{k}')\rangle$ using the closure relation $I = \sum_m^{\text{HS}} \iiint_{BZ} d^3k'\,|\psi_m(\mathbf{k}')\rangle\,\langle\psi_m(\mathbf{k}')|$, that is

$$|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle = \sum_m^{\text{HS}} \iiint_{BZ} d^3k'\,\langle\psi_m(\mathbf{k}')|\partial_{\mathbf{k}}\psi_n(\mathbf{k})\rangle\,|\psi_m(\mathbf{k}')\rangle\,,$$

which gives

$$\begin{aligned}(\,\mathbf{r} - \langle\mathbf{r}\rangle_n)\,|u_n(\mathbf{k})\rangle = {} & i\left|\widetilde{\partial}_{\mathbf{k}}u_n(\mathbf{k})\right\rangle \\ & -i\sum_m^{\text{HS}} \iiint_{BZ} d^3k'\,\langle\psi_m(\mathbf{k}')|\partial_{\mathbf{k}}\psi_n(\mathbf{k})\rangle\;e^{i(\Lambda(\mathbf{k}') - \Lambda(\mathbf{k}))}e^{i(\mathbf{k}' - \mathbf{k}).\mathbf{r}}\;|u_m(\mathbf{k}')\rangle \\ & +i\,\langle\Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle\,|u_n(\mathbf{k})\rangle\,.\end{aligned}$$

and then use the Hermitian conjugate of Eq. (B.12) to evaluate the orbital magnetic moment of the electron, that is

$$\mathbf{m}_n(\mathbf{k}) = -\frac{e}{2c\hbar}\text{Im}[\,i\,\langle u_n(\mathbf{k})|\,(\mathbf{r} - \langle\mathbf{r}\rangle_n)\;\times\;(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k}))\,|\partial_{\mathbf{k}}u_n(\mathbf{k})\rangle\,]. \tag{B.12}$$

This way Eq. (B.12) takes the form

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) &= -\frac{e}{2c\hbar}\mathrm{Im}[\left\langle \widetilde{\partial}_{\mathbf{k}} u_n(\mathbf{k})\right| \times \left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\right)\left|\partial_{\mathbf{k}} u_n(\mathbf{k})\right\rangle] \\ &+\frac{e}{2c\hbar}\mathrm{Im}[\sum_m^{\mathrm{HS}} \iiint_{BZ} d^3k'\, e^{i(\Lambda(\mathbf{k})-\Lambda(\mathbf{k}'))}\, \langle \Psi_m(\mathbf{k}')|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle^* \\ &\times \left\langle u_m(\mathbf{k})\right| e^{i(\mathbf{k}-\mathbf{k}').\mathbf{r}}\left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\left|\partial_{\mathbf{k}} u_n(\mathbf{k})\right\rangle\right] \\ &-\frac{e}{2c\hbar}\mathrm{Im}[\langle \Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_n(\mathbf{k})\rangle^* \times \langle u_n(\mathbf{k})|\, H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle\,].\end{aligned}$$

Assuming then that the states, $\partial_{\mathbf{k}} u_n(\mathbf{r},\mathbf{k})$ as well as $u_m(\mathbf{r},\mathbf{k})$ and the Hamiltonian $H_k(\mathbf{r},\mathbf{k})$, are periodic in space within the material, then, Eq. (B.13) takes the form

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) &= -\frac{e}{2c\hbar}\mathrm{Im}[\left\langle \widetilde{\partial}_{\mathbf{k}} u_n(\mathbf{k})\right| \times \left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\right)\left|\partial_{\mathbf{k}} u_n(\mathbf{k})\right\rangle] \\ &+\frac{e}{2c\hbar}\mathrm{Im}[\sum_m^{\mathrm{HS}} \iiint_{BZ} d^3k'\, e^{i(\Lambda(\mathbf{k})-\Lambda(\mathbf{k}'))}\, \langle \partial_{\mathbf{k}}\Psi_n(\mathbf{k})|\Psi_m(\mathbf{k}')\rangle \\ &\times \delta(\mathbf{k}-\mathbf{k}')\,\langle u_m(\mathbf{k})|\left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle\right] \\ &-\frac{e}{2c\hbar}\mathrm{Im}\left[\langle \partial_{\mathbf{k}}\Psi_n(\mathbf{k})|\Psi_n(\mathbf{k})\rangle \times \langle u_n(\mathbf{k})|\, H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle\right].\end{aligned} \tag{B.13}$$

which finally gives

$$\begin{aligned}\mathbf{m}_n(\mathbf{k}) &= -\frac{e}{2c\hbar}\mathrm{Im}\left[\left\langle \widetilde{\partial}_{\mathbf{k}} u_n(\mathbf{k})\right| \times \left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\right)\left|\partial_{\mathbf{k}} u_n(\mathbf{k})\right\rangle\right] \\ &-\frac{e}{2c\hbar}\mathrm{Im}\left[\sum_{m\neq n}^{\mathrm{HS}} \langle \Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle \times \langle u_m(\mathbf{k})|\left(H_k(\mathbf{r},\mathbf{k}) - E_n(\mathbf{k})\,|\partial_{\mathbf{k}} u_n(\mathbf{k})\rangle\right]\end{aligned} \tag{B.14}$$

where we have used $\langle \partial_{\mathbf{k}}\Psi_n(\mathbf{k})|\Psi_m(\mathbf{k})\rangle = -\langle \Psi_n(\mathbf{k})|\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\rangle$ that is valid due to $m \neq n$. Eq. (B.14) is Eq. (4.31) of the main text. As a final step, we find an expression for $\langle \psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle$, provided that $n \neq m$, and then replace it in the sum of Eq. (B.14). This is accomplished by the off-diagonal Hellmann-Feynman theorem that we derive in the Appendix C.

Appendix C

Off-diagonal Hellmann-Feynman theorem and the matrix elements $\langle\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle$

We develop an off-diagonal Hellmann-Feynman theorem by starting from the eigenvalue equation

$$\left(H(\mathbf{r}) - E_m(\mathbf{k})\right)\,|\psi_m(\mathbf{k})\rangle = 0. \tag{C.1}$$

where $H(\mathbf{r})$ is the initial system's Hamiltonian. Specifically, for the purpose of calculations of this work, we use the initial Hamiltonian of the system which does not depend on the wavevector $\mathbf{k}$, that is, $\partial_{\mathbf{k}}H(\mathbf{r}) = 0$. The result that we derive, is easily extended to include a Hamiltonian that has explicit parameter dependence by simply adding to it the term that has the derivative of the Hamiltonian with respect to the parameter.

By assuming that the crystal momentum takes continuous values, we act with the momentum gradient operator $\partial_{\mathbf{k}}$ on Eq. (C.1) obtaining

$$-\,\partial_{\mathbf{k}}E_n(\mathbf{k})\,|\psi_m(\mathbf{k})\rangle \;+\; \left(H(\mathbf{r}) - E_n(\mathbf{k})\right)|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle = 0. \tag{C.2}$$

and then take the inner product of Eq. (C.2) with $\langle\psi_n(\mathbf{k})|$ which gives

$$-\,\partial_{\mathbf{k}}E_n(\mathbf{k})\delta_{nm} \;+\; \langle\psi_n(\mathbf{k})|\left(H(\mathbf{r}) - E_n(\mathbf{k})\right)|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle = 0. \tag{C.3}$$

We now take into account a possible anomaly of the momentum gradient operator due to the non-Hermitian effect, that emerges whenever the gradient operator $\partial_{\mathbf{k}}$ breaks the domain of definition D_H of the Hamiltonian $H(\mathbf{r})$. In this framework, the wavefunctions $\psi_m(\mathbf{r},\mathbf{k})$ and $\partial_{\mathbf{k}}\psi_m(\mathbf{r},\mathbf{k})$ fulfill different boundary conditions over the edges of the system, and as a result they don't belong within the same domain of definition, that is, $\psi_m(\mathbf{r},\mathbf{k}) \in D_H$ while $\partial_{\mathbf{k}}\psi_m(\mathbf{r},\mathbf{k}) \notin D_H$. Therefore, whenever the non-Hermitian effect emerges, the term $\langle\psi_n(\mathbf{k})|\left(H(\mathbf{r}) - E_m(\mathbf{k})\right)|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle$ entering Eq. (C.3) is not zero as a result of the follow-

ing non-trivial inequality

$$\begin{aligned}\langle H_k(\mathbf{r},\mathbf{k})\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle &= \big\langle\psi_n(\mathbf{k})|H_k(\mathbf{r},\mathbf{k})^{+}\partial_{\mathbf{k}}\psi_m(\mathbf{k})\big\rangle \\ &\neq \langle\psi_n(\mathbf{k})|H_k(\mathbf{r},\mathbf{k})\,\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle\,.\end{aligned}$$

We treat this non-Hermitian effect by expressing the term $\langle\psi_n(\mathbf{k})|H(\mathbf{r})\,\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle$ as

$$\langle\psi_n(\mathbf{k})|H(\mathbf{r})\,\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle = \langle H(\mathbf{r})\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle - \mathbf{S}_{nm}(\mathbf{k}) \tag{C.4}$$

where the $\mathbf{S}_{nm}(\mathbf{k})$ term represents the non-Hermitian effect and is a boundary quantity. Its explicit boundary integral form is given below. In this respect, by taking into account Eq. (C.4), Eq. (C.3) takes the form

$$\partial_{\mathbf{k}}E_n(\mathbf{k})\,\delta_{nm} = (E_n(\mathbf{k}) - E_m(\mathbf{k}))\,\langle\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle - \mathbf{S}_{nm}(\mathbf{k}), \tag{C.5}$$

which for $n \neq m$ gives $\langle\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle$ as a function of $\mathbf{S}_{nm}(\mathbf{k})$, given by

$$\langle\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_m(\mathbf{k})\rangle = \frac{\mathbf{S}_{nm}(\mathbf{k})}{(E_n(\mathbf{k}) - E_m(\mathbf{k}))}. \tag{C.6}$$

We now give the explicit integral form of $\mathbf{S}_{nm}(\mathbf{k})$. Specifically, (i) by using Eq. (C.4) as the definition of the $\mathbf{S}_{nm}(\mathbf{k})$, (ii) by working in the position representation, and (iii) after an integration by parts (assuming a 3D system), the matrix elements of the non-Hermitian term $\mathbf{S}_{nm}(\mathbf{k})$ are always transformed, due to symmetry of the integrands, into a boundary quantity that is given by

$$\mathbf{S}_{nm}(\mathbf{k}) = \frac{i\hbar}{2}\oiint_S \mathbf{n}\cdot\big(\,(\mathbf{v}\,\psi_n)^* + \psi_n^*\,\mathbf{v}\,\big)\,\partial_{\mathbf{k}}\psi_m\,dS, \tag{C.7}$$

where $\psi_m = \psi_m(\mathbf{r},\mathbf{k})$ are the Bloch eigenfunctions, $\mathbf{v}$ is the standard velocity operator and $\mathbf{n}$ is the unit vector that is locally normal to the surface S. The corresponding abstract form of $\mathbf{S}_{nm}(\mathbf{k})$ is given by

$$\mathbf{S}_{nm}(\mathbf{k}) = \big\langle\Psi_n(\mathbf{k})|\,\big(H(\mathbf{r})^{+} - H(\mathbf{r})\,\big)\,\partial_{\mathbf{k}}\Psi_m(\mathbf{k})\big\rangle\,.$$

It is now intuitively useful to give the extension of Eq. (C.5) to the one that includes the explicit dependence of the Hamiltonian on a static parameter, in order to show the necessity of a non-Hermitian boundary term that solves a "paradox" concerning the band theory. First we present the "paradox" and then we show how this is resolved by taking into account the non-Hermitian term $\mathbf{S}_{nm}(\mathbf{k})$. When one uses the cell periodic eigenstates and applies the Hellmann-Feynman theorem into the equation $\langle u_n(\mathbf{k})|\,H_k(\mathbf{r},\mathbf{k})|u_n(\mathbf{k})\rangle = E_n(\mathbf{k})$, one finds the standard velocity expectation value with respect to the dispersion relation derivative, that is $\langle u_n(\mathbf{k})|\,\partial_{\mathbf{k}}H_k(\mathbf{r},\mathbf{k})|u_n(\mathbf{k})\rangle = \partial_{\mathbf{k}}E_n(\mathbf{k}) \neq 0$. On the other hand, if one

uses the Bloch eigenstates, that is applies the Hellmann-Feynman theorem into the equation $\langle\psi_n(\mathbf{k})|\, H(\mathbf{r})|\psi_n(\mathbf{k})\rangle = E_n(\mathbf{k})$, one deduces that $\partial_{\mathbf{k}} E_n(\mathbf{k}) = 0$. These sorts of subtleties are attributed to non-Hermitian boundary terms that are not properly taken into account. Specifically, by assuming a Hamiltonian $H(\mathbf{r}, \mathbf{R})$, where $\mathbf{R}$ is a general parameter, then Eq. (C.5) takes the form

$$\begin{aligned} \partial_{\mathbf{R}} E_n(\mathbf{R})\, \delta_{nm} \;\; &= \;\; (E_n(\mathbf{R}) - E_m(\mathbf{R}))\, \langle\psi_n(\mathbf{R})|\partial_{\mathbf{R}}\psi_m(\mathbf{R})\rangle \\ &\quad + \langle\psi_n(\mathbf{R})|\, \partial_{\mathbf{R}} H(\mathbf{r}, \mathbf{R})\, |\psi_m(\mathbf{R})\rangle \, - \, \mathbf{S}_{nm}(\mathbf{R}) \end{aligned} \tag{C.8}$$

where $|\psi_n(\mathbf{R})\rangle$ are the eigenstates of the Hamiltonian. By way of an example, using the diagonal form of Eq. (C.5) and assuming $\mathbf{R} \equiv \mathbf{k}$ as well as an initial Hamiltonian $H(\mathbf{r})$ we find $\partial_{\mathbf{k}} E_n(\mathbf{k}) = -\,\mathbf{S}_{nn}(\mathbf{k})$. In this manner, one will deduce that the bands are always flat (or equivalently that the group velocity is always zero) if the non-Hermitian boundary contribution is not taken into account, which will lead to an apparent "paradox". Using now the Bloch form eigenstate $|\Psi_n(\mathbf{k})\rangle = e^{i\mathbf{k}.\mathbf{r}}\, e^{i\Lambda(\mathbf{k})}\, |u_n(\mathbf{k})\rangle$ into the boundary term $\mathbf{S}_{nn}(\mathbf{k}) = \langle H(\mathbf{r})\psi_n(\mathbf{k})|\partial_{\mathbf{k}}\psi_n(\mathbf{k})\rangle - \langle\psi_n(\mathbf{k})|H(\mathbf{r})\partial_{\mathbf{k}}\psi_n(\mathbf{k})\rangle$, as well as by taking into account Eq. (2.30) and the explicit form of the boundary velocity definition Eq. (2.3) of the main text, the relation between the boundary velocity and the standard (group) velocity for stationary states $\langle\mathbf{v}_b\rangle_n = -\,\langle\mathbf{v}\rangle_n$ is restored and the "paradox" is resolved.

Appendix D

Boundary operator expectation value

We assume a Hermitian operator $\mathbf{G}$ that may be a function of $\mathbf{G}(\mathbf{r}, \boldsymbol{\pi}, t, \boldsymbol{\sigma})$. Using a Cartesian coordinate system, the operator components are given by

$$\mathbf{G} = G_x \mathbf{e}_x + G_\psi \mathbf{e}_\psi + G_z \mathbf{e}_z. \tag{D.1}$$

In order to analytically evaluate the expectation value of the boundary operator Eq. (3.6) we need the explicit form of the Hamiltonian of the system. Therefore, we assume the Hamiltonian Eq. (3.7) which is convenient to separate into

$$H(\mathbf{r}, \mathbf{t}) = H_1(\mathbf{r}, \mathbf{t}) + H_2(\mathbf{r}, \mathbf{t}), \tag{D.2}$$

where

$$H_1(\mathbf{r}, \mathbf{t}) = \frac{1}{2m} \mathbf{\Pi}(\mathbf{r}, t)^2 + V(\mathbf{r}, t) \tag{D.3}$$

is the spinless part and

$$H_2(\mathbf{r}, \mathbf{t}) = -\frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{B}(\mathbf{r}, t) + \boldsymbol{\alpha}(\mathbf{r}, t, \boldsymbol{\sigma}) \cdot \mathbf{\Pi}(\mathbf{r}, t) \tag{D.4}$$

is the relativistic correction term. In this respect, the expectation value of the boundary operator Eq. (3.9) is given by

$$\langle \boldsymbol{\mathcal{O}}_b \rangle = \langle \boldsymbol{\mathcal{O}}_{b1} \rangle + \langle \boldsymbol{\mathcal{O}}_{b2} \rangle \tag{D.5}$$

where

$$\langle \boldsymbol{\mathcal{O}}_{b1} \rangle = \frac{i}{\hbar} \left(\langle H_1(\mathbf{r}, t) \Psi(t) | \mathbf{G} \Psi(t) \rangle - \langle \Psi(t) | H_1(\mathbf{r}, t) \mathbf{G} \Psi(t) \rangle \right) \tag{D.6}$$

is the non-Hermitian boundary contribution due to the spinless part of the Hamiltonian and

$$\langle \boldsymbol{\mathcal{O}}_{b2} \rangle = \frac{i}{\hbar} \left(\langle H_2(\mathbf{r}, t) \Psi(t) | \mathbf{G} \Psi(t) \rangle - \langle \Psi(t) | H_2(\mathbf{r}, t) \mathbf{G} \Psi(t) \rangle \right) \tag{D.7}$$

is the boundary contribution due to the relativistic correction (spin dependent) terms. In this framework we will evaluate separately Eq. (D.6) and Eq. (D.7), and then add them

to get Eq. (D.5).

Analytic calculation of $\langle \boldsymbol{\mathcal{O}}_{b1} \rangle$

By taking into account that the scalar potential that enters the Hamiltonian $H_1(\mathbf{r},t)$ is a real quantity, the expectation value of the boundary operator $\boldsymbol{\mathcal{O}}_{b1}$ is given by

$$\langle \boldsymbol{\mathcal{O}}_{b1} \rangle = \frac{i}{2m\hbar} \iiint_V \Big((\boldsymbol{\Pi}^2\Psi)^\dagger \, \mathbf{G}\Psi - \Psi^\dagger \boldsymbol{\Pi}^2 \, \mathbf{G}\Psi \Big) \, dV, \tag{D.8}$$

where $\Psi \equiv \Psi(\mathbf{r},t)$ is the two component spinor wavefunction. The x component of Eq. (D.8) is given from

$$\langle \boldsymbol{\mathcal{O}}_{b1} \rangle_x = \frac{i}{2m\hbar} \mathbf{e}_x \iiint_V \Big((\boldsymbol{\Pi}^2\Psi)^\dagger \, G_x\Psi - \Psi^\dagger \boldsymbol{\Pi}^2 \, G_x\Psi \Big) \, dV, \tag{D.9}$$

where we have make use of the constant direction of the Cartesian unit vector $\mathbf{e}_x$. Using the explicit form of the kinematic momentum operator $\boldsymbol{\Pi} = -i\hbar\nabla - \frac{e}{c}\mathbf{A}(\mathbf{r},t)$, Eq. (D.9) takes the form

$$\langle \boldsymbol{\mathcal{O}}_{b1} \rangle_x = \frac{i}{2m\hbar} \mathbf{e}_x \iiint_V \Big((-i\hbar\nabla - \frac{e}{c}\mathbf{A}) \cdot \boldsymbol{\Pi}\Psi \,)^\dagger \, G_x\Psi \; - \; \Psi^\dagger \, (-i\hbar\nabla - \frac{e}{c}\mathbf{A}) \cdot \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV \tag{D.10}$$

that leads to

$$\begin{aligned} \langle \boldsymbol{\mathcal{O}}_{b1} \rangle_x \;\; = \;\; & \frac{i}{2m\hbar} \mathbf{e}_x (i\hbar) \iiint_V \nabla \cdot \Big((\boldsymbol{\Pi}\Psi)^\dagger \, G_x\Psi \; + \; \Psi^\dagger \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV \\ & - \frac{i}{2m\hbar} \mathbf{e}_x (i\hbar) \iiint_V \Big((\boldsymbol{\Pi}\Psi)^\dagger \cdot \nabla(G_x\Psi) \; + \; \nabla\Psi^\dagger \cdot \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV \\ & - \frac{i}{2m\hbar} \mathbf{e}_x \frac{e}{c} \iiint_V \Big((\mathbf{A} \cdot \boldsymbol{\Pi}\Psi)^\dagger \, G_x\Psi \; - \; \Psi^\dagger \mathbf{A} \cdot \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV \end{aligned} \tag{D.11}$$

which gives

$$\begin{aligned} \langle \boldsymbol{\mathcal{O}}_{b1} \rangle_x \;\; = \;\; & -\frac{1}{2m} \mathbf{e}_x \oiint_S \Big((\boldsymbol{\Pi}\Psi)^\dagger \, G_x\Psi(\mathbf{r},t) + \Psi^\dagger \boldsymbol{\Pi} \, G_x\Psi \Big) \cdot d\mathbf{s} \\ & + \frac{i}{2m\hbar} \mathbf{e}_x \iiint_V \Big((\boldsymbol{\Pi}\Psi)^\dagger \cdot (-i\hbar)(\nabla G_x\Psi) \; - \; (-i\hbar\nabla\Psi)^\dagger \cdot \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV \\ & - \frac{i}{2m\hbar} \mathbf{e}_x \frac{e}{c} \iiint_V \mathbf{A} \cdot \Big((\boldsymbol{\Pi}\Psi)^\dagger \, G_x\Psi \; - \; \Psi^\dagger \boldsymbol{\Pi} \, G_x\Psi \Big) \, dV. \end{aligned} \tag{D.12}$$

Replacing now $-i\hbar\nabla = \mathbf{\Pi} + \frac{e}{c}\mathbf{A}$ in the second term of the right hand side of Eq. (D.12) we find

$$\begin{aligned}\langle \boldsymbol{\mathcal{O}}_{b1}\rangle_x &= -\frac{1}{2m}\mathbf{e}_x \oiint_S \Big((\,\mathbf{\Pi}\Psi\,)^\dagger\, G_x\Psi \,+\, \Psi^\dagger \mathbf{\Pi}\, G_x\Psi \Big)\cdot d\mathbf{s} \\ &+\frac{i}{2m\hbar}\mathbf{e}_x \iiint_V \Big((\,\mathbf{\Pi}\Psi\,)^\dagger \cdot (\mathbf{\Pi}+\frac{e}{c}\mathbf{A})(G_x\Psi) \,-\, ((\mathbf{\Pi}+\frac{e}{c}\mathbf{A})\Psi)^\dagger \cdot \mathbf{\Pi}\, G_x\Psi \Big)\, dV \\ &-\frac{i}{2m\hbar}\mathbf{e}_x\frac{e}{c} \iiint_V \mathbf{A}\cdot \Big((\,\mathbf{\Pi}\Psi\,)^\dagger\, G_x\Psi \,-\, \Psi^\dagger \mathbf{\Pi}\, G_x\Psi \Big)\, dV \end{aligned} \tag{D.13}$$

which finally gives

$$\langle \boldsymbol{\mathcal{O}}_{b1}\rangle_x = -\frac{1}{2m}\mathbf{e}_x \oiint_S \Big((\,\mathbf{\Pi}\Psi\,)^\dagger\, G_x\Psi \,+\, \Psi^\dagger \mathbf{\Pi}\, G_x\Psi \Big)\cdot d\mathbf{s}. \tag{D.14}$$

Taking now into account that $d\mathbf{s} = \mathbf{n}\, ds,$ where $\mathbf{n}$ is the unit vector that is locally normal to the surface $S,$ Eq. (D.14) can be recast in the form

$$\langle \boldsymbol{\mathcal{O}}_{b1}\rangle_x = -\frac{1}{2}\mathbf{e}_x \oiint_S \mathbf{n}\cdot \Big((\,\frac{\mathbf{\Pi}}{m}\Psi\,)^\dagger \,+\, \Psi^\dagger \frac{\mathbf{\Pi}}{m} \Big)\, G_x\Psi\, ds \tag{D.15}$$

where we have use $\mathbf{n}\cdot\nabla = n_x\frac{\partial}{\partial_x} + n_\psi\frac{\partial}{\partial_\psi} + n_z\frac{\partial}{\partial_z},$ in order to restructure the term $\Psi(\mathbf{r},t)^\dagger\,(\mathbf{\Pi}\, G_x\Psi(\mathbf{r},t)\,)\cdot d\mathbf{s}$ in the form $\mathbf{n}\cdot\big(\Psi(\mathbf{r},t)^\dagger\mathbf{\Pi}\big)\, G_x\Psi(\mathbf{r},t)\, ds.$

By adding all of the Cartesian components $\langle \boldsymbol{\mathcal{O}}_{b1}\rangle = \langle \boldsymbol{\mathcal{O}}_{b1}\rangle_x + \langle \boldsymbol{\mathcal{O}}_{b1}\rangle_\psi + \langle \boldsymbol{\mathcal{O}}_{b1}\rangle_z$ we find the form of the $\langle \boldsymbol{\mathcal{O}}_{b1}\rangle$ that is given by

$$\langle \boldsymbol{\mathcal{O}}_{b1}\rangle = -\frac{1}{2} \oiint_S \mathbf{n}\cdot \Big((\,\frac{\mathbf{\Pi}}{m}\Psi\,)^\dagger \,+\, \Psi^\dagger \frac{\mathbf{\Pi}}{m} \Big)\, \mathbf{G}\Psi\, ds \tag{D.16}$$

Analytic calculation of $\langle \boldsymbol{\mathcal{O}}_{b2}\rangle$

The expectation value of the boundary contribution $\langle \boldsymbol{\mathcal{O}}_{b2}\rangle$ does not depend on the Zeeman term; this is because each one of the Pauli matrices satisfies $\sigma_i = \sigma_i^\dagger,$ therefore, $(\boldsymbol{\sigma}\cdot\mathbf{B})^\dagger = \mathbf{B}\cdot\boldsymbol{\sigma} = \boldsymbol{\sigma}\cdot\mathbf{B},$ which leads to the zero contribution

$$\begin{aligned}\frac{i}{\hbar}\langle\Psi(t)|\,\big({H_Z}^+ - H_Z\big)\mathbf{G}\,|\Psi(t)\rangle &= -\frac{ie}{2mc}\iiint_V \Big(\,((\boldsymbol{\sigma}\cdot\mathbf{B})\Psi)^\dagger\, \mathbf{G}\Psi \,-\, \Psi^\dagger\,(\boldsymbol{\sigma}\cdot\mathbf{B})\mathbf{G}\Psi\Big)\, dV \\ &= -\frac{ie}{2mc}\iiint_V \Big(\Psi^\dagger \Big((\boldsymbol{\sigma}\cdot\mathbf{B}) - (\boldsymbol{\sigma}\cdot\mathbf{B})\Big)\, \mathbf{G}\Psi\Big)\, dV = 0.\end{aligned}$$

In this respect Eq. (D.7) is given from $\langle \boldsymbol{\mathcal{O}}_{b2}\rangle = \frac{i}{\hbar}\langle\Psi(t)|\,\big({H_{S.O}}^+ - H_{S.O}\big)\mathbf{G}\,|\Psi(t)\rangle$ and the x component of it by

$$\langle \boldsymbol{\mathcal{O}}_{b2}\rangle_x = \frac{i}{\hbar}\mathbf{e}_x \iiint_V \Big(\,(\boldsymbol{\alpha}\cdot\mathbf{\Pi}\,\Psi)^\dagger\, G_x\Psi \,-\, \Psi^\dagger\, \boldsymbol{\alpha}\cdot\mathbf{\Pi}\, G_x\Psi\Big)\, dV. \tag{D.17}$$

Using $\boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})^\dagger = \boldsymbol{\alpha}(\mathbf{r},t,\boldsymbol{\sigma})$ that gives $(\boldsymbol{\alpha}\,\Psi(\mathbf{r},t))^\dagger = \Psi(\mathbf{r},t)^\dagger\,\boldsymbol{\alpha}$, as well as $\boldsymbol{\alpha}\cdot\boldsymbol{\Pi} = \boldsymbol{\Pi}\cdot\boldsymbol{\alpha} + i\hbar(\nabla\cdot\boldsymbol{\alpha})$,
and the following properties:

$$\begin{aligned}
(\boldsymbol{\alpha}\cdot\boldsymbol{\Pi}\,\Psi)^\dagger &= (\boldsymbol{\Pi}\cdot\boldsymbol{\alpha}\,\Psi)^\dagger \,+\, (\,i\hbar(\nabla\cdot\boldsymbol{\alpha})\,\Psi)^\dagger \\
&= +i\hbar\left(\nabla\cdot(\boldsymbol{\alpha}\,\Psi)^\dagger\right) \,-\, \frac{e}{c}\mathbf{A}\cdot(\boldsymbol{\alpha}\,\Psi)^\dagger \,-\, i\hbar\,\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha}) \\
&= +i\hbar\left(\nabla\cdot(\Psi^\dagger\boldsymbol{\alpha})\right) \,-\, \frac{e}{c}\mathbf{A}\cdot(\Psi^\dagger\boldsymbol{\alpha}) \,-\, i\hbar\,\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha}) \\
&= +i\hbar\nabla\Psi(\mathbf{r},t)^\dagger\cdot\boldsymbol{\alpha} \,+\, i\hbar\,\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha}) \,-\, \frac{e}{c}\mathbf{A}\cdot(\Psi^\dagger\boldsymbol{\alpha}) \,-\, i\hbar\,\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha}) \\
&= +i\hbar\nabla\Psi^\dagger\cdot\boldsymbol{\alpha} \,-\, \frac{e}{c}\Psi^\dagger\,\mathbf{A}\cdot\boldsymbol{\alpha}
\end{aligned} \tag{D.18}$$

together with

$$\begin{aligned}
\boldsymbol{\alpha}\cdot\boldsymbol{\Pi}\,G_x\Psi &= \boldsymbol{\Pi}\cdot\boldsymbol{\alpha}\,G_x\Psi \,+\, i\hbar(\nabla\cdot\boldsymbol{\alpha})\,G_x\Psi \\
&= -i\hbar\nabla\cdot(\boldsymbol{\alpha}\,G_x\,\Psi) \,-\, \frac{e}{c}\mathbf{A}\cdot(\boldsymbol{\alpha}\,G_x\,\Psi) \,+\, i\hbar(\nabla\cdot\boldsymbol{\alpha})\,G_x\,\Psi,
\end{aligned} \tag{D.19}$$

we find

$$\begin{aligned}
\langle\boldsymbol{\mathcal{O}}_{b2}\rangle_x &= \frac{i}{\hbar}\mathbf{e}_x\iiint_V\left(\,i\hbar\nabla\Psi^\dagger\cdot\boldsymbol{\alpha}\,G_x\Psi \,-\, \frac{e}{c}\Psi^\dagger\,\mathbf{A}\cdot\boldsymbol{\alpha}\,G_x\Psi\right)dV \\
&- \frac{i}{\hbar}\mathbf{e}_x\iiint_V\left(-i\hbar\Psi^\dagger\,\nabla\cdot(\boldsymbol{\alpha}\,G_x\,\Psi) \,-\, \frac{e}{c}\Psi^\dagger\,\mathbf{A}\cdot(\boldsymbol{\alpha}\,G_x\,\Psi) \,+\, i\hbar\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha})\,G_x\,\Psi\right)dV \\
&= \frac{i}{\hbar}\mathbf{e}_x(i\hbar)\iiint_V\nabla\cdot\left(\Psi^\dagger\,\boldsymbol{\alpha}\,G_x\Psi\right)dV \,-\, \frac{i}{\hbar}\mathbf{e}_x(i\hbar)\iiint_V\Psi^\dagger\,(\nabla\cdot\boldsymbol{\alpha})\,G_x\,\Psi dV \\
&= -\mathbf{e}_x\oiint_S\left(\Psi^\dagger\,\boldsymbol{\alpha}\,G_x\Psi\right)\cdot d\mathbf{s}
\end{aligned} \tag{D.20}$$

where we have used

$$\nabla\cdot\boldsymbol{\alpha} = \frac{\hbar}{4m^2c^2}\nabla\cdot(\boldsymbol{\sigma}\times\nabla V(\mathbf{r},t)) = \frac{\hbar}{4m^2c^2}\left(\,\nabla V(\mathbf{r},t)\cdot(\nabla\times\boldsymbol{\sigma}) - \boldsymbol{\sigma}\cdot(\nabla\times\nabla V(\mathbf{r},t))\,\right) = 0.$$

By adding all of the Cartesian components $\langle\boldsymbol{\mathcal{O}}_{b2}\rangle = \langle\boldsymbol{\mathcal{O}}_{b2}\rangle_x + \langle\boldsymbol{\mathcal{O}}_{b2}\rangle_\psi + \langle\boldsymbol{\mathcal{O}}_{b2}\rangle_z$ we find the form of the $\langle\boldsymbol{\mathcal{O}}_{b2}\rangle$ that is given by

$$\langle\boldsymbol{\mathcal{O}}_{b2}\rangle = -\oiint_S\mathbf{n}\cdot(\Psi^\dagger\,\boldsymbol{\alpha})\,\mathbf{G}\Psi ds. \tag{D.21}$$

Using $(\boldsymbol{\alpha}\,\Psi(\mathbf{r},t))^\dagger = \Psi(\mathbf{r},t)^\dagger\,\boldsymbol{\alpha}$ in Eq. (D.21) we restructure it in the symmetrical form

$$\langle\boldsymbol{\mathcal{O}}_{b2}\rangle = -\frac{1}{2}\oiint_S\mathbf{n}\cdot\left((\boldsymbol{\alpha}\Psi)^\dagger \,+\, \Psi^\dagger\boldsymbol{\alpha}\right)\,\mathbf{G}\Psi ds. \tag{D.22}$$

Boundary operator expectation value: $\langle \boldsymbol{\mathcal{O}}_{b1} \rangle + \langle \boldsymbol{\mathcal{O}}_{b2} \rangle$

Noting that $\boldsymbol{\alpha} = \frac{i}{\hbar}[\, H_{S.O}\,, \mathbf{r}\,]$, the expectation value of $\langle \boldsymbol{\mathcal{O}}_{b} \rangle$ is finally given by

$$\begin{aligned} \langle \boldsymbol{\mathcal{O}}_{b} \rangle &= \langle \boldsymbol{\mathcal{O}}_{b1} \rangle + \langle \boldsymbol{\mathcal{O}}_{b2} \rangle \\ &= -\frac{1}{2} \oiint_S \mathbf{n}\cdot \left(((\frac{\mathbf{\Pi}}{m} + \boldsymbol{\alpha})\Psi)^\dagger \, + \, \Psi^\dagger (\frac{\mathbf{\Pi}}{m} + \boldsymbol{\alpha}) \right) \mathbf{G}\Psi \, ds \\ &= -\frac{1}{2} \oiint_S \mathbf{n}\cdot \big(\mathbf{v}\Psi)^\dagger \, + \, \Psi^\dagger \mathbf{v} \big) \, \mathbf{G}\Psi \, ds \end{aligned} \tag{D.23}$$

where $\mathbf{v} = \frac{i}{\hbar}\,[H(\mathbf{r},t), \mathbf{r}] = \frac{\mathbf{\Pi}}{m} + \boldsymbol{\alpha}$.

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