IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

Non-Hermitian Contributions to the Off-Diagonal Ehrenfest Theorem: Their Impact on Optical Properties of Semiconducting Materials

Georgios Konstantinou[1], Konstantinos Moulopoulos[2]

Special Scientist (PhD Solid State Physics), FOSS Research Centre for Sustainable Energy, PV Technology, University of Cyprus, Nicosia, Cyprus [1]

Associate Professor, Department of Physics, University of Cyprus, Nicosia, Cyprus [2]

Abstract: We show the emergence of surface Non-Hermitian boundary terms that appear in an extended form of the quantum Ehrenfest theorem and are crucial in the calculation of optical matrix elements that govern the Optical Transitions in semiconductors, e.g. solar cells. Their inevitable existence, strongly related to the boundary conditions of a given quantum mechanical problem, is far-reaching in the sense that they play a dramatic role in the dynamics of solar absorption and the corresponding optical transitions that follow. Processes like optical transitions in localized and delocalized states and probabilities of intermolecular transitions can be investigated through this generalized off-diagonal Ehrenfest theorem, employed in the present work in the form of various physical examples. As a byproduct, an explicit demonstration of bulk-boundary correspondence is shown, as the extended Ehrenfest theorem can be separated into bulk and surface contributions, each behaving separately from the other, but at the end collaborating to give the correct time-derivative of the desired optical element. An additional use is speculated in the case of topological materials.

Keywords: Non-Hermiticity, Ehrenfest Theorem, Optical transitions, solar cells.

I. INTRODUCTION

The well-known Ehrenfest theorem of Quantum Mechanics describes the time-flow of the mean value of a vector operator $\vec{B}$ through the following relation (the so-called Heisenberg equation):

$$\frac{d}{dt}\langle\Psi|\vec{B}|\Psi\rangle = \left\langle\Psi\left|\frac{\partial\vec{B}}{\partial t}\right|\Psi\right\rangle + \frac{i}{\hbar}\langle\Psi|[H,\vec{B}]|\Psi\rangle \quad \textbf{(1)}$$

where $|\Psi\rangle$ is **any** state $|\Psi(t)\rangle$ of the system, solution of the t-dependent Schrödinger equation, and $[H,\vec{B}]$ denotes the commutator of $\vec{B}$ with H. The above, if viewed as a continuity equation, states that the operator $\vec{B}$ **is conserved** (its mean value is independent of time) if either $\vec{B}$ is time-independent and commutes with H, or whenever $\frac{\partial\vec{B}}{\partial t} = -\frac{i}{\hbar}[H,\vec{B}]$, i.e. in the case that $\vec{B}$ is an invariant operator [3]. This statement is not however generally true (in the sense that a local form of the above theorem may lack a divergence of a current density); indeed it has been explicitly proved in [1] that the following generalized Ehrenfest theorem is valid (with B_l a certain Cartesian component of the vector operator $\vec{B}$):

$$\frac{d}{dt}\langle\Psi|B_l|\Psi\rangle = \left\langle\Psi\left|\frac{\partial}{\partial t}B_l\right|\Psi\right\rangle + \frac{i}{\hbar}\langle\Psi|[H,B_l]|\Psi\rangle - \oint\vec{J}_{gen}\,.\,d\vec{S} \quad \textbf{(2)},$$

$$\text{with } \vec{J}_{gen} = \frac{i\hbar}{2m}\left(\vec{\nabla}\Psi^* B_l\Psi - \Psi^*\vec{\nabla}(B_l\Psi)\right) - \frac{q}{mc}\vec{A}\Psi^* B_l\Psi \quad \textbf{(3)}$$

the generalized current density of the quantity B_l, and $\vec{A}$ is any magnetic vector potential present in the system. The last flux term across the system boundaries describes non-Hermitian effects that are emergent (and are strictly resulting from the boundary conditions). Although we have used notation for the surface flux of $\vec{J}_{gen}$ (proper for a 3D system), eq. (2) is also valid for any dimensionality (with the last term being a line integral of the component of $\vec{J}_{gen}$ perpendicular to the displacement element $d\vec{l}$ for 2D systems), or the difference of values of $\vec{J}_{gen}$ between two points (the ends of a 1D system). If we also define

$$\rho_{gen} = \Psi^* B_l\Psi \quad \textbf{(4)}$$

a generalized density of B_l, then eq. (2) can also be written in differential form, namely:

$$\vec{\nabla}.\vec{J}_{gen} + \frac{\partial\,\rho_{gen}}{\partial t} = \Psi^*\left(\frac{\partial}{\partial t}B_l + \frac{i}{\hbar}[H,B_l]\right)\Psi \quad \textbf{(5)}$$

Eq. (5) is actually a generalized local conservation law: the local contribution to $\langle\Psi|B_l|\Psi\rangle$ together with its flow, satisfy a continuity balance only if the source term that appears on the right hand side of (5) vanishes. The above extended

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

form of the Ehrenfest theorem is more complete and has potential consequences on many elementary Quantum Mechanical problems (see Ref. [1] for a few examples). Also, it resolves some previously noticed Quantum Mechanical paradoxes (see Ref. [4], as well as Ref. [5] for an observation on the Hypervirial theorem). In what follows, we will develop a new methodology that extends even beyond the above Ehrenfest theorem (2) and applies mostly in the case of optical transitions by again involving the non-Hermitian boundary terms of eq. (2) and by generalizing even further to non-diagonal matrix elements (hence not only to the expectation values of (2)) and to left and right states that follow different Hamiltonians (but mutually related, their difference being an additive t-dependent perturbation term). Even more generally, our extended theorem can describe processes occurring in molecular orbitals as well as hoppings between different atoms or molecules.

II. THE OFF-DIAGONAL EHRENFEST THEOREM

We now generalize even further the above discussion: Suppose that we have a static Hamiltonian denoted by H^0, given by the following expression

$$H^0 = \frac{\left(\vec{p}+\frac{e}{c}\vec{A}^0(\vec{r})\right)^2}{2m} + V^0(\vec{r}),$$

with $\vec{A}^0(\vec{r})$ the magnetic vector potential and $V^0(\vec{r})$ a scalar potential energy with e being the electronic charge. At a given time $t> 0$, H^0 transforms into another, time-dependent Hamiltonian $H(t)$ by some mechanism (i.e. solar photon absorption) that can be interpreted as adiabatic perturbation of some parameter or by adding to H^0 an extra time-dependent perturbation term:

$$H(t) = H^0 + H'(\vec{r},t)$$

where $H'(\vec{r},t)$ is a perturbative term that can be introduced through the position and the momentum operators always in position representation ($\vec{p} = -i\hbar\vec{\nabla}_r$). We suppose that the perturbation occurs at a specific instance t=0, so that we can write $H'(\vec{r},t) = F(\vec{r},t)\theta(t)$. Let $f(\vec{r},t)$ and $\Psi(\vec{r},t)$ be the most general solutions of the following Schrödinger equations:

$$H^0 f = i\hbar\frac{df}{dt} \textbf{ (6)} \text{ and } H(t)\Psi = i\hbar\frac{d\Psi}{dt} \textbf{ (7)}$$

In what follows, we will deal with cases of optical transitions between the states f and Ψ when an optical matrix element can be represented by the inner product $\langle f|B_l|\Psi\rangle$, with $\vec{B}$ being generally a vector operator whose a certain Cartesian component is B_l; normally, it can be either the momentum or the position operator, but in general it can be any operator. The time-evolution of the matrix element then reads:

$$\frac{d}{dt}\langle f|B_l|\Psi\rangle = \left\langle\frac{\partial}{\partial t}f\middle|B_l\middle|\Psi\right\rangle + \left\langle f\middle|\frac{\partial}{\partial t}B_l\middle|\Psi\right\rangle + \left\langle f\middle|B_l\middle|\frac{\partial}{\partial t}\Psi\right\rangle = \left\langle f\middle|\frac{\partial}{\partial t}B_l\middle|\Psi\right\rangle + \frac{i}{\hbar}\langle H^0 f|B_l|\Psi\rangle - \frac{i}{\hbar}\langle f|B_l|H'\Psi\rangle, \textbf{ (8)}$$

where we have made use of the above Schrödinger equations (eq. (6) and (7)). Next, we add and subtract the term $\frac{i}{\hbar}\langle f|B_l|H^0\Psi\rangle$ and make use of the fact that $\langle f|B_l|H^0\Psi\rangle = -\langle f|[H^0,B_l]|\Psi\rangle + \langle f|H^0B_l|\Psi\rangle$ to find:

$$\frac{d}{dt}\langle f|B_l|\Psi\rangle = \left\langle f\middle|\frac{\partial}{\partial t}B_l\middle|\Psi\right\rangle + \frac{i}{\hbar}\langle f|[H^0,B_l]|\Psi\rangle - \frac{i}{\hbar}\langle f|B_l|H'\Psi\rangle, + \frac{i}{\hbar}\langle H^0 f|B_l|\Psi\rangle - \frac{i}{\hbar}\langle f|H^0B_l|\Psi\rangle \textbf{ (9)}$$

We now calculate the last two terms (which, generally, do not cancel out, due to the appearance of possible emergent non-Hermiticity of the kinetic energy of H^0, as seen in [1]), namely:

$$\langle H^0 f|B_l|\Psi\rangle - \langle f|H^0B_l|\Psi\rangle = -\frac{\hbar^2}{2m}\langle\nabla^2 f|B_l|\Psi\rangle + \frac{\hbar^2}{2m}\langle f|\nabla^2 B_l|\Psi\rangle + \frac{i\hbar e}{mc}\left\langle\vec{A}.\vec{\nabla}f\middle|B_l\middle|\Psi\right\rangle + \frac{i\hbar e}{mc}\left\langle f\middle|\vec{A}.\vec{\nabla}B_l\middle|\Psi\right\rangle \textbf{ (10)}$$

so that, by using the Green's theorem (in a very similar manner as was proved in [1]) we conclude to the following equation that rigorously describes the dynamical development of the optical element:

$$\frac{d}{dt}\langle f|B_l|\Psi\rangle = \left\langle f\middle|\frac{\partial}{\partial t}B_l\middle|\Psi\right\rangle + \frac{i}{\hbar}\langle f|[H^0,B_l]|\Psi\rangle - \frac{i}{\hbar}\langle f|B_l|H'\Psi\rangle - \oint\vec{J}^{f,\Psi}_{gen}.d\vec{S}, \textbf{ (11)}$$

or, in differential form (using the fact that the above is valid for any volume element of the system), we obtain the following extension of the continuity equation:

$$\vec{\nabla}.\vec{J}^{f,\Psi}_{gen} + \frac{d\,\rho^{f,\Psi}_{gen}}{dt} = f^*\left(\frac{\partial}{\partial t}B_l + \frac{i}{\hbar}[H^0,B_l] - \frac{i}{\hbar}B_lH'\right)\Psi \textbf{ (12)}$$

with $\vec{J}^{f,\Psi}_{gen} = \frac{i\hbar}{2m}\left(\vec{\nabla}f^*B_l\Psi - f^*\vec{\nabla}(B_l\Psi)\right) + \frac{e}{mc}\vec{A}f^*B_l\Psi$ **(13)** an off-diagonal generalization of flow density (which is an off-diagonal version of the previously mentioned $\vec{J}_{gen}$) and $\rho^{f,\Psi}_{gen} = f^*B_l\Psi$ **(14)** an off-diagonal generalization of the density of the Hermitian operator B_l. Eq. (11) can be viewed as a generalization of eq. (2) (to $f \neq \Psi$ and to $H' \neq 0$). In the special case where $B_l = 1$, the identity operator, eq. (12) becomes:

$$\vec{\nabla}.\vec{J}^{f,\Psi}_{gen} + \frac{d\,\rho^{f,\Psi}_{gen}}{dt} = -\frac{i}{\hbar}f^*H'\Psi \textbf{ (15)} \text{ with } \rho^{f,\Psi}_{gen} = f^*\Psi \textbf{ (16)}$$

A few comments are then worth making here: The off-diagonal generalized density is actually the probability amplitude to make a transition from the initial (single-) eigenstate f to the final (linear combination) state Ψ. Because the system (or the perturbation) is time-dependent, the off-diagonal generalized current density plays the role of the transition probability flow, i.e. there is a finite chance of the particle being energetically transported to a final state due to the action of the perturbation. The right hand-side of eq. (15) generates the transition probability in a type of local continuity equation, and acts as a source term. Eq. (11) gives another insight to the problem: the time flow of $\langle f|B_l|\Psi\rangle$

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

is governed by bulk terms and a surface term (the surface integral of $\vec{J}^{f,\Psi}_{gen}$) which gives one the opportunity to study a given problem from a dual perspective: the bulk physics and the surface physics, as we shall see below. It should be noted that eq. (12) is valid as written only if Ψ is a solution of (7) (with Hamiltonian H) and f is a solution of (6) (with Hamiltonian H^0). At this point, to make sure that things are as clear as possible, we turn our attention to the solution Ψ; we reemphasize that this is a solution of $H(t)\Psi = i\hbar\frac{d\Psi}{dt}$, and is generally not connected with f, which is a solution of a different Schrödinger equation: $H^0 f = i\hbar\frac{df}{dt}$. In cases of solar absorption, it is reasonable to assume that Ψ can be written as a linear combination on all f s-eigenstates of H^0. Equation (12) is actually modified in form if one chooses to use - instead of Ψ- another eigenstate of H^0; Suppose that we are interested in the time evolution of the matrix element $\langle f_i|B_l|f_n\rangle$, with f_i, f_n two orthogonal eigenstates of H^0 and B_l is either the momentum or the position operator. In this case, after following a similar methodology as the one used to derive eq. (12), we arrive at the following generalized continuity equation:

$$\vec{\nabla}.\vec{J}^{i,n}_{gen} + \frac{d\,\rho^{i,n}_{gen}}{dt} = f_i^*\left(\frac{\partial}{\partial t}B_l + \frac{i}{\hbar}[H^0, B_l]\right)f_n \text{ with } \rho^{i,n}_{gen} = e^{\frac{i}{\hbar}(\varepsilon_i - \varepsilon_n)t} f_i^* f_n \quad \textbf{(17)}$$

which lacks - if compared to (12) - the perturbation term. This equation will be used quite often in what follows.

III. APPLICATION OF THE GENERALIZED EHRENFEST THEOREM IN CASES WITH FERMI GOLDEN RULE

To estimate the probability of an optical transition from the initial Quantum Mechanical state $f_l(\vec{r})$ (a single eigenfunction of H^0, solution of $H^0 f_l = \varepsilon_l f_l$), in which case $f = f_l(\vec{r})e^{-\frac{i}{\hbar}\varepsilon_l t}$, to the final state $\Psi = \sum_n a_n(t) f_n(\vec{r}) e^{-\frac{i}{\hbar}\varepsilon_n t}$ (a general solution of $H\Psi = i\hbar\frac{\partial\Psi}{\partial t}$) that can always be written as a linear combination of all $f_n(\vec{r})$ states of H^0 with time dependent coefficients $a_n(t)$, we must calculate the time evolution of $\langle f|1|\Psi\rangle$. Using eq. (15) we find:

$$\frac{d[f^*(\vec{r},t)\Psi(\vec{r},t)]}{dt} = -\vec{\nabla}.\vec{J}^{f,\Psi}_{gen} - \frac{i}{\hbar}\sum_n e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t} a_n(t) H'_{l,n} \quad \textbf{(18)}$$

with $H'_{l,n} = f_l{}^* H' f_n$ and the $\vec{\nabla}.\vec{J}^{f,\Psi}_{gen}$ term can be determined as follows: From eq. (13) and the definitions of f and Ψ we have that (always for B_l = identity operator and assuming that no vector potentials are present, as typical in solar cells)

$$\vec{J}^{f,\Psi}_{gen} = \frac{i\hbar}{2m}\left(\vec{\nabla}f^*\Psi - f^*\vec{\nabla}\Psi\right) = \frac{i\hbar}{2m}\sum_n a_n(t)\, e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t}\left(\vec{\nabla}f_l{}^*(\vec{r})f_n(\vec{r}) - f_l{}^*(\vec{r})\vec{\nabla}f_n(\vec{r})\right) = \sum_n a_n(t)\,\vec{J}^{l,n}_{gen}$$

with $\vec{J}^{l,n}_{gen} = \frac{i\hbar}{2m}e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t}\left(\vec{\nabla}f_l{}^*(\vec{r})f_n(\vec{r}) - f_l{}^*(\vec{r})\vec{\nabla}f_n(\vec{r})\right)$. Now, according to eq. (17), and the fact that both f_l and f_n are eigenfunctions of H^0, we have that this generalized current obeys $\vec{\nabla}.\vec{J}^{l,n}_{gen} + \frac{d\,\rho^{l,n}_{gen}}{dt} = 0$, with $\rho^{l,n}_{gen} = e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t} f_l{}^*(\vec{r})f_n(\vec{r})$ so that

$$\vec{\nabla}.\vec{J}^{f,\Psi}_{gen} = \sum_n a_n(t)\,\vec{\nabla}.\vec{J}^{l,n}_{gen} = -\sum_n a_n(t)\frac{d\,\rho^{l,n}_{gen}}{dt} = -\frac{i}{\hbar}\sum_n a_n(t)\,(\varepsilon_l - \varepsilon_n)e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t} f_l{}^*(\vec{r})f_n(\vec{r}) \quad \textbf{(19)}$$

with ε_n the energy levels of the unperturbed Hamiltonian H^0. Integrating then eq. (18) over the whole volume of the system, we get:

$$\frac{d\left(\int d^3r f^*\Psi\right)}{dt} = \frac{da_l(t)}{dt}, \text{ and}$$

$$\frac{da_l(t)}{dt} = -\frac{i}{\hbar}\sum_n a_n(t)e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t}\left[(\varepsilon_n - \varepsilon_l)\int d^3r f_l{}^* f_n(\vec{r}) + \langle H'\rangle_{l,n}\right] = -\frac{i}{\hbar}\sum_n a_n(t)e^{\frac{i}{\hbar}(\varepsilon_l - \varepsilon_n)t}\langle H'\rangle_{l,n} \quad \textbf{(20)}$$

Due to the orthonormality of $f_l(\vec{r})$ and $f_n(\vec{r})$. We observe that in this case, where the state Ψ can be written as a linear combination of all independent eigenstates of the unperturbed Hamiltonian the integral of the $\vec{\nabla}.\vec{J}_{gen}$ term vanishes. As a result, in the $B_l = 1$ case, the probability amplitude is not influenced by the appearance of boundary terms, but in a more general case, where the initial and final states may not be orthogonal (e.g. transitions between different molecular orbitals), boundary terms will indeed be needed. The result (20) is the standard textbook result that leads to Fermi Golden Rule (after the usual approximations on the coefficients are made).

which lacks - if compared to (12) - the perturbation term. This equation will be used quite often in what follows.

IV. APPLICATION IN OPTICAL TRANSITIONS

The off-diagonal non-Hermitian boundary terms may have potential consequences on the optical properties of semiconducting systems if one appropriately applies the extended Ehrenfest theorem for the optical matrix elements. In what follows, we will make use of eqs. (11), (12) and (17) to some quantum mechanical problems that are affected by a time-dependent perturbation (i.e. a solar photon absorption) and calculate the dipole matrix element and the momentum matrix element (in case that we have a scalar or a vector potential to describe the interaction of matter with the electric field of light). The interaction term H' will be set to zero, because we will only be interested in single eigenstates of the unperturbed Hamiltonian H^0 as the initial and final states. Let us start from the time-dependence of the transition dipole

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

matrix element $\langle f|\vec{r}|\Psi\rangle$ with $f(\vec{r},t)=f_i(\vec{r})e^{-\frac{i}{\hbar}\varepsilon_i t}$ and $\Psi(\vec{r},t)=f_n(\vec{r})e^{-\frac{i}{\hbar}\varepsilon_n t}$, both solutions of H^0. The usefulness of our results is demonstrated in the following way: For single eigenstates, and time-independent operators, we have that the following relation holds:

$$\frac{d}{dt}\langle f|B_l|\Psi\rangle = i\omega_{i,n}\langle f_i|B_l|f_n\rangle \textbf{ (21)} \text{ with } \omega_{i,n}=\frac{\varepsilon_i-\varepsilon_n}{\hbar}$$

i.e. the matrix element between single eigenkets of any physical observable is proportional to its time-derivative. In contrast, when the diagonal matrix element is used instead, the time derivative gives a null result, as indeed expected, because the time-phase factor of the single eigenkets is eliminated. This result gives one the potential to express the optical transition element in terms of its time derivative (simplifying, as we shall see, in many cases the calculation load). We proceed with three important examples.

A. Free particle in 1 and 2 dimensions

It is convenient to first present a simple example in 2D: Consider a particle in the interior of a 2D rectangle ($L_x \times L_y$) with vanishing vector and scalar potentials $(\vec{A},V)=0$ and periodic boundary conditions along the sides L_x and L_y : In this free particle case, the normalized eigenfunctions of the Hamiltonian are:

$$f_{\vec{k}}(\vec{r})=\frac{1}{\sqrt{L_x L_y}}e^{i\vec{k}.\vec{r}},\ \textbf{(22)} \text{ with } k_x=2\pi\frac{n_x}{L_x},\ k_y=2\pi\frac{n_y}{L_y}\ \textbf{(23),}\ n_x,n_y=0,\pm1,\pm2,\ldots. \text{ with eigenenergies: } \varepsilon_k^0=\frac{\hbar^2k^2}{2m}\ \textbf{(24)}$$

Let us then consider the x-component of the position as our input operator in eq. (17) to find (with $f=|\vec{k}'\rangle$ and $\Psi=|\vec{k}\rangle$ being two different, orthonormal eigenfunctions):

$$\frac{d}{dt}\langle x\rangle_{\vec{k},\vec{k}'}=i\omega_{\vec{k},\vec{k}'}\langle x\rangle_{\vec{k},\vec{k}'}=\frac{\langle p_x\rangle_{\vec{k},\vec{k}'}}{m}-\oint \vec{J}^{\vec{k},\vec{k}'}_{gen\perp}dl,\ \textbf{(25)}$$

with $\langle p_x\rangle_{\vec{k},\vec{k}'}=0$ and the line integral along the line boundary is the integral of the transverse component of $\vec{J}^{\vec{k},\vec{k}'}_{gen}$ ($\vec{J}^{\vec{k},\vec{k}'}_{gen\perp}$) to the edges of the rectangle, namely:

$$\oint \vec{J}^{\vec{k},\vec{k}'}_{gen\perp}dl=\int_0^{L_x}\vec{J}^{\vec{k},\vec{k}'}_y(x,0)dx-\int_0^{L_x}\vec{J}^{\vec{k},\vec{k}'}_y(x,L_y)dx-\int_0^{L_y}\vec{J}^{\vec{k},\vec{k}'}_x(0,y)dy+\int_0^{L_y}\vec{J}^{\vec{k},\vec{k}'}_x(L_x,y)dy=\frac{\hbar}{2m}e^{i\omega_{\vec{k},\vec{k}'}t}\frac{1}{L_xL_y}\left(k_y'+\right.$$
$$\left.ky0Lxxeikx-kx'.xdx-\hbar2meiωk,k't1LxLyky'+ky0Lxxeikx-kx'.xdx-0+0=0\right)\ \textbf{(26)}$$

where we used $\vec{J}^{\vec{k},\vec{k}'}_x(x,y)=\frac{i\hbar}{2m}e^{i\omega_{\vec{k},\vec{k}'}t}\left(\frac{\partial f^*_{\vec{k}'}}{\partial x}xf_{\vec{k}}-f^*_{\vec{k}'}f_{\vec{k}}-xf^*_{\vec{k}'}\frac{\partial f_{\vec{k}}}{\partial x}\right)$, $\vec{J}^{\vec{k},\vec{k}'}_y(x,y)=\frac{i\hbar}{2m}e^{i\omega_{\vec{k},\vec{k}'}t}\left(\frac{\partial f^*_{\vec{k}'}}{\partial y}xf_{\vec{k}}-xf^*_{\vec{k}'}\frac{\partial f_{\vec{k}}}{\partial y}\right)$ and $\omega_{\vec{k},\vec{k}'}=\frac{\varepsilon^0_{k'}-\varepsilon^0_k}{\hbar}$.

If we put everything into eq. (25), the final result seems to be:

$$\frac{d}{dt}\langle x\rangle_{\vec{k},\vec{k}'}=0,\ \text{for } k\neq k'\ \textbf{(27)}$$

To independently check the validity of this result, we straightforwardly proceed with the verification of eq. (27) (always for $\vec{k}\neq\vec{k}'$):

$$\frac{d}{dt}\langle x\rangle_{\vec{k},\vec{k}'}=\frac{i\omega_{\vec{k},\vec{k}'}}{L_xL_y}e^{i\omega_{\vec{k},\vec{k}'}t}\int_0^{L_x}dx\,xe^{i(k_x-k_x')x}\int_0^{L_y}dy\,e^{i(k_y-k_y')y}=\frac{i\omega_{\vec{k},\vec{k}'}}{L_xL_y}e^{i\omega_{\vec{k},\vec{k}'}t}\int_0^{L_x}dx\,xe^{i(k_x-k_x')x}\left[\frac{e^{i(k_y-k_y')L_y}-1}{i(k_y-k_y')}\right]=0$$

(the last vanishing due to eq. (23)). In two dimensions we get a null result, but it is interesting to note that if we had carried out our calculations in the case of 1D (an electron in a linear length L_x, with periodic boundary conditions), namely:

$f_k(x)=\frac{1}{\sqrt{L_x}}e^{ikx}$, with $k_x=2\pi\frac{n_x}{L_x}$, and $\varepsilon^0_k=\frac{\hbar^2k^2}{2m}$ we would have found that (after applying the integrated version of eq. (17)):

$$\frac{d}{dt}\langle x\rangle_{k,k'}=\frac{\langle p_x\rangle_{k,k'}}{m}-\vec{J}^{k,k'}_{gen}\Big|_0^{L_x}$$

with $\langle p_x\rangle_{k,k'}=0$ and $\vec{J}^{k,k'}_{gen}\Big|_0^{L_x}=\frac{i\hbar}{2mL_x}e^{i\omega_{\vec{k},\vec{k}'}t}e^{i(k-k')x}(-1-i(k+k')x)\Big|_0^{L_x}=\frac{\hbar\pi}{mL_x}e^{i\omega_{\vec{k},\vec{k}'}t}(n_x+n_x')$

so that $\frac{d}{dt}\langle x\rangle_{k,k'}=-\frac{\hbar\pi}{mL_x}(n_x+n_x')e^{i\omega_{\vec{k},\vec{k}'}t}$, hence a non-vanishing result.

This can again be verified for the case of $k\neq k'$, by straightforwardly calculating the time derivative, namely:

$$\frac{d}{dt}\langle x\rangle_{k,k'}=\frac{1}{L_x}e^{i\omega_{\vec{k},\vec{k}'}t}\int_0^{L_x}dx\,xe^{i(k-k')x}=\frac{i}{L_x}\omega_{\vec{k},\vec{k}'}e^{i\omega_{\vec{k},\vec{k}'}t}\int_0^{L_x}dx\,xe^{i(k-k')x}=\frac{i}{L_x}\omega_{\vec{k},\vec{k}'}e^{i\omega_{\vec{k},\vec{k}'}t}x\,\frac{e^{i(k-k')x}}{i(k-k')}\Big|_0^{L_x}=$$
$$\frac{1}{(k-k')}\omega_{\vec{k},\vec{k}'}e^{i\omega_{\vec{k},\vec{k}'}t}=-\frac{\hbar\pi}{mL}(n_x+n_x')e^{i\omega_{\vec{k},\vec{k}'}t}\ \textbf{(28)}$$

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

One can also add here the expected $\frac{d}{dt}\langle x\rangle_{k,k'} = 0$ in the case of $k = k'$ (as the expectation value in a single-eigenstate is indeed t-independent, meaning that the time-derivative will result to zero) that actually motivated the discussion in [1] and was developed there in full detail.
We notice from the above example that the dimensionality of a given problem is very important because the extra spatial degrees of freedom may affect the photon absorbance differently; for the previous 1D case, transition probabilities between different wave-number states are possible, as given by eq. (28). In the 2D case however, this is not always possible (as predicted by eq. (27)) for a linearly polarized electric field. Transitions are possible, however, in the case of circularly polarized (or any directionally time-varying) electric field, in which case the above electric dipole element may not vanish. Similar conclusions can be also drawn for the 3D case.

B. Quantum bouncing ball

After the previous example, viewed as a preliminary step, we now turn our attention to the off-diagonal momentum optical matrix element $\langle\vec{\Pi}\rangle_{i,n}$, with $\vec{\Pi} = \vec{p} + \frac{e}{c}\vec{A}$ the kinetic momentum, in cases where the perturbation enters the Hamiltonian as a time-dependent vector potential. Using for simplicity a specific component of the vector operator $\vec{\Pi}$, i.e. $B_l = \Pi_x = p_x + \frac{e}{c}A_x$ (and for the case $H' = 0$) in eq. (17) we arrive at the following equation:

$$\vec{\nabla}.\vec{J}^{f,\Psi}_{gen} + \frac{d\,\rho^{f,\Psi}_{gen}}{dt} = f^*\left(-\frac{eB_z}{mc}\Pi_y + \frac{eB_y}{mc}\Pi_z - \frac{\partial V}{\partial x}\right)\Psi \textbf{ (29)}$$

Then, for $H' = 0$, and $\omega_i = eB_i/mc$ (i.e. f and Ψ are regarded as two distinct eigenfunctions (hence, there is no need of including H', as explained before) of the same Hamiltonian), and by using eq. (21) we have:

$$\frac{d\,\rho^{f,\Psi}_{gen}}{dt} = \frac{d}{dt}\left(e^{i\frac{(\varepsilon_f-\varepsilon_\psi)t}{\hbar}}f^*(\vec{r})\Pi_x\Psi(\vec{r})\right) = i\omega_{f,\psi}\rho^{f,\Psi}_{gen}(\vec{r}) \textbf{ (30)}$$

with $\omega_{f,\psi} = \frac{(\varepsilon_f-\varepsilon_\psi)}{\hbar}$, from which we obtain that:

$$i\omega_{f,\psi}\langle\Pi_x\rangle_{f,\psi} = -\omega_z\langle\Pi_y\rangle_{f,\psi} + \omega_y\langle\Pi_z\rangle_{f,\psi} - \langle\frac{\partial V}{\partial x}\rangle_{f,\psi} - \oint\vec{J}^{f,\Psi}_{gen}(\Pi_x).d\vec{S} \textbf{ (31)}$$

with $\vec{J}^{f,\Psi}_{gen}(\Pi_x)$ given by eq. (13). In [2], the authors use the Ehrenfest theorem to calculate $\langle\Pi_x\rangle_{f,\Psi}$ neglecting the boundary terms, which terms however can in principle be very important and can contribute equally to the overall result. The above equation (31) has the advantage that, it can relate the optical element $\langle\Pi_i\rangle_{f,\Psi}$ with the effective bulk force acting on the particle and with a boundary term (a surface force) as a result of the interaction with the electromagnetic field.

To underline the important physical consequences of the new non-Hermitian terms, we will calculate the last term appearing in (31) for the case of an electron in a triangular well (described by a homogeneous electric field E) in 1D without any magnetic fields or vector potentials present. In this case, the wavefunctions are represented by the Airy functions: $\Psi_n = C_n Ai\left[\left(x - {\varepsilon_n}/{eE}\right)/l_f\right]$, with C_n a normalization constant, Ai[x] the Airy functions, ε_n the energy levels and $l_f = (\hbar^2/2meE)^{1/3}$. Let $f = C_{n'}Ai\left[\left(x - {\varepsilon_{n'}}/{eE}\right)/l_f\right]$ and $\Psi = C_n Ai\left[\left(x - {\varepsilon_n}/{eE}\right)/l_f\right]$ two different, linearly independent solutions of the Schrödinger equation:

$$\Psi'' - \frac{2meE}{\hbar^2}\left(x - \frac{\varepsilon_n}{eE}\right)\Psi = 0 \textbf{ (32)}$$

The boundary condition at x=0 allows us to directly relate the energy eigenvalues ε_n to the roots a_n of the Airy function:

$$Ai\left[-{\varepsilon_n}/{eEl_f}\right] = 0 \Rightarrow \varepsilon_n = -eEl_f a_n \text{ with n=1,2… } \textbf{(33)}$$

The generalized current density (eq. (13)) then reads:

$$\vec{J}^{f,\Psi}_{gen}(p_x) = e^{i\omega_{n,n'}t}\frac{\hbar^2}{2m}C^*_{n'}C_n\left(Ai^{*\prime}\left[\frac{x}{l_f} + a_{n'}\right]Ai'\left[\frac{x}{l_f} + a_n\right] - Ai^*\left[\frac{x}{l_f} + a_{n'}\right]Ai''\left[\frac{x}{l_f} + a_n\right]\right) \textbf{ (34)}$$

with $\omega_{n,n'} = \frac{\varepsilon_{n'}-\varepsilon_n}{\hbar}$. Because the Airy function $Ai\left[\frac{x}{l_f} + a_{n'}\right]$ (and its derivative) at the asymptotic limit $x\to\infty$ vanishes, and so does at x=0 (due to the infinite potential wall), we find that the only surviving term is the product of derivatives at x=0:

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

$$\vec{J}_{gen}^{f,\Psi}(p_x)\Big|_0^\infty = -\frac{\hbar^2}{2ml_f^2} C_{n'}^* C_n e^{i\omega_{n,n'}t}(Ai^{*\prime}[a_{n'}]Ai'[a_n]) \textbf{ (35)}$$

By then using the normalization constant $C_n = 1/\left[\sqrt{l_f}Ai'(a_n)\right]$ we find that:

$$\vec{J}_{gen}^{f,\Psi}(p_x)\Big|_0^\infty = -\frac{\hbar^2}{2ml_f^3} e^{i\omega_{n,n'}t} \textbf{ (36)}$$

Now, considering that $\langle \Pi_y \rangle_{n,n'} = 0$, $\langle \Pi_z \rangle_{n,n'} = 0$ (for a 1D case) and that $\frac{\partial V}{\partial x} = eE$ (the bulk force, which is homogeneous) it is immediate that $\langle \frac{\partial V}{\partial x} \rangle_{n.n'} = 0$, due to the orthogonality of n and n′ (in eq. (31)) and we therefore note that $\langle \Pi_x \rangle_{n,n'}$ is proportional to the boundary term. On the other hand, we should point out that the full potential profile consists of both bulk and boundary terms, namely:

$$V = \lim_{V_0 \to \infty} V_0 \theta(-x) + eEx\theta(x) \textbf{ (37)}$$

with $\theta(x)$ the Heaviside step function, so that the full force equation should be related to $\frac{\partial V}{\partial x} = \lim_{V_0 \to \infty} V_0 \delta(x) + eE\theta(x)$, with $\delta(x)$ the Dirac delta function. But, in doing so, there is a danger of double-counting the force contribution. What eq. (29) actually achieves, is to divide the problem into a bulk term and a surface term, which can be treated separately. To correctly calculate $\langle \frac{\partial V}{\partial x} \rangle_{n.n'}$ in eq. (29) we only need to use the bulk force element, $eE\theta(x)$, which actually gives a null result. All surface terms (forces, momentum transfer etc.) are automatically built-in the last term of eq. (31), and no further calculations to determine the wave function are needed. Having this in mind, we conclude to:

$$\frac{d\langle p_x \rangle_{n,n'}}{dt} = i\omega_{f,\psi}\langle p_x \rangle_{n,n'} \Rightarrow \langle p_x \rangle_{n,n'} = \frac{-i\hbar^2}{2ml_f^3\omega_{n,n'}} e^{i\omega_{n,n'}t} \textbf{ (38)}$$

and we can see that eqs (38) and (36) are indeed consistent with eq. (31) with the vanishing of $\langle \frac{\partial V}{\partial x} \rangle_{n.n'}$. It should also be noted that, in spite of the claim in [2], it is possible to find a way to analytically show the above result independently, with use of Airy function properties, and this is presented in Appendix 1. Furthermore, for completeness, we here carry out corresponding calculations, but now using the position operator in the integral version of eq. (17) as an input operator (for comparison purposes - assuming that the electromagnetic field is now coupled through a dipole moment interaction term), namely:

$$i\omega_{n',n}\langle \Psi_{n'}|x|\Psi_n \rangle = \frac{1}{m}\langle \Psi_{n'}|p_x|\Psi_n \rangle + \vec{J}_{gen}^{f,\Psi}\Big|_0^\infty,$$

with $\langle \Psi_{n'}|p_x|\Psi_n \rangle = \frac{-i\hbar^2}{2ml_f^3\omega_{n,n'}} e^{i\omega_{n,n'}t}$ as given by eq. (38) and

$$\vec{J}_{gen}^{f,\Psi}\Big|_0^\infty = \frac{i\hbar}{2m}\Psi_{n'}' x\Psi_n - \Psi_{n'}(\Psi_n + x\Psi_n')\Big|_0^\infty = 0$$

So that we get the expected result (that demonstrates the duality between the choices of the momentum and position to describe the electromagnetic radiation), namely:

$$\langle \Psi_{n'}|x|\Psi_n \rangle = \frac{\hbar^2}{2ml_f^3\omega_{n,n'}^2} e^{i\omega_{n,n'}t}$$

It is important to notice that in higher dimensionality cases, where line and surface integrals of the non-Hermitian terms appear, the boundary terms might not be zero; in these cases a more careful calculation is necessary (and this will be the focus of a future work).

C. Particle in an infinite potential well

Let us finally see a simpler example from elementary Quantum Mechanics where the new surface terms proposed here might be important: Consider an electron in a quantum potential well with infinite walls and $(\vec{A}, V) = 0$ inside the cell, with normalized eigenfunctions:

$$\Psi_n = \sqrt{\frac{2}{d}} \sin\left(\frac{n\pi x}{d}\right) e^{-\frac{i\varepsilon_n t}{\hbar}} \textbf{ (39)}$$

and eigenenergies $\varepsilon_n = \frac{\hbar^2\pi^2n^2}{2md^2}$ with n = 1,2.. and d is the quantum well's length. We have that $\frac{\partial \Psi}{\partial x} = \sqrt{\frac{2}{d}}\frac{n\pi}{d}\cos\left(\frac{n\pi x}{d}\right)$ and $\frac{\partial^2 \Psi}{\partial x^2} = -\sqrt{\frac{2}{d}}\left(\frac{n\pi}{d}\right)^2 \cos\left(\frac{n\pi x}{d}\right)$, so that for $l \neq n$ we obtain:

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

$$\vec{J}_{gen}^{l,n} = \frac{i\hbar}{2m}\left(\vec{\nabla}\Psi_l^* p_x \Psi_n - \Psi_l^* \vec{\nabla}(p_x \Psi_n)\right) = \frac{i\hbar}{2m}\left[-i\hbar \frac{2n\pi}{d^2}\frac{l\pi}{d}\cos\left(\frac{n\pi x}{d}\right)\cos\left(\frac{l\pi x}{d}\right)\right]\Big|_0^d e^{i\omega_{l,n}t} = \hbar^2 \frac{nl\pi^2}{md^3}[\cos(n\pi)\cos(l\pi) - 1]e^{i\omega l,nt}$$ **(40)**

so that by using the integral form of eq. (17) we find that (after using $\frac{\partial V}{\partial x} = 0$):

$$\frac{d}{dt}\langle p_x\rangle_{l,n} = -\hbar^2 \frac{nl\pi^2}{md^3}[cos(n\pi)cos(l\pi) - 1]e^{i\omega_{l,n}t}$$ **(41)**

In (41), only terms that satisfy the condition n-l =odd survive, and they give:

$$\frac{d}{dt}\langle p\rangle_{l,n} = -2i\hbar^2 \frac{nl\pi^2}{md^3\omega_{l,n}} e^{i\omega_{l,n}t}$$ **(42)**

For the case $l = n$, we also have that $\vec{J}_{gen}^{l,l} = 0$ and $\frac{d}{dt}\langle p\rangle_{l,l} = 0$.

We therefore conclude that the non-Hermitian terms are of vital importance when it comes to calculate the time dependence of optical matrix elements, and should always be included. Generally, we can see from eq. (31) that, if the surface term were indeed zero, we could write directly a certain component of the optical matrix element $\langle \Pi_i \rangle_{f,\psi}$ as a function of the 'effective force', $\langle \vec{\nabla} V \rangle_{f,\psi}$ and simplify the calculations as already been done in [2]. However, this is not always the case, as the non-Hermitian terms appear as a consequence of a generalized conservation theorem. This is demonstrated more clearly in the comments that follow.

If, for example, the momentum is chosen as an input operator in eq. (31), there is a bulk force contribution from the gradient of the potential and a surface contribution from the non-Hermitian term. While the potential gradient refers to the (off-diagonal) bulk force acting on the particle, the surface term incorporates the surface force directly (which is generally proportional to the product of the derivatives of the two transverse wave functions-as will be demonstrated below). At this point, to clear things out, we will present a simple example: Consider once again the simple case of an electron in a 1D quantum well of length L (with no-vector potential) and the equation (31) in 1D:

$$i\omega_{f,\psi}\langle p_x\rangle_{f,\psi} = -\langle \frac{\partial V}{\partial x}\rangle_{f,\psi} - \vec{J}_{gen}^{f,\Psi}(p_x)\Big|_0^L$$ **(43)**

with $\vec{J}_{gen}^{f,\Psi}(p_x) = \frac{i\hbar}{2m}\left(\frac{\partial}{\partial x}f^* p_x \Psi - f^* \frac{\partial}{\partial x}(p_x \Psi)\right) = \frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x}f^* \frac{\partial}{\partial x}\Psi - f^* \frac{\partial^2}{\partial x^2}\Psi\right)$ **(44).** In this case, the potential profile reads:

$$V = lim_{V_0\to\infty} V_0[\theta(-x) + \theta(x - L)]$$ **(45)**

The gradient, $\frac{\partial V}{\partial x}$ reads: $\frac{\partial V}{\partial x} = lim_{V_0\to\infty} V_0[\delta(-x) + \delta(x - L)]$ (**46**). This is the surface force operator acting on the particle, while the bulk force operator is obviously $\frac{\partial V}{\partial x} = 0$. Eq. (43) can then be utilized in a twofold manner: If one chooses to use the boundary terms as in eq. (43), then, because the surface force information is already included in $\vec{J}_{gen}^{f,\Psi}(p_x)\Big|_0^L$, (which is actually proportional to the product of the derivatives of the wavefunctions, because the second term in eq. (44) vanishes, and only the first term survives) and $\frac{\partial V}{\partial x}$ must only be the bulk force which is zero.
On the other hand, if one wishes to neglect the boundary terms in (43), then the full potential profile (eq. (46)) must be used. Extra care is therefore needed in order to avoid double counting of the force contribution to $\langle p_x\rangle_{f,\psi}$. As a byproduct we note that, if in a problem there are periodic boundary conditions, then, the full version of eq. (43) must be used, because of the difficulty in obtaining the exact form of the surface potential.

Finally, we should re-emphasize that the generality of our results permits one to conduct calculations beyond the stationary states and consider delocalized states or even states that belong to a different Hamiltonians, which is why states f and Ψ are left intentionally unspecified.

V. CONCLUSION

We have shown an extended form of the Ehrenfest theorem that applies in case of calculations of optical matrix elements. This generalized form, including non-Hermitian boundary terms defines a continuity equation describing the flow of a specific optical matrix element $\langle f_l|B_l|f_n\rangle$, with B_l a Hermitian operator of the system. The generalized Ehrenfest theorem has been applied to some elementary quantum mechanical problems demonstrating the necessity of inclusion of the non-Hermitian terms. Dimensionality and given boundary conditions are crucial in the determination of these boundary currents, which completely separate the problem from its bulk response. For example, in some problems, the quantum force originates completely from the boundaries, while, in other problems, both the boundary and the surface play equivalent roles. It can furthermore be speculated that a more careful consideration of this separation (into a bulk and a surface contribution) may reflect the recently observed bulk-boundary correspondence that is found in Quantum Hall systems [6] and even in more general topological materials, such as Topological Insulators [7,8] or 3D Dirac and Weyl semimetals [9].

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
ISO 3297:2007 Certified
Vol. 4, Issue 12, December 2017

APPENDIX

We here prove the result (38) analytically:

$$\langle p_x \rangle_{n,n'} = -i\hbar \int_0^\infty dx\, \Psi_{n'}^* \frac{\partial \Psi_n}{\partial x} = \frac{-i\hbar^2}{2ml_f^3 \omega_{n,n'}} e^{i\omega_{n,n'}t}$$

Let $\Psi_{n'}^* = C_{n'} Ai\left[\left(x - {}^{\varepsilon_{n'}}/_{eE}\right)/l_f\right] e^{\frac{i\varepsilon_{n'}t}{\hbar}}$ and $\Psi_n^* = C_n Ai\left[\left(x - {}^{\varepsilon_n}/_{eE}\right)/l_f\right] e^{-\frac{i\varepsilon_n t}{\hbar}}$ be two orthogonal solutions of the Schrodinger equation:

$$\Psi_{n'}'' - \frac{2meE}{\hbar^2}\left(x - \frac{\varepsilon_{n'}}{eE}\right)\Psi_{n'} = 0 \quad \text{(A1)}$$

$$\Psi_n'' - \frac{2meE}{\hbar^2}\left(x - \frac{\varepsilon_n}{eE}\right)\Psi_n = 0 \quad \text{(A2)}$$

Multiply (A1) with Ψ_n' and (A2) with $\Psi_{n'}'$, and add them by parts to find:

$$\Psi_{n'}''\Psi_n' + \Psi_n''\Psi_{n'}' - \frac{2meE}{\hbar^2}\left(x\Psi_{n'}\Psi_n' - \frac{\varepsilon_{n'}}{eE}\Psi_{n'}\Psi_n' + x\Psi_n\Psi_{n'}' - \frac{\varepsilon_n}{eE}\Psi_n\Psi_{n'}'\right) = 0 \text{ (A3)}$$

Integrate eq. (A3) with respect to x:

$$\int_0^\infty dx \left[\Psi_{n'}''\Psi_n' + \Psi_n''\Psi_{n'}' - \frac{2meE}{\hbar^2}\left(x\Psi_{n'}\Psi_n' - \frac{\varepsilon_{n'}}{eE}\Psi_{n'}\Psi_n' + x\Psi_n\Psi_{n'}' - \frac{\varepsilon_n}{eE}\Psi_n\Psi_{n'}'\right)\right] = 0 \text{ (A4)}$$

We will now make use of the properties of the Airy functions to simplify the results:

$$\int_0^\infty dx\, \Psi_{n'}''\Psi_n' = \Psi_{n'}'\Psi_n'\Big|_0^\infty - \int_0^\infty dx\, \Psi_{n'}'\Psi_n'' \text{ (A5)}$$

$$\int_0^\infty dx\, x\Psi_{n'}\Psi_n' = x\Psi_{n'}\Psi_n\Big|_0^\infty - \int_0^\infty dx\, x\Psi_n\Psi_{n'}' = -\int_0^\infty dx\, x\Psi_n\Psi_{n'}' \text{ (A6)}$$

$$\int_0^\infty dx\, \Psi_{n'}\Psi_n' = -\int_0^\infty dx\, \Psi_n\Psi_{n'}' \text{ (A7)}$$

Substituting (A5), (A6) and (A7) into (A4) we conclude to:

$$\Psi_{n'}'\Psi_n'\Big|_0^\infty - \frac{2m}{\hbar^2}\left(\varepsilon_n - \varepsilon_{n'}\right)\int_0^\infty dx\, \left(\Psi_{n'}\Psi_n'\right) = 0 \text{ (A8)}$$

Because $\langle p_x \rangle_{n,n'} = -i\hbar \int_0^\infty dx\, \Psi_{n'}^* \frac{\partial \Psi_n}{\partial x}$ we get: $-i\hbar \int_0^\infty dx \left(\Psi_{n'}\Psi_n'\right) = -i\frac{\hbar^2 \Psi_{n'}'\Psi_n'\Big|_0^\infty}{2m\omega_{n,n'}}$. Note that in the asymptotic limit x→ ∞, both the wavefunction and its derivative vanish, so that $\Psi_{n'}'\Psi_n'\Big|_0^\infty = -\Psi_{n'}'(0)\Psi_n'(0) = -\frac{1}{l_f^3}$ and therefore

$$\langle p_x \rangle_{n,n'} = -i\frac{\hbar^2}{2m\omega_{n,n'}l_f^3} e^{i\omega_{n,n'}t} \text{ (A9)}$$

which coincides with eq. (38) that has been derived with much less effort in the main text, with use of the non-Hermitian boundary terms.

REFERENCES

[1] G. Konstantinou, K. Kyriakou, K. Moulopoulos, Emergent Non-Hermitian Contributions to the Ehrenfest and Hellmann-Feynman Theorems, International Journal of Engineering Innovations and Research, vol. 5, Issue 4 (2016)
[2] A. G. Petrov and A. Shik, Interlevel optical transitions in quantum wells, Physical Review B, vol. 48, 11883 (1993)
[3] H. R. Lewis Jr. and W. B. Riesenfeld, An Exact Quantum Theory of the Time-Dependent Harmonic Oscillator and of a Charged Particle in a Time-Dependent Electromagnetic Field, J. Math. Phys. Vol. 10, 1458 (1969)
[4] R. N. Hill, A Paradox Involving the Quantum Mechanical Ehrenfest Theorem, Am. J. Phys. vol. 41, 736 (1973)
[5] F. M. Fernández and E. A. Castro, Lecture Notes in Chemistry: Hypervirial Theorems, Springer-Verlag (1987)
[6] G. M. Graf, Aspects of the Integer Quantum Hall Effect, Pure Mathematics: vol. 76 (2007)
[7] M. Z. Hasan & C. L. Kane, Colloquium: , Topological Insulators, Rev. Mod. Phys. 82, 3045 (2010)
[8] X.-L. Qi and S.-C. Zhang, Topological insulators and superconductors, Rev. Mod. Phys. vol. 83, 1057 (2011)
[9] X. Wan, A. M. Turner, A. Vishwanath and S. Y. Savrasov, Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates, Phys. Rev. B vol. 83, 205101 (2011).