

Adiabatic electronic flux in molecules and in condensed matter

Cite as: J. Chem. Phys. **156**, 204118 (2022); <https://doi.org/10.1063/5.0087883>

Submitted: 10 February 2022 • Accepted: 10 May 2022 • Accepted Manuscript Online: 11 May 2022 •

Published Online: 26 May 2022

 Raffaele Resta



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Defining the temperature of an isolated molecule](#)

The Journal of Chemical Physics **156**, 204304 (2022); <https://doi.org/10.1063/5.0090205>

[Numerical calculation of Green's function and momentum distribution for spin-polarized fermions by path integral molecular dynamics](#)

The Journal of Chemical Physics **156**, 204117 (2022); <https://doi.org/10.1063/5.0093472>

[Practical guide to replica exchange transition interface sampling and forward flux sampling](#)

The Journal of Chemical Physics **156**, 200901 (2022); <https://doi.org/10.1063/5.0080053>

[Learn More](#)

The Journal
of Chemical Physics **Special Topics** Open for Submissions



Adiabatic electronic flux in molecules and in condensed matter

Cite as: J. Chem. Phys. 156, 204118 (2022); doi: 10.1063/5.0087883

Submitted: 10 February 2022 • Accepted: 10 May 2022 •

Published Online: 26 May 2022



View Online



Export Citation



CrossMark

Raffaele Resta^{a)} 

AFFILIATIONS

Istituto Officina dei Materiali IOM-CNR, Strada Costiera 11, 34151 Trieste, Italy and Donostia International Physics Center, 20018 San Sebastián, Spain

^{a)} Author to whom correspondence should be addressed: resta@iom.cnr.it. URL: <http://www-dft.ts.infn.it/~resta/>

ABSTRACT

The theory of adiabatic electron transport in a correlated condensed-matter system is rooted in a seminal paper by Niu and Thouless [J. Phys. A: Math. Gen. 17, 2453 (1984)]; I adopt here an analogous logic in order to retrieve the known expression for the adiabatic electronic flux in a molecular system [L. A. Nafie, J. Chem. Phys. 79, 4950 (1983)]. Its derivation here is considerably simpler than those available in the current quantum-chemistry literature; it also explicitly identifies the adiabaticity parameter, in terms of which the adiabatic flux and the electron density are both exact to first order. It is shown that the continuity equation is conserved to the same order. For the sake of completeness, I also briefly outline the relevance of the macroscopic electronic flux to the physics of solids and liquids.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0087883>

I. INTRODUCTION

Several recent and less recent papers in molecular physics have addressed the long-standing problem of evaluating the electronic flux within the adiabatic approximation and beyond;^{1–9} in its simplest formulation, the main issue is as follows. Whenever the instantaneous electronic Hamiltonian is time-reversal invariant, its ground eigenfunction can be chosen as real, and therefore, it carries an identically vanishing flux, while instead the electron density $n(\mathbf{r}, t)$ from the same instantaneous eigenstate is clearly time-dependent. Hence, to this order, the continuity equation is obviously violated; it has been first shown by Nafie¹ in 1983 how to evaluate the flux in order to restore the continuity equation.

If the time-dependent term in the electronic Hamiltonian evolves periodically in time at frequency ω , then $\partial n(\mathbf{r}, t)/\partial t$, when evaluated on the instantaneous ground eigenstate, is linear in ω . The adiabatic limit is by definition the limit $\omega \rightarrow 0$; it makes sense whenever the ground state is nondegenerate. In the following, the frequency ω is chosen as the main adiabaticity parameter: it is therefore clear that in order to conserve the continuity equation, one needs an expression for the electronic flux correct—like the density—to the first order in ω .

In condensed matter physics, the electronic-flux problem has been solved by Thouless^{10,11} (in an independent-electron

framework) and by Niu and Thouless¹² (in a many-body framework); to the best of the author's knowledge, the relevance of the Niu–Thouless (hereafter quoted as NT) approach to molecular physics has never been elucidated. Therefore, I present here a molecular-physics formulation of the adiabatic electronic flux, strongly inspired by the NT seminal paper. The NT-based logic yields a very concise, pedagogically appealing, derivation and a clear understanding of what the adiabatic limit is.

The word “adiabatic” as adopted here—as well as generally in condensed matter physics^{11,12}—requires a semantical specification. When the Hamiltonian evolves at frequency ω , the NT electronic flux is (as said above) exact to the first order in our adiabaticity parameter ω ; it will be shown below that its entries are the eigenvalues and eigenstates of the instantaneous Hamiltonian at a given time. At variance with the adiabatic electron density, the microscopic electronic flux has *not* a single-state expression (here as well in the previous literature); because of this, the term “complete adiabatic” is adopted in the previous chemical-physics literature.¹

Section II presents a proof of the one-body continuity equation in a correlated many-electron system and establishes the notations adopted throughout. In Sec. III, the lowest-order expression for the one-body electronic flux is derived following the NT simple logic, as adapted to a molecular system; the adiabatic continuity equation is

proved in Sec. IV. In Sec. V, I briefly address the adiabatic electronic flux in condensed matter systems, either insulators or metals and either solids or liquids.

II. CONTINUITY EQUATION

I am going to address throughout the (spin-integrated) one-body flux $\mathbf{j}(\mathbf{r}, t)$ and one-body density $n(\mathbf{r}, t)$ of a correlated N -electron system, whose continuity equation reads

$$\nabla_{\mathbf{r}} \cdot \mathbf{j}(\mathbf{r}, t) = -\frac{\partial}{\partial t} n(\mathbf{r}, t). \quad (1)$$

In order to establish the notations used in the following, I start deriving Eq. (1) in a many-body setting. The Schrödinger equation for any given time-dependent many-body state $|\Psi\rangle$ is

$$(\hat{T} + \hat{V})|\Psi\rangle = i\hbar \frac{\partial}{\partial t} |\Psi\rangle, \quad \hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2, \quad (2)$$

where the time-dependent potential \hat{V} comprises one-body and two body terms and is a multiplicative operator in the Schrödinger representation. The one-body electron density and electron flux are

$$n(\mathbf{r}, t) = \langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle, \quad (3)$$

$$\mathbf{j}(\mathbf{r}, t) = \langle \Psi | \hat{\mathbf{j}}(\mathbf{r}) | \Psi \rangle, \quad (4)$$

$$\hat{\mathbf{j}}(\mathbf{r}) = -\frac{i\hbar}{2m} \sum_{i=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \nabla_{\mathbf{r}_i}]. \quad (5)$$

The divergence of the current operator $\hat{\mathbf{j}}(\mathbf{r})$ is then

$$\nabla_{\mathbf{r}} \cdot \hat{\mathbf{j}}(\mathbf{r}) = -\frac{i\hbar}{2m} \sum_{i=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \nabla_{\mathbf{r}_i}^2], \quad (6)$$

where we have used $\delta'(y)f(y) = -\delta(y)f'(y)$ and $[\partial_x \delta(x-y)]f(y) = \delta(x-y)f'(y)$.

We further note that $[\delta(\mathbf{r} - \mathbf{r}_i), \nabla_{\mathbf{r}_j}^2] = 0$ for $i \neq j$, and therefore, we may replace the sum in Eq. (6) with a double sum,

$$\begin{aligned} \nabla_{\mathbf{r}} \cdot \hat{\mathbf{j}}(\mathbf{r}) &= -\frac{i\hbar}{2m} \sum_{i,j=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \nabla_{\mathbf{r}_j}^2] \\ &= \frac{i}{\hbar} \sum_{i=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \hat{T}] \\ &= \frac{i}{\hbar} \sum_{i=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \hat{H}], \end{aligned} \quad (7)$$

where the last line owes to the multiplicative nature of \hat{V} .

The divergence of the electron flux reads then, using the Schrödinger equation,

$$\begin{aligned} \nabla_{\mathbf{r}} \cdot \mathbf{j}(\mathbf{r}, t) &= \frac{i}{\hbar} \left(\langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \hat{H} | \Psi \rangle - cc \right) \\ &= -\langle \Psi | \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \frac{\partial}{\partial t} | \Psi \rangle + cc, \end{aligned} \quad (8)$$

where “cc” stays for the complex conjugate; Eq. (8) is indeed the continuity equation.

III. NIU-THOULESS ADIABATIC FLUX

We consider the time-independent Schrödinger equation,

$$\begin{aligned} \hat{H}_{\lambda} |\Psi_n\rangle &= E_n |\Psi_n\rangle, \quad \hat{H}_{\lambda} = \hat{T} + \hat{V}_{\lambda} \\ \hat{T} &= \frac{1}{2m} \sum_{i=1}^N |\mathbf{p}_i|^2 = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2, \end{aligned} \quad (9)$$

where the potential depends on a single parameter λ that summarizes the nuclear configuration; it could be replaced by an explicit set of nuclear coordinates at the only price of burdening the notations. The time-independent potential \hat{V}_{λ} comprises one-body and two-body terms and is multiplicative; it also includes the classical nuclear–nuclear repulsion energy (a λ -dependent constant, not an operator). We assume a singlet ground state, and we neglect irrelevant spin variables.

We leave the λ -dependence of the eigenvalues and eigenstates as implicit throughout; the time-independent N -body density matrix (also known as ground-state projector) is then

$$\hat{\rho}_{\lambda} = |\Psi_0\rangle \langle \Psi_0|. \quad (10)$$

In order for the adiabatic expansion to be possible, we require the ground-state to be nondegenerate for all λ values.

When λ is varied in time, the Hamiltonian becomes time-dependent, and we write the exact density matrix as

$$\hat{\rho}(t) = \hat{\rho}_{\lambda} + \delta\hat{\rho}(t). \quad (11)$$

Since \hat{H}_{λ} commutes with $\hat{\rho}_{\lambda}$, the equation of motion is

$$[\hat{H}_{\lambda}, \delta\hat{\rho}] = i\hbar \left(\frac{\partial}{\partial t} \hat{\rho}_{\lambda} + \frac{\partial}{\partial t} \delta\hat{\rho} \right). \quad (12)$$

The lowest-order adiabatic flux is obtained, following NT, by neglecting the second term in parentheses,

$$\hat{H}_{\lambda} \delta\hat{\rho} - \delta\hat{\rho} \hat{H}_{\lambda} = i\hbar \dot{\lambda}(t) (|\partial_{\lambda} \Psi_0\rangle \langle \Psi_0| + |\Psi_0\rangle \langle \partial_{\lambda} \Psi_0|). \quad (13)$$

Upon multiplying all terms in the equation by $\langle \Psi_n |$ on the left and by $|\psi_0\rangle$ on the right, we get

$$(E_n - E_0) \delta\rho_{n0} = i\hbar \dot{\lambda}(t) \langle \Psi_n | \partial_{\lambda} \Psi_0 \rangle, \quad (14)$$

where we have set

$$\delta\rho_{nn'} = \langle \Psi_n | \delta\hat{\rho} | \Psi_{n'} \rangle. \quad (15)$$

Inversion of Eq. (14) yields

$$\delta\rho_{n0} = -i\hbar \dot{\lambda}(t) \frac{\langle \Psi_n | \partial_{\lambda} \Psi_0 \rangle}{E_0 - E_n}, \quad n \neq 0. \quad (16)$$

The time-dependence of $\delta\rho_{n0}$ is explicit in $\dot{\lambda}(t)$ and implicit in the time-dependence of the instantaneous eigenvalues and eigenstates at $\lambda = \lambda(t)$.

Since \hat{H}_{λ} is time-reversal invariant, the eigenfunctions are real and $\delta\rho_{n0} = -\delta\rho_{0n}$; owing to norm conservation, $\delta\rho_{00} = 0$, and the

matrix elements with both $n \neq 0$ and $n' \neq 0$ are of higher order. The lowest-order expression for the complete $\delta\hat{\rho}$ is, therefore,

$$\delta\hat{\rho} = \sum_n \delta\rho_{n0} (|\Psi_n\rangle\langle\Psi_0| - |\Psi_0\rangle\langle\Psi_n|). \quad (17)$$

As pointed out in the Introduction, the first term in Eq. (11) does not contribute to the electronic flux, which, therefore, is

$$\begin{aligned} \mathbf{j}(\mathbf{r}, t) &= \sum_n \delta\rho_{n0} (\langle\Psi_0|\hat{\mathbf{j}}(\mathbf{r})|\Psi_n\rangle - \text{cc}) \\ &= 2\sum_n \delta\rho_{n0} \langle\Psi_0|\hat{\mathbf{j}}(\mathbf{r})|\Psi_n\rangle \\ &= -2i\hbar\dot{\lambda}(t) \sum_{n \neq 0} \frac{\langle\Psi_0|\hat{\mathbf{j}}(\mathbf{r})|\Psi_n\rangle\langle\Psi_n|\partial_\lambda\Psi_0\rangle}{E_0 - E_n}, \end{aligned} \quad (18)$$

since $\langle\Psi_0|\hat{\mathbf{j}}(\mathbf{r})|\Psi_n\rangle$ is purely imaginary. The only entries in the NT electronic flux [Eq. (18)] are the eigenvalues and eigenstates of the instantaneous Hamiltonian \hat{H}_λ at time t ; the flux is proportional to $\dot{\lambda}(t)$, which is infinitesimal in the adiabatic limit.

At this point, the “lowest order” expansion leading to the electronic-flux formula above can be better specified. The term neglected in Eq. (12) is clearly proportional to $\ddot{\lambda}(t)$; therefore, whenever $\lambda(t)$ evolves periodically in time at frequency ω , then—as anticipated in the Introduction—the NT adiabatic flux is linear in ω and neglects terms of order ω^2 and higher. On practical grounds, the adiabatic approximation holds whenever $\hbar\omega$ is much smaller than the first excitation energy.

IV. ADIABATIC CONTINUITY EQUATION

The lowest-order NT density matrix is $\hat{\rho}_\lambda + \delta\hat{\rho}$, with $\delta\hat{\rho}$ given by Eq. (17): Only its second term contributes to the flux, while instead only its first term contributes to the density. The lowest-order time-derivative of $n(\mathbf{r}, t)$ is then (owing to time-reversal invariance)

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = 2\dot{\lambda}(t) \langle\Psi_0|\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) |\partial_\lambda\Psi_0\rangle. \quad (19)$$

Therefore, at variance with the electronic flux [Eq. (18)], $\partial n(\mathbf{r}, t)/\partial t$ is obtained—to the same adiabatic order—from a single-state expression.

Equations (7) and (18) yield

$$\begin{aligned} \nabla_{\mathbf{r}} \cdot \mathbf{j}(\mathbf{r}, t) &= \frac{2i}{\hbar} \sum_n \delta\rho_{n0} \langle\Psi_0|\sum_{i=1}^N [\delta(\mathbf{r} - \mathbf{r}_i), \hat{H}_\lambda] |\Psi_n\rangle \\ &= \frac{2i}{\hbar} \sum_n \delta\rho_{n0} (E_n - E_0) \langle\Psi_0|\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) |\Psi_n\rangle \\ &= -2\dot{\lambda}(t) \sum_n \langle\Psi_0|\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) |\Psi_n\rangle\langle\Psi_n|\partial_\lambda\Psi_0\rangle, \end{aligned} \quad (20)$$

whence the continuity equation follows by exploiting completeness.

V. ELECTRONIC FLUX IN CONDENSED MATTER

We have implicitly considered so far a bounded N -electron system, whose wave functions vanish far away from the sample:

such boundary conditions are dubbed “open” in condensed-matter-theory jargon. Next, we address instead an unbounded many-electron system within Born–von–Kármán periodic boundary conditions (PBCs): the many-body wave functions are periodic with period L over each electron Cartesian coordinate $r_{i\alpha}$ independently. One considers, therefore, a system of N interacting electrons in a cubic box—often called “supercell”—of volume L^3 , together with its periodic replicas. The Hamiltonian has the same form as of Eq. (9), where the potential V_λ now obeys PBCs and includes the classical nuclear–nuclear repulsion; the supercell is charge-neutral. The limit $N \rightarrow \infty$, $L \rightarrow \infty$, $N/L^3 = \langle n \rangle$ constant is understood. It is not required that the system is crystalline, only that it is macroscopically homogeneous. When the potential V_λ is adiabatically varied, the microscopic electronic flux is provided by Eq. (18) as it stands if the PBC eigenstates are normalized to one over the supercell.

The additional feature here is the *macroscopic* electronic flux $\langle \mathbf{j}(t) \rangle$, defined as the sample average of $\mathbf{j}(\mathbf{r}, t)$, which obviously is divergenceless. Suppose that the flux is along the positive x -direction: such flux may exist owing ideally to an electron source at $x = -\infty$ and a drain at $x = +\infty$. The electrical current density that flows through the sample when V_λ is adiabatically varied in time equals $-e\langle \mathbf{j}(t) \rangle$. This is the current due to the electrons only; the nuclear charges may also contribute to the electrical current.

If one defines the many-body velocity operator as

$$\hat{\mathbf{v}} = -\frac{i\hbar}{m} \sum_{i=0}^N \nabla_{\mathbf{r}_i} = \frac{1}{m} \sum_{i=0}^N \mathbf{p}_i, \quad (21)$$

then the macroscopic average of Eq. (18) is

$$\langle \mathbf{j}(t) \rangle = -\frac{i\hbar\dot{\lambda}(t)}{L^3} \sum_{n \neq 0} \left(\frac{\langle\Psi_0|\hat{\mathbf{v}}|\Psi_n\rangle\langle\Psi_n|\partial_\lambda\Psi_0\rangle}{E_0 - E_n} - \text{cc} \right). \quad (22)$$

A powerful transformation, inspired once more by NT—although somewhat different from the original formalism—allows eliminating the sum over the excited states, as shown in the following.

One generalizes the Hamiltonian in Eq. (9) by considering the family of Hamiltonians,

$$\hat{H}_{\kappa\lambda} = \hat{T}_\kappa + \hat{V}_\lambda \quad \hat{T}_\kappa = \frac{1}{2m} \sum_{i=1}^N |\mathbf{p}_i + \hbar\boldsymbol{\kappa}|^2. \quad (23)$$

The PBC eigenvalues and eigenstates now depend on both $\boldsymbol{\kappa}$ and λ . The vector parameter $\boldsymbol{\kappa}$, having the dimensions of an inverse length, corresponds to perturbing the Hamiltonian with a vector potential $\mathbf{A} = \hbar c\boldsymbol{\kappa}/e$, constant in space and in time: it is, therefore, a pure gauge transformation. As observed back in 1964 by Kohn,¹³ PBCs violate gauge-invariance in the conventional sense (at any finite L): for instance, E_0 may depend on $\boldsymbol{\kappa}$. The virtue of Eq. (23) is that the many-body velocity operator [Eq. (21)] and the average flux [Eq. (22)] can be recast as

$$\hat{\mathbf{v}} = \frac{1}{\hbar} \partial_\kappa \hat{H}_{\kappa\lambda}, \quad \boldsymbol{\kappa} = 0, \quad (24)$$

$$\langle \mathbf{j}(t) \rangle = -\frac{i\dot{\lambda}(t)}{L^3} \sum_{n \neq 0} \left(\frac{\langle\Psi_0|\partial_\kappa \hat{H}_{\kappa\lambda} |\Psi_n\rangle\langle\Psi_n|\partial_\lambda\Psi_0\rangle}{E_0 - E_n} - \text{cc} \right). \quad (25)$$

Then, we note that perturbation theory yields

$$|\partial_{\kappa}\Psi_0\rangle = \sum_{n\neq 0} |\Psi_n\rangle \frac{\langle \Psi_n | \partial_{\kappa} \hat{H}_{\kappa\lambda} | \Psi_0 \rangle}{E_0 - E_n}, \quad (26)$$

$$\langle \mathbf{j}(t) \rangle = -\frac{i\dot{\lambda}(t)}{L^3} (\langle \partial_{\kappa}\Psi_0 | \partial_{\lambda}\Psi_0 \rangle - \langle \partial_{\lambda}\Psi_0 | \partial_{\kappa}\Psi_0 \rangle). \quad (27)$$

The extensive quantity in parentheses, multiplied by i , takes, at the present time, the name of many-body Berry curvature in the (κ, λ) variables;¹¹ here, it is evaluated at $\kappa = 0$.

The expressions provided above for both the microscopic flux $\mathbf{j}(\mathbf{r}, t)$ and the macroscopic one $\langle \mathbf{j}(t) \rangle$ apply to either metals or insulators and to either solids or liquids. In the special case of a crystalline insulator, the adiabatic current $-e\langle \mathbf{j}(t) \rangle$ coincides by definition with the time derivative of the macroscopic electrical polarization^{11,14} (electronic term thereof; the classical nuclear term has to be added). In the case of an insulating liquid, whenever the nuclear configuration $\lambda(t)$ is a periodic function—i.e., $\lambda(T) = \lambda(0)$, where T is a macroscopic time—the integrated transported charge in time T is integer: this outstanding fact is the theoretical basis for Faraday's laws of electrolysis.¹⁵ Finally, in the case of a metal, the current $-e\langle \mathbf{j}(t) \rangle$ linearly induced by a dc electric field defines the Drude weight of the material.¹⁶

VI. CONCLUSIONS

After defining in the Introduction the adiabaticity parameter ω , I have shown how the concise and elegant NT approach can be extended to molecular physics, thus yielding the electronic flux to linear order in adiabaticity in terms of the eigenstates and eigenvalues of the instantaneous Hamiltonian at a given time; it is then shown that the continuity equation is conserved to the same order. The major result here—Eq. (18)—is not new: it has been first obtained in Ref. 1 from a different logic, in a different formalism, and even in a different semantics from NT (i.e., “complete” adiabatic approximation).

In the chemical-physics literature, the flux problem has been dealt with so far in the more general context of the Born–Oppenheimer (also called Born–Huang) decoupling of the equations of motion for a system of electrons and nuclei.^{1,2,9} At variance with the previous literature, here, I have solely addressed the adiabatic approximation by itself and the flux problem therein, keeping—for the sake of clarity—the issue as conceptually distinct from the validity (or otherwise) of the Born–Oppenheimer approximation in a given molecular-dynamics phenomenon.

The final part of this paper switches to condensed matter physics within Born–von–Kármán periodic boundary conditions in order to summarize some of the known results about adiabatic electron transport therein. In particular, I discuss the macroscopic adiabatic flux, which was indeed the original focus of NT back in 1984.

ACKNOWLEDGMENTS

I have thoroughly discussed electron transport with S. Baroni; his invaluable contribution is gratefully acknowledged. This work was supported by the Office of Naval Research (USA) under Grant No. N00014-20-1-2847.

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

- 1 L. A. Nafe, *J. Chem. Phys.* **79**, 4950 (1983).
- 2 S. Patchkovskii, *J. Chem. Phys.* **137**, 084109 (2012).
- 3 D. J. Diestler *et al.*, *J. Phys. Chem. A* **117**, 8519 (2013).
- 4 A. Schild, F. Agostini, and E. K. U. Gross, *J. Phys. Chem. A* **120**, 3316 (2016).
- 5 A. Schild, *Phys. Rev. A* **98**, 052113 (2018).
- 6 T. Schaupp and V. Engel, *J. Chem. Phys.* **150**, 164110 (2019).
- 7 T. Schaupp and V. Engel, *J. Chem. Phys.* **152**, 204310 (2020).
- 8 T. Schaupp, K. Renziehausen, I. Barth, and V. Engel, *J. Chem. Phys.* **154**, 064307 (2021).
- 9 K. Hanasaki and K. Takatsuka, *J. Chem. Phys.* **154**, 164112 (2021).
- 10 D. J. Thouless, *Phys. Rev. B* **27**, 6083 (1983).
- 11 D. Vanderbilt, *Berry Phases in Electronic Structure Theory* (Cambridge University Press, Cambridge, 2018).
- 12 Q. Niu and D. J. Thouless, *J. Phys. A: Math. Gen.* **17**, 2453 (1984).
- 13 W. Kohn, *Phys. Rev.* **133**, A171 (1964).
- 14 R. Resta, *J. Chem. Phys.* **154**, 050901 (2021).
- 15 R. Resta, *J. Chem. Phys.* **155**, 244503 (2021).
- 16 R. Resta, *J. Phys.: Condens. Matter* **30**, 414001 (2018).