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3 Outline of density-functional perturbation theory

In this section we give an outline of the basic concepts of DFPT, also known as linear-response theory or, in the quantum-chemistry context, “analytic

3. Sơ lược về lý thuyết nhiễu loạn hàm mật độ

Trong phần này, chúng tôi trình bày khái niệm cơ bản về DFPT, hay còn gọi là lý thuyết đáp ứng tuyến tính, hoặc trong hóa lượng tử gọi là các phương pháp “đạo hàm giải tích”.

derivative” methods. DFPT has an outstanding role in addressing many crystalline properties besides dielectric ones, including lattice-dynamical, elastic, and electron-phonon coupling properties. A comprehensive review of DFPT in crystalline solids is available in Ref. [16]. We will emphasize the formulation and application of DFPT for evaluating derivatives of the macroscopic polarization to compute such quantities as the Born effective charge from Eq. (5) [27-30] or the dielectric constant $\epsilon = 1 + 4\pi\chi$ with χ from Eq. (2). Since the nuclear contribution to the macroscopic polarization is trivial, we focus on the electronic term only, indicating it with P for the sake of simplicity. We stress, however, that the nuclear term is essential to ensure charge neutrality and translational invariance.

Let us start with a large but finite insulating system having discrete single particle orbitals $\{|\psi_i\rangle\}$ which vanish outside the sample. We will switch to the crystalline case, with periodic boundary conditions, only later in this Section. We write the electron density as $n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$, where the sum is over occupied (“valence”) states i , and a factor of 2 may be inserted in all formulas for the spin-degenerate case. The electronic term in the macroscopic polarization is then, from Eqs. (1) and (6),

DFPT có vai trò nổi bật trong việc xác định nhiều tính chất của tinh thể cũng như tính chất của điện môi bao gồm tính chất động học mạng, đàn hồi và sự ghép electron-phonon. Tài liệu tham khảo [16] trình bày khá toàn diện về phương pháp DFPT trong chất rắn tinh thể.

Chúng ta sẽ tập trung vào việc xây dựng và áp dụng DFPT để tính đạo hàm của độ phân cực vĩ mô và suy ra các đại lượng như điện tích hiệu dụng Bohr từ PT (5) [27-30] hoặc hằng số điện môi $\epsilon = 1 + 4\pi\chi$, với χ được cho trong PT.(2). Do đóng góp của hạt nhân vào độ phân cực vĩ mô không đáng kể, chúng tôi chỉ tập trung vào số hạng điện tử, kí hiệu là P để đơn giản. Tuy nhiên, chúng tôi nhấn mạnh rằng số hạng hạt nhân là cần thiết để đảm bảo sự trung hòa điện tích và sự bất biến tịnh tiến.

Giả sử chúng ta xét một hệ cách điện lớn nhưng hữu hạn có orbital của từng hạt rời rạc $|\psi_i\rangle$ và bằng không bên ngoài mẫu. Chúng ta sẽ chuyển sang trường hợp tinh thể, với điều kiện biên tuần hoàn trong phần sau của mục này. Biểu diễn mật độ electron dưới dạng

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2, \quad (6)$$



(7) where L^3 is the volume of the finite sample.

Suppose now that we switch on a given perturbation—e.g. a sublattice displacement as in Eq. (5)—whose amplitude we measure by a dimensionless parameter A . We expand all relevant quantities in powers of A , e.g.,

$$V_{\text{ext}}(\mathbf{r}) = V_{\text{ext}}^{(0)}(\mathbf{r}) + V_{\text{ext}}^{(1)}(\mathbf{r}) + V_{\text{ext}}^{(2)}(\mathbf{r}) + \dots, \quad (8)$$

where $V_{\text{ext}}^{(n)}$ contains the terms of order A^n . Here $V_{\text{ext}}^{(0)}$ is the bare (or unscreened) potential felt by the electrons, so that $V_{\text{ext}}^{(1)}$ is the first-order perturbing term in the KS Hamiltonian [31]. We write similar expansions for the self-consistently screened total potential $V(\mathbf{r})$, the electron density $n(\mathbf{r})$, the wavefunctions $|\psi_i^*\rangle$, etc. Using Eq. (7), we wish to evaluate the corresponding first-order change in the polarization,

$$P^{(1)} = -\frac{e}{L^3} \sum_i \langle \psi_i^* | \mathbf{r} | \psi_i \rangle + \text{c.c.}; \quad (9)$$

where the sum is over occupied (“valence”) states and “c.c.” is the complex conjugate.

For a finite system, Eq. (9) is straightforward to evaluate as soon as $|\psi_i^{(0)}\rangle$ is available. The latter can be obtained by ordinary first-order perturbation theory

$$|\psi_i^{(1)}\rangle = \sum_{j \neq i} \frac{V_{ji}^{(1)}}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle \quad (10)$$

involving a sum over all other states, including all unoccupied

$$P = -\frac{e}{L^3} \sum_i \langle \psi_i | \mathbf{r} | \psi_i \rangle, \quad (7)$$

$$V_{\text{ext}}(\mathbf{r}) = V_{\text{ext}}^{(0)}(\mathbf{r}) + V_{\text{ext}}^{(1)}(\mathbf{r}) + V_{\text{ext}}^{(2)}(\mathbf{r}) + \dots, \quad (8)$$

$$P^{(1)} = -\frac{e}{L^3} \sum_i \langle \psi_i^{(0)} | \mathbf{r} | \psi_i^{(1)} \rangle + \text{c.c.}, \quad (9)$$

$$|\psi_i^{(1)}\rangle = \sum_{j \neq i} \frac{V_{ji}^{(1)}}{E_i^{(0)} - E_j^{(0)}} |\psi_j^{(0)}\rangle \quad (10)$$

states. Because such sums often converge very slowly, it is a common practice to obtain $|\psi_i^{(1)}\rangle$ instead by solving the equivalent implicit Sternheimer equation

$$(\mathcal{E}_i - H) Q_i |\psi_i^{(1)}\rangle = Q_i V^{(1)} |\psi_i^{(0)}\rangle \quad (11)$$

for $|\psi_i^{(1)}\rangle$, where $Q_i = 1 - P_i$. This can be accomplished using standard iterative techniques.

Finally, since $V = V_{\text{ext}} + V_H + V_{\text{xc}}$, it is also necessary to iterate an outer self-consistent screening loop to solve for $n^{(1)}(\mathbf{r}) = \sum_i |\psi_i^{(1)}(\mathbf{r})|^2 + \text{c.c.}$ (12)

It is permissible to replace the sum over $j = i$ in Eq. (10) by a sum over unoccupied states only, and also the projector Q_i in Eq. (11) by a projector onto unoccupied states only, for the purposes of computing any physical change such as $P^{(1)}$ of Eq. (9). This is almost always done in practice, but for simplicity we will not follow this path here.

$$V^{(1)} = V_{\text{ext}} + f_H \cdot n^{(1)} + f_{\text{xc}} \cdot n^{(1)}$$

together with Eq. (11). Here the dot product indicates an integral over \mathbf{r}' ; f_H is the (linear) Hartree potential kernel, and

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$$

is the exchange-correlation kernel, where E_{xc} is the KS exchange-correlation energy functional [31]. This completes the solution of Eq. (9) in the case of a finite sample.

$$(E_i^{(0)} - H) Q_i |\psi_i^{(1)}\rangle = Q_i V^{(1)} |\psi_i^{(0)}\rangle \quad (11)$$

$$n^{(1)}(\mathbf{r}) = \sum_i \psi_i^{(0)*}(\mathbf{r}) \psi_i^{(1)}(\mathbf{r}) + \text{c.c.} \quad (12)$$

$$V^{(1)} = V_{\text{ext}}^{(1)} + f_H \cdot n^{(1)} + f_{\text{xc}} \cdot n^{(1)} \quad (13)$$

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{\text{xc}}(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \quad (14)$$

We now prepare to apply the thermodynamic limit and let the size of the sample become infinite. Then the occupied and empty states $|\psi_j^{(0)}\rangle$ will become Bloch states $|\psi_{\mathbf{k}}^{(0)}\rangle$. However, it is not permissible to leave the position operator r in place in Eq. (9), because matrix elements of r between Bloch functions are ill-defined. Therefore, before taking the thermodynamic limit, we first introduce an alternative method for obtaining $|\psi_{\alpha,i}^{(1)}\rangle = \langle \psi_{\alpha,i}^{(1)} | \psi_i^{(0)} \rangle$ that avoids this problem. In particular, we compute it from

$$\dots\dots\dots (15)$$

as can easily be checked using the definition

$$\mathbf{v} = -\frac{i}{\hbar} [r, H] \quad (16)$$

of the velocity operator. This approach appears to reintroduce an undesirable sum over unoccupied states, but in view of the similarity of Eq. (15) to Eq. (10), we can once again replace it by a Sternheimer equation

$$(E_i^{(0)} - H) Q_i |\psi_{\alpha,i}^{(1)}\rangle = Q_i (i\hbar v_{\alpha}) |\psi_i^{(0)}\rangle \quad (17)$$

which will be solved by iterative methods. Then Eq. (9) becomes $P_{\alpha}^{(1)} = \sum_j \langle \psi_{\alpha,i}^{(1)} | \psi_j^{(0)} \rangle \psi_j^{(0)} + \text{c.c.}$ (18)

The velocity operator \mathbf{v} coincides with \mathbf{p}/m in the simple case where all potentials are local. The generalization to nonlocal pseudopotentials—either norm-conserving or ultrasoft [32]—has been

$$|\tilde{\psi}_{\alpha,i}^{(1)}\rangle = \sum_{j \neq i} \frac{|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|}{E_i^{(0)} - E_j^{(0)}} (i\hbar v_{\alpha}) |\psi_i^{(0)}\rangle, \quad (15)$$

$$\mathbf{v} = -\frac{i}{\hbar} [\mathbf{r}, H] \quad (16)$$

$$(E_i^{(0)} - H) Q_i |\tilde{\psi}_{\alpha,i}^{(1)}\rangle = Q_i (i\hbar v_{\alpha}) |\psi_i^{(0)}\rangle \quad (17)$$

$$P_{\alpha}^{(1)} = -\frac{e}{L^3} \sum_i \langle \tilde{\psi}_{\alpha,i}^{(1)} | \psi_i^{(1)} \rangle + \text{c.c.} \quad (18)$$

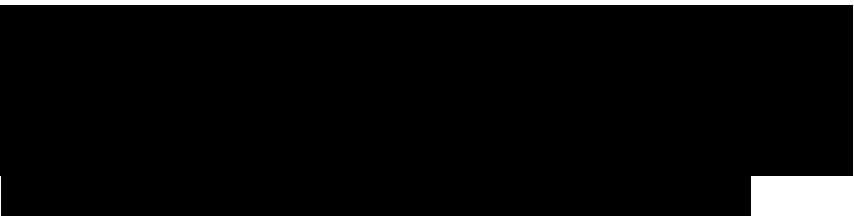
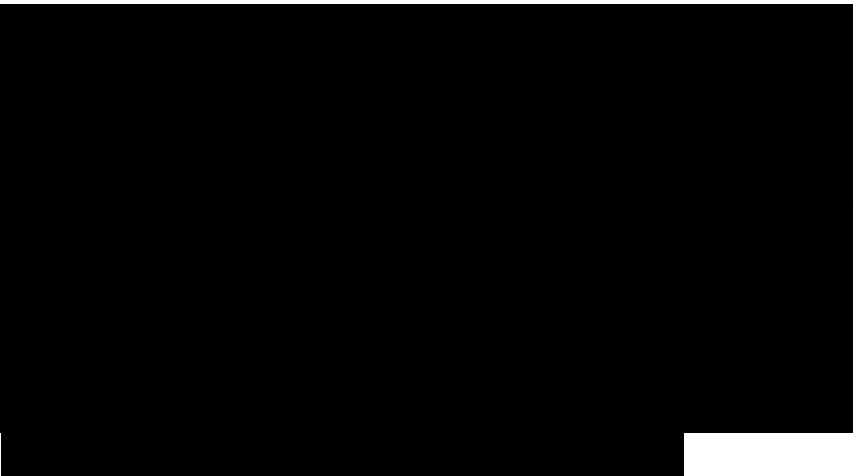
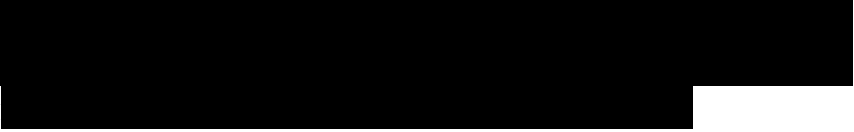
considered in Ref. [16].

A conceptually similar scheme was first proposed in the 1950s by Sternheimer [33] for evaluating atomic polarizabilities.

We emphasize that the replacement of \mathbf{r} by \mathbf{v} at this point essentially corresponds to switching from a formulation based on charge to one based on current. If we are actually dealing with a finite system, Eqs. (9) and (18) are equally valid. But in taking the thermodynamic limit, matrix elements of \mathbf{r} become ill-defined, for essentially the same reason that Eq. (1) is ill-defined. For an extended system in the thermodynamic limit, it is then mandatory to use the velocity formula, hence the current, as in Eq. (18). Focusing on currents has thus been crucial to the development of the modern theory of polarization, as illustrated further in the following Section.

Let us now make the transition to the crystalline case, with periodic boundary conditions, and let the index i be identified with the band index n and the Bloch vector \mathbf{k} . At this point we also drop the superscript “(0)” from unperturbed quantities, so that, e.g., $|\psi_{n\mathbf{k}}^{(0)}\rangle \equiv |\psi_{n\mathbf{k}}\rangle$. Then Eq. (18) becomes

where n runs over the occupied valence bands of the insulator and the integral is over the Brillouin zone (BZ). In combination with Eq. (10) or



$$\mathbf{P}^{(1)} = \frac{i\hbar e}{(2\pi)^3} \sum_n \sum_{m \neq n \text{ BZ}} \int d\mathbf{k} \frac{\langle \psi_{n\mathbf{k}} | \mathbf{v} | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | \psi_{n\mathbf{k}}^{(1)} \rangle}{E_{n\mathbf{k}} - E_{m\mathbf{k}}} + \text{c.c.}, \quad (19)$$

(11), this provides the solution to the problem of computing the first-order linear response of the polarization in response to a perturbation, such as a sublattice displacement, that preserves the crystal periodicity.

While such linear-response or DFPT methods have satisfactorily provided P derivatives over the years, the problem of evaluating the “polarization itself” remained an open and confusing one until the mid-1990s, when the advent of the modern theory of polarization provided a resolution. This is the subject of the next Section.

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4 The Berry-phase theory of polarization

In this Section, we provide a brief derivation of the central results that were uncovered in the early 1990s, which are often referred to as the “modern theory of polarization.” The basic idea is to consider the change in polarization of a crystal as it undergoes some slow change, e.g., a slow displacement of one sublattice relative to the others, and relate this to the current that flows during this adiabatic evolution of the system. These considerations will allow us to arrive at an expression for the polarization that does not take the form of an expectation value of an operator, as is normally the case. Rather, it takes the form of a “Berry phase,” which is a



geometrical phase property of a closed manifold (the Brillouin zone) on which a set of vectors (occupied Bloch states) are defined.

Once again, we assume that the crystal Hamiltonian H_A depends smoothly on parameter A and has Bloch eigenvectors obeying $H_A|\psi_{n\mathbf{k}}\rangle = E_{n\mathbf{k}}|\psi_{n\mathbf{k}}\rangle$ (the A subscripts will often be suppressed for clarity). We also assume that A changes slowly with time, so that the adiabatic approximation is appropriate. With a slight change of notation (introducing $dA = d/dA$), the principal result (19) of the previous Section becomes

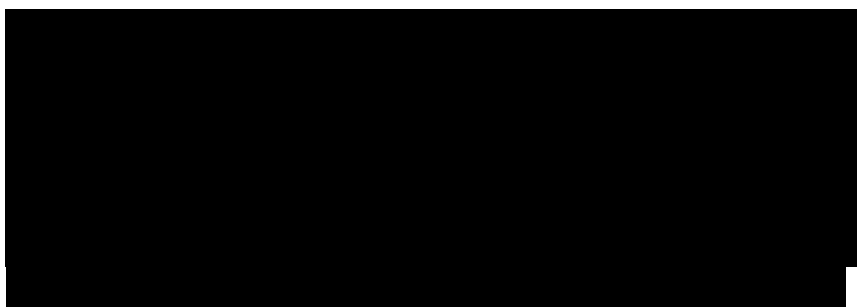
.....
 Since the spatially averaged current density is just $\mathbf{j} = d\mathbf{P}/dt = (d\mathbf{P}/dA)A$, this equation can be converted into the statement that the instantaneous current is given by

$$\mathbf{j} = \frac{i\hbar e}{2\pi^3} \sum_n \sum_{m \neq n} \int_{BZ} d\mathbf{k} \frac{\langle \psi_{n\mathbf{k}} | \mathbf{v} | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | dA | \psi_{n\mathbf{k}} \rangle}{E_{n\mathbf{k}} - E_{m\mathbf{k}}} + \text{c.c.} \quad (21)$$

We can then say that the change in polarization during some time interval is

$$\Delta \mathbf{P} = \int \mathbf{j}(t) dt \quad (22)$$

where $\mathbf{j}(t)$ is given by Eq. (21). This formulation is particularly intuitive, since it is phrased in terms of the current density that is physically flowing through the crystal as the system traverses some adiabatic path. But since $\mathbf{j} = d\mathbf{P}/dt$ is proportional to $A = dA/dt$ in Eq. (21), the dt can be factored out, and we can equivalently go back to



$$\partial_\lambda \mathbf{P} = \frac{i\hbar e}{(2\pi)^3} \sum_n \sum_{m \neq n} \int_{BZ} d\mathbf{k} \frac{\langle \psi_{n\mathbf{k}} | \mathbf{v} | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | \partial_\lambda \psi_{n\mathbf{k}} \rangle}{E_{n\mathbf{k}} - E_{m\mathbf{k}}} + \text{c.c.} \quad (20)$$



$$\mathbf{j} = \frac{i\hbar e \dot{\lambda}}{(2\pi)^3} \sum_n \sum_{m \neq n} \int_{BZ} d\mathbf{k} \frac{\langle \psi_{n\mathbf{k}} | \mathbf{v} | \psi_{m\mathbf{k}} \rangle \langle \psi_{m\mathbf{k}} | \partial_\lambda \psi_{n\mathbf{k}} \rangle}{E_{n\mathbf{k}} - E_{m\mathbf{k}}} + \text{c.c.} \quad (21)$$



$$\Delta \mathbf{P} = \int \mathbf{j}(t) dt \quad (22)$$



$$\Delta \mathbf{P} = \int (\partial_\lambda \mathbf{P}) d\lambda \quad (23)$$

integrating Eq. (20) directly to obtain

$$AP = j(dxP) dA \quad (23)$$

where dAP is given by Eq. (20). This is the formally more direct path.

In the case that the Hamiltonian is just $p^2/2m_e$ plus a local potential, it follows that $v = p/m_e$, and it is possible to evaluate Eq. (20) directly (or, to avoid the sum over unoccupied states, to obtain $\langle \psi_{nk} | v | \psi_{nk} \rangle$ by the method of Eq. (17)). However, we can proceed in a more general fashion, which also eliminates the energy denominator in Eq. (20), using ordinary $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. Here we introduce the effective Schrodinger equation $H_k |u_{nk}\rangle = E_{nk} |u_{nk}\rangle$ where $u_{nk}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} \psi_{nk}(\mathbf{r})$ and $H_k = e^{-i\mathbf{k}\cdot\mathbf{r}} H e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{2m_e} (\mathbf{p} + \hbar\mathbf{k})^2 + e^{-i\mathbf{k}\cdot\mathbf{r}} V e^{i\mathbf{k}\cdot\mathbf{r}}$. (24)

(The last term reduces back to V if the potential commutes with \mathbf{r} , but this is often not the case when dealing with modern pseudopotentials.)

By elementary perturbation theory, the first-order change of $|u_{nk}\rangle$ with wavevector is just $|\nabla_{\mathbf{k}} u_{nk}\rangle = \sum_{m \neq n} \frac{(\nabla_{\mathbf{k}} H_k) |u_{mk}\rangle}{E_{nk} - E_{mk}}$. (25)

But using the definition (16) of the velocity operator, and $\mathbf{v}_k H_k = -i[\mathbf{r}, H_k]$ (which follows immediately from $H_k = e^{-i\mathbf{k}\cdot\mathbf{r}} H e^{i\mathbf{k}\cdot\mathbf{r}}$), the first matrix element in the numerator of Eq. (20) becomes

$$\langle -\nabla_{\mathbf{k}} u_{nk} | \mathbf{v} | u_{mk} \rangle = \hbar^{-1} \langle u_{nk} | [\mathbf{r}, H_k] | u_{mk} \rangle = \hbar^{-1} \langle u_{nk} | (\nabla_{\mathbf{k}} H_k) | u_{mk} \rangle. \quad (26)$$

$$\langle H_{\mathbf{k}} | u_{\mathbf{m}\mathbf{k}} \rangle - \hbar \langle u_{\mathbf{n}\mathbf{k}} | \nabla_{\mathbf{k}} H_{\mathbf{k}} | u_{\mathbf{m}\mathbf{k}} \rangle \cdot (26)$$

Then Eq. (20) turns into
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or, using Eq. (25), simply

$$d\mathbf{P} = \sum_n \int_{BZ} d\mathbf{k} \{ \nabla_{\mathbf{k}} u_{\mathbf{n}\mathbf{k}} | \partial_{\lambda} u_{\mathbf{n}\mathbf{k}} \rangle + \text{C.C.} \} \cdot (28)$$

Remarkably, the sum over empty states has been eliminated from this formula, showing that the rate of change of polarization with A is a property of the occupied bands only, as one expects on physical grounds. This expression can be integrated with respect to A to obtain [6]

$$P(A) = \sum_n \int_{BZ} d\mathbf{k} \langle u_{\mathbf{n}\mathbf{k}} | \nabla_{\mathbf{k}} | u_{\mathbf{n}\mathbf{k}} \rangle \cdot (29)$$

as may be verified by taking the A derivative of both sides of Eq. (29) and comparing with Eq. (28). The result is independent of the particular path of $A(t)$ in time, and depends only on the final value of A , as long as the change is slow in the adiabatic sense. We therefore associate $P(A)$ with the physical polarization of state A , and henceforth drop the A label. Since $\langle \nabla_{\mathbf{k}} (u_{\mathbf{n}\mathbf{k}} | u_{\mathbf{n}\mathbf{k}} \rangle) = 0$, the integrand is pure imaginary, and Eq. (29) can alternatively be written as

To be more precise, this is the electronic contribution to the polarization; to this must be added the nuclear (or “ionic”)

$$\partial_{\lambda} \mathbf{P} = \frac{ie}{(2\pi)^3} \sum_n \sum_{m \neq n, BZ} \int d\mathbf{k} \frac{\langle u_{\mathbf{n}\mathbf{k}} | \nabla_{\mathbf{k}} H_{\mathbf{k}} | u_{\mathbf{m}\mathbf{k}} \rangle \langle u_{\mathbf{m}\mathbf{k}} | \partial_{\lambda} u_{\mathbf{n}\mathbf{k}} \rangle}{E_{\mathbf{n}\mathbf{k}} - E_{\mathbf{m}\mathbf{k}}} + \text{c.c.} \quad (27)$$

$$\partial_{\lambda} \mathbf{P} = \frac{ie}{(2\pi)^3} \sum_n \int_{BZ} d\mathbf{k} \langle \nabla_{\mathbf{k}} u_{\mathbf{n}\mathbf{k}} | \partial_{\lambda} u_{\mathbf{n}\mathbf{k}} \rangle + \text{c.c.} \quad (28)$$

$$\mathbf{P}(\lambda) = \frac{-ie}{(2\pi)^3} \sum_n \int_{BZ} d\mathbf{k} \langle u_{\mathbf{n}\mathbf{k}} | \nabla_{\mathbf{k}} | u_{\mathbf{n}\mathbf{k}} \rangle \cdot (29)$$

$$\mathbf{P} = \frac{e}{(2\pi)^3} \text{Im} \sum_n \int_{BZ} d\mathbf{k} \langle u_{\mathbf{n}\mathbf{k}} | \nabla_{\mathbf{k}} | u_{\mathbf{n}\mathbf{k}} \rangle \cdot (30)$$

contribution

$$P_{\text{ion}} = Q^{-1} \sum_s Z_s r_s, \quad (31)$$

where the sum is over atoms s having core charge Z_s and location r_s in the unit cell of volume Q .

Equation (30) is the central result of the modern theory of polarization. It says that the electronic contribution to the polarization of a crystalline insulator may be expressed as a Brillouin-zone integral of an “operator” $i\nabla_k$ that plays the role of an r operator in a heuristic sense. However, $i\nabla_k$ is not a normal operator; it involves taking the derivative of the state vector $|u_k\rangle$ with respect to wavevector. In particular, the quantity $i\nabla_k|u_k\rangle$ depends on the choice of relative phases of the Bloch functions at different k ; such a sensitivity is not expected for a “normal” quantum-mechanical operator.

To explore this point, we specialize for the moment to a single band for a one-dimensional (1D) crystal of lattice constant a , so that $P = -e_0/2n$, where

$$0 = -\text{Im} \int dk \langle u_k | \nabla_k | u_k \rangle. \quad (32)$$

Now suppose that a new set of Bloch functions is defined by $|\tilde{u}_k\rangle = e^{-i\beta(k)} |u_k\rangle$, (33) with an equivalent relation between $|\tilde{U}_k\rangle$ and $|u_k\rangle$, where $P(k)$ is some smooth real function of k . As mentioned in the Introduction, such a twist of the phases is often referred to as a “change of gauge.” Then

$$P_{\text{ion}} = \Omega^{-1} \sum_s Z_s r_s, \quad (31)$$

$$\phi = -\text{Im} \int_0^{2\pi/a} dk \langle u_k | \partial_k | u_k \rangle. \quad (32)$$

$$|\tilde{\psi}_k\rangle = e^{-i\beta(k)} |\psi_k\rangle, \quad (33)$$

$$\langle u_k | dk | u_k \rangle = \langle u_k | dk | u_k \rangle - i \frac{d\beta}{dk}, \quad (34)$$

Fig. 3. At left, a sketch of the Brillouin zone of a 1D crystal, regarded as a segment of the real k axis. At right, a sketch of the same Brillouin zone regarded as a topologically closed loop.

showing that the integrand of Eq. (32) depends on the choice of gauge. One may then wonder whether Eq. (30) is well-defined at all.

However, it turns out that the entire integral in Eq. (32) is independent of gauge. The demonstration of this claim depends on the fact that the eigenvectors $|\psi_0(k)\rangle$ are periodic functions of k with

$$|\psi_0(k + 2\pi/a)\rangle = |\psi_0(k)\rangle, \quad (35)$$

which is known as the “periodic gauge condition.” Indeed, it is natural to regard the Brillouin zone not as an interval of the real axis, but as a closed space (i.e., a ring), as illustrated in Fig. 3. Thus, to be sensible, the gauge change should obey

$$\beta(k + 2\pi/a) = \beta(k) + 2\pi m, \quad (36)$$

where m is an integer, so that $\exp(-i\beta)$ will match seamlessly at the Brillouin zone boundary. We shall assume here that $m = 0$, returning to the possibility of $m = 0$ in Sec. 6. The integral of the last term of Eq. (34) over the entire Brillouin zone therefore vanishes, so that $0 = 0$, and the polarization is indeed gauge-invariant. The quantity 0 is

$$\langle \bar{u}_k | \partial_k | \bar{u}_k \rangle = \langle u_k | \partial_k | u_k \rangle - i \frac{d\beta}{dk}, \quad (34)$$

$$|\psi_{2\pi/a}\rangle = |\psi_0\rangle, \quad (35)$$

$$\beta(2\pi/a) = \beta(0) + 2\pi m, \quad (36)$$

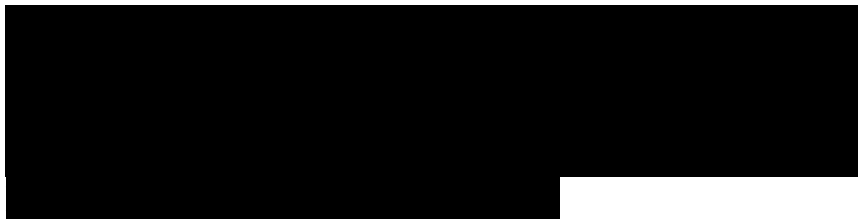
known a “Berry phase” [9]; it is a global phase property of the Bloch bands as the wavevector k is carried around the Brillouin zone.

In order to perform practical calculations using Eq. (30), it is necessary to reformulate the theory on a discrete k mesh. We illustrate this again in the context of the 1D single-band case, where we note that Eq. (32) can be discretized as

$$\phi = - \text{Im} \ln \prod_{j=0}^{M-1} \langle u_{k_j} | u_{k_{j+1}} \rangle \quad (37)$$

where $k_j = 2\pi j/Ma$ is the j ’th k -point in the Brillouin zone. That this reproduces Eq. (32) can be checked by plugging the expansion $u_{k+A} = u_k + A \frac{d}{dk} u_k + O(A^2)$ into Eq. (37) and keeping the leading term as $A \rightarrow 0$. Eq. (37) says to take the complex phase of the product of $\langle u_{k_1} | u_{k_2} \rangle$ with $\langle u_{k_2} | u_{k_3} \rangle$, etc., all the way around the Brillouin zone (as in the right panel of Fig. 3). The gauge-invariance is manifest: changing the phase of one Bloch function $|u_k\rangle$ obviously has no effect, since it appears in the product once as a bra and once as a ket. (Note that, in evaluating Eq. (37), one should apply the periodic gauge condition of Eq. (35) in the form $u_{k+2\pi/a}(x) = e^{-2\pi i x/a} u_k(x)$ in evaluating the last inner product needed to close the loop.)

In three dimensions (3D), the Brillouin zone can be regarded



$$\phi = - \text{Im} \ln \prod_{j=0}^{M-1} \langle u_{k_j} | u_{k_{j+1}} \rangle \quad (37)$$



as a closed 3-torus obtained by identifying boundary points $-0n\mathbf{k} = \wedge_{n,\mathbf{k}+\mathbf{G}_j}$, where \mathbf{G}_j are the three primitive reciprocal lattice vectors. Then the electronic polarization can be written as

where \mathbf{R}_j is the real-space primitive translation corresponding to \mathbf{G}_j , and the Berry phase for band n in direction j is

To compute the $0n_j$ for a given direction j , the sampling of the Brillouin zone is arranged as in Fig. 4, where k_y is the direction along \mathbf{G}_j and \mathbf{k}^\wedge refers to the 2D space of wavevectors spanning the other two primitive reciprocal lattice vectors. For a given \mathbf{k}^\wedge , the Berry phase $0n_j(\mathbf{k}^\wedge)$ is computed along the string of M k -points extending along k_y as in Eq. (37), and finally a conventional average is taken over the \mathbf{k}^\wedge via $K = \text{tt}—Z^\wedge(\mathbf{k}-0 \cdot$ (40)

This is the form in which the Berry-phase theory of polarization is implemented in modern electronic-structure codes. Further details and discussion, including the appropriate reformulation of Eqs. (39-40) for the case of connected multiple bands (i.e., bands with symmetry-induced degeneracies at certain locations in the Brillouin zone) may be found in Refs. [6] and [7].

$$\mathbf{P}_n = \frac{-e}{2\pi\Omega} \sum_j \phi_{nj} \mathbf{R}_j \quad (38)$$

$$\phi_{nj} = -\frac{\Omega}{(2\pi)^3} \text{Im} \int_{\text{BZ}} d^3k \langle u_{n\mathbf{k}} | \mathbf{G}_j \cdot \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle . \quad (39)$$

$$\phi_{nj} = \frac{1}{N_{\mathbf{k}_\perp}} \sum_{\mathbf{k}_\perp} \phi_n(\mathbf{k}_\perp) . \quad (40)$$

