Density-Polarization Functional Theory of the Response of a Periodic Insulating Solid to an Electric Field

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The response of an infinite, periodic, insulating solid to an infinitesimally small electric field is investigated in the framework of density functional theory. We find that the applied perturbing potential is not a unique functional of the periodic density change; it depends also on the change in the macroscopic *polarization*. Moreover, the dependence of the exchange-correlation energy on polarization induces an exchange-correlation electric field. These effects are exhibited for a model semiconductor. We also show that the scissor-operator technique is an approximate way of bypassing this polarization dependence.

Density functional theory (DFT) [1,2] has become the standard method for first-principles calculations of the properties of solids. Within the local density approximation (LDA) [2], the accuracy obtained for a wide set of properties is of the order of a few percent [3]. Notable exceptions to this gratifying picture are the cohesive energy of solids, the energy gap of semiconductors, and their dielectric susceptibility. The first of these failures is attributed to the LDA [3], while the second comes from a discontinuity in the DFT exchange-correlation potential when an electron is added across the gap [4].

The third failure is striking in that it is not easy to see whether it comes from the LDA approximation or from some fundamental feature of DFT. At first sight, the dielectric susceptibility, being the second derivative of the ground state energy with respect to an applied electric field, should be obtained exactly within DFT. Although the corresponding potential change is linear in space, and breaks the periodicity of the solid techniques were found to bypass this problem [5,6]. Unfortunately, the LDA results [5–7] are usually much larger (more than 10%) than the experimental data. Dal Corso, Baroni, and Resta [8] argued that any attempt to improve the LDA calculated value should go in the direction of better approximations to the true functional. The latter authors tried to compute the dielectric response of Si in the generalized gradient approximation (GGA) [8], but with limited success.

Earlier, Levine and Allan had proposed a simple "LDA + scissor correction" approach to the dielectric tensor [6], in which a constant shift Δ is imposed on the conduction bands with respect to the valence bands, to reproduce the correct band gap. The dielectric tensor in this approximation has been found to be within a few percent of the experimental data for more than a dozen semiconductors and insulators [6,7]. But, as emphasized by Dal Corso, Baroni, and Resta, there was no immediate justification within DFT of this successful procedure.

In recent work by Godby, Sham, and Schlüter [9], it was shown that the exchange-correlation potential near

a semiconductor interface acquires a slow linear spatial variation, related to the discontinuity Δ that occurs on addition of an electron to the bulk semiconductor. This variation corresponds to an ultranonlocal "vertex correction" in the Kohn-Sham formulation of the dielectric response of the semiconductor, and depends *crucially* on the electron density at the interface [10]. A connection between the scissor-operator correction and this linear behavior of the exchange-correlation potential was also pointed out.

In this paper we reexamine the response of a periodic solid to an electric field within DFT, and observe that the original proof of Hohenberg and Kohn [1] does not apply to this case. We then prove the equivalent of the Hohenberg and Kohn theorem in perturbation theory, and show that knowledge of both the change in periodic density *and* the change in polarization is needed to recover the change of periodic potential and change of electric field that induced them. The exchange-correlation energy thus depends on the polarization, and this dependence, not taken into account previously, will generate an exchange-correlation electric field, identified with the slow linear variation of the exchange-correlation potential observed by Godby, Sham, and Schlüter [9]. We then explore a simple model that exhibits the crucial features of our theory, and explain the relationship to the scissor-correction approach to the dielectric tensor.

In the DFT approach to the many-body problem, it is shown that the knowledge of the density $n(\mathbf{r})$ of the ground state of a system with Hamiltonian $H_v = T + V_{e-e} + v$ (sum of the kinetic T, electron-electron interaction V_{e-e}, and one-body local potential v operators), uniquely determines the local potential $v(\mathbf{r})$ of this Hamiltonian up to a constant.

Unfortunately, the straightforward application of a homogeneous electric field (linear potential) to a system with a periodic potential does not allow for a ground state solution [11]: A translation against the direction of the field by a whole number of lattice constants would

always lower the electronic energy. The impossibility of a ground state in the presence of a finite electric field renders *invalid* the original proof [1] of density functional theory for this case.

The use of perturbation theory allows us to bypass this problem. We choose to work in the long wave method [12] (an infinitesimal sinusoidal perturbation whose wave vector tends to zero). Equivalent results may be obtained using other techniques mentioned in Ref. [12]. Atomic units, for which the electronic charge is -1, are used. The change of total potential corresponding to an infinitesimal electric field $\delta\mathcal{E}$ is (written in one dimension for brevity)

$$\delta v_{\mathcal{E}}(r) = \lim_{q\to 0}\delta\mathcal{E}\,\frac{\sin(qr)}{q} = \lim_{q\to 0}\frac{\delta\mathcal{E}}{2iq}(e^{iqr} - e^{-iqr}). \quad (1)$$

We also allow for changes of potential that are periodic in space, with the same periodicity as the unperturbed system: $\delta v_G(r) = \delta v(G)\,e^{iGr}$ with $\delta v(G) = [\delta v(-G)]^*$, where G is a nonzero vector of the reciprocal lattice. These changes of potential are obtained, in the long wave method, from the Fourier components of the potential

$$\delta v_G(r) = \lim_{q\to 0}\{\delta v(G+q)e^{i(G+q)r} + \delta v(G-q)e^{i(G-q)r}\} \quad (2)$$

such that $\delta v(G)/2 = \delta v(G+q) = \delta v(G-q)$.

In response to these perturbations, at finite q, the system will develop changes in density described similarly by $\delta n(G\pm q)$. The long wave part of this change in density, for $q\to 0$, will be [12]

$$\delta n_{\mathcal{P}}(r) = \lim_{q\to 0}\delta\mathcal{P}q\sin(qr), \quad (3)$$

where $\delta\mathcal{P}$ is the change of polarization for $q = 0$.

The elaboration of a density functional theory for these perturbations must answer the following question: What quantities do we need in order to determine $\delta\mathcal{E}$ and the set of $\delta v(G)$ uniquely?

Keeping in mind that we must stay within perturbation theory and treat only infinitesimal electric fields, we now provide a perturbative analog of the first Hohenberg-Kohn theorem [1]: The knowledge of the *change* in density everywhere uniquely determines the *change* in potential. This theorem could be proved by taking the infinitesimal limit of *finite* differences of the first Hohenberg-Kohn theorem [1], but this approach cannot be followed for electric fields, since *only* infinitesimal electric fields are allowed. The following demonstration stays strictly within perturbation theory.

We consider the Hylleraas minimum principle [13]: A trial change in wave function $\delta\phi_t$ gives an upper bound on the second-order change in energy

$$\delta^2 E \leq \langle\delta\phi_t|H - E|\delta\phi_t\rangle + (\langle\delta\phi_t|\delta v|\phi\rangle + \text{c.c.}). \quad (4)$$

This principle is valid under the constraint $\langle\delta\phi_t|\phi\rangle + \langle\phi|\delta\phi_t\rangle = 0$. The minimum is reached *only* for the $\delta\phi$ that is the response of the quantum-mechanical system to the change of potential δv. When this change of potential

is a one-body local operator, Eq. (4) becomes

$$\delta^2 E \leq \langle\delta\phi_t|H - E|\delta\phi_t\rangle + \int \delta v(r)\delta n_t(r)dr, \quad (5)$$

where the change in density $\delta n_t(r)$ is easily derived from the knowledge of the unperturbed wave function and the trial change in wave function. Now consider two changes in potentials $\delta v_1(r)$ and $\delta v_2(r)$ such that $\delta v_1(r) \neq \delta v_2(r) + \text{const.}$ The Hylleraas minimum principle applied to the perturbation $\delta v_1(r)$ gives

$$\langle\delta\phi_1|H - E|\delta\phi_1\rangle + \int \delta v_1(r)\delta n_1(r)dr$$

$$< \langle\delta\phi_2|H - E|\delta\phi_2\rangle + \int \delta v_1(r)\delta n_2(r)dr, \quad (6)$$

while for the perturbation $\delta v_2(r)$, a similar inequality, where 1 and 2 are interchanged, is obtained. Summing these two inequalities leads to

$$0 < \int [\delta v_1(r) - \delta v_2(r)][\delta n_2(r) - \delta n_1(r)]dr. \quad (7)$$

Setting $\delta n_1(r) = \delta n_2(r)$ would lead to a contradiction, showing that two different changes in potential must induce two different changes in density. Thus the knowledge of $\delta n(r)$ everywhere uniquely defines the $\delta v(r)$ that induced it.

The same line of argument can be used in the case of perturbations of periodic systems with finite wave vector q, as previously defined. All quantities have to be normalized to the unit cell volume. This normalization, and a Fourier transform, applied to the term $\int \delta v(r)\delta n(r)dr$ in Eq. (5), changes it into $\Omega_{\text{cell}}\sum_G\{\delta v^*(G + q)\delta n(G + q) + \delta v^*(G - q)\delta n(G - q)\}$. The limit $q\to 0$ is now taken for two different perturbations described by $\{\delta\mathcal{E}_1, \delta v_1(G)\}$ and $\{\delta\mathcal{E}_2, \delta v_2(G)\}$. The $G = 0$ term is isolated, and the long wave values from Eqs. (1) and (3) are used, leading to the following extension of Eq. (7):

$$0 < \frac{\Omega_{\text{cell}}}{2}\left\{(\delta\mathcal{E}_1 - \delta\mathcal{E}_2)(\delta\mathcal{P}_2 - \delta\mathcal{P}_1)\right.$$

$$+ \sum_{G\neq 0}[\delta v_1^*(G) - \delta v_2^*(G)]$$

$$\left.\times [\delta n_2(G) - \delta n_1(G)]\right\}. \quad (8)$$

If we now suppose $\delta\mathcal{P}_1 = \delta\mathcal{P}_2$ and $\delta n_1(G) = \delta n_2(G)$, the expected contradiction is obtained. From this result we conclude that the change in potential *and* electric field can be deduced from the knowledge of the change in density *and* polarization that were induced by them. Note that the knowledge of the change of polarization is crucial, since it is the quantity *conjugate* to the change of electric field in Eq. (8): If $\delta\mathcal{P}_1$ were allowed to be different from $\delta\mathcal{P}_2$, Eq. (8) could be satisfied for some $\delta\mathcal{E}_1 \neq \delta\mathcal{E}_2$. The dependence on polarization is a remnant of the ultranonlocal dependence on the long wave part of the change in density, Eq. (3), that *vanishes* for $q = 0$.

Equation (8) also shows that *if* no change in electric field is allowed, the knowledge of the polarization is not needed: A density-polarization functional theory is required for the *specific* case of the response to an electric field [14].

In the Kohn-Sham construction [2], an exchange-correlation energy functional of the density is introduced. Following the Kohn-Sham argument, now applied to the response to an electric field, this functional will depend on both the periodic density *and* the polarization: $E_{xc}[n_G; \mathcal{P}]$. This functional is defined only for values of $\mathcal{P}$ in an infinitesimally small neighborhood of the zero-field polarization [15].

We show now that this polarization dependence of the exchange-correlation energy leads to the existence of a new "exchange-correlation electric field."

First, we mention that the treatment of the electric field as a perturbation makes use of the following link between the operator r and the derivative with respect to the wave vector [5]:

$$\delta \mathcal{E} P_c r |u_{j,k}\rangle = \delta \mathcal{E} P_c i \frac{\partial}{\partial k} |u_{j,k}\rangle, \qquad (9)$$

where P_c is the projector on the conduction bands, and $u_{j,k}$ is the periodic part of the Bloch function of band j with wave vector k.

Also, the recent theory of polarization proposed by King-Smith and Vanderbilt [16] leads to the expression for the polarization [15]

$$\mathcal{P} = \sum_j 2i \int \langle u_{j,k} | \frac{\partial}{\partial k} |u_{j,k}\rangle \frac{dk}{2\pi}, \qquad (10)$$

where the sum is over the valence bands.

When wave functions are varied in order to find the Kohn-Sham self-consistent equations, the exchange-correlation energy changes, because of the implicit dependence of the density on wave functions, but also because of the implicit dependence of the polarization on wave functions [see Eq. (10)]. The term $P_c \delta v_{xc}|u_{j,k}\rangle$ that appears in the perturbative equivalent of the Kohn-Sham equation (the Sternheimer equation [5]) is replaced by

$$P_c \delta v_{xc}|u_{j,k}\rangle + \delta \mathcal{E}_{xc} P_c i \frac{\partial}{\partial k} |u_{j,k}\rangle, \qquad (11)$$

where $\delta \mathcal{E}_{xc} = (\partial^2 E_{xc}/\partial \mathcal{P})^2 \delta \mathcal{P} + \sum_G (\partial^2 E_{xc}/\partial \mathcal{P} \partial n_G) \delta n_G$.

The second term of Eq. (11), missing in previous theories of the dielectric constant [5], is to be interpreted as an additional electric field [compare with Eq. (9)], created by the polarization dependence of the exchange-correlation energy. It vanishes in zero applied electric field.

We will now analyze the model one-dimensional semiconductor used by Godby and Sham in Ref. [10], and show that it exhibits the main features of our theory: (1) The knowledge of the density change alone is not sufficient to deduce the periodic potential change and electric field change; (2) an exchange-correlation electric field appears.

In this model, the periodic solid plus electric field is treated by the long wave method in a supercell consisting

of N basic unit cells of length a. The external potential plus the Hartree potential $V_{ext}(x) + V_H(x)$ is taken to be the sum of two different contributions: $V_0 \cos(2\pi x/a) + \lambda \sin(2\pi x/Na)$. The first term has the periodicity of one unit cell, while the second, with the periodicity of the supercell, corresponds to a slowly varying potential of amplitude λ. For an infinitely long supercell, the second term mimics the action of an electric field.

The self-energy operator is taken to be the nonlocal potential: $\Sigma(x, x', \omega) = \{[f(x) + f(x')]/2\}g(|x - x'|)$, where $f(x) = -F_0[1 - \cos(2\pi x/a)]$ is a negative function with the periodicity of one unit cell and $g(y)$ is a normalized Gaussian of width $w = 2$ a.u.

We keep the same set of parameters as in Ref. [10]. First, the many-body problem is solved by direct diagonalization of the equations containing the self-energy operator, using a plane-wave basis set and a Brillouin zone sampling at the Γ point only. From this result, we construct an *exact* density functional theory by determining the local potential $V_{eff,1}(x)$ which, when filled with *noninteracting* electrons (no self-energy operator), reproduces the same electron density as in the many-body case (see Fig. 4 of Ref. [10]). Standard iterative nonlinear optimization techniques are used for that purpose. Independently, we also extract the (polarized) density of the single unit cell $\pm\frac{1}{2}a$, where the slowly varying potential is most linear, and, again using optimization techniques, we reproduce this density with *another* potential, $V_{eff,2}(x)$, having period a. In this case, to retain the sampling of the Brillouin zone at the Γ point, we repeat the density periodically in the supercell. The only problem in reproducing the "target" density comes from the slight nonlinearity of the slowly varying potential, and disappears progressively for larger supercells. Figure 1 presents the results obtained with an $80a$ supercell and $\lambda = 0.95$ eV, for which the rms differ-
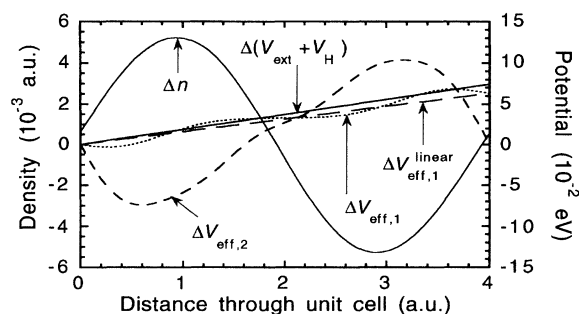

FIG. 1. The unit cell of our model one-dimensional semiconductor, where the slowly varying applied potential $\Delta(V_{ext} + V_H)$, that changes the interacting electron density by Δn, is the most linear. Both $\Delta V_{eff,1}$ and $\Delta V_{eff,2}$, used in the noninteracting Kohn-Sham equations, yield the same Δn. $\Delta V_{eff,2}$ is a periodic potential with no linear slope, while $\Delta V_{eff,1}$, whose linear part is $\Delta V_{eff,1}^{linear}$, reproduces not only Δn but also the change of polarization due to $\Delta(V_{ext} + V_H)$. This illustrates the need for polarization dependence in E_{xc}. For clarity, the potential curves have been aligned so that they all start from zero.

ence between the target and computed density is 4 parts per 10^3.

This example illustrates that the action of a linear potential $\Delta(V_{\text{ext}} + V_H)$, superimposed on a periodic potential, in the case of an interacting-electron model system can be mimicked by *two* different potentials $\Delta V_{\text{eff},1}$ and $\Delta V_{\text{eff},2}$, acting upon the corresponding noninteracting electron system, in contrast to a naive application of DFT theorems. However, $\Delta V_{\text{eff},2}$ is not able to reproduce the polarization (0.037 electron) associated with the long-wavelength charge density. Moreover, $\Delta(V_{\text{ext}} + V_H)$ and the linear component $\Delta V_{\text{eff},1}^{\text{linear}}$ of the Kohn-Sham potential $\Delta V_{\text{eff},1}$ differ by 15%, because of the existence of the exchange-correlation electric field.

We now discuss briefly the implications of our theory for practical calculations. LDA or GGA techniques can be used to approximate the periodic density dependence of E_{xc}. Unfortunately, since the homogeneous electron gas is metallic, we do not see any easy way to modify LDA or GGA in order to obtain a polarization-dependent exchange-correlation energy that would generate the second term in Eq. (11). Nevertheless, our theory allows the scissor-operator correction to be understood as an *approximate* way of *bypassing* this dependence.

Indeed, in Ref. [10], it was shown that the effect of a slowly varying potential ΔV that induces transitions between valence and conduction bands with a gap E_g [see Eq. (10) of Ref. [10]] is approximately equivalent to the effect of a slowly varying potential $\Delta V + \Delta V_{\text{xc}}$ that induces transitions between valence and conduction bands with a gap E_g^{DFT} [see Eq. (11) of Ref. [10]]. Hence, the *exact* density-polarization functional theory calculation in a field $\delta \mathscr{E} + \delta \mathscr{E}_{\text{xc}}$, with a gap E_g^{DFT}, can be *approximately* replaced by a LDA calculation in a field $\delta \mathscr{E}$, with a modified gap E_g; this is the LDA + scissor correction, which gives a dielectric constant for Si of 11.2 (experiment, 11.4–11.7, LDA 12.9–13.5, GGA 12.4–12.6) [6–8].

In conclusion, because the original Hohenberg-Kohn theorem is not valid for the case of the response to a homogeneous electric field, we have set up a density-polarization functional theory, of which an approximate form is the LDA + scissor correction.

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