Exchange-Correlation Hole in Polarized Insulators: Implications for the Microscopic Functional Theory of Dielectrics

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We present a simple and direct proof that the exchange-correlation hole, and therefore the exchange-correlation energy, in a polarized insulator is not determined by the bulk density alone. It is uniquely characterized by the density and the macroscopic electric polarization of the dielectric medium. [S0031-9007(97)04962-4]

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In a notable paper in 1964 Hohenberg and Kohn [1] established the basic principle of density functional theory (DFT): any property of an interacting time-reversal invariant many-particle system is uniquely determined as a functional of its ground state density $n_0(\mathbf{r})$. The proof rests upon the demonstration that a given $n_0(\mathbf{r})$ is consistent with only *one* external scalar potential $v_{\text{ext}}(\mathbf{r})$ (except for an arbitrary constant), which determines the entire Hamiltonian since kinetic and particle-interaction (V_{e-e}) terms are known from the fundamental constants $\hbar$, m_e, and e. Together with the Kohn-Sham (KS) [2] ansatz that the interacting ground state density can be represented by noninteracting fermions in an effective local potential, this has provided the foundation for much of the current theoretical calculations in atomic, nuclear, and condensed matter physics [3].

In the past DFT has often been applied uncritically to condensed matter, assuming implicitly that the properties of bulk matter in the thermodynamic limit are functionals only of the density in the bulk. However, the Hohenberg-Kohn (HK) proofs are only for the entire density (including the surface), and they provide no guarantee that the functionals of the density are well defined in the thermodynamic limit. In particular, the use of Born–von Karman (BvK) boundary conditions may introduce additional considerations not included in their original analysis. Although it is well known that the long-range Coulomb terms must be treated carefully and are not absolutely convergent in the thermodynamic limit, it has been implicitly assumed that the key quantity describing many-body effects in the KS approach, the exchange-correlation (x-c) energy E_{xc}, is an intrinsic functional of the bulk density. Recently, however, Gonze, Ghosez, and Godby (GGG) [4] have argued that in an insulator E_{xc} must also be a function of the macroscopic (average) electric polarization in the limit of an infinite system. This has led to much controversy and proposals concerning the nature of exchange and correlation [5–8] and the KS functional [9,10] in insulators.

In this Letter we provide a simple direct demonstration that the x-c hole in a polarized insulating crystal is modified in a manner *not described solely by the density in the bulk region of the crystal*, even though the hole around an electron in the bulk is localized to the bulk region. We show that the hole is determined only if the bulk macroscopic electric polarization is specified in addition to the bulk density. This can be interpreted as the "polarization" of the x-c hole [6,8], providing the physical mechanism leading to the generalized form of the KS equations required to have an in-principle-exact description of polarized extended matter [4,8].

In a dielectric with a macroscopic electric field $\mathbf{E}_{\text{mac}}$, the energy can be expressed in terms of the polarization [11]. In the case of a macroscopic region of a periodic crystal of volume Ω, external effects can be incorporated [6,8] by terms of the form ($\hbar = m_e = -e = 1$ in a.u.)

$$E_{\text{ext}} = -\Omega \mathbf{E}_{\text{mac}} \cdot \mathbf{P}_{\text{mac}} + \int_{\Omega} d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}), \qquad (1)$$

where the field couples to the macroscopic polarization $\mathbf{P}_{\text{mac}}$, and the second term is explicitly restricted to only the periodic part of the external potential $v_{\text{ext}}(\mathbf{r})$ coupled to the electronic (number) density $n(\mathbf{r})$, which is periodic. The key point for our purposes is that $\mathbf{P}_{\text{mac}}$ is *not directly* determined by the density in Ω. Although variations in the polarization density field are related to $n(\mathbf{r})$ by $\nabla \cdot \mathbf{P}(\mathbf{r}) = +n(\mathbf{r})$, its average value $\mathbf{P}_{\text{mac}}$ can be found only as a change from a reference polarization $\mathbf{P}^0_{\text{mac}}$, in terms of an integrated polarization current that flows *through* the volume Ω [12]. This result for $\mathbf{P}_{\text{mac}}$ is a consequence of the BvK boundary conditions used to describe the extended system [13]; it is not needed in finite systems and was not considered in the original analysis of HK who, implicitly, assumed open (vanishing) boundary conditions. Thus, the bulk density $n(\mathbf{r})$ and changes in polarization $\delta \mathbf{P}_{\text{mac}} = \mathbf{P}_{\text{mac}} - \mathbf{P}^0_{\text{mac}}$ are independent experimentally measurable quantities. Furthermore, each is uniquely determined by the *bulk* ground state wave function, with $\delta \mathbf{P}_{\text{mac}}$ given by its Berry's geometric phase [13–15].

The case of zero macroscopic field, $\mathbf{E}_{\text{mac}} = \mathbf{0}$, is of special interest because it can be considered the standard reference state of the insulator: then its total energy is not *explicitly* dependent upon $\mathbf{P}_{\rm mac}$ [8], and the original analysis of HK is sufficient to conclude that all bulk properties must be *functionals* only of the bulk density $n(\mathbf{r})$; in particular, this includes the ground state spontaneous polarization $\mathbf{P}^0_{\rm mac}$. On the other hand, if $\mathbf{E}_{\rm mac}$ is not zero, the same reasoning requires that all physical quantities must be functions of $\delta\mathbf{P}_{\rm mac}$ as well as functionals of the bulk density. Therefore, the intrinsic description of a dielectric material in the presence of an electric field requires generalization of the HK theorems [8].

In the KS approach, E_{xc} is defined to be the difference between the internal energy of the interacting many-body system and that of a noninteracting system of electrons of the same density $n(\mathbf{r})$. The generalization for a polarized system requires that the noninteracting system also has the same zero-field polarization $\mathbf{P}^0_{\rm mac}$ and change $\delta\mathbf{P}_{\rm mac}$ in the presence of a field. As shown in Ref. [8], E_{xc} is related to the interacting N-particle wave function Ψ by a generalized constrained Levy formulation,

$$E_{xc}[n;\mathbf{P}_{\rm mac}] = \min_{\Psi\to n(\mathbf{r}),\mathbf{P}_{\rm mac}} \langle\Psi| -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + V_{e-e}|\Psi\rangle - T_{\rm ind}[n;\mathbf{P}_{\rm mac}] - E_H[n], \tag{2}$$

where $T_{\rm ind}$ is the kinetic energy of independent fermions and E_H is the Coulomb Hartree energy [8]. This may also be expressed in terms of the Coulomb interaction between the electron density at point $\mathbf{r}$ and the density at $\mathbf{r}+\mathbf{u}$ of the x-c hole $n_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u})$ defined by a coupling constant integration [3] over all values of the interaction λ from $\lambda = 0$ to its full strength $\lambda = 1$,

$$\begin{aligned} E_{xc} &= \frac{1}{2}\int_\Omega d\mathbf{r}\, n(\mathbf{r}) \int_\Omega d\mathbf{u}\, \frac{1}{|\mathbf{u}|}\, n_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u}) \\ &= \frac{N}{2}\int_\Omega d\mathbf{u}\, \frac{1}{|\mathbf{u}|}\, \langle n_{xc}(\mathbf{u})\rangle, \end{aligned} \tag{3}$$

where $\langle n_{xc}(\mathbf{u})\rangle$ is the density-weighted average of the x-c hole. Equivalently, E_{xc} can be written in terms of the coupling constant averaged (symmetric) pair correlation function g^λ through the relation $n_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u}) = \int_0^1 d\lambda\,[g^\lambda(\mathbf{r},\mathbf{r}+\mathbf{u}) - 1]n(\mathbf{r}+\mathbf{u})$.

The energy E_{xc}/N can be interpreted as the electrostatic interaction between an electron of charge -1 and the charge distribution $-\langle n_{xc}(\mathbf{u})\rangle$, the total charge of which is $+1$, as required by a sum rule. Thus E_{xc} is determined by the *shape* of $\langle n_{xc}(\mathbf{u})\rangle$. The shape is also restricted by other considerations; e.g., it is straightforward to show that the density-weighted average of $n_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u})$ over the entire volume of any finite system Ω must be symmetric in $\mathbf{u}$, i.e., $\langle n_{xc}(\mathbf{u})\rangle = \langle n_{xc}(-\mathbf{u})\rangle$. This follows from the fact that correlations among electrons are symmetric in particle exchanges. In addition, it can be shown that averages over $\mathbf{r}$ in a cell of a periodic region of a material also lead to a symmetric $\langle n_{xc}(\mathbf{u})\rangle$ as long as the hole is localized in the relative coordinate $\mathbf{u}$, so that $\mathbf{r}+\mathbf{u}$ is also limited to the periodic region. This applies to a crystal in an electric field, where the (metastable) ground state wave function is invariant to lattice translations even though the Hamiltonian is not. In this case, however, we note that other averages of the x-c hole, such as the simple average over position, $\int_\Omega d\mathbf{r}\, n_{xc}(\mathbf{r},\mathbf{r}+\mathbf{u})$, are not symmetric.

Now let us consider the case of an insulator in an electric field (or, as we will see, the case of a spontaneously polarized insulator). In order to establish the desired result, it is sufficient to consider the noninteracting case where the exchange (x) hole can be determined exactly. This is an approach often used in DFT [3] and arguments that the x energy, E_x, should depend on polarization were given in Ref. [7]. It then follows from the fact that E_{xc} can be expressed as the coupling constant averaged form, for which the noninteracting x hole is one limit, that the same conclusions must apply to the exact x-c hole. We consider a one-dimensional (1D) insulating crystal with potential energy $V(x) = V_0(x) + V_L(x)$, where $V_0(x)$ is periodic in the crystal lattice constant a, and $V_L(x)$ is an additional long wavelength potential with periodicity $L = Ma$, $M \gg 1$. In order to mimic a constant electric field near $x = 0$ we have chosen $V_L(x) = V_b[\frac{75}{64}\sin(\tilde{x}) - \frac{25}{384}\sin(3\tilde{x}) + \frac{3}{640}\sin(5\tilde{x})]$, with $\tilde{x} \equiv 2\pi x/L$, which is a symmetric form that is $\propto x + \mathcal{O}(x^7)$. Figure 1 shows the potential energy $V(x)$ and the change in density, $\Delta n(x) = n(x) - n(x)_{V_b=0}$, in the region around $x = 0$. Although the potential clearly has a linear component, the density is very nearly periodic. In the middle panel is also shown the change in the periodic density generated by a potential $V^{\rm fit}(x)$ which has periodicity a chosen to reproduce the density of the central part of the supercell. Since the curves are essentially indistinguishable, this illustrates the point made by GGG that the same periodic density can be generated by two potentials differing by more than a constant.

Consider the density-weighted average x hole around an electron in the periodic region around $x = 0$ of the supercell. We define this hole to be $\langle n_x^{(1)}(u)\rangle$ and the change from the zero applied field hole to be $\Delta\langle n_x^{(1)}(u)\rangle$, which is readily expressed in terms of the eigenstates of the supercell. We have verified that $\Delta\langle n_x^{(1)}(u)\rangle$ does not depend upon the unit cell chosen for the average in a region around the origin where the electric field is effectively constant. Also, the lowest order change in the hole must be quadratic in the field strength since the zero-field system has a center of inversion symmetry, and we have plotted in Fig. 1 the change per unit field *squared.* The result is compared with the corresponding change for the system with the same density and potential $V^{\rm fit}(x)$, which is defined to be $\Delta\langle n_x^{(2)}(u)\rangle$. It is apparent from the figure that $\Delta\langle n_x^{(1)}(u)\rangle$ is more extended than $\Delta\langle n_x^{(2)}(u)\rangle$. Since the two holes are different, we have established that the density is not sufficient to determine the x hole, and using the reasoning given above we conclude that E_{xc} is *not determined solely by the bulk periodic density.*

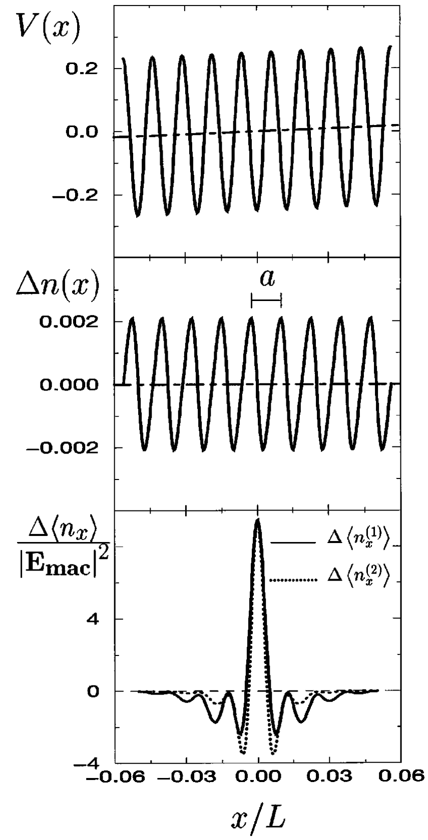

FIG. 1. Results (in a.u.) for a model of a nonpolar insulator with the lowest band occupied, i.e., 2 electrons/cell. The potential energy (see text) is given by $V_0(x) = -V_a \cos(2\pi x/a)$, $V_a = 1/4$, and $V_b = V_a/5$, with $a = 5a_0$ $[a_0 = \hbar^2/(m_e e^2)]$. We show the central 8 cells in a supercell of length $L = 80a$. ($L = 40a$ gives essentially identical results.) Top panel: $V(x)$; the average slope is $\mathbf{E}_{\text{mac}} = 2\pi V_b/L$. Middle panel: Change in electron density $\Delta n(x) = n(x) - n(x)_{V_b=0}$ in the supercell, and in the fitted system (indistinguishable). Lower panel: Change in the density-weighted average x hole divided by $[\mathbf{E}_{\text{mac}}]^2$ for two different potentials which give the same periodic density.

It is straightforward to prove that the hole is determined by the bulk density *and* the macroscopic polarization. This follows from the same reasoning as the original HK arguments except that now the external terms in the energy [Eq. (1)] involve *both* the bulk $n(\mathbf{r})$ and $\mathbf{P}_{\text{mac}}$. In our present example, we have calculated the polarization in the two cases to show explicitly that they are different. The average polarization $\mathbf{P}_{\text{mac}}^{(1)} = 3.44 \times 10^{-3}$ in cells near the origin of the supercell can be found from the density *in the supercell* using $d\mathbf{P}(x)/dx = +n(x)$, whereas the polarization $\mathbf{P}_{\text{mac}}^{(2)} = 2.11 \times 10^{-3}$ of the system with the fitted periodic potential can be found from the Berry's phase expressions [14,15]. To our knowledge, this is the first explicit demonstration of the polarization dependence of exchange, and therefore of the x-c energy.

It is instructive to consider the Clausius-Mossotti limit of localized, nonoverlapping wave functions in each cell. Then the two different ways of calculating $\mathbf{P}_{\text{mac}}$ lead to the same answer: the dipole moment per unit length of each isolated unit. The x hole is also localized in one cell, so that all properties are determined by the density in each cell. In general, however, an insulating crystal is not a sum of isolated units, and there is an explicit dependence upon $\mathbf{P}_{\text{mac}}$ due to transfer of electrons and delocalization of the x hole between cells.

There are other interesting conclusions which follow from the analysis of the periodic system in the presence of an electric field, e.g., the independent-particle kinetic energy T_{ind} is also a function of the polarization [8]. The generalized KS functional can be written [8]

$$E[n;\mathbf{P}_{\text{mac}}] = E_{\text{ext}}[n;\mathbf{P}_{\text{mac}}] + T_{\text{ind}}[n;\mathbf{P}_{\text{mac}}] + E_H[n] + E_{xc}[n;\mathbf{P}_{\text{mac}}], \tag{4}$$

where the first term is given in Eq. (1). The variational principle requires that E be stationary with respect to *both* $n(\mathbf{r})$ and $\mathbf{P}_{\text{mac}}$, and in terms of the lattice-periodic single-particle orbitals $\phi_{i,\mathbf{k}}$ of the KS approach, the Euler-Lagrange equations become [8]

$$\left[-\frac{1}{2}(\nabla + i\mathbf{k})^2 + V_{\text{eff}}(\mathbf{r}) + i\mathbf{E}_{\text{eff}} \cdot \nabla_{\mathbf{k}}\right]\phi_{i,\mathbf{k}}(\mathbf{r}) = \varepsilon_{i,\mathbf{k}}(\mathbf{r})\phi_{i,\mathbf{k}}(\mathbf{r}). \tag{5}$$

Here $V_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \delta(E_H + E_{xc})/\delta n(\mathbf{r})$ is an ordinary local potential and $\mathbf{E}_{\text{eff}} = \mathbf{E}_{\text{mac}} - \frac{1}{\Omega}\partial E_{xc}/\partial \mathbf{P}_{\text{mac}}$ is an effective electric field. Accordingly, the resulting generalized KS equations are formally the same as the usual *density-only* ones except that there is a term involving the derivative of the periodic orbitals with respect to the wave vector $\mathbf{k}$ (where $\mathbf{k} \in [-\frac{\pi}{a};\frac{\pi}{a}]$ in 1D). It must be mentioned that this additional term is a nontrivial extension; the variations with $\mathbf{k}$ must be properly incorporated to get a gauge-invariant result [8].

The term $\partial E_{xc}/\partial \mathbf{P}_{\text{mac}} = -\Omega \mathbf{E}_{xc}$ in the generalized KS equations can be identified with an "x-c electric field" [4,8] in analogy to the actual electric field term. It must be emphasized, however, that this is not a true electric field; it acts only on electrons and not on other charges; it may be longitudinal or transverse and is not related to any density by a Poisson-like equation. Since the changes are quadratic in $\mathbf{E}_{\text{mac}}$ and thus also in $\mathbf{P}_{\text{mac}}$, it follows that in the case of a symmetric crystal $\mathbf{E}_{xc} \propto \mathbf{E}_{\text{mac}}$ for small $\mathbf{E}_{\text{mac}}$. Thus for zero field the system is described by the usual *density-only* KS equations, but $\mathbf{E}_{xc}$ *affects* the dielectric properties. We do not attempt to estimate the size of the effect since the present 1D model does not fix the full 3D form of the x hole needed to calculate E_x.

If one considers a system with lower symmetry, in general the ground state polarization $\mathbf{P}_{\text{mac}}^0$ is nonzero, and there is no symmetry reason for $\mathbf{E}_{xc}$ to vanish. Our calculations also provide a microscopic basis for such a field. If we consider a 1D example in which the crystal potential is non-mirror-symmetric, the shape of the x hole changes linearly with the field $\mathbf{E}_{\text{mac}}$. An example of the

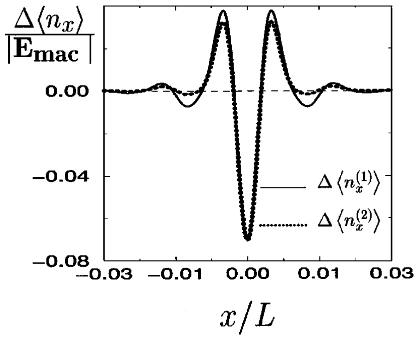

FIG. 2. Same as the lower panel in Fig. 1, but for a polar insulator with $V_0(x) = -V_a[\cos(2\pi x/a) - \frac{1}{4}\sin(4\pi x/a)]$, $V_a = 1/4$, and $V_b = V_a/20$, plotted per unit field $\mathbf{E}_{\rm mac}$. The spontaneous polarization is $\mathbf{P}^0_{\rm mac} = 1.321 \times 10^{-2}$, while the changes are $\delta\mathbf{P}^{(1)}_{\rm mac} = 0.86 \times 10^{-3}$, and $\delta\mathbf{P}^{(2)}_{\rm mac} = 0.53 \times 10^{-3}$.

change in the hole per unit field is shown in Fig. 2. Since $\mathbf{P}_{\rm mac}$ varies linearly with $\mathbf{E}_{\rm mac}$, it follows immediately that $\mathbf{E}_{xc} \neq \mathbf{0}$, even for $\mathbf{E}_{\rm mac} = \mathbf{0}$. Note that the sign of the change is relevant, and the positive direction for $\mathbf{E}_{\rm mac}$ in Fig. 2 is chosen to be in the same direction as $\mathbf{P}^0_{\rm mac}$. The existence of a spontaneous $\mathbf{E}_{xc}$ was discussed in a recent paper by GGG [9], who described the counterintuitive consequences if one attempts to incorporate it into the original density-only KS formulation. Vanderbilt [10] went on to find simple examples where straightforward application of the usual KS approach leads to "ultra-nonlocal dependence upon the charge density." In contrast, we have shown that the generalized KS framework provides a simple, direct description in terms of the dependence of the x-c hole upon the polarization as well as density.

It is interesting to note that the present theory of polarized insulators is formally analogous to the well-known case of spin density functionals, in which a spin-polarized system is described by KS equations with a spin-dependent effective potential even if there is no such magnetic-field-like terms in the original HK system. A general KS formulation involving properties other than the density has been developed by Jansen [16], who showed that such a theory must in general involve operators in the effective Hamiltonian which couple to the desired additional variable(s). Jansen's analysis leads to equations similar to our Eq. (2) in which the effective field in principle can be defined in terms of the exact many-body wave functions.

In conclusion, we have provided a simple proof that in an insulating crystal, the dielectric properties cannot be described solely in terms of the periodic bulk density. This leads to a generalized KS approach needed for all materials with nonzero polarization, in which there is an effective "x-c electric field" $\mathbf{E}_{xc}$ that can be represented as a nonlocal operator. Our central result is that the x-c hole itself is modified in a fundamental way in a polarized medium. This was explicitly demonstrated for the x hole in a noninteracting system, and it follows from well-known expressions involving a coupling constant integration [3] that the same conclusions apply to the x-c energy E_{xc} in the interacting system. Our conclusions have no effect upon work done within approximations such as local density and generalized gradient; instead, this work shows that a complete description of dielectrics is outside the framework of such approximations.

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