## Polarization Dependence of the Exchange Energy

In our 1995 Letter [1], we showed that the density-functional-theory (DFT) exchange-correlation energy of insulators submitted to external electric fields should depend not only on the bulk periodic density, but also on the macroscopic polarization. In a recent Letter Resta [2], after a careful discussion of the electrostatics of the exchange-correlation energy for macroscopic bodies, states "that, whenever the macroscopic polarization contributes to the bulk XC energy, the system shows long range correlation," and proposes that the integral of the exchange-correlation hole in the bulk may not be $-1$, some part of the hole being found on the surface.

Although we do not comment here on the latter interesting possibility, we now argue that the DFT *exchange* energy (without correlation) already shows dependence on the polarization, although the exchange hole integrates to $-1$ in the bulk. Thus we disagree with Resta's assertion [2] that long-range correlations must be present in order to observe the kind of behavior that we have discussed in our previous Letter.

A $O(\frac{1}{q})$ divergence in the long-wave part ($\mathbf{q} \to 0$) of the exchange potential $v_x(\mathbf{q}) = \frac{\delta E_x}{\delta n(\mathbf{q})}$ (corresponding to a homogeneous exchange electric field) is a necessary and sufficient condition for the exchange energy to depend on the polarization [1]. Here the exchange energy

$$E_x = -\frac{1}{4} \int\int \frac{\gamma(\mathbf{r}, \mathbf{r}')\gamma(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}', \qquad (1)$$

is computed from the first-order density matrix [3] obtained from Kohn-Sham (KS) wave functions [4]:

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i^{occ} \psi_{KS,i}^*(\mathbf{r})\psi_{KS,i}(\mathbf{r}') . \qquad (2)$$

A tractable scheme for computing the exchange potential was recently proposed by Görling and Levy [5], with the components of the KS potential taken as *independent* variables. In our case, using the chain rule,

$$v_x(\mathbf{q}) = \sum_{\mathbf{G}} \frac{\delta E_x}{\delta v_{KS}(\mathbf{q} + \mathbf{G})} \frac{\delta v_{KS}(\mathbf{q} + \mathbf{G})}{\delta n^*(\mathbf{q})}$$

$$= \sum_{\mathbf{G}} \chi_0^{-1}(\mathbf{q}, \mathbf{q} + \mathbf{G}) \frac{\delta E_x}{\delta v_{KS}(\mathbf{q} + \mathbf{G})} , \qquad (3)$$

where $\chi_0$ is the independent-particle polarizability of the KS electronic system. The important physics is contained in the $\mathbf{G} = 0$ component (while other reciprocal-lattice vectors describe local fields).

Thanks to the $O(\frac{1}{q^2})$ divergence of $\chi_0^{-1}$ in the long-wavelength limit, one requires a contribution of order $q$ from $\frac{\delta E_x}{\delta v_{KS}(\mathbf{q})}$ for the $O(\frac{1}{q})$ divergence of $v_x(\mathbf{q})$ to arise.

From (1), one finds

$$\frac{\delta E_x}{\delta v_{KS}(\mathbf{q})} = -\frac{1}{2} \int\int \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta \gamma(\mathbf{r}', \mathbf{r})}{\delta v_{KS}(\mathbf{q})} d\mathbf{r}\, d\mathbf{r}'. \quad (4)$$

The long-wave change in the KS potential can be written [1] as $\delta v_{KS}(\mathbf{q}) = \frac{\delta \mathcal{E}}{2iq}$ (where $\delta \mathcal{E}$ is the KS effective electric field), so that

$$\frac{\delta \gamma(\mathbf{r}', \mathbf{r})}{\delta v_{KS}(\mathbf{q})} = 2iq \frac{\delta \gamma(\mathbf{r}', \mathbf{r})}{\delta \mathcal{E}} . \qquad (5)$$

The final step in the proof comes from the fact that the density matrix built from KS wave functions indeed depends on the long-wave change in the KS potential or, equivalently, that the exchange hole polarizes [6] when placed in a KS effective electric field. This is easily seen in the following example. Consider a 3D periodic array of widely spaced helium atoms, with its corresponding KS potential and associated KS wave functions. The exchange hole, for an electron close to one helium atom, is equal to minus half the density surrounding this helium atom, and integrates to $-1$. If an independent KS electric field is now applied, the density around each atom, and hence also the exchange hole, will polarize.

The dependence of the DFT exchange energy on polarization is thus demonstrated.

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