The long-wavelength behaviour of the exchange-correlation kernel in the Kohn-Sham theory of periodic systems

Ph. Ghosez[1], X. Gonze[1] and R. W. Godby[2]
[1] *Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium*
[2] *Department of Physics, University of York, Heslington, York YO1 5DD, U. K.*
(February 1, 2008)

The polarization-dependence of the exchange-correlation (XC) energy functional of periodic insulators within Kohn-Sham (KS) density-functional theory requires a $\mathcal{O}(1/q^2)$ divergence in the XC kernel for small vectors $\mathbf{q}$. This behaviour, exemplified for a one-dimensional model semiconductor, is also observed when an insulator happens to be described as a KS metal, or vice-versa. Although it can occur in the exchange-only kernel, it is not found in the usual local, semi-local or even non-local approximations to KS theory. We also show that the test-charge and electronic definitions of the macroscopic dielectric constant differ from one another in exact KS theory, but are equivalent in the above-mentioned approximations.

PACS numbers: 71.10.+x, 77.22.Ej

I. INTRODUCTION

We have recently reexamined [1–3] the exchange-correlation potential, $V_{\rm xc}(\mathbf{r})$, that represents electronic exchange and correlation in the Kohn-Sham formulation of density-functional theory (DFT), in the case of macroscopic bodies. Our analysis focused on periodic solids with a uniform macroscopic polarization: a crystal subjected to a homogeneous external electric field, or a polar crystal. We showed that the exact $V_{\rm xc}$ inside the crystal is required to have an ultra-non-local dependence on the surface electron density, or, equivalently, on the macroscopic polarization. In the present paper, we will show that the exchange-correlation kernel, $K_{\rm xc}$, is a powerful vehicle for analyzing the presence of this dependence in the common approximations for exchange and correlation. The required wavevector-dependence of $K_{\rm xc}$ is illustrated in the exact DFT of a model system. Links with the polarizability in insulators and metals will also be established.

We first define some useful quantities and notation. Within the Kohn-Sham (KS) formulation of Density Functional Theory [4], a system of interacting electrons in its ground state, placed in an external potential, $V_{\rm ext}(\mathbf{r})$, is mapped onto a fictitious system of independent particles in an effective potential

$$V_{\rm KS}(\mathbf{r}) = V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + V_{\rm xc}(\mathbf{r}), \tag{1}$$

under the requirement that both generate the same density $n(\mathbf{r})$. The combined external $V_{\rm ext}(\mathbf{r})$ and Hartree $V_{\rm H}(\mathbf{r})$ potentials give the electrostatic potential $V_{\rm TC}(\mathbf{r})$ felt by a classical test charge (TC), while the exchange-correlation (XC) term, $V_{\rm xc}(\mathbf{r})$, that subsumes all the additional many-body effects, acts only on KS electrons.

The XC potential at point $\mathbf{r}$ is the first derivative of the XC energy with respect to the density at this point,

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})}. \tag{2}$$

The second derivative of this XC energy with respect to the densityis called the XC kernel:

$$K_{\rm xc}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E_{\rm xc}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}. \tag{3}$$

The explicit forms of $E_{\rm xc}$, $V_{\rm xc}$ or $K_{\rm xc}$ as functionals of the density are unfortunately unknown and calculations are usually performed within the local-density approximation (LDA), within semi-local approximations such as the generalized gradient approximations (GGA) [5], or even within non-local approximations such as the weighted-density approximation (WDA) [6].

In the same manner as $V_{\rm xc}$ constitutes a sizeable contribution to the KS effective potential, $K_{\rm xc}$ plays an important role in the investigation of the responses of the KS system to static external pertubations. The density response of the interacting electron system to an external perturbation is described by the polarizability matrix χ:

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r},\mathbf{r}')\ \delta V_{\rm ext}(\mathbf{r}')d\mathbf{r}'. \tag{4}$$

The so-called "proper part" of the density response, π [7], relates the change of density to the change of the test-charge potential:

$$\delta n(\mathbf{r}) = \int \pi(\mathbf{r},\mathbf{r}')\ \delta V_{\rm TC}(\mathbf{r}')d\mathbf{r}'. \tag{5}$$

From the relation between TC and external potentials, these matrices are related by the following expression (making use of matrix notations):

$$\pi^{-1} = \chi^{-1} + V_C, \tag{6}$$

where $V_{\rm C}$ stays for the Coulomb interaction. For periodic solids, the various quantities are most conveniently represented in reciprocal space, where $\chi(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$, for

example, may be thought of as a matrix in the reciprocal-space lattice vectors $\mathbf{G}$ and $\mathbf{G}'$, for each wavevector $\mathbf{q}$, with the element $\mathbf{G} = \mathbf{G}' = \mathbf{0}$ known as the head, the other elements in that row and column as the wings, and the rest of the matrix as the body [8].

For the KS system, an independent-particle polarizability matrix χ_o is usually introduced, relating the change of density to that of the effective KS potential:

$$\delta n(\mathbf{r}) = \int \chi_o(\mathbf{r}, \mathbf{r}')\ \delta V_{\rm KS}(\mathbf{r}') d\mathbf{r}'. \tag{7}$$

Using Eqs. (1) and (6), this independent-particle polarizability matrix is easily linked with the interacting-particle polarizability and its proper part:

$$\begin{aligned} \chi_o^{-1} &= \chi^{-1} + V_C + K_{\rm xc} \\ &= \pi^{-1} + K_{\rm xc}. \end{aligned} \tag{8}$$

Following the Adler and Wiser sum-over-state technique [9], χ_o can be directly computed from the KS wavefunctions. As shown by Eq. (8), the knowledge of $K_{\rm xc}$ is crucial in deducing χ or π from χ_o. This key role was recently recalled by Dal Corso, Baroni and Resta [10].

In connection with the KS band-gap problem it was shown by Godby and Needs [11], within certain approximations, that the ground state of a periodic insulator is sometimes described as a metal in KS theory. This is particularly striking in that the long-wavelength behaviour of the polarizability matrix χ for an insulator is qualitatively different from that of a metal, while χ is a ground-state quantity and should be correctly obtained within DFT. Godby and Needs emphasized that a highly nonanalytic $K_{\rm xc}$ could allow such a phenomenon.

Recently, we proposed that the exact XC energy functional is polarization-dependent in the case of periodic insulating solids submitted to a homogeneous electric field [1]. After exploring in some detail the consequences of this finding, Aulbur, Jönsson and Wilkins [12] showed the presence of a sizeable contribution of the polarization-dependence of $E_{\rm xc}$ to the linear and non-linear optical response of real materials. For polar solids, careful treatment of the polarization is mandatory, even if no homogeneous electric field is present [2]. Resta [13] tried to address the origin of these effects: he proposed that the polarization dependence should arise from the Coulomb coupling between the electron, in the bulk, and part of its correlation hole delocalized at the surface. At variance, Martin and Ortiz [14], pointed out that the shape of the XC hole may already depend on the surface charge, and we demonstrated [3] that a polarization-dependence is expected at the purely exchange level (without correlation). In another paper, Martin and Ortiz [15] placed the new density-polarization functional theory in the perspective of important works of the seventies, and presented an alternative formulation of it.

In Section II of the present paper, we link the polarization-dependence of the XC energy to a $\mathcal{O}(1/q^2)$ divergence of $K_{\rm xc}$ in the limit of $q \to 0$, briefly sketched in Ref. [16], and illustrate this behaviour in the case of a one-dimensional semiconductor. An analysis of related points was given in Ref. [12]. This requirement of the exact KS theory is not fulfilled in the usual approximations such as the LDA, the GGA, and the WDA, as shown in Section III. In Section IV, we observe that a $\mathcal{O}(1/q^2)$ behaviour of the exact XC kernel is able to resolve the "true insulator - KS metal" paradox. A unified treatment of $K_{\rm xc}$ for insulators and metals is given in Section V, together with an analysis of the exchange-only kernel. We will finally discuss (Section VI) the consequences of these facts for the different definitions of the macroscopic dielectric constant.

II. DIVERGENCE OF $K_{\rm XC}$

Working on periodic insulators first, we adopt the same perturbative approach (long-wave method) as in Ref. [1], and briefly recall one of its central result. The change of external potential $\delta V_{\rm ext}$ produced by an infinitesimal homogeneous electric field $\delta\mathcal{E}_{\rm ext}$ is (written in one dimension for brevity):

$$\begin{aligned} \delta V_{\rm ext}(r) &= \lim_{q\to 0}\ \delta V_{\rm ext}(q)\ (e^{iqr} - e^{-iqr}) \\ &= \lim_{q\to 0}\ \frac{\delta\mathcal{E}_{\rm ext}}{q}\ \sin(qr) \end{aligned} \tag{9}$$

In reponse to this perturbation, the system will develop a change of density $\delta n(r)$. Owing to local field effects (Umklapp processes), it may contain contributions at different $(q+G)$ vectors (where G belongs to the reciprocal lattice). Within linear response, the long-wave part of δn takes the form:

$$\delta n(r) = -\lim_{q\to 0}\ q\ \delta\mathcal{P}\ \sin(qr) \tag{10}$$

where $\delta\mathcal{P}$ is the change of polarization for $q = 0$ [17].

Generally, the self-consistent screening potential will also contain long-wave and more rapidly varying terms. Its long-wave part will include an Hartree contribution, corresponding to the screening of the applied field due to the Coulomb interaction. In Ref. [1], we demonstrated that the polarization dependence of $E_{\rm xc}$ will manifest itself through a homogeneous XC electric field $\delta\mathcal{E}_{\rm xc}$, so that for $q \to 0$:

$$\delta V_{\rm xc}(q) = \frac{\delta\mathcal{E}_{\rm xc}}{2iq}\ . \tag{11}$$

From Eqs. (2) and (3), the XC kernel and potential are related by $\delta V_{\rm xc} = K_{\rm xc}\,\delta n$. Isolating in this equation the long-wave terms from the other contributions, we obtain,

in a generalized matrix notation (in which G stands for *all* non-zero vectors of the reciprocal lattice):

$$\begin{pmatrix} \frac{1}{q}\frac{\delta \mathcal{E}_{\rm xc}}{2i} \\ \delta V_{{\rm xc},q+G} \end{pmatrix} = K_{\rm xc} \begin{pmatrix} -q\,\frac{\delta \mathcal{P}}{2i} \\ \delta n_{q+G} \end{pmatrix} . \qquad (12)$$

In order for the change in exchange-correlation field $\delta\mathcal{E}_{\rm xc}$ to be finite when a finite change of polarization $\delta\mathcal{P}$ takes place, the head of the exact exchange-correlation kernel matrix, $K_{\rm xc}(q,q)$, must exhibit a $\mathcal{O}(1/q^2)$ divergence in the limit of $q \to 0$ [16,12].

The previous results can be illustrated in the case of a simple model one-dimensional semiconductor, already used in Ref. [1], and for which $K_{\rm xc}$ can be computed exactly (within the model). In this model, the sum of the external and Hartree potential is taken to be:

$$V_{\rm ext}(x) + V_{\rm H}(x) = V_o \cos(2\pi x/a), \qquad (13)$$

where a is the unit cell length. Moreover, a simple non-local self-energy operator is present, with the aim of mimicking the relevant many-body effects. It has the same non-local form and same parameters as in Refs. [18,1]:

$$\Sigma(r,r',\omega) = \frac{f(x)+f(x')}{2}\, g(|x-x'|) \qquad (14)$$

where $f(x) = F_o\,[1-\cos(2\pi x/a)]$ is a negative function that has the cell periodicity and $g(y)$ is a normalized gaussian of width w. We construct an *exact* KS theory for this model system by determining the local potential $V_{\rm KS}$, which, when filled with non-interacting electrons, reproduces the density obtained when including the self-energy operator [18,1].

The proper part π of the polarizability of the model system can be obtained using the Adler and Wiser [9] sum-over-state technique applied to the eigenfunctions and eigenvalues of the reference Hamiltonian (that includes Σ, which is taken to be independent of changes in the external potential).

From our KS wavefunctions, that reproduce the same density, it is also possible to compute the KS independent-particle polarizability, χ_o, from the Adler and Wiser technique. The relationship between π and χ_o is given by Eq. (8), so that we obtain :

$$K_{\rm xc} = \chi_o^{-1} - \pi^{-1}. \qquad (15)$$

In Fig. 1 we have plotted the diagonal part of the computed $K_{\rm xc}$. The calculation was performed on a 80-unit-cell, which guarantees a convergence better than 0.7%. We observe a divergence in the limit of $q \to 0$. The inset exhibits its expected $\mathcal{O}(1/q^2)$ character.

We note that the divergence of $K_{\rm xc}$ has been obtained without including long-range correlation effects in our model semiconductor [19]. Inclusion of such effects would simply modify the coefficient of the $K_{\rm xc}(q,q)$ divergence.

III. APPROXIMATE FUNCTIONALS

In the previous Section, we have linked the polarization-dependence of the XC energy with an $\mathcal{O}(1/q^2)$ divergence of the XC kernel, and given an example of this behaviour. The link with a third concept, the ultra-non-local sensitivity of the exchange-correlation functional [18] was emphasized in Refs. [1,2]: a change in surface charge may have an influence on the bulk XC potential, independently of the distance between the point in the bulk and the surface. Any approximate XC functional can now be analyzed in the light of these characteristics of the exact functional. Although they have the same physical origin, each of them provides a different point of view.

As regards the ultra-non-locality requirement, the behaviour of LDA and GGA is clear: the corresponding exchange-correlation potentials at any point do *not* depend on the density outside the immediate neighborhood. The following analysis of the small wavevector dependence of the exchange-correlation kernel provides a more refined picture of the violation of this requirement.

To start with, we consider the XC kernel in the LDA,

$$K_{\rm xc}^{\rm LDA}(\mathbf{r},\mathbf{r}') = \left.\frac{\delta V_{\rm xc}^{\rm LDA}}{\delta n}\right|_{\mathbf{r}} . \delta(\mathbf{r}-\mathbf{r}'). \qquad (16)$$

The Fourier transform of this kernel, diagonal in real space, is such that $K_{\rm xc}^{\rm LDA}(\mathbf{q},\mathbf{q})$ is *independent* of $\mathbf{q}$ [20].

The gradient-corrected XC energy has the form

$$E_{\rm xc}^{\rm GGA}[n] = \int e_{\rm xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r}, \qquad (17)$$

with the corresponding potential :

$$V_{\rm xc}^{\rm GGA}(\mathbf{r}) = \left.\frac{\partial e_{\rm xc}}{\partial n}\right|_{\mathbf{r}} - \nabla \cdot \left.\frac{\partial e_{\rm xc}}{\partial \nabla n}\right|_{\mathbf{r}} \qquad (18)$$

The relationship between the long wavelength GGA-XC potential and the long wavelength density is therefore governed by the following kernel (compare with Eqs.(15) and (22) of Ref. [10]):

$$\begin{aligned} K_{\rm xc}^{\rm GGA}(\mathbf{q},\mathbf{q}) = \frac{1}{\Omega}\Bigg[& \int_\Omega \left.\frac{\partial^2 e_{\rm xc}}{\partial n^2}\right|_{\mathbf{r}} d\mathbf{r} \\ & -2i\sum_\alpha q_\alpha \int_\Omega \left.\frac{\partial^2 e_{\rm xc}}{(\partial n)(\partial(\partial_\alpha n))}\right|_{\mathbf{r}} d\mathbf{r} \\ & -\sum_{\alpha\beta} q_\alpha q_\beta \int_\Omega \left.\frac{\partial^2 e_{\rm xc}}{(\partial(\partial_\alpha n))(\partial(\partial_\beta n))}\right|_{\mathbf{r}} d\mathbf{r} \Bigg] \end{aligned} \qquad (19)$$

The first term of the right member of this equation is the Fourier transform of the term appearing in the LDA. Eq. (19) makes clear that the gradient corrections produces terms with *positive* powers of q, but not the required $\mathcal{O}(1/q^2)$ divergence.

Contrary to what is expected by Mazin and Cohen [21], the GGA has therefore no apparent ability to improve upon the LDA behaviour in this respect. Mazin and Cohen were also expecting the weighted-density approximation (WDA), in which the XC functional is truly non-local, to improve upon the LDA behaviour. We now analyze this case.

The exchange-correlation energy is given exactly by the adiabatic connection formula, in terms of the coupling-constant averaged pair-correlation hole, $G(\mathbf{r},\mathbf{r}';[n])$:

$$E_{\rm xc}[n] = \frac{1}{2}\iint n(\mathbf{r})\frac{G(\mathbf{r},\mathbf{r}';[n])}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}')d\mathbf{r}d\mathbf{r}' \qquad (20)$$

This exact expression was the starting point of the analysis of the XC hole by Resta [13]. In the WDA [6], the exact pair-correlation function at each point $\mathbf{r}$ is replaced by the pair-correlation evaluated for a homogeneous electron gas with "weighted" density, $G^{\rm hom}(\mathbf{r},\mathbf{r}';\bar{n}(\mathbf{r};[n]))$, where $\bar{n}(\mathbf{r};[n])$ is determined from the density in the whole space so as to satisfy the requirement that the exchange-correlation hole integrates to -1. The corresponding WDA-XC potential is made of three terms

$$\begin{aligned} V_{\rm xc}^{\rm WDA}(\mathbf{r}_0) = & \frac{1}{2}\int \frac{G^{\rm hom}(\mathbf{r}_0,\mathbf{r}';\bar{n}(\mathbf{r};[n]))}{|\mathbf{r}_0-\mathbf{r}'|}n(\mathbf{r}')d\mathbf{r}' \\ & + \frac{1}{2}\int n(\mathbf{r})\frac{G^{\rm hom}(\mathbf{r},\mathbf{r}_0;\bar{n}(\mathbf{r};[n]))}{|\mathbf{r}-\mathbf{r}_0|}d\mathbf{r} \\ & + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\frac{\delta G^{\rm hom}(\mathbf{r},\mathbf{r}';\bar{n}(\mathbf{r};[n]))}{\delta n(\mathbf{r}_0)}d\mathbf{r}d\mathbf{r}'. \qquad (21) \end{aligned}$$

If the WDA-XC energy functional were ultra-non-local, arbitrarily remote surface charges would influence the XC potential, so as to induce the possibility of a linear XC potential in the bulk. The first or second terms of Eq. (21) would present such a behaviour if the homogeneous gas pair-correlation function $G^{\rm hom}$ were replaced by some constant (independent of the distance between $\mathbf{r}$ and $\mathbf{r}'$): in this case they would be similar to a Hartree potential, that exhibits the desired dependence upon surface charge. A partly delocalized exchange-correlation hole would lead to the same kind of behaviour [13]. But the pair-correlation for a homogeneous gas, $G^{\rm hom}$, decays on average as the *inverse of the fifth power* of the distance between the points [6]. This decay will make these terms insensitive to the surface charge.

In the third term of Eq. (21), the derivative of the pair-correlation function with respect to some change of density appears. Ortiz and Martin have interpreted the corresponding term in the exact expression as coming from the polarizability of the exchange-correlation hole [14], sensitive to the TC or KS homogeneous electric field. But we will see that the WDA exchange-correlation hole is not as sensitive as the exact exchange-correlation hole. The derivative of the pair-correlation function can be obtained thanks to the chain rule,

$$\frac{\delta G^{\rm hom}(\mathbf{r},\mathbf{r}';\bar{n}(\mathbf{r};[n]))}{\delta n(\mathbf{r}_0)} = \frac{\delta G^{\rm hom}(\mathbf{r},\mathbf{r}';\bar{n}(\mathbf{r}))}{\delta \bar{n}(\mathbf{r})}\frac{\delta \bar{n}(\mathbf{r};[n]))}{\delta n(\mathbf{r}_0)}. \qquad (22)$$

The above-mentioned decay of $G^{\rm hom}$ affects both factors of the right-hand side. The first factor will exhibit the same decay as the homogeneous gas pair-correlation function, while the dependence of $\bar{n}(\mathbf{r};[n])$ upon $\delta n(\mathbf{r}_0)$, driven by the requirement that the exchange-correlation hole integrates to -1, will also be spatially short-ranged: a finite change of surface charge density on the surface of the crystal, times the r^{-5} decay and integrated over the whole surface, yields zero contribution in the thermodynamical limit. As a consequence, all the terms in Eq. (21) are insensitive to arbitrarily remote surface charges, so that no polarization-dependence is present in $V_{\rm xc}^{\rm WDA}$.

Thus, in opposition to the suggestion of Mazin and Cohen [21,22], we find that the possible non-locality of approximate functionals is not sufficient to generate a polarization-dependence: one needs an ultra-non-local dependence. This might be attained by considering either a model pair-correlation function that does not integrate to -1 in the bulk [13], or a polarizable exchange-correlation hole [14], as in the exact exchange approach [3].

IV. THE METAL – INSULATOR PARADOX

Godby and Needs [11] observed that the KS band structure of semiconductors might present the characteristics of a metallic state (the absence of a band gap). We now argue that it is precisely the *same* $\mathcal{O}(1/q^2)$ behaviour of $K_{\rm xc}(q,q)$ that allows this "true insulator–KS metal" paradox to be understood.

In order to make the analysis as simple as possible, we first ignore local field corrections, and also impose cubic symmetry. In this case, only the head of the different matrices appearing in Eq. (8) must be taken into account, which means that this equation reduces to a scalar equality. The small wavevector behaviours of χ and χ_o are well-known in both the metallic and the insulating case [7]. The independent-particle polarizability of a KS metallic ground-state behaves like

$$\lim_{q\to 0}\chi_o(q,q) = \gamma, \qquad (23)$$

while for a cubic KS insulator, one has

$$\lim_{q\to 0}\chi_o(q,q) = \alpha q^2, \qquad (24)$$

where γ and α are some negative constants. The head of the polarizability matrix $\chi(q,q)$ for a metal (interacting electrons, not KS electrons) behaves exactly as $-\frac{q^2}{4\pi}$ in the long-wavelength limit (which corresponds to complete screening of the Coulomb potential), while for cubic insulators, it is $-\frac{q^2}{4\pi}\beta$, where β is a positive constant smaller than one, describing the incomplete screening.

Now, one imposes no divergence in $\chi_o^{-1}(q,q)$ (metallic KS ground state), and non-cancelling divergences of $\chi^{-1}(q,q)$ and $V_{\rm C}$ (incomplete screening of the insulating system), so that Eq. (8) without local fields becomes

$$\frac{1}{\gamma} = -\frac{4\pi}{\beta q^2} + \frac{4\pi}{q^2} + K_{\rm xc}(q,q), \tag{25}$$

which proves that $K_{\rm xc}(q,q)$ *must* have a $\mathcal{O}(1/q^2)$ divergence. This result establish a connection between the "true insulator–KS metal" paradox and the polarization dependence of the XC energy for insulators: in both cases, the small-wavevector behaviour of the XC kernel is similar.

V. UNIFIED TREATMENT OF $K_{\rm XC}$ FOR INSULATORS AND METALS

We now consider the treatment of insulators and metals in a unique framework. By the way, we will also generalize the demonstration contained in the preceeding section to the case where local fields are included (we treat not only the head of $K_{\rm xc}$, χ_o^{-1} and π^{-1}, but also their wings and body).

Following the analysis by Pick, Martin and Cohen [7] of χ_o and π, we find that χ_o^{-1}, for the KS non-interacting system, and π^{-1}, for the interacting system, have the following, similar, non-analytic behaviour. In the insulating case, the head of these inverse matrices diverges like $\mathcal{O}(1/q^2)$, the wing elements diverge like $\mathcal{O}(1/q)$, while the body elements, though non-analytic, are non-divergent. In the metallic case, no element shows a divergence for small wavevectors. The divergences in $K_{\rm xc} = \chi_o^{-1} - \pi^{-1}$, following Eq.(15), are easy to deduce from these results, if we suppose that there is no fortuitous cancellation of divergences when the difference is taken.

For the (usual) "true metal–KS metal" case, since there is no divergence in χ_o^{-1} or π^{-1}, no element of $K_{\rm xc}$ need diverge for small wavevectors in order to correct the long-wavelength response (although separate non-analytic behaviour at non-zero wavevectors may be required to accommodate a disparity between the true and KS Fermi surfaces). In all the other conceivable cases (the usual "true insulator–KS insulator" case, the exotic "true insulator–KS metal" case, and the hypothetical "true metal–KS insulator" case), the head of $K_{\rm xc}$ will diverge like $\mathcal{O}(1/q^2)$, the wing elements will diverge like $\mathcal{O}(1/q)$, and the body elements will not diverge.

Although the exchange-only kernel is able to generate the right divergences in the "true insulator–KS insulator" case [3], it is unable to do so in the "true insulator–KS metal" case. Indeed, the argument developed in Ref. [3] relies on the following result :

$$V_{\rm x}(\mathbf{q}) = \sum_{\mathbf{G}} \chi_0^{-1}(\mathbf{q},\mathbf{q}+\mathbf{G}) \ \frac{\delta E_{\rm x}}{\delta V_{\rm KS}(\mathbf{q}+\mathbf{G})} \tag{26}$$

If the Kohn-Sham system is insulating, χ_o^{-1} will exhibit the appropriate divergences. Following Ref. [3], the exchange-hole polarizes in a homogeneous KS electric field, so that one obtains a polarization-dependence of the exchange-only kernel. On the other hand, if the Kohn-Sham system is metallic to start with, χ_o^{-1} has no divergence, and $V_{\rm x}(\mathbf{q})$ for short wavevectors will vanish.

Thus, the corrections needed to obtain an insulating-like polarizability while the Kohn-Sham system is metallic are entirely due to the correlation kernel. In the adiabatic coupling constant construction of the XC energy [6], the system at different value of the coupling constant λ will undergo a metal-insulator phase transition : at $\lambda = 0$, the characteristic system is the Kohn-Sham metallic system, while at $\lambda = 1$, one deals with the truly interacting, insulating, system.

VI. THE MACROSCOPIC DIELECTRIC CONSTANT

Now that the correct behaviour of $K_{\rm xc}$ has been discussed, we would like to investigate its consequences in the calculation of the macroscopic dielectric constant of insulators. At the macroscopic level, this quantity can be obtained as [23]:

$$\varepsilon_\infty = 1 + 4\pi \frac{\partial \mathcal{P}}{\partial \mathcal{E}} \tag{27}$$

where $\mathcal{P}$ is the macroscopic polarization and $\mathcal{E}$ is the macroscopic electric field.

In order to include the local-field effects in the computation of ε_∞, Adler and Wiser [9] relied on the dielectric matrix, relating effective and external potentials as follows

$$\sum_{\mathbf{q}+\mathbf{G}'} \varepsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')\delta V_{\rm eff}(\mathbf{q}+\mathbf{G}') = \delta V_{\rm ext}(\mathbf{q}+\mathbf{G}), \tag{28}$$

and connected the macroscopic dielectric constant to the head of the inverse dielectric matrix:

$$\varepsilon_\infty = \lim_{q\to 0} \frac{1}{\varepsilon^{-1}(\mathbf{q},\mathbf{q})}. \tag{29}$$

The demonstration of Eq. (29) was reported at the RPA level. The next step was to include correctly the correction induced by the exchange-correlation effects [24].

In the *test-charge* formulation of ε [24], the effective potential appearing in Eq. (28) is chosen as the one experienced by a hypothetical *classical* charge, $\delta V_{\rm TC} = \delta V_{\rm ext} + \delta V_{\rm H}$. Imposing the variations of the external potential $\delta V_{\rm ext}(\mathbf{q}+\mathbf{G})$ for $\mathbf{G} \neq \mathbf{0}$ to be zero, one deduces

$$\frac{1}{\varepsilon^{-1}_{\rm TC}(\mathbf{q},\mathbf{q})} = 1 - \frac{\delta V_{\rm H}(\mathbf{q})}{\delta V_{\rm ext}(\mathbf{q}) + \delta V_{\rm H}(\mathbf{q})} \tag{30}$$

$$= 1 - \frac{4\pi}{q^2}\frac{\delta n(\mathbf{q})}{\delta V_{\rm ext}(\mathbf{q}) + \delta V_{\rm H}(\mathbf{q})} \tag{31}$$

The relationship that exists in the long-wave approach between field and potential and between charge and polarization allows one to recover Eq. (27).

In the *electron* formulation, the effective potential appearing in Eq. (28) is replaced by the one felt by the Kohn-Sham electrons, $\delta V_{\rm KS} = \delta V_{\rm ext} + \delta V_{\rm H} + \delta V_{\rm xc}$. The dielectric constant is then :

$$\frac{1}{\varepsilon^{-1}_{e}(\mathbf{q},\mathbf{q})} = 1 - \frac{\delta V_{\rm H}(\mathbf{q}) + \delta V_{\rm xc}(\mathbf{q})}{\delta V_{\rm ext}(\mathbf{q}) + \delta V_{\rm H}(\mathbf{q}) + \delta V_{\rm xc}(\mathbf{q})}. \tag{32}$$

In the absence of polarization-dependence of $E_{\rm xc}$ ($\delta V_{\rm xc}(\mathbf{q}) = 0$), Eq. (32) reduces to Eq. (30). Within the LDA, GGA or WDA, *the test-charge and electron definitions of ε_∞ are therefore identical*.

Going beyond these approximations, we observe that the electron definition, Eq. (32), does not reduce to the test-charge one, Eq. (30), by a simple addition of the exchange-correlation contribution in the denominator (macroscopic field), but that the numerator must also include a modified Coulomb interaction. In addition, it can be checked that the test-charge definition of the macroscopic dielectric constant can be formulated as a second derivative of the (electric) free energy [25] with respect to a homogeneous electric field, which is not the case for the electron formulation.

It is also possible to analyze the direct effect of the divergence of head and wing elements of $K_{\rm xc}(q,q)$ on dielectric matrices. Following Singhal and Callaway [24], we use the equality

$$\delta n = \chi_o[\delta V_{\rm ext} + \delta V_{\rm H} + \delta V_{\rm xc}] \tag{33}$$

to find the form of the dielectric matrices in terms of χ_o, V_C and $K_{\rm xc}$:

$$\varepsilon_{\rm TC} = 1 - V_C\chi_o\,[1 - K_{\rm xc}\chi_o]^{-1}, \tag{34}$$

$$\varepsilon_e = 1 - V_C\chi_o - K_{\rm xc}\chi_o. \tag{35}$$

These expressions are governed by the products $V_C\chi_o$ and $K_{\rm xc}\chi_o$. The head and wing elements of χ_o behave like $\mathcal{O}(q^2)$ and $\mathcal{O}(q)$ in the limit of $q \to 0$ [7,20]. V_C is diagonal, with a divergent $\mathcal{O}(1/q^2)$ head. In the small wavevector limit, their product, an asymmetric matrix, will have finite head and body, while the upper wing will diverge like $\mathcal{O}(1/q)$ and the lower wing will behave like $\mathcal{O}(q)$. If we completely ignore the effect of the exchange-correlation terms in Eqs. (34) and (35), the latter form is also the form of the dielectric matrices.

If we take into account the effect of a *non-divergent* $K_{\rm xc}$, of the LDA type, the product $K_{\rm xc}\chi_o$ will behave like χ_o. The handling of such contributions in both Eqs. (34) and (35) will only affect the body of the dielectric matrices, in the small wavevector limit. By contrast, if we take into account the possible divergences of $K_{\rm xc}$, the product $K_{\rm xc}\chi_o$ will behave like $V_C\chi_o$. As such, it will be able to affect the leading behaviour of all elements in both formulations of the dielectric matrix.

The macroscopic dielectric constant being obtained from the head of the *inverse* dielectric matrix Eq. (29), the presence of $K_{\rm xc}$ will always affect its amplitude. However, if one deals with a LDA-type $K_{\rm xc}$, its influence will be mediated by local fields only , while the true $K_{\rm xc}$ will modify it more directly, in particular through a modification of the head of the dielectric matrix.

VII. CONCLUSIONS

In conclusion, we have seen that the polarization dependence of $E_{\rm xc}$ imposes a condition on the form of the exchange-correlation kernel: its head must diverge like $\mathcal{O}(1/q^2)$ in the limit of $q \to 0$. This condition is not satisfied within the LDA, GGA and WDA. The absence of this divergence in the approximate functionals will affect the amplitude of the computed macroscopic dielectric constant by a finite amount. A similar divergence is also needed, in order to reproduce the correct dielectric response, when insulators are described as metals in Kohn-Sham theory.

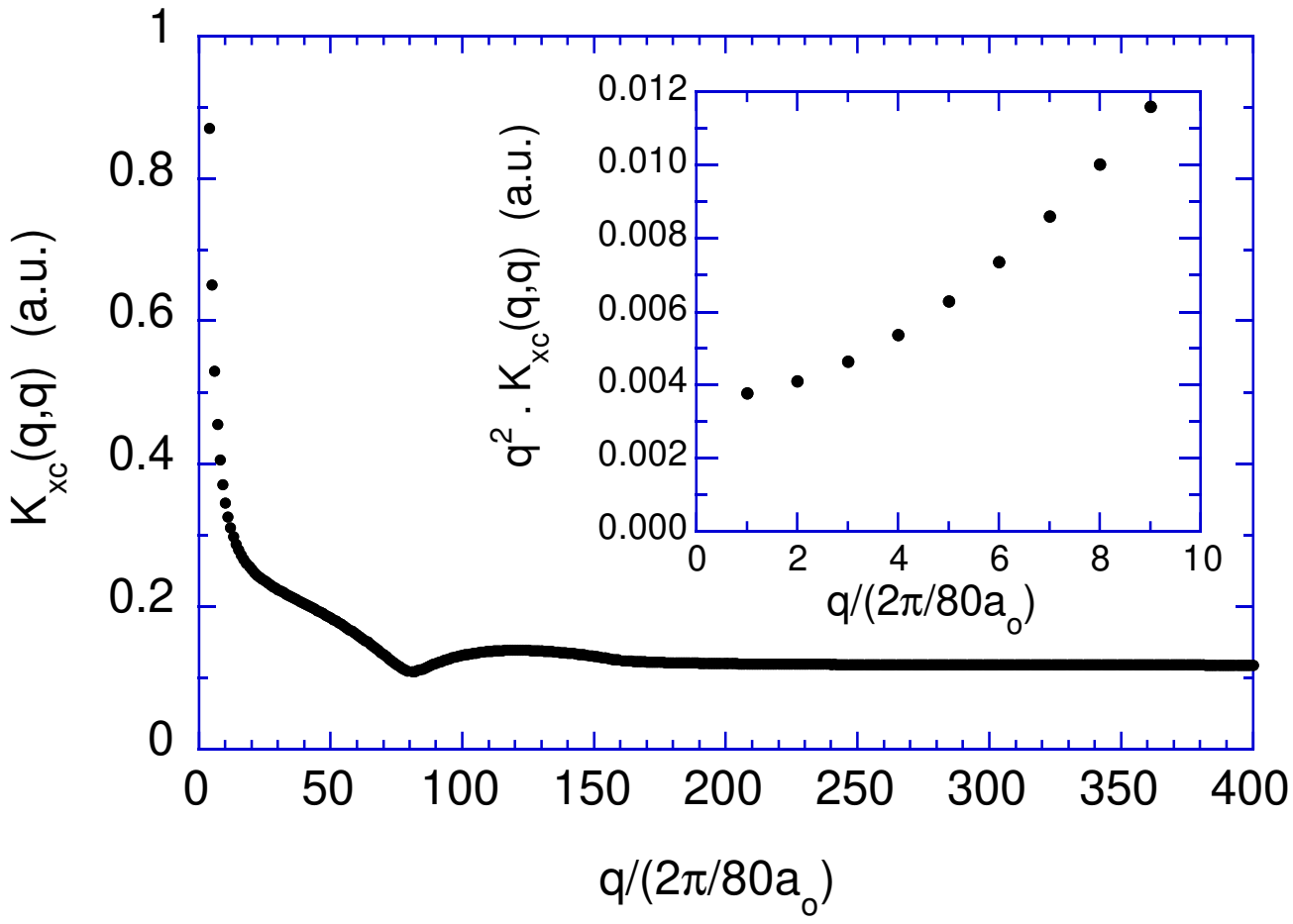
ACKNOWLEDGMENTS

We acknowledge numerous discussions with R. Martin, D. Vanderbilt, and R. Resta. We thank the latter for a careful reading of the final manuscript, Yong-Hoon Kim for questioning the effect of the exchange-only kernel in the metallic case, and the authors of Refs. [12–15] for providing copies of their manuscripts prior to publication. We acknowledge financial support from FNRS-Belgium and the Concerted Action programme 92-97.156 (X.G.), the EPSRC (R.W.G.), the European Union (HCM Program Contract CHRX-CT940462), and the Academic Research Collaboration Programme between the FNRS, the CGRI, and the British Council.

[1] X. Gonze, Ph. Ghosez and R. W. Godby, Phys. Rev. Lett. **74**, 4035 (1995).
[2] X. Gonze, Ph. Ghosez and R. W. Godby, Phys. Rev. Lett. **78**, 294 (1997).
[3] X. Gonze, Ph. Ghosez and R. W. Godby, Phys. Rev. Lett. **78**, 2029 (1997).

[4] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[5] See A. Khein, D. J. Singh and C. J. Umrigar, Phys. Rev. B **51**, 4105 (1995) and references therein.
[6] O. Gunnarsson, M. Jonson, and B.I. Lundqvist, Phys. Rev. B **20**, 3136 (1979); O. Gunnarsson and R. O. Jones, Phys. Scr. **21**, 394 (1980).
[7] R. M. Pick, M. H. Cohen, R. M. Martin, Phys. Rev. B **1**, 910 (1970).
[8] R. Resta and A. Baldereschi, Phys. Rev. B **23**, 6615 (1981); S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).
[9] S. L. Adler, Phys. Rev. **126**, 413 (1962); N. Wiser, Phys. Rev. **129**, 62 (1963).
[10] A. Dal Corso, S. Baroni and R. Resta, Phys. Rev. B **49**, 5323 (1994).
[11] R. W. Godby and R. J. Needs, Phys. Rev. Lett. **62**, 1169 (1989).
[12] W. G. Aulbur, L. Jönsson and J. W. Wilkins, Phys. Rev. B **54**, 8540 (1996). At variance with the present paper, they do not consider the influence of the local fields - or wings of matrices: compare their Eq.(7) with Eq.(11) of Ref. [1].
[13] R. Resta, Phys. Rev. Lett. **77**, 2265 (1996); Phys. Rev. Lett. **78**, 2030 (1997).
[14] R. Martin and G. Ortiz, Phys. Rev. Lett. **78**, 2028 (1997).
[15] R. Martin and G. Ortiz, submitted for publication in Phys. Rev. B.
[16] X. Gonze, Ph. Ghosez and R. W. Godby, Bull. Am. Phys. Soc. **41**, 340 (1996).
[17] Note that n is an electronic density, not a charge density. This equation differs from Eq.(3) in Ref. [1] because the choice of sign for the definition of the polarization in the latter paper was unconventional, albeit treated in a consistent way.
[18] R. W. Godby and L. J. Sham, Phys. Rev. B **49**, 1849 (1994).
[19] In Ref. [21], it was pointed out that the "exchange-correlation local field" (XCLF) correction to the Green's function approach diverges like $\mathcal{O}(1/q^2)$. Although this additional effect is not present in our model, a $\mathcal{O}(1/q^2)$ divergence is still observed.
[20] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987).
[21] I. I. Mazin and R. Cohen, Ferroelectrics **194**, 263 (1997).
[22] We disagree with other statements in Ref. [21]. For example, there are semiconductors described as metals in LDA, with formally infinite LDA dielectric constants, in contrast with the supposedly excellent accuracy of LDA mentioned in the beginning of Ref. [21]. This problem, in the context of exact KS theory, is analyzed in the present paper. Also, it is claimed in Ref. [21] that the most divergent term in the XC kernel is a delta function. Actually, in that paper, it is only proved that the XC kernel is infinite at $q = 0$, so that nothing prevents the stronger $\mathcal{O}(1/q^2)$ behaviour observed here. Finally, Ref. [21] fails to distinguish clearly between the limit $q \to 0$ and the case $q = 0$, particularly when attributing to Ref. [1] results about the validity of conventional DFT. We are in agreement with the alternative discussion of these issues, and their relationship to Ref. [1], given by Martin and Ortiz [15].
[23] Ch. Kittel, "Introduction to Solid State Physics", John Wiley & Sons Inc., New York, 1968.
[24] See S. P. Singhal and J. Callaway, Phys. Rev. B **14**, 2347 (1976) and references therein.
[25] S. de Gironcoli, S. Baroni and R. Resta, Phys. Rev. Lett. **62**, 2853 (1989).

FIG. 1. The diagonal part of the exchange-correlation kernel for the one-dimensional model semiconductor. The result was obtained for a 80 unit-cell supercell (320 a.u.). The $\mathcal{O}(1/q^2)$ character of the $K_{\rm xc}$ divergence is exhibited in the inset by the non-zero intercept of $q^2.K_{\rm xc}(q,q)$.


1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
350
400
K_xc(q,q) (a.u.)
q/(2π/80a_o)
0.012
0.010
0.008
0.006
0.004
0.002
0.000
0
2
4
6
8
10
q^2 . K_xc(q,q) (a.u.)
q/(2π/80a_o)