

Exact Dynamical Exchange-Correlation Kernel of a Weakly Inhomogeneous Electron Gas

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The dynamical exchange-correlation kernel f_{xc} of a nonuniform electron gas is an essential input for the time-dependent density-functional theory of electronic systems. The long-wavelength behavior of this kernel is known to be of the form $f_{xc} = \alpha/q^2$ where q is the wave vector and α is a frequency-dependent coefficient. We show that in the limit of weak nonuniformity the coefficient α has a simple and exact expression in terms of the ground-state density and the frequency-dependent kernel of a *uniform* electron gas at the average density. We present an approximate evaluation of this expression for Si and discuss its implications for the theory of excitonic effects.

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Since its introduction in works of Runge, Gross, and Kohn [1,2], the time-dependent density-functional theory (TDDFT) has evolved into a powerful tool of investigation of systems ranging from isolated atoms to bulk solids. In the important linear-response regime, the key quantity of TDDFT is the dynamical exchange-correlation (xc) kernel f_{xc} defined as the functional derivative

$$f_{xc}[n_0(\mathbf{r})](\mathbf{r}, \mathbf{r}', \omega) = \left. \frac{\delta V_{xc}[n](\mathbf{r}, \omega)}{\delta n(\mathbf{r}', \omega)} \right|_{n=n_0(\mathbf{r})}$$

of the dynamical xc potential V_{xc} with respect to the dynamical electron density n , taken at the ground-state value n_0 of the latter. With this definition, the density-response function χ can be represented in operator notation as [2]

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \{[1 - \chi_{KS}(C + f_{xc})]^{-1} \chi_{KS}\}(\mathbf{r}, \mathbf{r}', \omega), \quad (1)$$

where χ_{KS} is the Kohn-Sham (KS) density-response function of independent electrons, $C = e^2/|\mathbf{r} - \mathbf{r}'|$ is the Coulomb interaction, and e is the absolute value of the electron charge. While the density-response function of noninteracting electrons χ_{KS} can be straightforwardly calculated in many cases of interest [e.g., for homogeneous electron gases (EG) in three and two dimensions it is given by the analytical Lindhard's [3] and Stern's [4] formulas, respectively], the construction of f_{xc} , whose role is to account for dynamical many-body correlations, is a very challenging problem.

As an instructive specific case, let us consider the excitonic effect [5] in a semiconductor, which would manifest itself as an enhancement of the imaginary part of χ for frequencies close to the fundamental absorption edge. We neglect for a moment local-field effects [6,7] and write down the diagonal elements of the density response in momentum space as of Eq. (1)

$$\chi(\mathbf{q}, \mathbf{q}, \omega) = \frac{\chi_{KS}(\mathbf{q}, \mathbf{q}, \omega)}{1 - \chi_{KS}(\mathbf{q}, \mathbf{q}, \omega)[\frac{4\pi e^2}{q^2} + f_{xc}(\mathbf{q}, \mathbf{q}, \omega)]}, \quad (2)$$

where $4\pi e^2/q^2$ is the Fourier transform of the Coulomb interaction. On the one hand, the excitonic enhancement of χ is a many-body effect and, therefore, it needs a nonzero f_{xc} to be accounted for within TDDFT. On the other hand, because of the divergent Coulomb part $4\pi e^2/q^2$ in Eq. (2), any $f_{xc}(\mathbf{q}, \mathbf{q}, \omega)$ that remained finite at $q = 0$ would give no contribution in the long-wave limit $q \rightarrow 0$. This simple observation shows that in order to include the exciton, $f_{xc}(\mathbf{q}, \mathbf{q}, \omega)$ must be divergent in the long-wave limit at least as strongly as the Coulomb term; i.e., it must have the form

$$\lim_{q \rightarrow 0} f_{xc}(\mathbf{q}, \mathbf{q}, \omega) = \frac{e^2 \alpha(\omega)}{q^2} \quad (3)$$

(we introduce the e^2 so that α is dimensionless). And indeed, when the q^{-2} divergence has been introduced empirically in works dealing with the optical absorption spectrum of semiconductors [8–10], it has yielded a good TDDFT description of the excitonic effect.

From a theoretical standpoint the existence of the singularity in $f_{xc}(\mathbf{q}, \mathbf{q}, \omega)$ has long been known for periodic insulators both at zero frequency [11] and at finite frequency [12,13]. In metallic systems the singularity is believed to be absent at zero frequency, but still present at finite frequency [15]. Unfortunately, first-principle calculations of $\alpha(\omega)$ have not been forthcoming. Kim and Görling [12] have obtained a formal expression for $\alpha(\omega)$ for periodic insulators in the exact exchange approximation to the leading order in the Coulomb interaction—but the evaluation of this expression remains a formidable task. In this Letter we focus on weakly inhomogeneous electronic systems, and develop a theory that is exact to second order in the amplitude of the density modulation. Thus, at variance with the systems considered in Ref. [12], our

system is a metal and many-body effects are included beyond the exchange-only approximation to all orders in the Coulomb interaction. In particular, we will derive a simple and exact expression for $\alpha(\omega)$ in terms of the ground-state density and the dynamical xc kernel of a homogeneous EG evaluated at the average density of the inhomogeneous system.

Our approach is based on the general method recently derived from the time-dependent *current-density-functional theory* (TDCDFT) for constructing f_{xc} from the current-current response function [16]. This method is based on the exact relation that connects the scalar density-response function χ (density response to a scalar potential) to the tensor current-density-response function $\hat{\chi}$ (current-density response to a vector potential):

$$\chi(\mathbf{q}, \mathbf{q}', \omega) = \frac{c}{e\omega^2} \mathbf{q} \cdot \hat{\chi}(\mathbf{q}, \mathbf{q}', \omega) \cdot \mathbf{q}'. \quad (4)$$

Both response functions are expressed in terms of the corresponding Kohn-Sham response functions and xc kernels in the following manner:

$$\chi^{-1}(\mathbf{q}, \mathbf{q}', \omega) = \chi_{KS}^{-1}(\mathbf{q}, \mathbf{q}', \omega) - f_{xc}(\mathbf{q}, \mathbf{q}', \omega) - \frac{4\pi e^2}{q^2} \delta_{\mathbf{q}\mathbf{q}'} \quad (5)$$

and

$$\hat{\chi}^{-1}(\mathbf{q}, \mathbf{q}', \omega) = \hat{\chi}_{KS}^{-1}(\mathbf{q}, \mathbf{q}', \omega) - \hat{f}_{xc}(\mathbf{q}, \mathbf{q}', \omega) - \frac{4\pi e c}{\omega^2} \hat{L}_{\mathbf{q}} \delta_{\mathbf{q}\mathbf{q}'}, \quad (6)$$

where $\hat{L}_{\mathbf{q},ij} \equiv q_i q_j / q^2$, i , and j are Cartesian indices.

Equations (4)–(6) establish a connection between f_{xc} and its tensor counterpart \hat{f}_{xc} . The usefulness of this connection stems from the fact that the tensor quantities $\hat{\chi}_{KS}$ and \hat{f}_{xc} satisfy a broader set of exact sum rules than the corresponding scalar quantities. These sum rules were derived in Ref. [17]. Specializing to the case of periodic systems, the two most important sum rules for our purposes are

$$\hat{\chi}_{KS,ij}(\mathbf{G}, \mathbf{0}, \omega) = \frac{e}{mc} n_0(\mathbf{G}) \delta_{ij} - \frac{1}{m\omega^2} \times \sum_{\mathbf{G}',k} \hat{\chi}_{KS,ik}(\mathbf{G}, \mathbf{G}', \omega) G'_k G'_j V_{KS}(\mathbf{G}'), \quad (7)$$

and

$$\sum_{\mathbf{G}'} \hat{f}_{xc,ij}(\mathbf{G}, \mathbf{G}', \omega) n_0(\mathbf{G}') = \frac{c}{e\omega^2} G_i G_j V_{xc}(\mathbf{G}), \quad (8)$$

where \mathbf{G} are reciprocal lattice vectors. These sum rules connect three different types of components of, say, $\hat{\chi}_{KS}(\mathbf{G}, \mathbf{G}', \omega)$: the $(\mathbf{0}, \mathbf{0})$ (head), the $(\mathbf{0}, \mathbf{G} \neq \mathbf{0})$ and $(\mathbf{G} \neq \mathbf{0}, \mathbf{0})$ (wing), and the $(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0})$ (body) components.

Let us further restrict our attention to the case of a weakly inhomogeneous system: $|n_0(\mathbf{G})| \ll n_0(\mathbf{0}) \equiv \bar{n}_0$, and $|V_{KS}(\mathbf{G})| \ll \hbar^2 G^2 / 2m$ for $\mathbf{G} \neq \mathbf{0}$. Then Eq. (7) leads to

$$\hat{\chi}_{KS,ij}(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0}, \omega) = \left[\frac{e\omega^2}{cG^2} L_{G,ij} \chi_{KS}^{hL}(G, \omega) + T_{G,ij} \chi_{KS}^{hT}(G, \omega) \right] \delta_{\mathbf{G}\mathbf{G}'}, \quad (9)$$

$$\hat{\chi}_{KS,ij}(\mathbf{G} \neq \mathbf{0}, \mathbf{0}, \omega) = \hat{\chi}_{KS,ji}(\mathbf{0}, -\mathbf{G}, \omega) = \frac{en_0(\mathbf{G})}{mc} \left[\delta_{ij} - \frac{\chi_{KS}^{hL}(G, \omega)}{\chi_{KS}^{hL}(G, 0)} L_{G,ij} \right], \quad (10)$$

$$\hat{\chi}_{KS,ij}(\mathbf{0}, \mathbf{0}, \omega) = \frac{e\bar{n}_0}{mc} \delta_{ij} + \frac{e}{m^2\omega^2 c} \sum_{\mathbf{G} \neq \mathbf{0}} \frac{|n_0(\mathbf{G})|^2}{\chi_{KS}^{hL}(G, 0)^2} \times [\chi_{KS}^{hL}(G, \omega) - \chi_{KS}^{hL}(G, 0)] G_i G_j, \quad (11)$$

to the zeroth, first, and second order in $n_0(\mathbf{G} \neq \mathbf{0})$, respectively. Here χ_{KS}^{hL} and χ_{KS}^{hT} are, respectively, the longitudinal and transverse KS density-response functions of the homogeneous EG of density \bar{n}_0 , and $T_{G,ij} = \delta_{ij} - L_{G,ij}$. Equation (10) is obtained by the substitution for $\sum_k \hat{\chi}_{KS,ik}(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0}, \omega) G_k$ in the right-hand side of Eq. (7) of its homogeneous value of $(e\omega^2 G_i / cG^2) \chi_{KS}^{hL}(G, \omega) \delta_{\mathbf{G}\mathbf{G}'}$. Equation (11) is obtained by the substitution of Eq. (10) into the right-hand side of Eq. (7) after setting $\mathbf{G} = \mathbf{0}$. Equation (9) just replaces $\hat{\chi}_{KS}(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0}, \omega)$ by its homogeneous value. The relation $V_{KS}(\mathbf{G} \neq \mathbf{0}) = n_0(\mathbf{G}) / \chi_{KS}^{hL}(G, 0)$ valid to the first order in $n_0(\mathbf{G} \neq \mathbf{0})$ has been used. Similarly, for \hat{f}_{xc} we have from Eq. (8)

$$\hat{f}_{xc,ij}(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0}, \omega) = \frac{c}{e\omega^2} G^2 [f_{xc}^{hL}(G, \omega) L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij}] \delta_{\mathbf{G}\mathbf{G}'}, \quad (12)$$

$$\hat{f}_{xc,ij}(\mathbf{G} \neq \mathbf{0}, \mathbf{0}, \omega) = \hat{f}_{xc,ji}(\mathbf{0}, -\mathbf{G}, \omega) = -\frac{cG^2}{e\omega^2 \bar{n}_0} n_0(\mathbf{G}) \{ [f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0)] L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij} \}, \quad (13)$$

$$\hat{f}_{xc,ij}(\mathbf{0}, \mathbf{0}, \omega) = \frac{c}{e\omega^2 \bar{n}_0^2} \sum_{\mathbf{G} \neq \mathbf{0}} G^2 |n_0(\mathbf{G})|^2 \{ [f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0)] L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij} \}, \quad (14)$$

where f_{xc}^{hL} and f_{xc}^{hT} are the longitudinal and transverse, respectively, xc kernels of the homogeneous EG of density \bar{n}_0 .

The following steps, which involve repeated inversions of infinite matrices, rely on the mathematical fact that to find the head, wing, and body elements of the inverse matrix to the second, first, and zeroth order in the inhomogeneity, respectively, it is sufficient to know the corresponding elements of the original matrix to the same

orders, and then the inversion can be performed in a closed form (cf., Ref. [18]). The complete procedure is schematically illustrated in Fig. 1. Starting from Eqs. (9)–(14) for $\hat{\chi}_{KS}$ and \hat{f}_{xc} we (i) invert Eqs. (9)–(11) to get $\hat{\chi}_{KS}^{-1}$; (ii) combine $\hat{\chi}_{KS}^{-1}$ and \hat{f}_{xc} to get $\hat{\chi}^{-1}$ by virtue of Eq. (6); (iii) invert $\hat{\chi}^{-1}$ to get $\hat{\chi}$; (iv) use Eq. (4) and its KS analogue to find the scalar response function χ from $\hat{\chi}$ and χ_{KS} from $\hat{\chi}_{KS}$; (v) invert χ and χ_{KS} to get χ^{-1} and χ_{KS}^{-1} ; and, (vi) apply Eq. (5) to find f_{xc} . We note that in our analysis we are remaining within the domain of the equivalence between TDCDFT and TDDFT, keeping \mathbf{q} small but finite [19]. The final result of this procedure is

$$f_{xc}(\mathbf{G} \neq \mathbf{0}, \mathbf{G}' \neq \mathbf{0}, \omega) = f_{xc}^{hL}(G, \omega) \delta_{\mathbf{G}\mathbf{G}'}, \quad (15)$$

$$\begin{aligned} \lim_{q \rightarrow 0} f_{xc}(\mathbf{G} \neq \mathbf{0}, \mathbf{q}, \omega) &= f_{xc}(-\mathbf{q}, -\mathbf{G}, \omega) \\ &= -\frac{(\mathbf{G} \cdot \hat{\mathbf{q}})}{\bar{n}_0 q} [f_{xc}^{hL}(G, \omega) \\ &\quad - f_{xc}^{hL}(G, 0)] n_0(\mathbf{G}), \end{aligned} \quad (16)$$

$$\begin{aligned} \lim_{q \rightarrow 0} f_{xc}(\mathbf{q}, \mathbf{q}, \omega) &= \frac{1}{\bar{n}_0^2 q^2} \sum_{\mathbf{G} \neq \mathbf{0}} (\mathbf{G} \cdot \hat{\mathbf{q}})^2 [f_{xc}^{hL}(G, \omega) \\ &\quad - f_{xc}^{hL}(G, 0)] n_0(\mathbf{G})^2, \end{aligned} \quad (17)$$

where $\hat{\mathbf{q}}$ is the unit vector parallel to \mathbf{q} . It should be noted at this point that the above expression for the scalar kernel $f_{xc}(\mathbf{q}, \mathbf{q}, \omega)$ differs from what one would get by simply taking the longitudinal component of $\hat{f}_{xc,ij}(\mathbf{q}, \mathbf{q}, \omega)$, i.e., $f_{xc}(\mathbf{q}, \mathbf{q}, \omega) \neq \frac{e\omega^2}{cq^2} \sum_{i,j} \hat{q}_i \hat{f}_{xc,ij}(\mathbf{q}, \mathbf{q}, \omega) \hat{q}_j$. The implication is that the scalar xc potential (V_{xc}) of time-dependent DFT is *not* equivalent to the longitudinal component of the vector potential (\mathbf{A}_{xc}) of time-dependent CDFT: rather, it should be constructed through the careful inversion procedure described above. A recent interesting attempt to construct V_{xc} from \mathbf{A}_{xc} [20] should be reexamined in the light of this result.

From the result of the step (iv) for χ we obtain a formula for the macroscopic dielectric function of a crystal

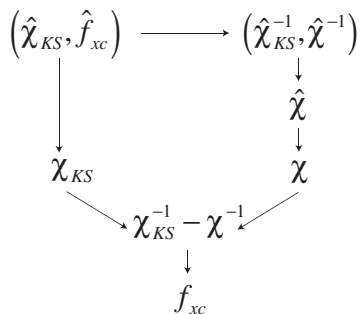


FIG. 1. Scheme of the procedure for calculating the xc kernel f_{xc} starting from the expressions (9)–(14) for $\hat{\chi}_{KS}$ and \hat{f}_{xc} .

$$\begin{aligned} \lim_{q \rightarrow 0} \epsilon_M(\mathbf{q}, \omega) &= 1 - \frac{4\pi e^2 \bar{n}_0}{m\omega^2} - \frac{e^2}{m^2 \omega^4} \sum_{\mathbf{G} \neq \mathbf{0}} |V_0(\mathbf{G})|^2 G^2 (\hat{\mathbf{q}} \cdot \mathbf{G})^2 \\ &\quad \times \left[\frac{1}{\epsilon^{hL}(G, \omega)} - \frac{1}{\epsilon^{hL}(G, 0)} \right], \end{aligned} \quad (18)$$

where V_0 is the bare crystalline potential and $\epsilon^{hL}(q, \omega)$ is the longitudinal dielectric function of the homogeneous electron liquid. Equation (18) is in agreement with the Hopfield's formula for optical conductivity [21], and reduces to the corresponding results of Refs. [7,18] in the random phase approximation [$f_{xc,L}^h(G, \omega) = 0$].

Equations (15)–(17) are the main result of this Letter. In the inhomogeneous case they replace the grossly inaccurate LDA formula [2,22–24] which does not contain the singularity in q . Identifying the $(\mathbf{0}, \mathbf{0})$ element of the microscopic matrix of the xc kernel in Eq. (17) as the averaged f_{xc} , we see that f_{xc} diverges for $q \rightarrow 0$ as described by Eq. (3), wherein $\alpha(\omega)$ is given by [25]

$$\alpha(\omega) = \sum_{\mathbf{G} \neq \mathbf{0}} \frac{(\mathbf{G} \cdot \hat{\mathbf{q}})^2}{e^2 \bar{n}_0^2} [f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0)] n_0(\mathbf{G})^2. \quad (19)$$

We notice that $\alpha(\omega) = 0$ in the uniform limit and $\alpha(0) = 0$ up to second order in $n_0(\mathbf{G} \neq \mathbf{0})$. This shows that the q^{-2} singularity is absent at zero frequency in systems that are perturbatively connected to the homogeneous electron liquid, i.e., metals [26].

In order to calculate $\alpha(\omega)$ from Eq. (19) we need the Fourier amplitudes of the ground-state electron density and the wave vector and frequency-dependent f_{xc}^{hL} of the homogeneous EG, evaluated at reciprocal lattice vectors. The first ingredient is straightforwardly obtained from standard electronic structure calculations. Unfortunately, the same cannot be said of the second ingredient $f_{xc}^{hL}(q, \omega)$: A reliable q - and ω -dependent xc kernel of the homogeneous EG which reproduces, at small q , what is presently believed to be the qualitatively correct form of the frequency dependence is not known to us. In spite of these difficulties, it must be emphasized that the calculation of $f_{xc}^{hL}(q, \omega)$ is still a much simpler problem than the calculation of the dynamical xc kernel of the nonuniform system. Thus, our Eq. (19) does not simply express an unknown quantity in terms of another unknown quantity, but actually opens the way to systematic calculations of α based on the many-body theory of the homogeneous EG. Further, Eqs. (15)–(17) for f_{xc} offer a promising alternative to the widespread practice of treating the dynamical xc effects in the LDA.

In Fig. 2, we plot $\alpha(\omega)$ from Eq. (19) vs frequency for crystalline silicon. The Fourier coefficients of the electron density were calculated with the code FHI98MD [27], and we approximated $f_{xc}^{hL}(q, \omega) \simeq f_{xc}^{hL}(0, \omega)$, taking the latter from Ref. [24]. In the range 0–22 eV, the real part of $\alpha(\omega)$ is negative, changing sign for positive above 22 eV. It reaches its minimum of $\alpha \approx -0.1$ at $\omega \approx 14$ eV. In the range 3–5 eV of the main absorption in silicon, $\text{Re } \alpha$

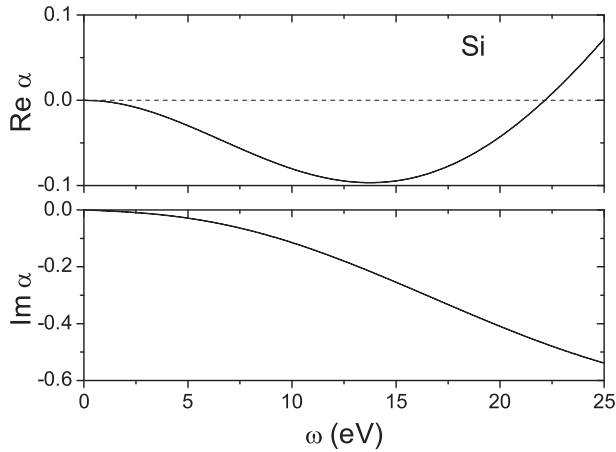


FIG. 2. The frequency dependence of the real (upper panel) and imaginary (lower panel) parts of the α coefficient in Eq. (3) for silicon calculated by Eq. (19).

changes from -0.01 to -0.03 , which is an order of magnitude smaller than the empirical value of $\alpha \approx -0.2$ found as the best fit to the experimental spectrum in Ref. [8]. This large difference may simply indicate that the nearly free electron model, while being adequate for simple metals and even for semiconductors in the high-frequency regime [18], is not sufficiently accurate for semiconductors at frequency lower than or comparable to the band gap. Another probable source of discrepancy is that our approach is a pure TDDFT, whereas the value of $\alpha \approx -0.2$ was obtained in Refs. [8,9] with the use of TDDFT together with the self-energies incorporated in the Green's function via the *GW* approximation.

In conclusion, we wish to comment on the relation between the present exact results and the approximate nonlocal f_{xc} that can be derived from the Vignale-Kohn (VK) local density approximation to TDCDFT [15,17,28]. The VK approximation is applicable in principle to strongly inhomogeneous systems (e.g., insulators), provided the density is slowly varying on the scale of the interparticle distance and $\omega \gg \max(qv_F, Gv_F)$ where v_F is the local Fermi velocity. In contrast, our Eq. (17) is only valid when the inhomogeneity is weak. When the inhomogeneity is both weak and slowly varying and $\omega \gg \max(qv_F, Gv_F)$, then our formula (17) is indeed equivalent to the VK approximation as it should.

A clear advantage of our formula is that it is based on controlled approximations. We believe that this formula will be useful in the study of the dynamical response of metals at all frequencies, and of insulators at not too low frequencies, provided the nonuniformity of the valence electron density is small.

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