Exact dynamical exchange-correlation kernel of a weakly inhomogeneous electron gas

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The dynamical exchange-correlation kernel \( f_{xc} \) of a non-uniform 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 \( \alpha \) is a frequency-dependent coefficient. We show that in the limit of weak non-uniformity the coefficient \( \alpha \) 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 potential \( \delta V_{xc} \) of the latter. With this definition, the density-response function \( \chi \) can be represented in operator notation as [2]

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

where \( \chi_{KS} \) is the Kohn-Sham (KS) density-response function of independent electrons, \( C = e^2/|r - r'| \) is the Coulomb interaction, and \( e \) is the absolute value of the electron charge. While the density-response function of non-interacting electrons \( \chi_{KS} \) can be straightforwardly calculated in many cases of interest (e.g., for homogeneous electron gases in three and two dimensions it is given by the analytical Lindhard’s [2] and Stern’s [4] formulas, respectively), the construction of \( f_{xc} \), whose role is to account for dynamical many-body correlations, is not straightforward.

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

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

where \( 4\pi e^2/q^2 \) is the Fourier transform of the Coulomb interaction. On the one hand, the excitonic enhancement of \( \chi \) 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 \( f_{xc}(q, q, \omega) \) that remained finite at \( q = 0 \) would give no contribution in the long-wave limit \( q \to 0 \). This simple observation shows that in order to include the exciton, \( f_{xc}(q, q, \omega) \) must be divergent in the long-wave limit at least as strongly as the Coulomb term. And indeed, when the \( q^{-2} \) divergence has been introduced empirically in papers dealing with the optical absorption spectrum of semiconductors [6, 7, 8], it has yielded a good TDDFT description of the excitonic effect.

Clearly it would be highly desirable to have a first-principle theory of the small-\( q \) behavior of the xc kernel, rather than relying on empirical parametrizations. In this Letter we take a step in this direction. We first show that the asymptotic relation

\[
\lim_{q \to 0} f_{xc}(q, q, \omega) = \frac{e^2\alpha(\omega)}{q^2} \tag{3}
\]

(where we introduce the \( e^2 \) so that \( \alpha \) is dimensionless) is a rigorous consequence of exact sum rules for the current density response function. Then, in the limit of weak non-uniformity we obtain a simple and exact expression for \( \alpha(\omega) \) in terms of the ground-state density and the dynamical \( xc \) kernel of a homogeneous electron gas at the average density [20].

We start by noting that the local density approximation (LDA) to \( f_{xc} \) is unable to produce the divergence. Indeed, within LDA [2]

\[
f_{xc}(r, r', \omega) = f^h_{xc}(r, \omega) \delta(r - r'), \tag{4}
\]

where \( f^h_{xc}(n, \omega) \) is the long-wave limit of the xc kernel of the homogeneous electron gas of density \( n \). The latter is known [2, 3, 10, 11] to be finite, no divergence arising, therefore, in the Fourier transform of Eq. (4).
To obtain an accurate non-local $f_{xc}$, we resort to the recently proposed general method \[12\] derived from the time-dependent current-density functional theory (TD-CDFT) \[13\]. This method is based on the exact relation that holds between the scalar density-response function $\chi$ (density response to a scalar potential) and the tensor current-density-response function $\hat{\chi}$ (current-density response to a vector potential):

$$\chi(\mathbf{q}, \mathbf{q}', \omega) = \frac{c}{e\omega^2} \mathbf{q} \cdot \tilde{\chi}(\mathbf{q}, \mathbf{q}', \omega) \cdot \mathbf{q}' , \quad (5)$$

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

$$\chi^{-1}(\mathbf{q}, \mathbf{q}', \omega) = \chi_{KS}^{-1}(\mathbf{q}, \mathbf{q}', \omega) - f_{xc}(\mathbf{q}, \mathbf{q}', \omega) - \frac{4\pi e^2}{q^2} \delta_{qq'} , \quad (6)$$

and

$$\hat{\chi}^{-1}(\mathbf{q}, \mathbf{q}', \omega) = \hat{\chi}_{KS}^{-1}(\mathbf{q}, \mathbf{q}', \omega) - \hat{f}_{xc}(\mathbf{q}, \mathbf{q}', \omega) - \frac{4\pi e c}{\omega^2} \bar{L}_{q}^{h} \delta_{qq'} , \quad (7)$$

where $\bar{L}_{q,ij} \equiv q_{q,j}/q^2$, $i$ and $j$ are cartesian indices.

Equations \[5,7\] 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. \[14\]. Specializing to the case of a periodic systems, the two most important sum rules for our purposes are

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

and

$$\sum_{\mathbf{G}'} \hat{f}_{xc,ij}(\mathbf{G}, \mathbf{G}', \omega) n_0(\mathbf{G}') = \frac{c}{e\omega^2} G_{i} G_{j} V_{xc}(\mathbf{G})$$

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

Let us further restrict our attention to the case of a weakly inhomogeneous system: $|n_0(\mathbf{G})| \ll n_0(0) \equiv \bar{n}_0$, and $|V_{KS}(\mathbf{G})| \ll \hbar^2 G^2/2m$ for $\mathbf{G} \neq 0$. Then it is easily shown that the homogenous electron gas approximation for the $(\mathbf{G} \neq 0, \mathbf{G}' \neq 0)$ components completely determines the $(0, \mathbf{G} \neq 0)$ and $(\mathbf{G} \neq 0, 0)$ components to first order in $n_0(\mathbf{G} \neq 0)$, which in turn completely determines the $(0, 0)$ component to second order in $n_0(\mathbf{G} \neq 0)$. Thus, for $\hat{\chi}_{KS}$ we obtain

$$\hat{\chi}_{KS,ij}(\mathbf{G} \neq 0, \mathbf{G}' \neq 0, \omega) = \left[ \frac{e\omega^2}{cG^2} L_{G,ij} \chi_{KS}^{hL}(G, \omega) + T_{G,ij} \chi_{KS}^{hT}(G, \omega) \right] \delta_{GG'} ,$$
$$\hat{\chi}_{KS,ij}(\mathbf{G} \neq 0, 0, \omega) = \hat{\chi}_{KS,ij}(0, -G, \omega) = \frac{e}{mc} \left[ n_0(\mathbf{G}) \delta_{ij} - L_{G,ij} \chi_{KS}^{hL}(G, \omega) V_{KS}(\mathbf{G}) \right] ,$$
$$\hat{\chi}_{KS,ij}(0, 0, \omega) = \frac{e\bar{n}_0}{mc} \delta_{ij} + \frac{e}{m^2 \omega^2} \sum_{\mathbf{G} \neq 0} G^2 L_{G,ij} V_{KS}(\mathbf{G})^2 \left[ \chi_{KS}^{hL}(G, \omega) - \chi_{KS}^{hL}(G, 0) \right] . \quad (10)$$

to the zero-th, first, and second order in $V_{KS}(\mathbf{G})$, respectively. Here $\chi_{KS}^{hL}$ and $\chi_{KS}^{hT}$ are, respectively, the longitudinal and transverse KS density-response functions of the homogeneous electron gas of density $\bar{n}_0$, and $T_{G,ij} = \delta_{ij} - L_{G,ij}$. Similarly, for $\hat{f}_{xc}$ we have

$$\hat{f}_{xc,ij}(\mathbf{G} \neq 0, \mathbf{G}' \neq 0, \omega) = \frac{c}{e\omega^2} G^2 \left[ f_{xc}^{hL}(G, \omega) L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij} \right] \delta_{GG'} ,$$
$$\hat{f}_{xc,ij}(\mathbf{G} \neq 0, 0, \omega) = \hat{f}_{xc,ij}(0, -G, \omega) = -\frac{cG^2}{e\omega^2 n_0(\mathbf{G})} \left\{ |f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0)| L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij} \right\} ,$$
$$\hat{f}_{xc,ij}(0, 0, \omega) = \frac{c}{e\omega^2 \bar{n}_0} \sum_{\mathbf{G} \neq 0} G^2 n_0(\mathbf{G})^2 \left\{ |f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0)| L_{G,ij} + f_{xc}^{hT}(G, \omega) T_{G,ij} \right\} , \quad (11)$$

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

The following steps, which involve repeated inversions of infinite matrices, rely on the mathematical fact that to find the $(0, 0)$, $(0, \mathbf{G} \neq 0)/(\mathbf{G} \neq 0, 0)$, and $(\mathbf{G} \neq 0, \mathbf{G}' \neq 0)$
The complete procedure is schematically illustrated in Fig. 1. Starting from Eqs. (10) and (11) for $\chi_{KS}$ and $f_{xc}$, we (i) invert Eqs. (10) to get $\chi_{KS}$; (ii) combine $\chi_{KS}$ and $f_{xc}$ to get $\chi$ by virtue of Eq. (7); (iii) invert $\chi^{-1}$ to get $\chi$; (iv) use Eq. (5) and its KS analogue to find the scalar response function $\chi$ from $\chi$ and $\chi_{KS}$ from $\chi_{KS}$; (v) invert $\chi$ and $\chi_{KS}$ to get $\chi^{-1}$ and $\chi_{KS}^{-1}$; and, (vi) apply Eq. (7) to find $f_{xc}$. The final result of this procedure is

\begin{equation}
\lim_{q \to 0} f_{xc}(G \neq 0, G' \neq 0, \omega) = f_{xc,L}(G, \omega) \delta_{G G'},
\end{equation}

\begin{equation}
\lim_{q \to 0} f_{xc}(G \neq 0, q, \omega) = f_{xc}(-q, -G, \omega) = \frac{(G \cdot \hat{q})}{\bar{n}_0 q} \left[ f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0) \right] n_0(G),
\end{equation}

\begin{equation}
\lim_{q \to 0} f_{xc}(q, q, \omega) = \frac{1}{\bar{n}_0 q^2} \sum_{G \neq 0} (G \cdot \hat{q})^2 \left[ f_{xc}^{hL}(G, \omega) - f_{xc}^{hL}(G, 0) \right] |n_0(G)|^2,
\end{equation}

where $\hat{q}$ is the unit vector parallel to $q$. It should be noted at this point that the above expression for the scalar kernel $f_{xc}(q, q, \omega)$ differs from what one would get by simply taking the longitudinal component of $f_{xc,i,j}(q, q, \omega)$, i.e. $f_{xc}(q, q, \omega) \neq \frac{\delta_{ij}}{q^2} \sum_{i,j} \hat{q}_i \hat{f}_{xc,i,j}(q, q, \omega) \hat{q}_j$. 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 ($\textbf{A}_{xc}$) 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 $\textbf{A}_{xc}$ [15] should be re-examined in the light of this result.

From the result of the step (iv) for $\chi$ and making use of the relation

\begin{equation}
\frac{1}{\epsilon_M(\omega)} = 1 + \lim_{q \to 0} \frac{4\pi e^2}{q^2} \chi(q, q, \omega),
\end{equation}

we obtain a formula for the macroscopic dielectric function of a crystal

\begin{equation}
\epsilon_M(\omega) = 1 - \frac{4\pi e^2 \bar{n}_0}{\hbar^2 \omega^2} - \frac{e^2}{\hbar^2 \omega^4} \sum_{G \neq 0} |V_0(G)|^2 G^2 (\hat{q} \cdot G)^2 \left[ \frac{1}{\epsilon^{hL}(G, \omega)} - \frac{1}{\epsilon^{hL}(G, 0)} \right].
\end{equation}

0) 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 accuracy, and then the inversion can be performed in a closed form [15].
and the wave vector and frequency-dependent $f^{xc}_{q, \omega}$ of the homogeneous electron gas, 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 $f^{xc}_{q, \omega}(q, \omega)$, for which we do not have reliable expressions. The best that can be done, at this time, is either to disregard the wave vector dependence, or to make use of the interpolation formula proposed in Ref. [18], which however fails to reproduce, at small $q$, what is presently believed to be the qualitatively correct form of the frequency dependence. In spite of these difficulties, it must be emphasized that the calculation of $f^{xc}_{q, \omega}(q, \omega)$ is still a much simpler problem than the calculation of the dynamical $xc$ kernel of the non-uniform system. Thus, our Eq. (18) does not simply express an unknown quantity in terms of another unknown quantity, but actually opens the way to systematic calculations of $\alpha$ based on the many-body theory of the homogeneous electron gas. Further, Eqs. (12)-(14) for $f^{xc}$ offer a promising alternative to the widespread practice of treating the dynamical exchange and correlations effects in the LDA.

In Fig. 2 we plot $\alpha(\omega)$ from Eq. (15) vs frequency for crystalline silicon. The Fourier coefficients of the electron density were calculated with the code FHI98MD [19], and we approximated $f^{xc}_{q, \omega}(q, \omega) \simeq f^{hL}_{xc}(0, \omega)$, taking the latter from Ref. [11]. 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, Re $\alpha$ 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. [6]. 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 [15], is not sufficiently accurate for semiconductors at frequency lower than or comparable to the band gap (see also footnote [21]). 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] and [7] with the use of self-energies incorporated in the Green’s function via the GW approximation.

In conclusion, within the nearly free electron approximation, we have constructed the otherwise exact exchange-correlation kernel for time-dependent density-functional theory. This kernel is nonlocal in space, exhibiting the $q^{-2}$ singularity in the reciprocal space. The strength of this singularity, which is frequency-dependent, has been directly related to the magnitude of the non-uniformity of the density of valence electrons, and this singularity disappears in the limiting case of the homogeneous electron liquid. We are proposing an improvement over the conventional LDA scheme of including the dynamical exchange and correlation effects into ab initio calculations of the linear response of crystalline solids which consistently accounts for the long-wave divergence in the exchange-correlation kernel.

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The existence of a divergence in the off-diagonal components $f_{xc}(q, k + q, \omega)$ for $q \to 0$ and $k$ finite was first pointed out in Ref. [13].

This is not to say that $f_{xc}(q, q, 0)$ is always free of the $q^{-2}$ singularity, but it means that such a singularity, if present, cannot be reached by a perturbative expansion about the homogeneous ground-state. Indeed, there is evidence that the $f_{xc}(q, q, 0)$ of band insulators has a $q^{-2}$ singularity, which is missed in the present approach.