

Local Density-Functional Theory of Frequency-Dependent Linear Response

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The linear density response of inhomogeneous electronic systems is discussed from a density-functional point of view. We derive a local-density approximation for the frequency-dependent exchange-correlation potential, which is compared with the "adiabatic" expression used in former work.

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The classical density-functional formalism of Hohenberg and Kohn¹ and of Kohn and Sham² is a ground-state theory. Although a time-dependent extension of the Thomas-Fermi model was derived long ago,³ the time-dependent counterpart to the Kohn-Sham (KS) equations was lacking for a long time. In 1980, Zangwill and Soven⁴ published an interesting paper in which they calculated atomic photoabsorption cross sections using a self-consistent KS-type method. Although they used a simple, frequency-independent exchange-correlation potential, the calculated photoabsorption cross sections turned out to give a rather good description of experimental data. A mathematical foundation of time-dependent density-functional theory has been discussed in a recent paper by Runge and Gross.⁵ The aim of the present note is to provide a local-density approximation for the frequency-de-

pendent exchange-correlation potential within linear-response theory.

We consider an unperturbed inhomogeneous electronic system with density $n_0(\mathbf{r})$ in the ground state (assumed nondegenerate) of the static external potential $v_0(\mathbf{r})$. Now consider a small perturbing potential $v_1(\mathbf{r}, t)$ and the corresponding density response $n_1(\mathbf{r}, t)$. The associated Fourier components $v_1(\mathbf{r}, \omega)$ and $n_1(\mathbf{r}, \omega)$ are then related by the equation

$$n_1(\mathbf{r}, \omega) = \int d^3r' \chi(\mathbf{r}, \mathbf{r}'; \omega) v_1(\mathbf{r}', \omega), \quad (1)$$

where $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ denotes the exact density-density response function.

We make the *assumption* that the density $n_0(\mathbf{r}) + n_1(\mathbf{r}, t)$ is "noninteracting v -representable," i.e., can be reproduced by a system of noninteracting electrons in an appropriate single-particle potential $v_0^{\text{eff}}(\mathbf{r}) + v_1^{\text{eff}}(\mathbf{r}, t)$. We can then write

$$n_1(\mathbf{r}, \omega) = \int d^3r' \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega) v_1^{\text{eff}}(\mathbf{r}', \omega), \quad (2)$$

where $\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega)$ is the density-density response function of the noninteracting (Kohn-Sham) ground state corresponding to $v_0^{\text{eff}}(\mathbf{r})$. It is given by (atomic units are used throughout)

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i(\mathbf{r})^* \phi_j(\mathbf{r}) \phi_j(\mathbf{r}')^* \phi_i(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\delta}, \quad (3)$$

where the $\phi_i(\mathbf{r})$ and ϵ_i are the KS eigenfunctions and eigenvalues, and the f_i ($= 1$ or 0) are occupation numbers.

Next we define the exchange-correlation (xc) part of v_1^{eff} by the equation

$$v_1^{\text{eff}}(\mathbf{r}, \omega) = v_1(\mathbf{r}, \omega) + \int \frac{n_1(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} d^3r' + v_{1,\text{xc}}(\mathbf{r}, \omega). \quad (4)$$

(Omission of $v_{1,\text{xc}}$ yields the time-dependent Hartree response.) In the spirit of density-functional theory we seek an expression of $v_{1,\text{xc}}(\mathbf{r}, \omega)$ as a linear functional of $n_1(\mathbf{r}, \omega)$,

$$v_{1,\text{xc}}(\mathbf{r}, \omega) = \int d^3r' f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) n_1(\mathbf{r}', \omega), \quad (5)$$

where f_{xc} depends on the unperturbed ground-state density, $n_0(\mathbf{r})$. Then Eqs. (2)–(5) represent a scheme for the self-consistent determination of the density response $n_1(\mathbf{r}, \omega)$. For the most general situation, we do not know whether f_{xc} exists, let alone how to construct it. However, a formal representation of f_{xc} can be derived from the definitions (1), (2), (4), and (5) as

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}'; \omega) = \chi_{\text{KS}}^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega) - 1/|\mathbf{r} - \mathbf{r}'|, \quad (6)$$

provided that the inverse response functions χ^{-1} and χ_{KS}^{-1} exist. (A mathematical discussion of the invertibility of the mapping of time-dependent single-particle potentials on time-dependent densities is given in Ref. 5.)

For initially *homogeneous* systems [$n_0(\mathbf{r}) = \text{const}$], the function f_{xc} is explicitly known: In that case, Eqs. (1)

and (2) read

$$n_1(\mathbf{r}, \omega) = \int d^3r' \chi^h(|\mathbf{r} - \mathbf{r}'|; \omega) v_1(\mathbf{r}', \omega) \quad (7)$$

and

$$n_1(\mathbf{r}, \omega) = \int d^3r' \chi_0(|\mathbf{r} - \mathbf{r}'|; \omega) v_1^{\text{eff}}(\mathbf{r}', \omega), \quad (8)$$

where χ^h denotes the density-density response function of the homogeneous electron gas and χ_0 is the Lindhard function. Fourier transformation to q space gives

$$f_{xc}^h(q, \omega) = 1/\chi_0(q, \omega) - 1/\chi^h(q, \omega) - 4\pi/q^2. \quad (9)$$

We may note that f_{xc}^h is related to the so-called local-field correction,⁶ $G(q, \omega)$, by the relation

$$f_{xc}^h(q, \omega) = -(4\pi/q^2) G(q, \omega). \quad (10)$$

In order to derive an approximation for $v_{1,xc}$ for inhomogeneous systems, we make a *double* local-density approximation (LDA): We assume that $n_0(\mathbf{r})$ is sufficiently slowly varying that f_{xc} can be replaced by f_{xc}^h , evaluated for the local density⁷ $n_0(\mathbf{r})$; and, secondly, that $n_1(\mathbf{r}', \omega)$ is sufficiently slowly varying that, in Eq. (5), it can be replaced by $n_1(\mathbf{r}, \omega)$.⁸ This results in the replacement of

$$f_{xc}(\mathbf{r}, \mathbf{r}'; \omega) \rightarrow \delta(\mathbf{r} - \mathbf{r}') f_{xc}^h(q=0, \omega; n_0(\mathbf{r})), \quad (11)$$

so that

$$v_{1,xc}(\mathbf{r}, \omega) \approx f_{xc}^h(q=0, \omega; n_0(\mathbf{r})) n_1(\mathbf{r}, \omega). \quad (12)$$

$$\begin{aligned} \text{Re} f_{xc}^h(q, \omega) - f_{xc}^h(q, \infty) &= P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\text{Im} f_{xc}^h(q, \omega')}{\omega' - \omega}, \\ \text{Im} f_{xc}^h(q, \omega) &= -P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\text{Re} f_{xc}^h(q, \omega') - f_{xc}^h(q, \infty)}{\omega' - \omega}. \end{aligned}$$

(vi) $\text{Im} f_{xc}^h(q=0, \omega \rightarrow \infty) = -c/\omega^{3/2}$. A second-order perturbation expansion¹¹ of the irreducible polarization propagator yields

$$c = 23\pi/15. \quad (13)$$

This perturbation result becomes exact at high densities; we conjecture that it is a good approximation over a wide density range.

(vii) By use of (vi) and the Kramers-Kronig relation (v), the real part can be shown to behave like $\text{Re} f_{xc}^h(q=0, \omega \rightarrow \infty) = f_{\infty} + c/\omega^{3/2}$.

The LDA (12) requires an approximation for only the long-wavelength limit of the function $f_{xc}^h(q, \omega)$. A parametrization satisfying all the exact features listed above is provided by the following Padé-type expression:

$$\text{Im} f_{xc}^h(q=0, \omega; n) = \frac{a(n) \cdot \omega}{[1 + b(n)\omega^2]^{5/4}}, \quad (14)$$

The LDA has proved very useful for time-independent problems. Its value for response theory remains to be tested.

By use of well-known features of the electron gas response functions $\chi^h(q, \omega)$ or $G(q, \omega)$, the exact function f_{xc}^h is easily shown to have the following properties:

$$(i) \lim_{q \rightarrow 0} f_{xc}^h(q, 0; n) = \frac{d^2}{dn^2} [n\epsilon_{xc}(n)] \equiv f_0(n),$$

with $\epsilon_{xc}(n)$ the xc energy per particle of a homogeneous electron gas with density n . This equation is a consequence of the compressibility sum rule.⁶

$$(ii) \lim_{q \rightarrow 0} f_{xc}^h(q, \infty; n) = -\frac{4}{5} n^{2/3} \frac{d}{dn} \left| \frac{\epsilon_{xc}(n)}{n^{2/3}} \right| = f_{\infty}(n).$$

This result follows from the third frequency moment sum rule.⁶

(iii) According to the best estimates of $\epsilon_{xc}(n)$,^{9,10} the relation $f_0(n) < f_{\infty}(n) < 0$ holds for all densities.

(iv) $f_{xc}^h(q, \omega)$ is a complex-valued function whose real (imaginary) part is an even (odd) function of frequency.

(v) $f_{xc}^h(q, \omega)$ is an analytic function of ω in the upper half of the complex ω plane which, for each q , approaches a *real* high-frequency limit $f_{xc}^h(q, \infty)$.⁶ Therefore, the following Kramers-Kronig relations are satisfied:

with

$$b(n) = (\gamma/c)^{4/3} [f_{\infty}(n) - f_0(n)]^{4/3}, \quad (15)$$

$$a(n) = -(\gamma/c)^{5/3} [f_{\infty}(n) - f_0(n)]^{5/3}, \quad (16)$$

$$\gamma = [\Gamma \frac{1}{4}]^2 / (32\pi)^{1/2}, \quad (17)$$

and c given by (13). The real part corresponding to (14) is calculated by use of the Kramers-Kronig relation (v). Figures 1 and 2 show the real and imaginary parts of $f_{xc}^h(q=0, \omega)$ for $r_s=2$ and $r_s=4$, where r_s is the Wigner-Seitz radius $(4\pi/3)r_s^3=1/n$. For the correlation part of $\epsilon_{xc}(n)$ we have used the parametrization given by Vosko, Wilk, and Nusair.¹⁰

The photoabsorption cross section is directly related to the linear density response $n_1(\mathbf{r}, \omega)$ via Fermi's "golden rule."⁴ In order to calculate $n_1(\mathbf{r}, \omega)$, Zangwill and Soven applied the self-consistent scheme (2)-(5) with the LDA (12), but using the adiabatic

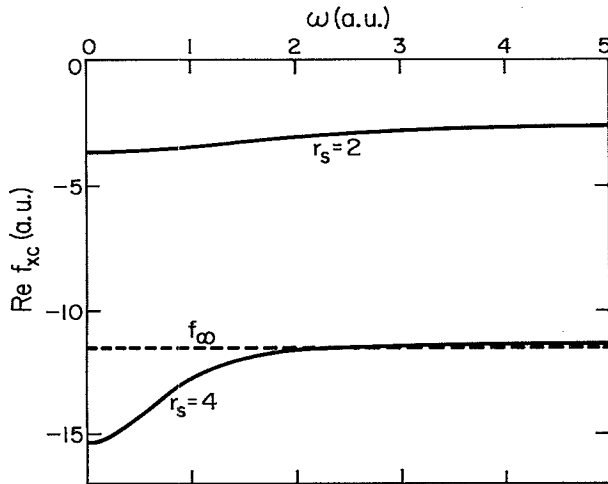


FIG. 1. Real part of the parametrization for $f_{xc}^h(q=0, \omega)$.

approximation $f_{xc}(r, r'; \omega) \rightarrow f_{xc}(r, r'; 0)$. This means that the real part of the function $f_{xc}^h(q=0, \omega)$ is replaced by its zero-frequency value f_0 for all ω , and that its imaginary part is neglected. To estimate the quality of this approximation, we first consider the fractional error of the real part, $\Delta = [f_0 - \text{Re} f_{xc}^h(q=0, \bar{\omega}; \bar{n})]/f_0$, where, for each subshell, $\bar{\omega}$ is a characteristic frequency and the total density, $\bar{n}$, is evaluated where the radial density of the subshell reaches its maximum. For the noble-gas subshells considered by Zangwill and Soven, Δ lies between 1% [for Ne(2p)] and 3% [for Xe(4d)]. On general grounds we expect the error due to neglect of $\text{Im} f_{xc}$ to be comparable. This shows that neglect of the frequency dependence of f_{xc} does not introduce significant errors in the case of these photoabsorption processes.

Finally, we remark on a connection with excited states: The *exact* frequency-dependent density response determines the positions of any discrete excited levels and absorption edges.

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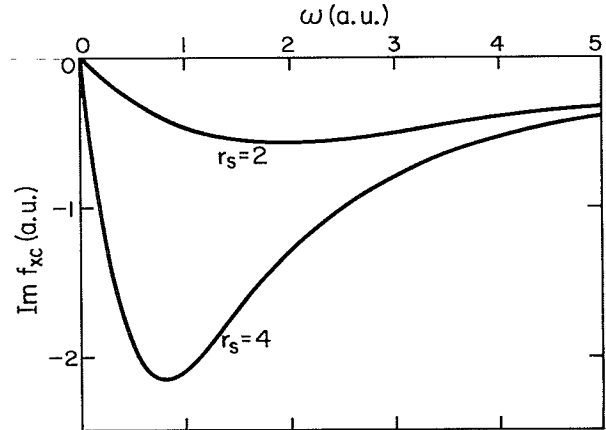


FIG. 2. Imaginary part of the parametrization for $f_{xc}^h(q=0, \omega)$.

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