Local Density-Functional Theory of Frequency-Dependent Linear Response

E. K. U. Gross and Walter Kohn

Department of Physics, University of California, Santa Barbara, California 93106
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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.

The classical density-functional formalism of Hohenberg and Kohn[1] and of Kohn and Sham[2] 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 Soven[4] 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 $n_0(r)$ in the ground state (assumed nondegenerate) of the static external potential $v_0(r)$. Now consider a small perturbing potential $v_1(r,t)$ and the corresponding density response $n_1(r,t)$. The associated Fourier components $v_1(r, \omega)$ and $n_1(r, \omega)$ are then related by the equation

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

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

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

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

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

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

where the $\phi_i(r)$ 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

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

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

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

where f_{xc} depends on the unperturbed ground-state density, $n_0(r)$. Then Eqs. (2)–(5) represent a scheme for the self-consistent determination of the density response $n_1(r, \omega)$. 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

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

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

and (2) read

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

and

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

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

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

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

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

In order to derive an approximation for $v_{1,\mathrm{xc}}$ 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 density[7] $n_0(\mathbf{r})$; 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

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

so that

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

$$\mathrm{Re}f_{\mathrm{xc}}^h(q, \omega) - f_{\mathrm{xc}}^h(q, \infty) = P \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\mathrm{Im}f_{\mathrm{xc}}^h(q, \omega')}{\omega' - \omega},$$

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

(vi) $\mathrm{Im}f_{\mathrm{xc}}^h(q = 0, \omega \rightarrow \infty) = -c/\omega^{3/2}$. A second-order perturbation expansion[11] of the irreducible polarization propagator yields

$$c = 23\pi/15. \tag{13}$$

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 $\mathrm{Re}f_{\mathrm{xc}}^h(q = 0, \omega \rightarrow \infty) = f_\infty + c/\omega^{3/2}$.

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

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

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

with $\epsilon_{\mathrm{xc}}(n)$ 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) $\lim_{q \to 0} f_{\mathrm{xc}}^h(q, \infty; n) = -\dfrac{4}{5} n^{2/3} \dfrac{d}{dn} \left| \dfrac{\epsilon_{\mathrm{xc}}(n)}{n^{2/3}} \right|$

$$\equiv f_\infty(n).$$

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

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

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

(v) $f_{\mathrm{xc}}^h(q, \omega)$ 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 $f_{\mathrm{xc}}^h(q, \infty)$.[6] Therefore, the following Kramers-Kronig relations are satisfied:

with

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

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

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

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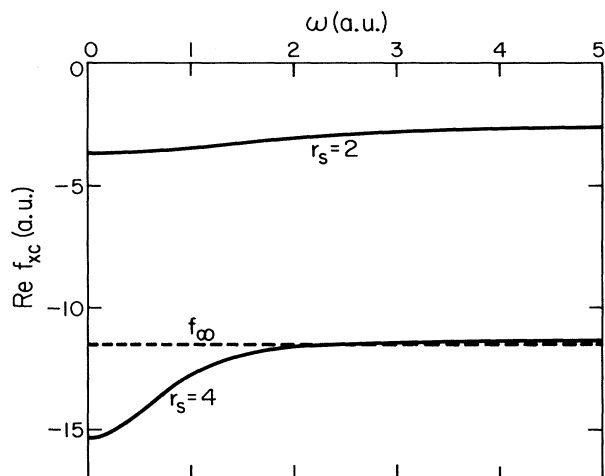
FIG. 1. Real part of the parametrization for $f_{xc}^h(q=0,\omega)$.

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

approximation $f_{xc}(\mathbf{r},\mathbf{r}';\omega) \rightarrow f_{xc}(\mathbf{r},\mathbf{r}';0)$. 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, $\Delta = [f_0 - \mathrm{Re}f_{xc}^h(q=0,\bar{\omega};\bar{n})]/f_0$, 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 $\mathrm{Im}f_{xc}$ 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.

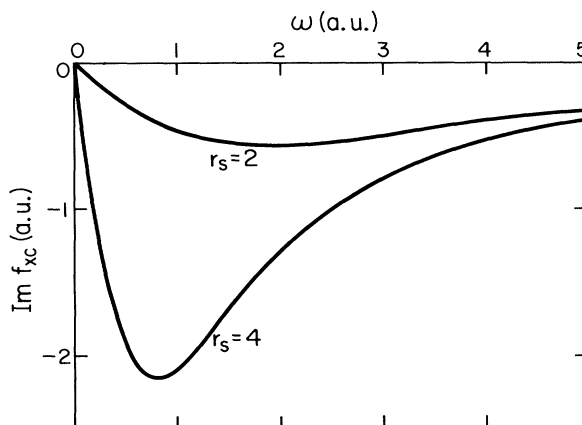This work has been supported in part by the National Science Foundation under Grant No. NSF DMR83-

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