

# Influence of the noninteracting density response function on the exchange-only kernel in time-dependent density-functional theory

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A formally exact expression for the interaction density response function  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  exists in terms of (i) its noninteracting counterpart  $\chi_0(\mathbf{r}, \mathbf{r}', \omega)$  and (ii) an exchange ( $x$ )-correlation ( $c$ ) kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ . In the absence of a first-principles theory for the  $\omega$  dependence of  $f_{xc}$ , the adiabatic approximation is most frequently made in this term, to construct a workable time-dependent density-functional theory. In the present study, a proposal is put forward to avoid the adiabatic approximation by working in the exchange-only limit in which  $f_{xc}$  is set equal to  $f_x(\mathbf{r}, \mathbf{r}', \omega)$ . We then refer to a result for the exchange energy given by Pines and Nozieres to motivate the assumption that  $f_x = f_x[\text{Im } \chi_0(\mathbf{r}, \mathbf{r}', \omega)]$ . The essential proposal here is therefore that the integral equation to be solved for the interacting density response function  $\chi$  is in the exchange-only case characterized entirely by the noninteracting response function  $\chi_0$ .

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## I. BACKGROUND AND OUTLINE

The calculation of excitation energies of molecules and clusters is an area of great current interest not only for quantum chemistry but also for molecular biophysics. This is made abundantly clear in the very recent review of Dreuw and Head-Gordon [1]. Following the lead of earlier authors [2–5], March, Rubio, and Alonso [6] (see also Ref. [7]) take the density response function  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  of the interacting electronic assembly as a starting point in a study of low-lying excitations in some light atomic ions. As set out, for example, in Ref. [7] [their Eq. (38)], the formally exact expression for  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  reads

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) = & \chi_0(\mathbf{r}, \mathbf{r}', \omega) + \int \int d\mathbf{r}'' d\mathbf{r}''' \chi(\mathbf{r}, \mathbf{r}'', \omega) \\ & \times \left( \frac{1}{|\mathbf{r}'' - \mathbf{r}'''} + f_{xc}(\mathbf{r}'', \mathbf{r}''', \omega) \right) \chi_0(\mathbf{r}''', \mathbf{r}', \omega). \end{aligned} \quad (1)$$

Setting  $f_{xc}$  equal to zero in Eq. (1) recovers the so-called random-phase approximation (RPA) to the response function. Unfortunately, given the noninteracting response function  $\chi_0$ , all the many-electron information required to determine  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  from the integral equation (1), is subsumed into the as yet unknown exchange-correlation kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ . This must therefore be one focus of any attempt to transcend existing treatments of TDDFT. Dreuw and Head-Gordon [1] stress that to date the adiabatic approximation is common in this context. Our aim in the present study is to make a start on a, of course still approximate, theory of calculating excitation energies via the poles of  $\chi(\mathbf{r}, \mathbf{r}', \omega)$  by releasing the adiabatic approximation. The price we pay for this generalization is to work here in the (time-dependent) exchange-only approximation in which the kernel  $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$  is replaced by

$f_x(\mathbf{r}, \mathbf{r}', \omega)$ . Our proposal is subsumed then into the statement, to be exemplified below, that

$$f_x(\mathbf{r}, \mathbf{r}', \omega) \equiv f_x[\text{Im } \chi_0(\mathbf{r}, \mathbf{r}', \omega)], \quad (2)$$

i.e., the frequency dependence of the exchange-only kernel  $f_x$  is, in essence, already embedded in  $\chi_0$ , which is given explicitly in the Appendix. To construct the functional of the right-hand side (RHS) of Eq. (2) is a nontrivial task, which we make a start on below.

## II. TOTAL EXCHANGE ENERGY $E_x$ IN TERMS OF THE NONINTERACTING FREQUENCY DEPENDENT RESPONSE FUNCTION $\chi_0(\mathbf{r}, \mathbf{r}', \omega)$

In the recent discussion of Howard and March [8] on the functional derivative of the noninteracting Dirac density matrix  $\gamma_0(\mathbf{r}_1, \mathbf{r}_2)$  with respect to the ground-state electron density  $\rho(\mathbf{r})$ , they refer to a result for the total exchange energy  $E_x$  of molecules and clusters given by Pines and Nozieres [9]. This result reads

$$\begin{aligned} E_x = & -\frac{1}{2} \int \frac{d\omega}{\pi} d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} [\text{Im } \chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega) \\ & + \pi \rho(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\omega)]. \end{aligned} \quad (3)$$

While TDDFT is usually discussed in terms of action functionals, we define the exchange potential in frequency space as a functional derivative of the exchange energy as given by Eq. (3),

$$v_x(\mathbf{r}, \omega) = \frac{\partial E_x}{\partial \rho(\mathbf{r}, \omega)}. \quad (4)$$

Since the exchange kernel is homogeneous in time, it can be computed by relating potentials and densities at the same frequency [10]. With the Pines and Nozieres expression for  $E_x$  we get immediately

$$\begin{aligned} f_x(\mathbf{r}, \mathbf{r}', \omega) &= \frac{\partial v_x(\mathbf{r}, \omega)}{\partial \rho(\mathbf{r}', \omega)} \\ &= -\frac{1}{2} \int \frac{d\omega'}{\pi} \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \text{Im} \frac{\partial^2 \chi_0(\mathbf{r}_1, \mathbf{r}_2, \omega')}{\partial \rho(\mathbf{r}, \omega) \partial \rho(\mathbf{r}', \omega)}, \end{aligned} \quad (5)$$

which confirms our proposition Eq. (2), that all frequency dependence of  $f_x$  is already embedded in the noninteracting susceptibility  $\chi_0$ .

To make further progress, we proceed along the lines of Shaginyan [11] and compute functional derivatives of  $\chi_0$  using the chain rule,

$$\begin{aligned} \frac{\partial \chi_0(\mathbf{r}', \mathbf{r}'', \bar{\omega})}{\partial \rho(\mathbf{r}, \omega)} &= \int \int \frac{\partial \chi_0(\mathbf{r}', \mathbf{r}'', \bar{\omega})}{\partial v_s(\mathbf{r}_1, \omega_1)} \frac{\partial v_s(\mathbf{r}_1, \omega_1)}{\partial \rho(\mathbf{r}, \omega)} d\mathbf{r}_1 d\omega_1 \\ &= \frac{1}{2\pi} \int \chi_0^{(2)}(\mathbf{r}', \mathbf{r}'', \mathbf{r}_1, \bar{\omega} - \omega, \omega) \chi_0^{-1}(\mathbf{r}, \mathbf{r}_1, \omega) d\mathbf{r}_1, \end{aligned} \quad (6)$$

where  $\chi_0 = \partial \rho / \partial v_s$  and  $\chi_0^{(2)} \sim \partial^2 \rho / \partial v_s^2$  is the quadratic response function as defined, e.g., in Ref. [12]. This result, together with Eqs. (3) and (4) constitutes an extension of the exact exchange potential obtained in Ref. [11] to the time-dependent case.

In order to compute the kernel  $f_x$ , a second functional derivative of  $\chi_0$  needs to be taken, which yields, after some algebra, the following expression:

$$\begin{aligned} \frac{\partial^2 \chi_0(\mathbf{r}', \mathbf{r}'', \bar{\omega})}{\partial \rho(\mathbf{r}, \omega) \partial \rho(\tilde{\mathbf{r}}, \omega)} &= \frac{1}{2\pi} \int \int \chi_0^{-1}(\tilde{\mathbf{r}}, \mathbf{r}_2, \omega) \chi_0^{(3)}(\mathbf{r}', \mathbf{r}'', \mathbf{r}_1, \mathbf{r}_2, \bar{\omega} \\ &\quad - 2\omega, \omega, \omega) \chi_0^{-1}(\mathbf{r}, \mathbf{r}_1, \omega) d\mathbf{r}_1 d\mathbf{r}_2 \\ &\quad - \frac{1}{(2\pi)^3} \int \int \int \int [\chi_0^{-1}(\mathbf{r}, \mathbf{r}_2, \omega) \chi_0^{(2)} \\ &\quad \times (\mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, 0, \omega) \chi_0^{-1}(\tilde{\mathbf{r}}, \mathbf{r}_4, \omega) \\ &\quad \times \chi_0^{-1}(\mathbf{r}_3, \mathbf{r}_1, \omega) \chi_0^{(2)}(\mathbf{r}', \mathbf{r}'', \mathbf{r}_1, \bar{\omega} - \omega, \omega)] \\ &\quad \times d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4. \end{aligned} \quad (7)$$

All response functions appearing in Eq. (7) are explicitly known in terms of Kohn-Sham single-particle orbitals [12] and could be used in conjunction with Eq. (5) to obtain a workable expression for the desired exchange-only kernel. Here, we are looking instead for an approximate description of  $f_x$ , in which the frequency dependence is easier to access. To this end we define the exchange energy density, say  $\epsilon_x(\mathbf{r}, \omega)$ , from Eq. (3) as

$$\begin{aligned} \epsilon_x(\mathbf{r}, \omega) &= -\frac{1}{2} \int \frac{d\mathbf{r}'}{\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|} [\text{Im} \chi_0(\mathbf{r}, \mathbf{r}', \omega) \\ &\quad + \pi \rho(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \delta(\omega)], \end{aligned} \quad (8)$$

which is evidently such that

$$E_x = \int \int \epsilon_x(\mathbf{r}, \omega) d\mathbf{r} d\omega. \quad (9)$$

We next invoke a generalization of the approximate exchange-potential,  $v_x^{\text{Sl}}$ , going back to the very early work of Slater [13], who wrote, in time-independent theory,

$$v_x^{\text{Sl}}(\mathbf{r}) = \frac{2\epsilon_x(\mathbf{r})}{\rho(\mathbf{r})}. \quad (10)$$

Combining the ground-state result (10) with the asymptotic result of one of us [14] that, as  $r$  becomes sufficiently large,

$$\lim_{r \rightarrow \infty} \epsilon_x(\mathbf{r}) = -\frac{e^2}{2r} \rho(\mathbf{r}), \quad (11)$$

we obtain the correct limiting term  $-e^2/r$  from Eqs. (10) and (11). This encourages us to postulate the frequency-dependent generalization of Eq. (10) as

$$v_x^{\text{Sl}}(\mathbf{r}, \omega) = \frac{2\epsilon_x(\mathbf{r}, \omega)}{\rho(\mathbf{r}, \omega)}, \quad (12)$$

where  $\epsilon_x(\mathbf{r}, \omega)$  is precisely defined in Eq. (8). This then leads to the following Slater approximation to the exchange-only kernel,

$$f_x(\mathbf{r}, \mathbf{r}', \omega) = \frac{2}{\rho(\mathbf{r}, \omega)} \frac{\partial \epsilon_x(\mathbf{r}, \omega)}{\partial \rho(\mathbf{r}', \omega)} - \frac{2\epsilon_x(\mathbf{r}, \omega)}{\rho(\mathbf{r}, \omega)^2} \delta(\mathbf{r} - \mathbf{r}'). \quad (13)$$

Here, the first term on the RHS of Eq. (13) has been evaluated above. The second term is local in space and its frequency dependence is dominated by the noninteracting density response function  $\chi_0$ , which has poles at the single-particle KS energy differences. This is in line with the work of Maitra *et al.* [15,16], who showed that the exact nonadiabatic exchange-correlation kernel  $f_{xc}$  needs to exhibit poles in frequency space to allow for a correct description of charge-transfer states and those of double excitation character. It therefore seems worthwhile to analyze the frequency dependence of Eq. (13) in more detail, which is however outside the scope of this paper and is left for future work.

*Note added.* Recently, we became aware of related earlier work by Görling [10] as well as Hirata *et al.* [17] on the exchange-only problem considered here. While aspects of

the treatment bear some similarity, we use as a central equation the Pines-Nozieres result, showing the crucial importance of  $\text{Im } \chi_0(\mathbf{r}, \mathbf{r}', \omega)$  in characterizing the exchange energy.

### APPENDIX

In contrast to the interacting density response function  $\chi$ , the independent-particle counterpart  $\chi_0$  is determined by the usual one-body wave functions  $\psi_i(\mathbf{r})$  of DFT plus the corresponding energies  $\epsilon_i$ . The result is

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{ij} (f_i - f_j) \frac{\psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\delta}, \quad (\text{A1})$$

the quantities  $f_i$  and  $f_j$  being Fermi occupation factors. The summations appearing in Eq. (A1) run over all one-body orbitals, including continuum states. The quantity  $\text{Im } \chi_0(\mathbf{r}, \mathbf{r}', \omega)$  entering the ansatz (2) which is central to the present study can be immediately determined in its frequency dependence from Eq. (A1). Thus at the exchange-only level of the present paper, the adiabatic approximation common to many current treatments is completely bypassed.

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