Many-body Diagrammatic Expansion for the Exchange-Correlation Kernel in Time Dependent Density Functional Theory

I. V. Tokatly,* R. Stübner, and O. Pankratov

Lehrstuhl für Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, 91058 Erlangen, Germany

(Dated: August 1, 2001)

A diagrammatic expansion for the dynamic exchange-correlation kernel \( f_{xc} \) of time dependent density functional theory is formulated. It is shown that \( f_{xc} \) has no singularities at Kohn-Sham transition energies in every order of the perturbation theory. However, it may diverge with the system size in extended systems. This signifies that any approximate perturbative substitute for \( f_{xc} \) requires a consistent perturbative treatment of the response function to avoid uncontrollable errors in the many-body corrections to excitations energies.

PACS numbers: 71.15.Mb, 31.15.Ew, 31.50.Df, 71.10.-w

The central problem of time dependent density functional theory (TDDFT)\(^1\) is to find an adequate approximation for the dynamic exchange-correlation (xc) potential \( v_{xc} \). In contrast to static DFT, where the local density approximation (LDA) has been extremely successful, no universal recipe for a dynamic \( v_{xc} \) has been found, and it remains unclear if such a recipe exists. The adiabatic LDA (ALDA), which is most popular in practical TDDFT calculations, is valid, by its nature, only in a quasistatic limit. This may suffice for a real-time dynamics of melting\(^2\) or desorption\(^3\), but is hardly relevant for electronic excitations in insulators, where ALDA predicts the same erroneous band gaps as the static LDA.\(^4\) The improvement in excitation spectra of atoms and molecules which has been obtained in TDDFT using ALDA or the optimized effective potential (OEP) approximation is not indicative in small systems the correction to the Kohn-Sham excitation energies is very small and approximations for \( f_{xc} \) play a secondary role in comparison to the accuracy of the static xc potential.\(^5,6\)

In general, electron-hole (e-h) excitation energies can be found as the poles of the density response function \( \chi(\mathbf{r},\mathbf{r}',\omega) \). TDDFT relates the exact \( \chi(\omega) \) to the susceptibility of non-interacting Kohn-Sham (KS) particles \( \chi_S(\omega) \) via the equation

\[
\chi(\omega) = \chi_S(\omega) + \chi_S(\omega)\tilde{V}(\omega)\chi(\omega) \quad (1)
\]

with \( \tilde{V}(\omega) = V_C + f_{xc}(\omega) \), where \( V_C \) is the Coulomb potential and the xc kernel \( f_{xc}(\mathbf{r},\mathbf{r}',\omega) = \delta v_{xc}(\mathbf{r},\mathbf{t})/\delta n(\mathbf{r}',\mathbf{t}') \) describes xc effects at the linear response level.\(^7\) Equation (1), which simultaneously accounts for the self-energy and the electron-hole correlations, may seem like an attractive alternative to the very laborious two-step approach involving a GW calculation for one-particle states with a subsequent solution of the Bethe-Salpeter (BS) equation for an e-h pair. Unfortunately, no approximation for \( f_{xc} \) is available which would be as efficient as LDA in the static DFT. In ALDA a time-dependent density is simply inserted in the LDA xc potential, and \( f_{xc} \) becomes an instantaneous point interaction, which is qualitatively different from a nonlocal and retarded xc kernel in systems with an energy gap. In fact, it is \textit{a priori} not clear whether \( f_{xc} \) allows any reasonable approximation, since its analytical properties in a non-homogeneous system are not known.

From the viewpoint of the standard many-body formalism \( \tilde{V}(\omega) \) in Eq. (1) acts as a mass operator for the density propagator \( \chi \), similar to the self-energy \( \Sigma = G^{-1} - G_0^{-1} \), with \( G \) and \( G_0 \) being interacting and non-interacting one-particle Green’s functions. In contrast to the Green’s function, \( \Sigma \) has no free-particle singularities in any order of the perturbation theory, as it contains only irreducible diagrams. Hence it allows perturbative approximations. Similarly, the introduction of the “density mass operator” \( \tilde{V} = \chi_{S}^{-1} - \chi^{-1} \) is motivated only if the latter does not possess the e-h singularities, which are present in \( \chi_S \) and any finite order approximation to \( \chi \).

In this paper we use the KS-based many-body diagrammatic technique of Ref. 8 to derive a perturbative expansion for \( f_{xc} \). We find that the kernel is indeed regular at KS frequencies. Yet, caution must be exercised in applying perturbative approximations [such as OEP (Refs. 7,9)] for \( f_{xc} \) in large systems to avoid uncontrollable errors or even unphysical divergences.

We start with the equation which relates \( \chi(\omega) \) to the proper polarizability \( \tilde{\chi} \)

\[
\chi(\omega) = \tilde{\chi}(\omega) + \tilde{\chi}(\omega)V_C\chi(\omega). \quad (2)
\]

It is convenient to split \( \tilde{\chi} \) as \( \tilde{\chi} = \chi_S + \pi_{xc} \) where the xc part \( \pi_{xc} \) can be represented as a series of graphs.\(^8\) The first-order contribution \( \pi_{xc}^{(1)} \) and examples of the second-order corrections \( \pi_{xc}^{(2)} \) are shown in Fig. 1, where solid and dashed lines stand for the KS Green’s functions and the Coulomb interaction respectively. To the wiggled line is assigned the inverse KS susceptibility \( \chi_S^{-1} \). It describes the scattering of KS particles by the xc potential \( v_{xc} \). By the definition of \( v_{xc} \), these processes exactly compensate the change of the density due to the self energy insertions in every order of the perturbation theory.\(^8\)

The graphical expansion of \( f_{xc} \) can be obtained from the relation \( f_{xc} = \chi_S^{-1} - \chi^{-1} \) (Ref. 7), which follows from Eqs. (1) and (2). The formal expansion of this equation
in terms of $\pi_{xc}$ gives the series

$$f_{xc} = \chi_S^{-1} \pi_{xc} \chi_S^{-1} - \chi_S^{-1} \pi_{xc} \chi_S^{-1} \pi_{xc} \chi_S^{-1} \ldots$$  \hspace{1cm} (3)$$

Inserting $\pi_{xc} = \pi_{xc}^{(1)} + \pi_{xc}^{(2)} + \pi_{xc}^{(3)} + \ldots$ and collecting the diagrams of the same order we obtain $f_{xc}^{(1)}$, $f_{xc}^{(2)}$, etc. The $n$-th order contribution $f_{xc}^{(n)}$ is a sum of the polarizability of the $n$-th order $\pi_{xc}^{(n)}$ with two attached wiggled lines and all diagrams with lower-order polarization loops connected by wiggled lines (Fig. 2). A closer inspection shows that all graphs with internal wiggled lines can be generated from a limited set of graphs with no internal but two external wiggled lines. This leads to the following rules for constructing $f_{xc}$: (i) Draw all standard diagrams for the proper polarization operator of the $n$-th order and attach wiggled lines to external points (construction of parent graphs). (ii) If possible, separate any given graph into two by cutting two fermionic lines. Join the external fermionic lines of these parts, connect them by a wiggled line and change the sign. Do not cut lines attached to the same wiggled line. (iii) Apply (ii) to all possible cuttings in all graphs, including those obtained previously. (iv) Keep only nonequivalent graphs. The arrows in Fig. 2 indicate application of these rules to the second-order parent graph in the upper left corner. 14

The same rules apply to the perturbation series for the “mass operator” $V$, except that in (i) the parent graphs are the diagrams for the total response function $\chi$. As discussed above, the introduction of $V$ (or $f_{xc}$) is justified only if this function is free of singularities related to the KS e-h pairs in every order of the perturbation theory. The analogy with the self-energy $\Sigma$ does not, by itself, ensure this property, and we apply our graphical method to prove that this is indeed the case.

Since the rules (ii)-(iv) deal only with the two-particle reducible graphs, a partial summation of the diagrams with the help of one- and two-particle irreducible elements (self-energies and vertices) is possible. An example of a summation of all parent graphs with $l$ vertex insertions (which divide each graph in $l + 1$ blocks) and with $m_k$ ($k = 1, \ldots, l + 1$) self-energies in every block is depicted in Fig. 3a. It is important that the diagrams generated by cutting two fermionic lines with the same frequency (e.g. in Fig. 1 and Fig. 2) have a similar structure. They all describe scattering of KS particles by the xc potential. The sum of these graphs and the parent graphs is again a diagram of the same type as in Fig. 3a with the self-energy $\Sigma_S = G_S^{-1} - G^{-1}$. This definition of $\Sigma_S$ ensures the equivalence of the KS and exact densities. The vertex $\Gamma$ is defined in the usual way as the sum of the four-point functions which are irreducible in the e-h channel. After summation, the graph in Fig. 3a can be considered as a new parent graph which generates further diagrams for $V$ by cutting only parallel e-h lines.

Let us now consider the general parent graph of Fig. 3a at KS frequency $\omega_{ij} = E_i - E_j$, where $E_j$ are the KS one-particle energies. This graph represents a $L$-th order correction (i.e. containing $L$ irreducible elements) to the response function $\chi$. When the frequency $\omega$ approaches $\omega_{ij}$, the graph in Fig. 3a diverges. Integrating over intermediate frequencies in every internal block we find that the most divergent term behaves as $1/(\omega - \omega_{ij})^{(L+1)}$. Application of our rules to the graph Fig. 3a generates a full set of diagrams for $V(\omega)$ i.e. the initial graph with only two external wiggled lines and the diagrams obtained by all possible cuttings of parallel e-h lines. All diagrams in this set have poles of various orders. However, they can be grouped in such a way that all singularities cancel. The general proof is straightforward but lengthy and will be published elsewhere. Here we show this cancellation for a graph with $L$ vertices, but with no self-energy insertions.

Application of the rules (i)-(iv) to this graph leads to replacement of all internal KS two-particle functions.
$K_S(\omega, \varepsilon) = G_S(\omega + \varepsilon)G_S(\varepsilon)$ by

$$J(\omega, \varepsilon, \varepsilon') = K_S(\omega, \varepsilon)\delta_{\varepsilon, \varepsilon'} - K_S(\omega, \varepsilon)\chi_S^{-1}(\omega)K_S(\omega, \varepsilon'),$$

where $\omega$ and $\varepsilon$ are transferred (external) and internal frequencies respectively. The resulting contribution to $V$ is shown graphically in Fig. 3b. The singularities at $\omega = \omega_j$ can potentially occur in the “resonant” part in every internal block $J_j(\omega, \varepsilon, \varepsilon')$, which contains an electron in the state $\varepsilon$ and a hole in the state $\varepsilon'$. A summation over internal frequency gives for the “dangerous” contribution

$$\sum_{\varepsilon, \varepsilon'} J_{ij}(\omega, \varepsilon, \varepsilon') = \frac{|ij\rangle\langle ij|}{\omega - \omega_{ij} - \omega - \omega_{ij}} \chi_S^{-1}(\omega)\frac{|ij\rangle\langle ij|}{\omega - \omega_{ij}},$$

(4)

where $|ij\rangle = \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}')$ is the wave function of the resonant e-h pair, $|ij\rangle = \psi_i(\mathbf{r})\psi_j^*(\mathbf{r})$ is the same function, but with equal coordinates of the electron and the hole and $\psi_i(\mathbf{r})$ are the KS orbitals. Both terms in Eq. (4) are apparently singular. To show that these divergences cancel, we single out the divergence in the KS susceptibility

$$\chi_S = |ij\rangle\langle ij|/(\omega - \omega_{ij}) + \chi_r,$nents, the effective interaction $\tilde{V}$.

where $\chi_r$ is the regular part. For the inverse $\chi_S^{-1}(\omega)$ we have

$$\chi_S^{-1}(\omega) = \chi_r^{-1}(\omega) - \frac{\chi_r^{-1}(\omega)\langle ij|\chi_r^{-1}(\omega)\rangle\langle ij|}{\omega - \omega_{ij} + \langle ij|\chi_r^{-1}(\omega)\rangle\langle ij|}.$$ (5)

Substitution of Eq. (5) to Eq. (4) gives a singularity-free result

$$\sum_{\varepsilon} J_{ij}(\omega_{ij}, \varepsilon) = \frac{|ij\rangle\langle ij|}{\langle ij|\chi_r^{-1}(\omega_{ij})\rangle\langle ij|}.$$ (6)

Similarly, zeroes of the external wiggled lines cancel the poles of the end blocks in Fig. 3b.\textsuperscript{16} Thus the graph Fig. 3b is regular at KS resonances in every order of the perturbation theory, and $\tilde{V}(\omega)$ can be viewed as a mass operator similar to the one-particle self energy $\Sigma$.

There is, however, one important difference. Whereas the self energy exactly reduces to the one-particle irreducible elements, the effective interaction $\tilde{V}(\omega)$, even after cancellation of singularities, still contains parts of the bare two-particle propagator with the resonant denominator being replaced by $\langle ij|\chi_r^{-1}(\omega_{ij})\rangle\langle ij|$ (see Eq. (6)). Since $\chi_r^{-1}(\mathbf{r}, \mathbf{r}')$ in general goes to zero at $|\mathbf{r} - \mathbf{r}'| \to \infty$ and the functions $|ij\rangle$ have a normalization factor $\sim 1/V$, the matrix element $\langle ij|\chi_r^{-1}(\omega_{ij})\rangle$ may vanish with the increase of the system size. For example, in a 3D semiconductor the inverse of the KS response function at $\omega = E_g$ has an asymptotic behavior $\chi_r^{-1}(E_g, \mathbf{r}, \mathbf{r}') \sim 1/|\mathbf{r} - \mathbf{r}'|$ (in this case $\chi_r$ means the principal value of $\chi_S$). Therefore the matrix element $\langle \mathbf{v}|\chi_r^{-1}(E_g)|\mathbf{v}\rangle$ vanishes as $V^{-1/3}$. This makes it problematic to construct approximations for $f_{xc}$ using perturbation theory, as is routinely done for $\Sigma$.

The simplest of the perturbative approximations corresponds to the first order in irreducible elements $\Sigma_S$ and $\Gamma$ (Fig. 4a), $\tilde{V}^{(1)} = \chi_S^{-1}(1)\chi_S^{-1},$ where $\chi^{(1)}$ is the first-order polarization loop. This class of approximations covers, for instance, the dynamic $x$-only OEP (Ref. 9) and the Richardson-Ashcroft approximation (RA).\textsuperscript{11} $\tilde{V}_{OEP}(\omega)$ is given by the graph of Fig. 4a with $\Sigma_S$ and $\Gamma$ taken in the first order in the Coulomb interaction $V_C$ (Ref. 8) in Fig. 4b. Similarly, $\tilde{V}_{RA}(\omega)$ has the same form of Fig. 4a, but with the self-energy $\Sigma_S$ and the vertex $\Gamma$ as shown in Fig. 4c. OEP and RA are state-of-the-art approximations which accurately reproduce the correlation energy and plasma excitations of a homogeneous electron gas.\textsuperscript{12} However, both approximations may give uncontrollable results for the e-h excitation energies. In the following we show this by an explicit calculation of the second-order corrections to the KS excitation energy $\omega_{ij}$.

The first-order (with respect to $\Sigma_S$ and $\Gamma$) correction $\Delta\omega_{ij}^{(1)} = \omega_{ij}^{(1)} - \omega_{ij}$ is given by

$$\Delta\omega_{ij}^{(1)} = \langle ij|\tilde{V}^{(1)}(\omega_{ij})|ij\rangle \equiv \langle ij|\tilde{W}|ij\rangle,$$ (7)

where the operator $\tilde{W}(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2')$ is defined as follows

$$\tilde{W} = \Sigma_S(\mathbf{r}_1, \mathbf{r}_2)\delta(\mathbf{r}_1' - \mathbf{r}_2') - \Sigma_S(\mathbf{r}_1', \mathbf{r}_2')\delta(\mathbf{r}_1 - \mathbf{r}_2') + \Gamma^{(1)}(\mathbf{r}_1, \mathbf{r}_1'; \mathbf{r}_2, \mathbf{r}_2').$$ (8)

The upper indexes in Eq. (8) indicate that the self-energies and the vertex are taken on the e-h mass shell. The equations (7)-(8) give a generalization of the x-only result,\textsuperscript{8} which is equivalent to the first-order of the Görling-Levy perturbation theory.\textsuperscript{13} Similarly we obtain the second-order correction

$$\Delta\omega_{ij}^{(2)} = \langle ij|\tilde{V}^{(2)}(\omega_{ij})|ij\rangle + \Delta\omega_{ij}^{(1)}\langle ij|\frac{\partial\tilde{V}^{(1)}}{\partial\omega}|ij\rangle + \sum_{k,l\neq i,j} \langle ij|\tilde{V}^{(1)}(\omega_{ij})|kl\rangle(\delta_{nk} - \delta_{nl})\langle kl|\tilde{V}^{(1)}(\omega_{ij})|ij\rangle$$ (9)

where $n_k$ is the occupation number of the $k$-th KS state and $\tilde{V}^{(2)}(\omega)$ is the effective interaction of the second order in $\Sigma_S$ and $\Gamma$. If we ignore $\tilde{V}^{(2)}$ and iteratively solve Eq. (1) using only the first-order function $\tilde{V}^{(1)}$ (e.g. in OEP or RA approximation) in place of the kernel, the second-order correction Eq. (9) would contain only the
last two terms. The last term can be written as
\[\{ij|\tilde{V}^{(1)}(\omega_{ij})\chi_r(\omega_{ij})\tilde{V}^{(1)}(\omega_{ij})|ij\} = \frac{(\Delta\omega)^2}{(ij|\chi_r^{-1}(\omega_{ij})|ij)},\]
where we used Eq. (7) and Eq. (5). A similar calculation of the second term in Eq. (9) shows that it contains the
same factor \(\{ij|\chi_r^{-1}(\omega_{ij})\}^{-1}\). Hence both terms in Eq. (9) which originate from \(\tilde{V}^{(1)},\) and which would be the only
contributions in OEP and RA, have exactly the same
denominator as the higher-order diagrams after the can-
cellation of the e-h singularities (see Eq. (6)). Clearly
this denominator must appear in \(\tilde{V}^{(2)}\) as well. The calculation shows that the first term in Eq. (9) indeed takes
the form
\[\{ij|\tilde{V}^{(2)}(\omega_{ij})|ij\} = \Delta_{ij}^{(2)} - \Delta\omega_{ij}^{(1)}\{ij|[\partial\tilde{V}^{(1)}/\partial\omega]|ij\}
- \{ij|\tilde{V}^{(1)}(\omega_{ij})\chi_r(\omega_{ij})\tilde{V}^{(1)}(\omega_{ij})|ij\},\]
where
\[\Delta_{ij}^{(2)} = \sum_{k,l\neq ij} \frac{(ij|\tilde{W}|kl)(kl|\tilde{W}|ij)}{\omega_{ij} - \omega_{kl}} + \Delta\omega_{ij}^{(1)}\{ij|[\partial\tilde{W}/\partial\omega]|ij\}.\]
The second and the third terms in Eq. (10) cancel the sec-
ond and the third terms in Eq. (9) and the second-order
energy shift is simply given by Eq. (11). This also follows
from a direct perturbative solution of the BS equation.
The cancellation found above is not accidental and can
be proven in every order of the perturbation theory.

Thus any finite-order approximation for \(\tilde{V}\) requires a
consistent perturbative treatment of Eq. (1) to obtain
a meaningful energy shift. In particular, the first-order
approximations like OEP or RA are appropriate for the
calculation of the excitation energies only in the first or-
der in \(\Sigma_S\) and \(\Gamma\). The naive second-order correction,
(last two terms in Eq. (9)) and higher-order corrections are wrong and can even diverge in extended systems. A
summation of all orders (exact solution of Eq. (1)) may
produce a finite result, but it will contain uncontrollable
errors. In recent TDDFT calculations for atoms it has
been indeed observed that exact (in contrast to pertur-
bative) solution of Eq. (1) does not necessarily improve
the results.\(^5\)

This work has been supported by the Deutsche Forschungsgemeinschaft under Grant PA 516/2-1. O. P.
is grateful for a partial support from the U.S. Depart-
ment of Energy, Office of Basic Energy Sciences, Divi-
sion of Materials Science by the University of California
Lawrence Livermore National Laboratory under contract
No. W-7405-Eng-48. The work of I. T. was partly sup-
ported by the Russian Federal Program “Integration”.

\(^1\) E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997
(1984).
\(^2\) J. Theilhaber, Phys. Rev. B 46, 12900 (1992).
\(^3\) Y. Miyamoto and O. Sugino, Phys. Rev. B 62, 2039 (2000).
\(^4\) F. Kootstra, P. L. de Boeij, and J. G. Snijders, J. Phys.
Chem. 112, 6517 (2000).
\(^5\) M. Petersilka, E. K. U. Gross, and K. Burke, Int. J. Quan-
tum Chem. 80, 534 (2000).
\(^6\) M. E. Casida and D. R. Salahub, Journ. Chem. Phys. 113,
8918 (2000).
\(^7\) M. Petersilka, U. J. Gossmann and E. K. U. Gross, Phys.
Rev. Lett. 76, 1212 (1996).
\(^8\) I. V. Tokatly and O. Pankratov, Phys. Rev. Lett. 86, 2078
(2001).
\(^9\) A. Göring, Int. J. Quant. Chem. 69, 265 (1998).
\(^10\) E. M. Lifshitz, L. P. Pitaevski, Statistical Physics, Part
2, Course of Theoretical Physics, Vol. 9 (Pergamon, New
York, 1980).
\(^11\) C. F. Richardson and N. W. Ashcroft, Phys. Rev. B 50,
8170 (1994).
\(^12\) M. Lein, E. K. U. Gross and J. P. Perdew, Phys. Rev.
B 61, 13431 (2001); K. Tatarczyk, A. Schindlmayr and
M. Scheffler, Phys. Rev. B 63, 235106 (2001).
\(^13\) A. Göring, Phys. Rev. A 54, 3912 (1996).
\(^14\) Interestingly, the rules (ii)-(iv) coincide with the diagr-
amic rules for the xc potential \(v_{xc}\) (Ref. 8). The only differ-
ence is the choice of the parent graphs in (i) (loops with one
or two external points for \(v_{xc}\) and \(f_{xc}\) respectively). This
by far nontrivial fact leads to the conjecture that these
rules should hold for any functional derivative \(\delta^nE_{xc}/\delta n^n\)
of the xc energy \(E_{xc}\).
\(^15\) To simplify the derivation we assumed that the resonant
transition \(\omega_{ij}\) is not degenerate. In the case of \(M\)-fold
degeneracy, the denominator in Eq. (6) is replaced by the
inverse of the \(M \times M\) matrix \(\{ij|\chi_r^{-1}|i'j'\}\), where \(|ij\) and
\(|i'j'\) belong to the set of degenerate states.