Many-body diagrammatic expansion in a Kohn-Sham basis: implications for Time-Dependent Density Functional Theory of excited states

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We formulate diagrammatic rules for many-body perturbation theory which uses Kohn-Sham (KS) Green’s functions as basic propagators. The diagram technique allows to study the properties of the dynamic nonlocal exchange-correlation (xc) kernel \( f_{xc} \). We show that the spatial non-locality of \( f_{xc} \) is strongly frequency-dependent. In particular, in extended systems the non-locality range diverges at the excitation energies. This divergence is related to the discontinuity of the xc potential.

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Time-dependent density functional theory (TDDFT) [1] offers a possibility to extend the powerful density-functional formalism [2] to excited states of many-body systems [3]. A substantial improvement of excitation energies with respect to KS eigenvalues was obtained for atoms and molecules [4] using a variety of approximations for a dynamic xc kernel \( f_{xc} = \delta v_{xc}(r, t)/\delta n(r’, t’) \) (\( v_{xc} \) is a xc potential). However in solids the wrong KS band gap remains unchanged regardless the approximations account for this behavior as they all employ the adiabatic (frequency-independent) xc kernels.

In this paper we develop a perturbative technique with KS Green’s functions as the bare propagators. In essence, it is a diagrammatic expansion of Sham-Schlüter equation [5], which maintains a correct electron density in every order of the perturbation theory. We find that at resonant frequencies the kernel \( f_{xc} \) is proportional to the discontinuity of \( v_{xc} \). This explains the anomalous non-locality of \( f_{xc} \), since a constant shift of a potential due to an extra particle is felt by another particle anywhere in the system.

In the framework of TDDFT the excitation energies are commonly calculated [6] from the poles of the linear response function \( \chi(r, r’, \omega) \). The latter is related to the KS susceptibility \( \chi_S(r, r’, \omega) \) by

\[
\chi(\omega) = \chi_S(\omega) + \chi_S(\omega) \left[ V_C + f_{xc}(\omega) \right] \tilde{\chi}(\omega),
\]

where \( V_C = e^2/|r - r'| \) is a bare Coulomb repulsion and the kernel \( f_{xc} \) enters as an additional dynamic interaction.

Alternatively, the poles of \( \chi(r, r’, \omega) \) can be found as the eigenvalues of a linearized equation for density matrix

\[
\left[ \omega - \hat{H}_S(r_1) + \hat{H}_S(r_2) \right] \delta \rho(r_1, r_2) - \rho_S(r_1, r_2) \int dr \left[ \hat{V}_{\omega}(r_1, r) - \hat{V}_{\omega}(r, r_2) \right] \delta \rho(r, r) = 0
\]

where \( \hat{V}_{\omega} = V_C + f_{xc}(\omega) \), \( \hat{H}_S(r) \) is the KS Hamiltonian, and \( \rho_S(r, r’) = \sum_j \psi_j^*(r) \psi_j(r’) \) is the equilibrium KS density matrix with the KS orbitals \( \psi_j(r) \). Equation (3) clearly shows that a correction to the KS excitation energies originates from the Hartree-type energy of the excitation-induced density fluctuation \( \delta n(r) = \delta \rho(r, r) \). In the KS basis equation (3) takes the form

\[
(\omega - \omega_{ij}^S) \delta \rho_{ij} - \gamma_{ij} \sum_{kl} \langle \Phi_{ij} | \hat{V}_{\omega} | \Phi_{kl} \rangle \delta \rho_{kl} = 0,
\]

where \( \omega_{ij}^S = E_i^S - E_j^S \) is a KS excitation energy, \( \gamma_{ij} = n_i - n_j \) is the difference of the occupation numbers and \( \Phi_{ij}(r) = \psi_i^*(r) \psi_j(r) \). The ordinary perturbation theory gives the energy shift \( \Delta \omega_{ij} = \omega_{ij} - \omega_{ij}^S \) in the first order as

\[
\Delta \omega_{ij}^{(1)} = \langle \Phi_{ij}(r) | V_C(r, r’) + f_{xc}(r, r’, \omega_{ij}^S) | \Phi_{ij}(r’) \rangle,
\]

which is identical to the result of the first-order Laurent expansion of \( \chi(r, r’, \omega) \) [7]. The perturbation theory easily allows to obtain the higher-order corrections as well. It is worth noting that equations (3) and (4) and the perturbative result (4) are equally valid for finite and for extended systems.

Let us consider the dependence of the first-order correction (4) on the size of a system \( L \sim V^{1/3} \) at fixed average density \( N/V \). As \( \Phi_{ij}(r) \) contains a normalization factor \( 1/V \), the first term in Eq. (4) is proportional to \( e^2/L \). This is the Coulomb energy of the density variation due to an electron-hole excitation, which is infinitesimally small in extended systems. The second term crucially depends on the non-locality of \( f_{xc} \) i.e. on the extension of a xc-hole. At \( \omega = 0 \) the non-locality range is about the interparticle distance \( \sim (V/N)^{1/3} \). This feature is reproduced by the popular OEP approximation [8] whereas in adiabatic LDA [9] \( f_{xc} \) is a point interaction. Assuming that at resonance frequency \( f_{xc}(\omega_{ij}) \) has a similar non-locality we find that the second term in Eq. (4) is
proportional to $1/N$ and vanishes as $L^{-3}$ (see, however, (10)). Thus any xc-kernel which is finite and decays at infinity does not contribute to $\omega_{ij}$ in extended systems. Using the many-body perturbative approach formulated below, we show that a non-vanishing xc correction arises due to the divergence of the non-locality scale of $f_{xc}(\omega_{ij})$.

\[
\hat{V} = \hat{W}' - \sum_{k=1}^{\infty} \int d\mathbf{r} v_{xc}^{(k)}(\mathbf{r}) \hat{n}(\mathbf{r}). \tag{5}
\]

In Eq. (5) $\hat{W}'$ is a two-particle interaction with the Hartree part being subtracted, $\hat{n}(\mathbf{r})$ is a density operator and we assume that the xc-potential $v_{xc}(\mathbf{r})$ and the ground state density are known, we represent the Hamiltonian of a system as a sum of the KS Hamiltonian $\hat{H}_S$ and the perturbation $\hat{V}$, where

\[
\hat{V} = \hat{W}' - \sum_{k=1}^{\infty} \int d\mathbf{r} v_{xc}^{(k)}(\mathbf{r}) \hat{n}(\mathbf{r}). \tag{5}
\]

We employ the Matsubara formalism at nonzero temperature $T$ which enables us to obtain any physical retarded function through analytic continuation [11]. Assuming that the xc-potential $v_{xc}(\mathbf{r})$ and the ground state density are known, we represent the Hamiltonian of a system as a sum of the KS Hamiltonian $\hat{H}_S$ and the perturbation $\hat{V}$, where $\hat{V} = \hat{W}'$ - $\sum_{k=1}^{\infty} \int d\mathbf{r} v_{xc}^{(k)}(\mathbf{r}) \hat{n}(\mathbf{r})$. (5)

Following the standard procedure [11] we define the Green’s function

\[
G(X, X') = -(T, \hat{\Psi}_S(X) \hat{\Psi}_S^{+}(X') \hat{\sigma}) / \langle \hat{\sigma} \rangle, \tag{6}
\]

where $X = (\mathbf{r}, \tau)$ ($\tau$ is an imaginary time), $\hat{\Psi}_S(X)$ is a field operator in a KS interaction representation and $\hat{\sigma}$ is a Matsubara S-matrix [11] which corresponds to the perturbation $\hat{V}$ of Eq. (5). The angular brackets in Eq. (6) denote averaging over the KS equilibrium state.

A formal graphical expansion of $G(X, X')$ contains along with the pair interaction terms the diagrams related to the scattering by the “external” potentials $v_{xc}^{(k)}$. To achieve a closed scheme one needs a complementary graphical representation of $v_{xc}(\mathbf{r})$, which can be obtained from the condition of density conservation. The Green’s function (6) can be written in the form $G = G_S + \sum_{k=1}^{\infty} G^{(k)}$, where $G_S$ is a KS Green’s function and $G^{(k)}$ is a $k$-th order correction. As the KS system possesses an exact density, the variation of the density due to the interaction (6) must vanish. Applying this requirement to every order we arrive at the system of equations:

\[
\delta n^{(k)}(\mathbf{r}) = T \sum_{n=-\infty}^{\infty} G^{(k)}(\mathbf{r}, \mathbf{r}, \omega_n) = 0, \tag{7}
\]

where $\omega_n = \pi T(2n + 1)$. This system is equivalent to well-known Sham-Schlüter equation (6) (see also (12)). A successive solution of Eq. (7) allows to construct $v_{xc}^{(k)}$ for every $k$. For example, the first-order correction $G^{(1)}$ is presented in Fig. 1a, where the solid line is the KS Green’s function and dashed line is the Coulomb interaction. Substituting $G^{(1)}$ into Eq. (6) we get $v_{xc}^{(1)}$ as shown in Fig. 2a, where the wiggled line stands for the inverse KS response function $\chi^{-1}_S(\mathbf{r}, \mathbf{r'})$. The final first-order correction to the Green’s function is shown in Fig. 1b. Note that $v_{xc}^{(1)}$ (Fig. 2a) exactly corresponds to the x-only OEP $v_x$. Given $v_{xc}^{(1)}$ we solve Eq. (6) for $k = 2$ and obtain eight graphs for $v_{xc}^{(2)}$ (Fig. 2b-i). From the further iterations we deduce the following diagrammatic rules for $v_{xc}$ in arbitrary order:

\begin{enumerate}
  \item Draw all graphs for density according to the usual rules [11] and attach wiggled lines to external point of each graph.
  \item Whenever it is possible separate the graphs into two parts by cutting two fermionic lines. Join the external fermionic lines of these parts and connect them by the wiggled line. Do not cut lines attached to the external wiggled line.
  \item If a new graph is separable, repeat ii.
  \item If there are several possible cross sections repeat ii and iii for every cross-section.
  \item Leave only nonequivalent graphs.
\end{enumerate}

For example, graphs a-e in Fig. 2 appear according to i. Graph f is obtained from d applying ii, whereas graphs g-i originate from the graph e by the successive application of ii-v.

Given a diagrammatic representation for $v_{xc}$ we can easily construct a graphical expansion for any quantity e.g. for one particle Green’s function, a response function or an energy. We find that the series for the energy coincides with the energy expansion obtained in a different context in Ref. [13] (see also Ref. [14]). As the diagrammatic expansion is derived maintaining the exact density in every order, the series for $v_{xc}$ is in fact a graphical representation of the Görling-Levy perturbation theory (GLPT) [15]. An obvious advantage of the graphical method is a possibility to construct $v_{xc}^{(k)}$ for every $k$ in a transparent form.
An important feature of the KS-based diagram technique is that every irreducible self-energy insertion \( \Sigma(\mathbf{r}, \mathbf{r}') \) is accompanied by the local counter term with the opposite sign which has the structure of the average of \( \Sigma: (G_S \Sigma G_S) (G_S G_S)^{-1} \). This term guarantees the density conservation and locally reduces the effective field \( \Sigma \). The first-order correction (Fig. 1b) gives an example of this compensation. It is interesting to note that also the standard diagram technique can be reformulated in a similar fashion. One has to explicitly introduce the correction to the chemical potential to compensate the change of the total number of particles (i.e., the averaged density) in every order of the perturbation theory. This leads to similar, but spatially-averaged counter terms. However the local compensation in the KS-based technique is obviously more efficient. This means that KS particles are much closer to the true quasiparticles than bare electrons.

Our graphical method has an obvious connection to the GW approximation [1]. Let us collect in every order of the perturbation theory only the bubble diagrams (e.g. the graph in Fig. 2c) and sum them up. The corresponding correction to the Green’s function is still given by Fig. 1b, but with the RPA-screened interaction. While the first graph in Fig. 1b is exactly the GW self-energy, the second one deviates from the common GW prescription. Instead of subtraction of the whole \( v_{xc} \) one has to use an approximate \( v_{xc} \), (even if the exact \( v_{xc} \) is known!). This is necessary for the purpose of internal consistency and facilitates the density conservation. From this point of view it is clear that KS eigenvalues should describe well quasiparticles in metals (e.g. the shape of the Fermi surface), but not in semiconductors. Indeed, for a short-ranged screened interaction in metals the first (nonlocal) and the second (local) term in Fig. 2b almost cancel (they would cancel exactly for a point interaction). Conversely, in insulators there is no pronounced cancellation since the interaction is long-ranged. As a result, the correction to the KS energies gets larger the larger the gap is.

To study the electron-hole excitations one has to consider the linear response function \( \chi(\mathbf{r}, \mathbf{r}', \omega_n) \). An integral equation for this function

\[
\chi(\omega_n) = \tilde{\chi}(\omega_n) + \tilde{\chi}(\omega_n) V_C \chi(\omega_n),
\]

contains irreducible polarization operator \( \tilde{\chi}(\omega_n) \). We split \( \tilde{\chi}(\omega_n) \) into two parts: \( \tilde{\chi}(\omega_n) = \chi_S(\omega_n) + \Pi(\omega_n) \), where \( \Pi(\omega_n) \) includes all (self-energy and vertex) corrections to the irreducible susceptibility \( \tilde{\chi}(\omega_n) \). The first-order corrections to \( \chi(\omega_n) \) are shown in Fig. 3, where the first four terms correspond to the first-order correction \( \Pi^{(1)}(\omega_n) \). Thus the total response function in the first order is

\[
\chi(\omega_n) \approx \chi_S(\omega_n) + \Pi^{(1)}(\omega_n) + \chi_S(\omega_n) V_C \chi_S(\omega_n).
\]
energies Eq. (1) depends, however, on the kernel at resonance $f_{xc}(\omega_i^S)$. Let us consider a spatial extension of this kernel using Eq. (14). To calculate $\chi_S(\omega)^{-1}$ at resonance $\omega_i^S$ one has to keep both a singular and a regular parts of $\chi_S(\omega)$. Following Ref. [13] we write $\chi_S = \gamma_{ij}\Phi_{ij}(r)\Phi_{ij}(r')/(\omega - \omega_i^S) + \chi_r(r, r')$, where $\chi_r$ is a regular part. Substituting $\Pi(1)(\omega)$ (4) to Eq. (13) and performing calculations we arrive at the following result

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega_{ij}) = \Delta_{ij} \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \chi_r^{-1}(\mathbf{r}, \mathbf{r}_1) \Phi_{ij}(\mathbf{r}_1) \Phi_{ij}(\mathbf{r}_2) \chi_r^{-1}(\mathbf{r}_2, \mathbf{r}') [\int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{ij}^*(\mathbf{r}_2) \chi_r^{-1}(\mathbf{r}_2, \mathbf{r}_1) \Phi_{ij}(\mathbf{r}_1)]^2}{(\int d\mathbf{r}_1 d\mathbf{r}_2 \Phi_{ij}^*(\mathbf{r}_2) \chi_r^{-1}(\mathbf{r}_2, \mathbf{r}_1) \Phi_{ij}(\mathbf{r}_1))^2}. \quad (14)$$

It is seen from Eq. (14) that a spatial scale of $f_{xc}(\mathbf{r}, \mathbf{r}', \omega_{ij})$ is dictated by the functions $\Phi_{ij}(r)$ which extend over the whole volume. Thus the non-locality range $\langle \omega_{ij} \rangle$ with this which is defined by the first four graphs in Fig. 3, but static approximation. But also any LDA-based dynamic approximation, including any gradient corrections) for $f_{xc}$ cannot provide a consistent results for excitation energies and a construction of explicit orbital- and frequency-dependent functionals similar to Eq. (4) is required. A possible alternative is a direct calculation of the irreducible polarization operator using the diagram method outlined above. This formally allows to express excitation energies as functionals of the KS orbitals and consequently of the ground state density.

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