Many-body quantum dynamics by the TDDFT-based theory of the density matrix

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We introduce a method of evaluating the density matrix of an arbitrary quantum mechanical system in terms of the quantities pertinent to the solution of the time-dependent density functional theory (TDDFT) problem. Our theory utilizes the adiabatic connection perturbation method [Görling and Levy, Phys. Rev. A 50, 196 (1994), Görling, ibid. 55, 2630 (1997)], from which the expansion of the density matrix in powers of the interaction constant $\lambda$ naturally arises. By this, we obtain the one-density-matrix $\rho_\lambda(r, r', t)$, which, by construction, has the $\lambda$-independent diagonal elements $\rho_\lambda(r, r, t) = n(r, t)$, where $n(r, t)$ is the particle density. The off-diagonal elements of $\rho_\lambda(r, r', t)$ importantly contribute to the processes beyond the reach of TDDFT, of which we consider the momentum-resolved photoemission, doing this to the first order in $\lambda$ (exact exchange).

In an illustrative calculation of photoemission from the quasi-2D electron gas with one filled subband we find strong deviations from the independent-particle Fermi golden rule formula.

**I. INTRODUCTION**

The time-dependent density functional theory (TDDFT) \cite{gorling-levy-94, gorling-97} is a powerful and now widely used method to study the time-evolution and excitation processes in quantum mechanical systems. Its success is due to the crucial simplification arising from the substitution of the prohibitively complicated many-body problem with the reference single-particle one, keeping, apart from the additional approximations invoked, the exact time-dependent electron density of the original many-body system. The description of a number of physical processes (e.g., optical absorption \cite{nazarov-97}, slowing of ions in matter \cite{nazarov-97}, etc.) can be reduced to finding the time-dependent electron density, and, therefore, TDDFT is the method of choice in studying such phenomena.

There exist, at the same time, important processes and the corresponding experimental methods, the theory of which cannot, on the very general physical grounds, be formulated in terms of the particle density. For a clear example, the momentum-resolved photoemission requires the knowledge of the single-particle probability in the momentum space, which, if we want to remain within the framework of a consistent quantum mechanics, cannot be found from the probability in the coordinate space, the latter giving the particle density. The minimal sufficient information is, in this case, contained in the reduced single-particle density matrix $\rho$ \cite{nazarov-97}. The real space $\rho(r, r', t)$ and the momentum space $\rho(p, p', t)$ representations of $\rho$ are related by the double Fourier transform, while it is impossible to directly relate the diagonal elements (probabilities) in the corresponding representations.

To find the density matrix is a complicated problem, generally speaking, taking us back to the many-body theory. In this Letter we come up with the idea that the solution of this problem can be much facilitated if the TDDFT problem for the same system is already solved. We use the power of the adiabatic connection perturbation method \cite{gorling-levy-94, gorling-97} and show that, while changing the interaction constant $\lambda$ from zero (the reference system value) to one (the physical system value), keeping the particle density $n_\lambda(r) = n(r)$ unchanged, we define not only the Kohn-Sham potential $v_{\lambda}(r, t)$, but also the many-body density matrix $\rho_\lambda$. The latter can be quite generally reduced to the one-density matrix $\rho_\lambda(r, r', t)$ expressed in terms of the KS orbitals of the TDDFT problem, giving us all the information required for the solution of such problems as the photoemission, heat transfer, etc.

**II. REAL-TIME THEORY TO THE 1-ST ORDER IN THE $\epsilon$-$\epsilon$ INTERACTION**

We start by writing the adiabatic connection Hamiltonian \cite{nazarov-97, nazarov-97}

$$\hat{H}^\lambda(t) = \sum_i \left[ -\frac{1}{2} \Delta_i + v_{\text{ext}}(r_i, t) + \tilde{v}^\lambda(r_i, t) \right] + \sum_{i<j} \frac{\lambda}{|r_i - r_j|},$$

(1)

where $\lambda \in [0, 1]$ is the $\epsilon$-$\epsilon$ interaction parameter. The corresponding many-body density-matrix satisfies the Liouville’s equation

$$i \frac{\partial \hat{\rho}^\lambda(t)}{\partial t} = [\hat{H}^\lambda(t), \hat{\rho}^\lambda(t)].$$

(2)

Expanding to the first order in $\lambda$ (but making, so far, no assumptions on the strength of the externally applied field), we can write

$$\hat{H}^\lambda(t) = \hat{H}_0(t) + \lambda \hat{H}_1(t),$$

(3)

$$\hat{\rho}^\lambda(t) = \hat{\rho}_0(t) + \lambda \hat{\rho}_1(t),$$

(4)

$$\tilde{v}^\lambda(r, t) = \tilde{v}_0(r, t) + \lambda \tilde{v}_1(r, t),$$

(5)

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where

\[ i \frac{\partial \rho_0(t)}{\partial t} = [\hat{H}_0(t), \rho_0(t)], \tag{6} \]
\[ i \frac{\partial \hat{\rho}_1(t)}{\partial t} = [\hat{H}_0(t), \hat{\rho}_1(t)] + [\hat{H}_1(t), \hat{\rho}_0(t)], \tag{7} \]
\[ \hat{H}_0(t) = \sum_i \left[ -\frac{1}{2} \Delta_i + v_{\text{ext}}(r_i, t) + \tilde{v}_0(r_i, t) \right], \tag{8} \]
\[ \hat{H}_1(t) = \sum_i \tilde{v}_1(r_i, t) + \sum_{i < j} \frac{1}{|r_i - r_j|}. \tag{9} \]

Let for \( t \leq 0 \) the external potential be time-independent and the system be in its ground state with the KS (Slater-determinant) wave-function \( |0\rangle \), where \(|\alpha\rangle\) is the orthonormal complete set of the KS eigenfunctions of the Hamiltonian \( \hat{H}_0(0) \). Let at \( t = 0 \) the time-dependent part of the external potential switch on. Then, \(|\alpha(t)\rangle\), which satisfies

\[ i \frac{\partial |\alpha(t)\rangle}{\partial t} = \hat{H}_0(t)|\alpha(t)\rangle, \tag{10} \]
\[ |\alpha(0)\rangle = |\alpha\rangle, \tag{11} \]

is also the orthonormal complete set of the Slater-determinant wave-functions at each particular time \( t \). Taking matrix elements of Eq. (7), we write with the help of Eq. (10)

\[ i \langle\alpha(t)| \frac{\partial \hat{\rho}_1(t)}{\partial t}|\beta(t)\rangle = \langle i \frac{\partial |\alpha(t)\rangle}{\partial t}|\hat{\rho}_1(t)||\beta(t)\rangle - \langle \alpha(t)|\hat{\rho}_1(t)|i \frac{\partial |\beta(t)\rangle}{\partial t}\rangle + (\delta_{\alpha 0} - \delta_{\alpha \beta})\langle \alpha(t)|\hat{H}_1(t)|\beta(t)\rangle \tag{12} \]

or

\[ i \frac{\partial }{\partial t} \langle\alpha(t)|\hat{\rho}_1(t)|\beta(t)\rangle = (\delta_{\alpha 0} - \delta_{\alpha \beta})\langle \alpha(t)|\hat{H}_1(t)|\beta(t)\rangle. \tag{13} \]

Equation (13) gives

\[ \langle\alpha(t)|\hat{\rho}_1(t)|\beta(t)\rangle = -i(\delta_{\alpha 0} - \delta_{\alpha \beta}) \int_0^t \langle\alpha(t')|\hat{H}_1(t')|\beta(t')\rangle dt'. \tag{14} \]

We can write

\[ \rho_1(r, r', t) = \sum_{i \in \text{occ}} \sum_{j \in \text{unocc}} \rho_1(t)|\hat{\rho}_1(t)|0_{ij}(t)\rangle \langle \phi_i(r, t)|\phi_j^*(r', t) + 0_{ij}(t)\rangle. \tag{15} \]

where \( 0_{ij}(t) \) is the ground-state Slater determinant with the occupied \( i \)-th orbital replaced with the vacant \( j \)-th one. Matrix elements of the type \( \langle 0(t)|\hat{\rho}_1(t)|0_{ij}(t)\rangle \) are the only non-vanishing ones, and, after they are worked out in terms of the orbitals, we obtain

\[ \rho_1(r, r', t) = -i \sum_{i \in \text{occ}} \sum_{j \in \text{unocc}} \int_{-\infty}^t dt' \left[ \int v_x(r_1, t')\phi_i^*(r_1, t')\phi_j(r_1, t')dr_1 + \int \phi_i^*(r_1, t')\rho_0(r_1, 2, t')\phi_j(r_2, t')dr_1dr_2 \right] \phi_i(r, t)\phi_j^*(r', t) + (r \leftrightarrow r')^*, \tag{16} \]

where \( v_x(r, t) = v_x(r, t) - v_{\text{ext}}(r, t) - v_{\text{H}}(r, t) \). Setting \( r' = r \) in Eq. (16) and equating its right-hand side to zero, immediately retrieves the equation for the exact exchange potential \( v_{\text{ex}}(r, t) \). It is directly verifiable that \( \rho_1(r, r', t) \) of Eq. (16) satisfies the Liouville-type equation

\[ i \frac{\partial \rho_1(t)}{\partial t} = [\hat{h}_a(t), \rho_1(t)] - [v_x(t), \rho_0(t)] \]
\[ + \int \rho_0(r_1, t)\rho_0(r_1, t') \left[ \frac{1}{|r_1 - r'|} - \frac{1}{|r_1 - r|} \right] dr_1. \tag{17} \]

III. LINEAR-RESPONSE THEORY IN THE FREQUENCY DOMAIN

From now we assume that the photon field is weak. We expand

\[ \rho(t) = \rho^{(0)} + \rho^{(1)}(t) + \rho^{(2)}(t) + ..., \tag{18} \]

where the superscripts indicate the order in the expansion in powers of the photon field, while the subscripts remain reserved for the order in the \( e-e \) interaction. First we easily show that

\[ \langle \phi_f|\rho_0^{(2)}(t)|\phi_f \rangle \sim \frac{\pi \hbar}{2} \sum_{m \in \text{occ}} |\langle \phi_f|v_s^{(1)}(\omega)|\phi_m \rangle|^2 \delta(\omega - \epsilon_f + \epsilon_m), \tag{19} \]

which reproduces the classical Fermi golden rule formula for the photoelectrons emission. To the first order in the interaction, and this is the main result of our work, we obtain
responding eigenenergy, and similarly for the final state. The TDDFT problem has recently been solved analytically in the linear-response regime for two-dimensional systems, where the filled subband.

\[
\langle \phi_f | r^{(2)}_1(t) | \phi_f \rangle \sim -\pi t Re \sum_{m \in \text{occ}} \delta(\omega - \epsilon_f + \epsilon_m) \langle \phi_f | \nu_s^{(1)}(\omega) | \phi_m \rangle^* \times
\]

\[
\left\{ \frac{\langle \phi_f | \nu_x^{(1)}(\omega) | \phi_m \rangle}{\epsilon_k - \epsilon_l - \omega} + \sum_k \frac{\langle \phi_f | \nu_x^{(1)}(\omega) | \phi_k \rangle}{\epsilon_m - \epsilon_k} + \frac{\langle \phi_f | \nu_x^{(1)}(\omega) | \phi_m \rangle}{\epsilon_f - \epsilon_k} + \int \phi_k(r_1) \phi_f^*(r_1) \phi_m(r) \cdot \phi_l(r) \cdot \phi_f(r) \cdot \phi_m(r) \, dr \right\}.
\]

This system ideally suits to illustrate our results by means of a very simple calculation. The general equations (19) and (20) reduce, respectively, to

\[
\langle \nu_x^{(1)}(\omega) | \mu_l^{(2)}(t) | \nu_x^{(1)}(\omega) \rangle \sim -H(k_F - k_{\parallel}) \frac{\pi t}{2} \times \left| \frac{\langle \mu_f(z) | \nu_s^{(1)}(z, \omega) | \mu_0(z) \rangle}{\delta(\omega - \lambda_f + \lambda_0)} \right|^2.
\]

where

\[
F_2(u) = 1 + \frac{L_1(2u) - I_1(2u)}{u},
\]

\[
L_1 \text{ and } I_1 \text{ are the 1st-order modified Struve and Bessel functions, respectively, } n_{2D} = \int_{-\infty}^{\infty} n(z, t) \, dz \text{ is the 2D density, and } k_F \text{ is the corresponding 2D Fermi radius. In the linear-response regime the exchange kernel, accordingly, is}
\]

\[
f_x(z, z', \omega) = -\frac{1}{n_{2D}} \frac{F_2(k_F | z - z' |)}{|z - z'|}.
\]

FIG. 1. Left: Schematics of the quasi-2D electron gas with one filled subband; Right: Schematics of the wave-function of the filled subband.

For quasi-2D electron gas with one filled subband and normally applied electric field (schematized in Fig. 1), the TDDFT problem has recently been solved analytically within the TDEXX [9] to the following results

\[
v_x(z, t) = -\frac{1}{n_{2D}} \int \frac{F_2(k_F | z - z' |)}{|z - z'|} n(z', t) \, dz',
\]

where \( H \) is the Heaviside step function, \( \mu_0(z) \) is the wavefunction of the only occupied subband, and \( \lambda_0 \) is the corresponding eigenenergy, and similarly for the final state.
and

\[ S_{k_\parallel}(z) = k_F \int_0^\infty \frac{J_1(x)J_0(k_\parallel x/k_F)}{\sqrt{x^2 + k_F^2 z^2}} \, dx, \]  

(25)

\[ G_{k_\parallel}(z) = v^{(0)}_z(z) + \int |\mu_0(z')|^2 S_{k_\parallel}(z - z') \, dz', \]  

(26)

where \( J_n(x) \) is the Bessel function of the order \( n \). The function of Eq. (25) is plotted in Fig. 2 for three values of the in-plane momentum \( k_\parallel \) of the emitted electron.

FIG. 2. Function \( S_{k_\parallel}(z) \) of Eq. (25) for three values of the lateral momentum \( k_\parallel \) of the emitted electron.

V. NUMERICAL RESULTS AND THEIR DISCUSSION

In Fig. 3 we plot results of the photoemission spectra calculations using our theory and compare them to the conventional Fermi golden rule results. The role of \( e-e \) interaction can be judged very important from this figure, leading to the interacting spectrum lying between the screened and the unscreened non-interacting ones, largely different from the both.

Figure 4 reveals a fundamental difference between the many-body and the KS dynamics, contained in the one-density-matrix and captured by our theory. Namely, in the quasi-2D electron gas we consider, the in-plane potential is flat and, therefore, the \( xy \) and \( z \) variables separate in the KS dynamics. As a result, the spectrum obtained with the use of the Fermi golden rule of Eq. (24) (dashed-dotted curve in Fig. 4) is the same for all the in-plane momenta of the emitted electrons. This is not the case when the interaction between electrons are included, leading to a fascinating and highly instructive correlation between the in-plane and the perpendicular motion in the many-body dynamics of the quasi-2D electron gas, the uniformity in the \( xy \) plane notwithstanding. Mathematically, the \( k_\parallel \) dependence is contained in the function \( S_{k_\parallel}(z) \) of Eq. (25), which enters Eq. (24) and which is plotted in Fig. 2.

FIG. 3. Spectra of photoemission from the quasi-2D electron gas with one subband filled. The density parameter is \( r_s = 5 \). The solid, dashed, and dotted lines are results obtained with the use of the present theory [Eq. (24)], Fermi golden rule with the screened (KS) potential [Eq. (23)], and Fermi golden rule with the unscreened (external) potential [Eq. (24)] with \( v_s(z, \omega) \) replaced with \( v_{\text{ext}}(z, \omega) \), respectively. The photon electric field is perpendicular to the layer. Electrons with the lateral momentum \( k_\parallel = k_F/2 \) are collected. The dashed vertical line indicates the work function value.

FIG. 4. Spectra of photoemission from the quasi-2D electron gas with one subband filled with the density parameter \( r_s = 5 \) obtained through Eq. (24). The solid, dashed, and dotted lines correspond to the emission of electrons with the lateral momentum of \( k_\parallel = 0, k_F/2, \) and \( k_F \), respectively. The dashed-dotted line shows the spectrum obtained with Fermi golden rule [Eq. (23)], which is one and the same for all the in-plane momenta.
VI. CONCLUSIONS

The TDDFT problem assumed to be solved, we have derived a general expression for the reduced one-density matrix $\rho(r, r', t)$ to the first order in the $e-e$ interaction at the fixed particle density, as TDDFT requires. Expressed in terms of the TDDFT orbitals and orbitals’ energies, our $\rho(r, r', t)$ extends the theory to phenomena beyond the reach of TDDFT. In particular, we derive an expression for the photoelectron spectra with the momentum resolution with account for the $e-e$ interaction, which would be impossible to do in the traditional TDDFT.

Our illustrative calculation for quasi-2D electron gas with one filled subband manifests a dramatic influence of the $e-e$ interactions on the photoelectron spectra. It also shows a remarkable effect of the correlation between the in-plane and the normal motion in a system uniform in the $xy$-plane, which correlation is impossible in the pure KS dynamics.

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