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

Vladimir U. Nazarov

Moscow Institute of Physics and Technology (National Research University), Dolgoprudny, Russian Federation (nazarov.vu@mipt.ru)

TDDFT-based many-body quantum dynamics by the reduced density matrix

DFT and TDDFT are powerful methods. They are successfully used to theoretically describe such properties and processes as

1. Molecular and crystal structure;
2. Optical absorption;
3. Stopping power of matter for moving ions;
4. Electronic transport;
5. *etc.*

Powerful, but not omnipotent:

DFT and TDDFT can only be usefull if *observables are expressible through the density* $n(\mathbf{r}, t)$**.**

Example of the contrary:

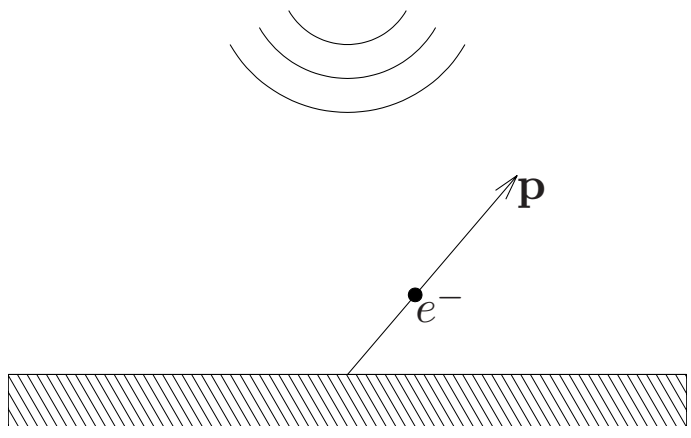


Figure 1: Photoemission process

Reduced one-particle density matrix (one-matrix):

$$\rho(\mathbf{r},\mathbf{r}',t) = N \int \rho(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\mathbf{r}',\mathbf{r}_2,\ldots,\mathbf{r}_N;t) d\mathbf{r}_2 \ldots d\mathbf{r}_N. \quad (1)$$

Then

$$\boxed{n(\mathbf{r},t)} = \rho(\mathbf{r},\mathbf{r},t). \quad (2)$$

On the other hand

$$\boxed{n(\mathbf{p},t)} = \rho(\mathbf{p},\mathbf{p},t), \quad (3)$$

where

$$\rho(\mathbf{p},\mathbf{p}',t) = \frac{1}{2\pi} \int \rho(\mathbf{r},\mathbf{r}',t) e^{i(\mathbf{p}'\cdot\mathbf{r}' - \mathbf{p}\cdot\mathbf{r})} d\mathbf{r} d\mathbf{r}'. \quad (4)$$

$n(\mathbf{p},t)$ cannot be (directly) obtained from $n(\mathbf{r},t)$ – the knowledge of $\rho(\mathbf{r},\mathbf{r}',t)$ is necessary.

$$\begin{aligned} n(\mathbf{r},t) &= n_{KS}(\mathbf{r},t). \\ \rho(\mathbf{r},\mathbf{r}',t) &\neq \rho_{KS}(\mathbf{r},\mathbf{r}',t). \end{aligned} \quad (5)$$

Time-domain formalism to the 1st order in interaction

$$\hat{H}(t;\lambda)=\sum_{i=1}^{N}\left[-\frac{1}{2}\Delta_i+v_{ext}(\mathbf{r}_i,t)+\tilde{v}(\mathbf{r}_i,t;\lambda)\right]+\sum_{i<j}^{N}\frac{\lambda}{|\mathbf{r}_i-\mathbf{r}_j|},\ \lambda\in[0,1],^{1} \tag{6}$$

$$i\frac{\partial\hat{\rho}(t;\lambda)}{\partial t}=[\hat{H}(t;\lambda),\hat{\rho}(t;\lambda)]. \tag{7}$$

$$\begin{bmatrix}\hat{H}(t;\lambda)\\ \hat{\rho}(t;\lambda)\\ \tilde{v}(t;\lambda)\end{bmatrix}=\begin{bmatrix}\hat{H}_0(t)\\ \hat{\rho}_0(t)\\ \tilde{v}_0(t)\end{bmatrix}+\lambda\begin{bmatrix}\hat{H}_1(t)\\ \hat{\rho}_1(t)\\ \tilde{v}_1(t)\end{bmatrix}, \tag{8}$$

$$\hat{H}_0(t)=\sum_{i=1}^{N}\left[-\frac{1}{2}\Delta_i+v_{ext}(\mathbf{r}_i,t)+\tilde{v}_0(\mathbf{r}_i,t)\right], \tag{9}$$

$$\hat{H}_1(t)=\sum_{i=1}^{N}\tilde{v}_1(\mathbf{r}_i,t)+\sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{10}$$

$$i\frac{\partial\hat{\rho}_0(t)}{\partial t}=[\hat{H}_0(t),\hat{\rho}_0(t)], \tag{11}$$

$$i\frac{\partial\hat{\rho}_1(t)}{\partial t}=[\hat{H}_0(t),\hat{\rho}_1(t)]+[\hat{H}_1(t),\hat{\rho}_0(t)]. \tag{12}$$

[1] Görling & Levy, PRA **50**, 196 (1994).

Formalism to the 1st order in interaction

With the adiabatic connection perturbation method, we arrive at[2]

$$i\frac{\partial\hat{\rho}_0(t)}{\partial t} = [\hat{h}_s(t), \rho_0(t)], \tag{13}$$

$$\begin{aligned} i\frac{\partial\hat{\rho}_1(t)}{\partial t} &= [\hat{h}_s(t), \rho_1(t)] - [v_x(t), \rho_0(t)] + \\ &\int \rho_0(\mathbf{r}, \mathbf{r}'', t)\rho_0(\mathbf{r}'', \mathbf{r}', t)\left[\frac{1}{|\mathbf{r}'' - \mathbf{r}'|} - \frac{1}{|\mathbf{r}'' - \mathbf{r}|}\right] d\mathbf{r}''. \end{aligned} \tag{14}$$

$\hat{h}_s(t)$ is the KS Hamiltonian, $\hat{\rho}_0(t)$ is the KS one-matrix.

$$P_f = \sum_{i\in occ}\left[\frac{\pi}{2}|\langle\phi_f|v_s^{(1)}(\omega)|\phi_i\rangle|^2 + \Delta A_{fi}\right]\delta(\omega - \epsilon_f + \epsilon_i + \Delta\omega_i), \tag{15}$$

$$\Delta\omega_i = -\langle\phi_i|v_x^{(0)}|\phi_i\rangle - \int\rho_0^{(0)}(\mathbf{r}, \mathbf{r}')\frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{16}$$

[2] VUN, PRL **123**, 095302 (2019).

Example I: Photoemission from atoms

Table 1: KS EXX orbital eigenvalues ϵ_i, energy shifts $\Delta\omega_i$, and the corresponding interaction-corrected IP $-(\epsilon_i + \Delta\omega_i)$ for several spherically symmetric spin neutral atoms, compared to the experimental and the Hartree-Fock values. EXX HOMO

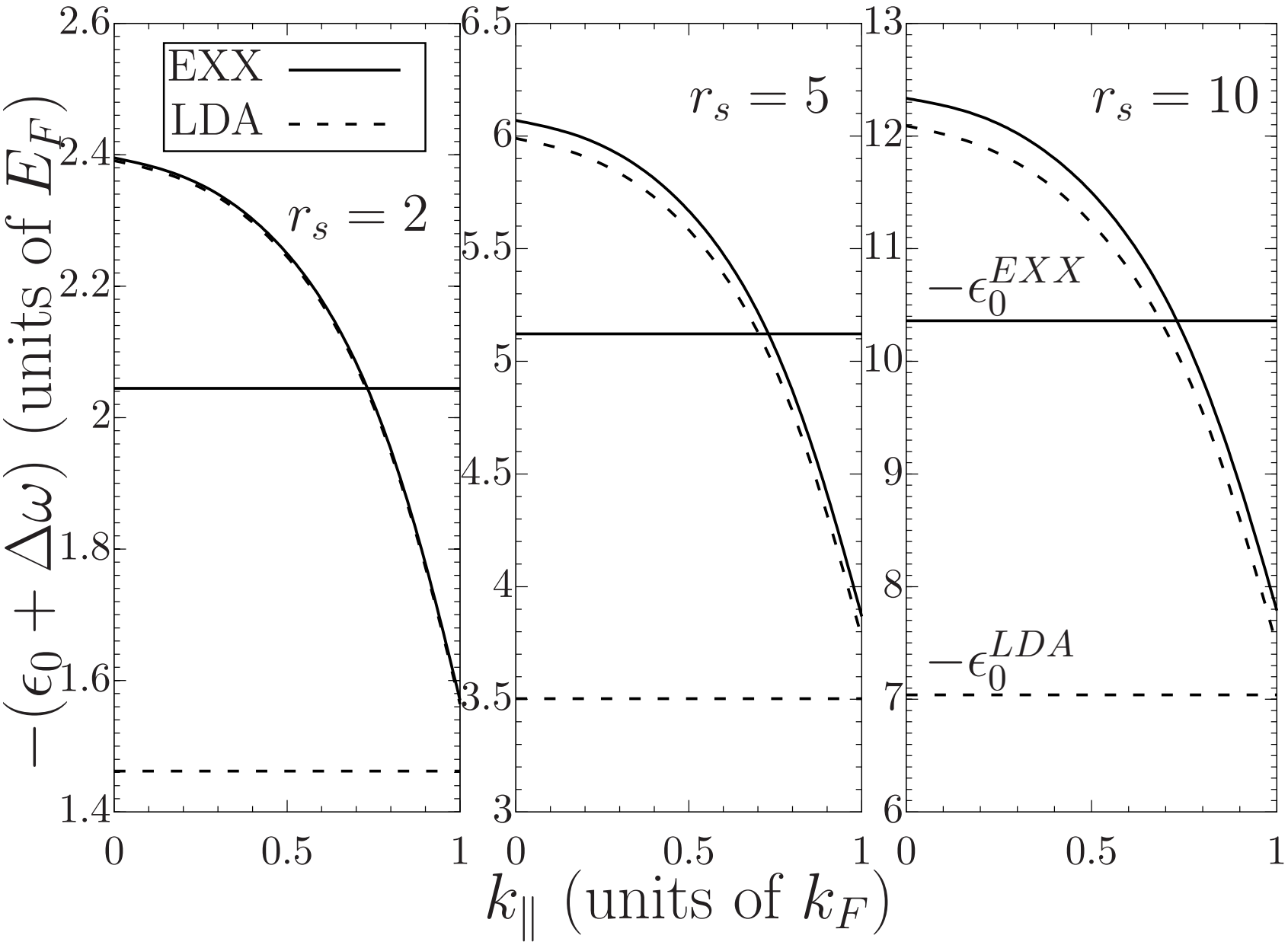
atom	$-\epsilon_i$	$-\Delta\omega_i$	$-(\epsilon_i+\Delta\omega_i)$	$-\epsilon_i^{exp}$	$-\epsilon_i^{HF}$
He(1s)	0.9179	-9.6$\times10^{-14}$	0.9179	0.9036	0.9179
Be(1s)	4.1147	0.6169	4.7316	4.384	4.7327
(2s)	0.3091	-2.7$\times10^{-6}$	0.3091	0.3425	0.3093
Ne(1s)	30.767	1.9951	32.762	31.985	32.772
(2s)	1.7054	0.2187	1.9241	1.781	1.9304
(2p)	0.8478	-5.4$\times10^{-5}$	0.8477	0.7960	0.8504
Mg(1s)	46.267	2.7567	49.024	48.174	49.032
(2s)	3.0927	0.6697	3.7624	3.454	3.7677
(2p)	1.8696	0.4114	2.2811	2.0212	2.2822
(3s)	0.2526	3.2$\times10^{-5}$	0.2526	0.2811	0.2531

Photoemission from atoms (continued)

Table 2: KS LDA and EXX orbital eigenvalues and the corresponding interaction-corrected IP of the atoms in Table 1. LDA HOMO

atom	$-\epsilon_i^{LDA}$	$-\epsilon_i^{EXX}$	$-(\epsilon_i^{LDA}+\Delta\omega_i^{LDA})$	$-(\epsilon_i^{EXX}+\Delta\omega_i^{EXX}$
He(1s)	0.5170	0.9179	0.9354	0.9179
Be(1s)	3.7956	4.1147	4.7547	4.7316
(2s)	0.1736	0.3091	0.3123	0.3091
Ne(1s)	30.229	30.767	32.849	32.762
(2s)	1.2656	1.7054	1.9741	1.9241
(2p)	0.4428	0.8478	0.8958	0.8477
Mg(1s)	45.890	46.267	49.090	49.024
(2s)	2.8454	3.0927	3.7874	3.7624
(2p)	1.6615	1.8696	2.3102	2.2811
(3s)	0.1423	0.2526	0.2542	0.2526

Example II: Q2DEG with one filled mini-band



Conclusions

- Assuming a solution to the TDDFT problem for a quantum mechanical system known, we have evaluated the reduced density matrix $\rho(\mathbf{r}, \mathbf{r}', t)$ to the first order in the e-e interaction;
- The knowledge of $\rho(\mathbf{r}, \mathbf{r}', t)$ extends the theory to phenomena, which are beyond the reach of the pure TDDFT with presently existing observable functionals;
- As an application, we have derived an extension to the Fermi's golden rule for the momentum-resolved PES;
- Our example calculations for (i) Q2DEG with one filled subband and (ii) for atoms manifest an important role of the e-e interactions in the TDDFT of PES.