

# Time-Dependent Density Functional Theory of Excitation Energies of Closed-Shell Quantum Dots

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The electronic structure and dynamics of quantum dots have recently been a subject of intense study. A knowledge of electronic excited state of quantum dots is important for many applications, including optical spectroscopy, quantum dot lasers and coherent control of electron and spin dynamics of quantum dots. Therefore, theoretical methods to provide accurate and efficient excitation energies of quantum dots are needed. Time-dependent density functional theory (TDDFT) is a rigorous extension of the ground stationary state SDFT in the time domain, thus allowing a number of dynamic and excited-state properties to be obtained [1]. Here we apply TDDFT for the low excitation energies of two-dimensional elliptical quantum dots with closed-shell structures and compare the excited energies with those obtained by exact diagonalization.

We use two different methods to obtain the excitation energies from the time-dependent Kohn-Sham equations. The first is to use the theorem that the frequency-dependent response function of a finite interacting system has discrete poles at the excited-state energies. Based on linear-response theory for the time-dependent Kohn-Sham equation, the following eigenvalue problem is derived for the excitation energies  $\Omega$  [2,3];

$$\Omega^2 = (\epsilon_{i\sigma} - \epsilon_{j\sigma})^2 \delta_{ik} \delta_{jl} \delta_{\sigma\tau} + 2\sqrt{(f_{i\sigma} - f_{j\sigma})(\epsilon_{j\sigma} - \epsilon_{i\sigma})} K_{ij\sigma,kl\tau} \sqrt{(f_{k\tau} - f_{l\tau})(\epsilon_{l\tau} - \epsilon_{k\tau})}$$

$$K_{ij\sigma,kl\tau} = \int \int \psi_{i\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \left\{ \frac{e^2}{\kappa} \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\delta \rho_{\sigma}(\mathbf{r}) \delta \rho_{\tau}(\mathbf{r}')} \right\} \psi_{k\tau}(\mathbf{r}') \psi_{l\tau}^*(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (1)$$

where  $\psi_{i\sigma}(\mathbf{r})$ ,  $\psi_{k\tau}(\mathbf{r})$  are occupied and  $\psi_{j\sigma}(\mathbf{r})$ ,  $\psi_{l\tau}(\mathbf{r})$  are unoccupied Kohn-Sham orbitals for the ground-state energies [4] and  $K_{ij\sigma,kl\tau}$  give the shift of excitation energies due to interactions. This formula represents one photon excitation process based on the linear response formalism. We use the adiabatic local-density-approximation (ALDA) for the exchange-correlation functional  $E_{xc}$ .

The second method we employ is to directly time integrate the time-dependent Kohn-Sham equations [5]. The time integration for the  $i$ -th Kohn-Sham orbital is implemented

by the split-operator method [6],

$$\begin{aligned}\Psi_i(\mathbf{r}, t + \Delta t) &= e^{-i \int_t^{t+\Delta t} (H_0(\mathbf{r}) + \delta V(\mathbf{r}, t)) dt / \hbar} \Psi_i(\mathbf{r}, t) \\ &\approx e^{-i H_0(\mathbf{r}) \Delta t / 2 \hbar} e^{-i \delta V(\mathbf{r}, t + \Delta t / 2) \Delta t / \hbar} e^{-i H_0(\mathbf{r}) \Delta t / 2 \hbar} \Psi_i(\mathbf{r}, t)\end{aligned}\quad (2)$$

where  $H_0(\mathbf{r})$  is the Kohn-Sham Hamiltonian for the ground-state energy [4] and the  $\delta V(\mathbf{r}, t)$  is the Coulomb-interaction contribution. The excitation energies are obtained from the frequency spectrum of the projection of  $\Psi_i(\mathbf{r}, t)$  onto the various ground-state Kohn-Sham orbitals. Both procedures produce the same results for the low excitation energies.

The table below shows the excitation energies of two-dimensional elliptical quantum dot with closed-shell structure (N=2 spin-unpolarized case) obtained by the exact-diagonalization method and by TDDFT. The 1st and 2nd levels correspond to  $S = 1$  states and the 3rd, 4th, and 5th levels correspond to  $S = 0$  states. We see that the TDDFT produces fairly accurate results and describes the spin singlet-triplet transition due to the exchange energy. The deviations from the exact-diagonalization results are always less than 0.13 meV.

level	Exact [meV]	TDDFT [meV]	Error [meV]
1st	1.125 (S=1)	0.993	0.132
2nd	1.449 (S=1)	1.352	0.097
3rd	2.873 (S=0)	2.872	0.001
4th	3.124 (S=0)	3.122	0.001
5th	3.559 (S=0)	3.652	0.093

We have also obtained photoabsorption spectra for the excited states and the dependence of excitation energies on the strength of the Coulomb interaction.

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