Excitons are completely missing for simple xc functionals like ALDA!
Optical absorption in solids probes primarily $q=0$. In the TDDFT response equation, the Coulomb interaction and the xc kernel only appear as a sum ($v+ f_{xc}$). Hence results are close to $f_{xc}=0$ (RPA) in the $q\to 0$ limit.

**Conclusion**: Approximations for $f_{xc}$ are needed which, for $q\to 0$, correctly diverge like $1/q^2$. Such approximations can be derived from many-body perturbation theory (see, e.g., L. Reining, A. Rubio, G. Onida, PRL 88, 066404 (2002)).
Two problems of LDA/ALDA need to be fixed:

- Onset of absorption is dictated by $\chi_{\omega}$, i.e. is identical to the LDA gap for $\omega$-independent kernel (such as ALDA).
- Description of excitons requires $1/q^2$ behavior of $f_{xc}(\omega)$.

Two problems of LDA/ALDA need to be fixed:
Two problems of LDA/ALDA need to be fixed:

- Description of excitons requires $1/q^2$ behavior of $f_{xc}$.
- Use better ground-state functional, such as HSE, which yields a reliable gap (in GKS) and reliable response function $\tilde{\chi}(q,\omega)$, i.e. is identical to the LDA gap for $\omega$-independent kernel (such as ALDA).

Onset of absorption is dictated by $\chi_s$, which is identical to the $\chi_s(q,\omega)$ of $\chi(q,\omega)$.

$$\varepsilon^{-1}(q,\omega) = 1 + \chi_s(q,\omega) \approx f_{xc}(q,\omega) \chi_s(q,\omega) \left[ 1 - (v(q) + f_{approx}(q,\omega)) \chi_s(q,\omega) \right]^{-1}$$
Two problems of LDA/ALDA need to be fixed:

1. Onset of absorption is dictated by $\chi_S$, i.e., identical to the LDA gap for $\omega$-independent kernel (such as ALDA) and reliable response function $\chi (b, \omega)$.
   - Use better ground-state functional, such as HSE, which yields a reliable gap (in GKS) and reliable response function $\chi (b, \omega)$.

2. Description of excitons requires $1/q^2$ behavior of $f_{xc}$.

Bootstrap Kernel

\[
\left[ \omega, b \right] \chi \left( \left[ \omega, b \right] \chi \left( \left[ \omega, b \right] f_{\text{approx}} + \left( b \right) \lambda \right) - 1 \right] \left( b \right) \lambda \left( \omega, b \right) \chi + 1 = \left[ \omega, b \right]_3
\]
$\frac{(0 = \infty, b)_{00} \chi}{(0 = \infty, b)_{1-3} 3} = (\infty, b)_{100_bq_f}^{xc}$

(Sharma, Dewhurst, Sanna, EKUC, PR, 107, 186401 (2011))
Bootstrap kernel

(Sharma, Dewhurst, Sanna, EKUG, PRL 107, 186401 (2011))
Linear response TDDFT is now being used to predict and to interpret experimental optical spectra in essentially all corners of physics and chemistry. Some examples:

- Linear-response TDDFT is now being used to predict...
Abstract: The electronic and excited state and luminescence properties of metal–organic framework MOF-5 were investigated using relativistic density functional theory (DFT) and time-dependent DFT (TDDFT). The geometry, IR spectra, and UV–vis spectra of MOF-5 in the ground state were calculated using DFT-M06-2X. The triplet–ground electronic excited state was calculated using DFT, leading to good agreement with the experimental results. The triplet–ground electronic excited state was calculated using DFT, leading to good agreement with the experimental results.

Chen, J., Xin Lan, Zhemping Han, Ce Hao, and Jiemin Qu

Investigations

Relativistic Time-Dependent Density Functional Theory

A NANOPLOASMONIC SWITCH BASED ON MOLECULAR MACHINES

ABSTRACT

Plasmonic devices can be used as the active components in nanoscale molecular machines. The observations suggest that the theory (TD-DFT) is consistent with experimental data. Plasmonic switches are localized surface plasmon resonance (LSPR) devices formed with few-nanometers thick gold layers. The switching is based on the localized plasmon resonance (LSPR) and it has been observed that the plasmonic switches can be used in nanoelectromechanical systems (NEMS) and molecular machines.
First-principles calculation of electronic spectra of light-harvesting Complex II

Carpigni, Bronis and Johannes Neugebaeurer

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Cite this: Phys. Chem. Chem. Phys., 2011, 13, 10475-10490