Time-dependent density functional theory in GPAW

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Introduction

In recent years, the time-dependent density functional theory (TDDFT) has become a popular tool for calculating excited-state properties such as linear and non-linear optical response. The most general realization of the TDDFT is the time-propagation scheme, in which the Kohn-Sham (KS) equations are integrated over the time-domain. In the linear-response regime, the excitation energies can also be calculated in the frequency space by solving a matrix equation in particle-hole basis.

We have implemented the TDDFT using real-space projector-augmented wave (PAW) method into the electronic structure program GPAW. The real-space PAW has several advantages for both ground state and time-dependent calculations: single convergence parameter (grid spacing), different boundary conditions, reduced number of grid points (compared to pseudopotentials), and efficient parallelization using domain decomposition.

Theory

Projector-augmented wave

The projector-augmented wave (PAW) method is an all-electron method, which is computationally comparable to ultrasoft pseudopotentials (USPP). It utilizes non-norm conserving pseudo wavefunctions, which are similar to the ones used in USPPs. However, instead of applying an approximate effective potential, the PAW method applies linear transformations from pseudo space to atomic orbital spaces, $\psi_n(\vec{r}) = \mathcal{T}\tilde{\psi}_n(\vec{r})$, to obtain the exact effective potential for the pseudo wavefunctions

$$\begin{aligned}\hat{H}\psi_n(\vec{r}) &= E\psi_n(\vec{r}) \\ \Longrightarrow \mathcal{T}^\dagger\hat{H}\mathcal{T}\tilde{\psi}_n(\vec{r}) &= E\mathcal{T}^\dagger\mathcal{T}\tilde{\psi}_n(\vec{r} \\ \Longrightarrow \tilde{H}\tilde{\psi}_n(\vec{r}) &= E\tilde{S}\tilde{\psi}_n(\vec{r})\end{aligned}$$

Linear-response

In linear-response scheme by Casida, one solves for the eigenstates of the matrix

$$\Omega_{ij\sigma,pq\tau} = \delta_{ip}\delta_{jq}\delta_{\sigma\tau}\varepsilon_{ij\sigma}^2 + 2\sqrt{f_{ij\sigma}f_{pq\tau}\varepsilon_{ij\sigma}\varepsilon_{pq\tau}}K_{ij\sigma,pq,\tau}$$

where $\varepsilon_{ij\sigma}$ are the KS eigenvalue differences and $f_{ij\sigma}$ are the occupation number differences. The coupling matrix ***K*** consists of the random phase approximation part

$$K^{\mathrm{RPA}}_{ij\sigma,pq,\tau} = \int d\vec{r}_1 d\vec{r}_2 \frac{n^*_{ij\sigma}(\vec{r}_1)n_{pq\tau}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

and the exchange-correlation part

$$K^{\mathrm{xc}}_{ij\sigma,pq,\tau} = \int d\vec{r}_1 d\vec{r}_2 n^*_{ij\sigma}(\vec{r}_1)\frac{\delta^2 E_{\mathrm{xc}}}{\delta_{\rho_\sigma(\vec{r}_1)}\delta_{\rho_\tau(\vec{r}_2)}}n_{pq\tau}(\vec{r}_2)\,.$$

Theory (cont.)

Time-propagation

In the time-propagation scheme, the time-dependent Kohn-Sham equations are transformed to the PAW-space

$$\begin{aligned}i\hbar\frac{\partial\psi_n(\vec{r},t)}{\partial t} &= \hat{H}\psi_n(\vec{r},t) \\ \Longrightarrow i\hbar\tilde{S}\frac{\partial\tilde{\psi}_n(\vec{r},t)}{\partial t} &= \tilde{H}\tilde{\psi}_n(\vec{r},t)\end{aligned}$$

where $\tilde{S} = \mathcal{T}^\dagger\mathcal{T}$ and $\tilde{H} = \mathcal{T}^\dagger\hat{H}\mathcal{T}$, and propagated using the Crank-Nicolson propagator with a predict-correct scheme

$$\begin{aligned}\left(\tilde{S} + i\tilde{H}(t)\Delta t/2\hbar\right)\tilde{\psi}_n^{\mathrm{pred}}(\vec{r},t+\Delta t) &= \\ \left(\tilde{S} - i\tilde{H}(t)\Delta t/2\hbar\right)\tilde{\psi}_n(\vec{r},t) + \mathcal{O}(\Delta t^2)&\end{aligned}$$

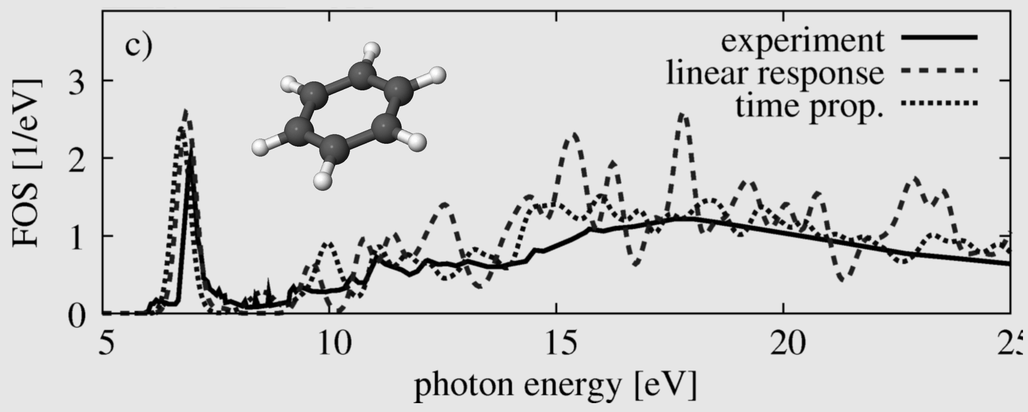
$$\begin{aligned}\left(\tilde{S} + i\tilde{H}(t+\Delta t/2)\Delta t/2\hbar\right)\tilde{\psi}_n^{\mathrm{corr}}(\vec{r},t+\Delta t) &= \\ \left(\tilde{S} - i\tilde{H}(t+\Delta t/2)\Delta t/2\hbar\right)\tilde{\psi}_n(\vec{r},t) + \mathcal{O}(\Delta t^3)&\end{aligned}$$

where the Hamiltonian at the middle of the step is approximated by

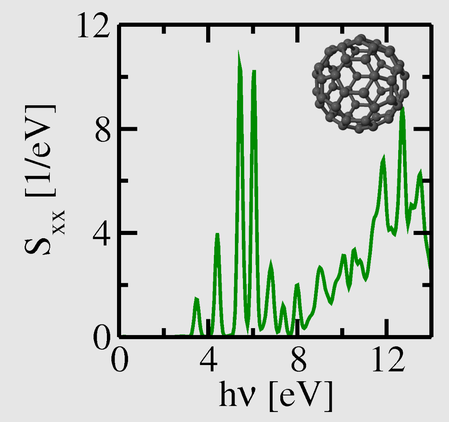
$$\tilde{H}(t+\Delta t/2) = \frac{1}{2}\left(\tilde{H}[\tilde{\psi}_n(\vec{r},t)] + \tilde{H}[\tilde{\psi}_n^{\mathrm{pred}}(\vec{r},t+\Delta t)]\right).$$

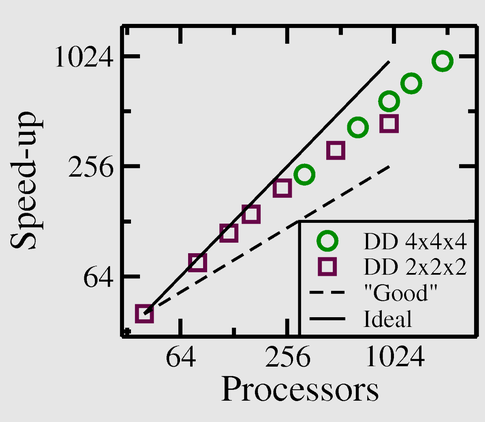
Results and Summary

Simulated linear-response optical absorption spectrum of benzene molecule, C_6H_6:



Simulated linear-response optical absorption spectrum of fullerene molecule, C_{60}, and the parallel scaling of the time-propagation approach in Cray XT4 for fullerene:





Summary

The time-dependent density functional theory implementations in ***GPAW*** provide tools for calculating ***all-electron excited state properties*** within linear and ***nonlinear*** regime with ***excellent parallel scaling***.

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For more infomation about GPAW see: wiki.fysik.dtu.dk/gpaw

For more details about TDDFT in GPAW see: M. Walter, H. Häkkinen, L. Lehtovaara, M. Puska, J. Enkovaara, C. Rostgaard and J. J. Mortensen
Time-dependent density-functional theory in the projector augmented-wave method
Journal of Chemical Physics, Vol. 128, 244101, 2008