**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, to obtain the exact effective potential for the pseudo wavefunctions

\[ \hat{H}_\psi(r) = \hat{E}_\psi(r) \]

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

\[ \Omega_{\sigma\sigma'} = \delta_{\sigma\sigma'} \delta_{\alpha\alpha'} \varepsilon_{\sigma}^2 + 2 \sqrt{\int_{\sigma} \int_{\sigma'} \varepsilon_{\sigma} \varepsilon_{\sigma'} K_{\sigma\sigma'}(r_1, r_2) } \]

where \( \varepsilon_{\sigma} \) are the KS eigenvalue differences and \( r_1, r_2 \) are the occupation number differences. The coupling matrix \( K \) consists of the random phase approximation part

\[ K^{\text{RPA}}_{\sigma\sigma'}(r_1, r_2) = \int d\tilde{r}_1 d\tilde{r}_2 n_{\sigma}(\tilde{r}_1) n_{\sigma'}(\tilde{r}_2) \]

and the exchange-correlation part

\[ K^{\text{xc}}_{\sigma\sigma'}(r_1, r_2) = \int d\tilde{r}_1 d\tilde{r}_2 n_{\sigma}(\tilde{r}_1) \frac{\delta^2 E_{\text{xc}}}{\delta n_{\sigma}(r_1) \delta n_{\sigma'}(r_2)} n_{\sigma'}(\tilde{r}_2). \]

**Results and Summary**

Simulated linear-response optical absorption spectrum of benzene molecule, \( \text{C}_6\text{H}_6 \):

Simulated linear-response optical absorption spectrum of fullerene molecule, \( \text{C}_{60} \), 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.