Introduction to Octopus:
Optical properties of finite systems

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Electronic response of finite systems to external fields

The dynamical polarizability is the ratio of the induced dipole moment to the perturbing electric field:

\[ \alpha(\omega) = \frac{\delta p(\omega)}{E(\omega)} = \frac{1}{E(\omega)} \int d\mathbf{r} \, \mathbf{r} \, \delta n(\mathbf{r}, \omega) \]

\( \alpha(\omega) \) is related to the optical absorption cross-section:

\[ \sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \{ \text{Tr} [\alpha(\omega)] \} \]
Real-time TDDFT

The dynamical polarizability can be computed by solving directly the time-dependent Kohn-Sham equations:

- Take the DFT ground state wavefunctions $\varphi_i(r)$.
- Excite all the frequencies of the system by applying the appropriate instantaneous perturbation $\delta v(r, t) = -E x_j \delta(t)$.
- Use TDDFT to propagate the wavefunctions in time:

$$
\varphi_i(r, t + \Delta t) = \hat{T} \exp \left\{ -i \int_t^{t+\Delta t} dt \hat{H}_{KS} \varphi_i(r, t) \right\}
$$

and keep track of the density $n(r, t)$.
- Compute the polarizability $\alpha_{ij}(\omega) = \frac{1}{E(\omega)} \int d\mathbf{r} \, x_i \delta n(\mathbf{r}, \omega)$. 
Casida equations:

- Pseudo-eigenvalue equation of the form:

\[ \hat{R} F_q = \Omega_q^2 F_q \]

- Eigenvalues $\Omega_q^2$ are the square of the excitation energies
- Eigenvectors are related to the oscillator strengths
- $\hat{R}$ is a matrix that involves pairs of occupied and unoccupied KS states
Sternheimer equations:

- Relies on the calculation of the first order variations of the KS wavefunctions $\psi'_m(r, \pm \omega)$
- Equations have the following form

\[
\left[ \hat{H}_{KS} - \epsilon_m \pm \omega + i\eta \right] \psi'_{m,i}(r, \pm \omega) = -\hat{P}_c \hat{H}'(\pm \omega) \psi_m(r),
\]

- $\hat{H}'$ is the first order variation of the Kohn-Sham Hamiltonian:

\[
\hat{H}'(\omega) = x_i + \int dr' \frac{\delta n_i(r', \omega)}{|r - r'|} + \int dr' f_{xc}(r, r', \omega) \delta n_i(r', \omega).
\]
Pros and cons

Real time propagation

Pros

- Favourable scaling with system size
- Does not require the calculation of empty states
- Easy to extend to other perturbations/responses
- Allows to go beyond linear-response
- Only requires knowledge of $v_{xc}$

Cons

- Slow for small systems
Pros and cons

Casida equations

Pros
- Fast for small systems

Cons
- Requires calculation of empty states
- Requires computation of large matrices
- Unfavourable scaling with system size
Pros and cons

Sternheimer equations

Pros

- Favourable scaling with system size
- Does not require the calculation of empty states
- Allows to go beyond linear-response

Cons

- Equations needs to be solved one frequency at a time
You can find the tutorials under this link: https://octopus-code.org/wiki/Tutorials

Optical response series:

- Lesson 1: Optical spectra from time-propagation
- Lesson 2: Convergence of the optical spectra
- Lesson 3: Optical spectra from Casida
- Lesson 4: Optical spectra from Sternheimer
- Lesson 5: Triplet excitations
- Lesson 6: Use of symmetries in optical spectra from time-propagation
The tutorials

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Have Fun!