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:

$$\alpha(\omega) = \frac{\delta \boldsymbol{p}(\omega)}{\boldsymbol{E}(\omega)} = \frac{1}{\boldsymbol{E}(\omega)} \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{r}\, \delta n(\boldsymbol{r}, \omega)$$

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

$$\sigma(\omega) = \frac{4\pi\omega}{c} \mathfrak{Im} \left\{ \mathrm{Tr} \left[\alpha(\omega) \right] \right\}$$

Real-time TDDFT

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

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

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

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

Other methods implemented in Octopus

Casida equations:

- Pseudo-eigenvalue equation of the form:

$$\hat{R}F_q = \Omega_q^2 F_q$$

- Eigenvalues Ω_q^2 are the square of the excitation energies
- Eigenvectors are related to the oscilator strenghts
- $\hat{R}$ is a matrix that involves pairs of occupied and unoccupied KS states

Other methods implemented in Octopus

Sternheimer equations:

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

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

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

$$\hat{H}'(\omega) = x_i + \int \mathrm{d}\boldsymbol{r}' \, \frac{\delta n_i(\boldsymbol{r}', \omega)}{|\boldsymbol{r} - \boldsymbol{r}'|} + \int \mathrm{d}\boldsymbol{r}' \, f_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \omega)\delta n_i(\boldsymbol{r}', \omega) \,.$$

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

The tutorials

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 !