

# 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:

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

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

$$\sigma(\omega) = \frac{4\pi\omega}{c} \Im \{ \text{Tr} [\alpha(\omega)] \}$$

# Real-time TDDFT

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

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

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

and keep track of the density  $n(\mathbf{r}, t)$ .

- Compute the polarizability  $\alpha_{ij}(\omega) = \frac{1}{E(\omega)} \int d\mathbf{r} x_i \delta n_j(\mathbf{r}, \omega)$ .

## Other methods implemented in Octopus

Casida equations:

- Pseudo-eigenvalue equation of the form:

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

- Eigenvalues  $\Omega_q^2$  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

# Other methods implemented in Octopus

Sternheimer equations:

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

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

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

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

## 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

## Casida equations

### Pros

- Fast for small systems

### Cons

- Requires calculation of empty states
- Requires computation of large matrices
- Unfavourable scaling with system size

## 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/documentation/13/tutorial/>

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

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**Have Fun !**

