TDDFT in linear response

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- Different theoretical approach

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- Different (easier) theoretical approach

TDDFT in linear response

- Different (easier) theoretical approach
- Practical scheme for spectroscopy and excitation energies

$$v_{ext}(\mathbf{r},t) = v_{ext}(\mathbf{r},0) + \delta v_{ext}(\mathbf{r},t)$$

$$n(\mathbf{r},t) = n(\mathbf{r},0) + \delta n(\mathbf{r},t) + \delta^{(2)} n(\mathbf{r},t) + ...$$

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$$\delta n(\mathbf{r},t) \longleftrightarrow \delta v_{ext}(\mathbf{r}',t')$$

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$$\delta n(\mathbf{r},t) = \int d\mathbf{r}' dt' \, \chi(\mathbf{r},\mathbf{r}',t-t') \delta v_{ext}(\mathbf{r}',t')$$

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polarizability

polarizability :: density-density response function

$$\chi(\mathbf{r},\mathbf{r}',t-t') = i\,\langle\Psi_0|[\hat{n}(\mathbf{r},t),\hat{n}(\mathbf{r}',t')]|\Psi_0\rangle$$

$$\hat{n}(\mathbf{r},t) = e^{iHt}\hat{n}(\mathbf{r})e^{-iHt} \qquad \hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$$

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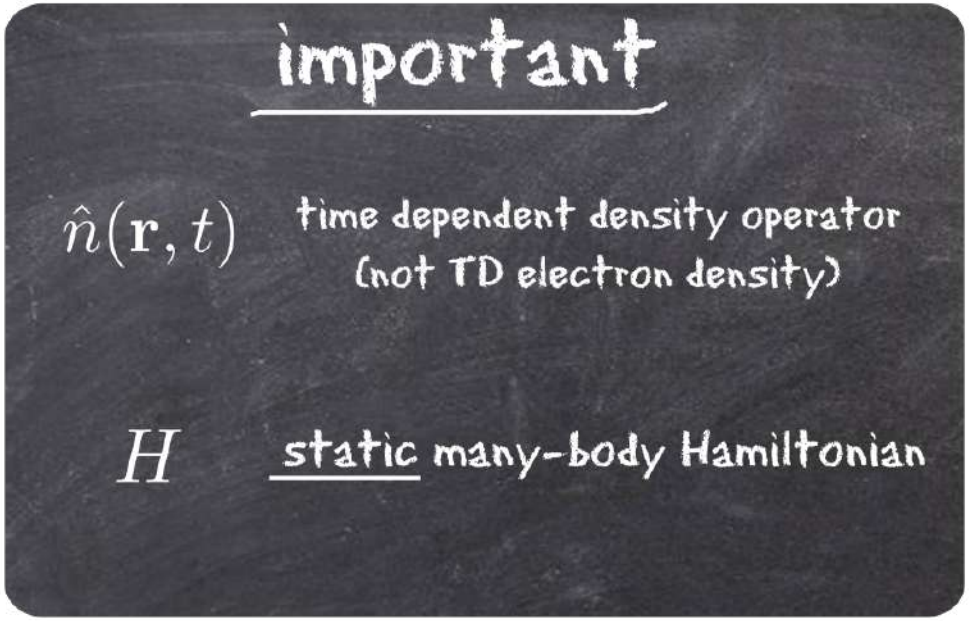

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Exercise

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \left[\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_I\rangle\,\langle\Psi_I|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - \underbrace{(E_I - E_0)}_{\Omega_I} + i0^+} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_I\rangle\,\langle\Psi_I|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega + (E_I - E_0) + i0^+} \right]$$

Ω_I excitations energies

polarizability :: density-density response function

$$\chi(\mathbf{r},\mathbf{r}',t-t') = i\,\langle\Psi_0|[\hat{n}(\mathbf{r},t)$$

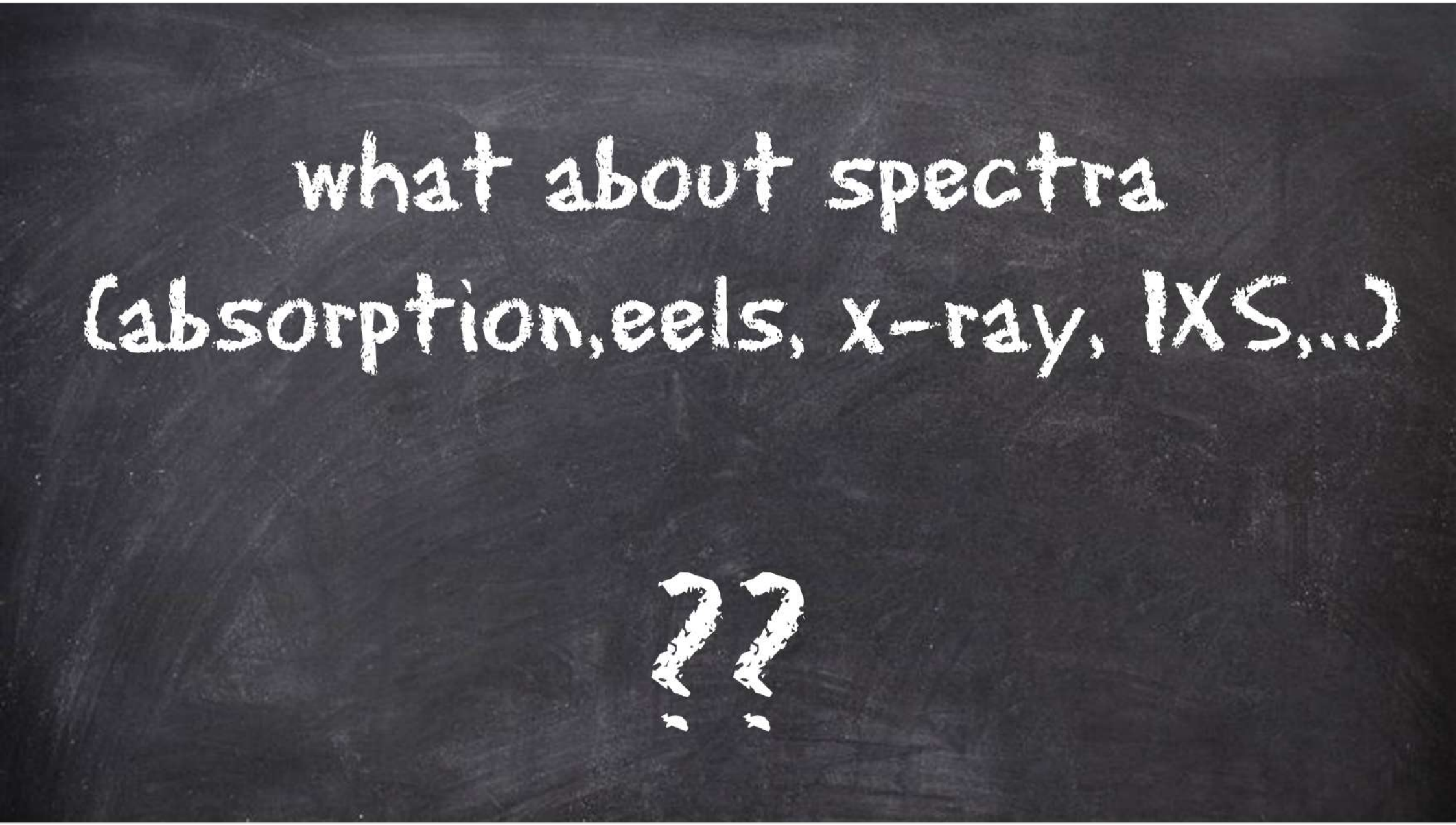
χ contains (poles) the excitation energies

$$\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$$

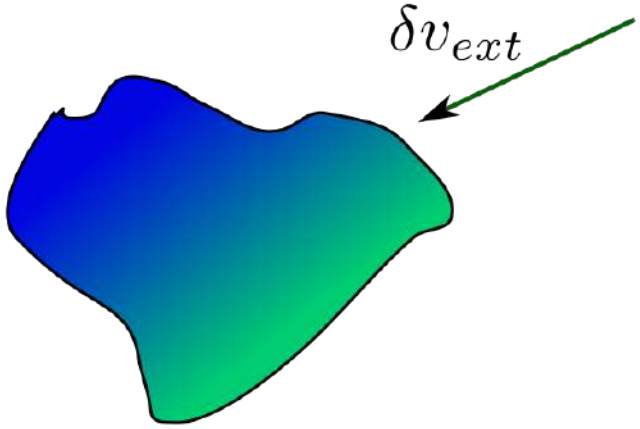
Exercise

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \left[\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_I\rangle\,\langle\Psi_I|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - \underbrace{(E_I - E_0)}_{\Omega_I} + i0^+} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_I\rangle\,\langle\Psi_I|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega + (E_I - E_0) + i0^+} \right]$$

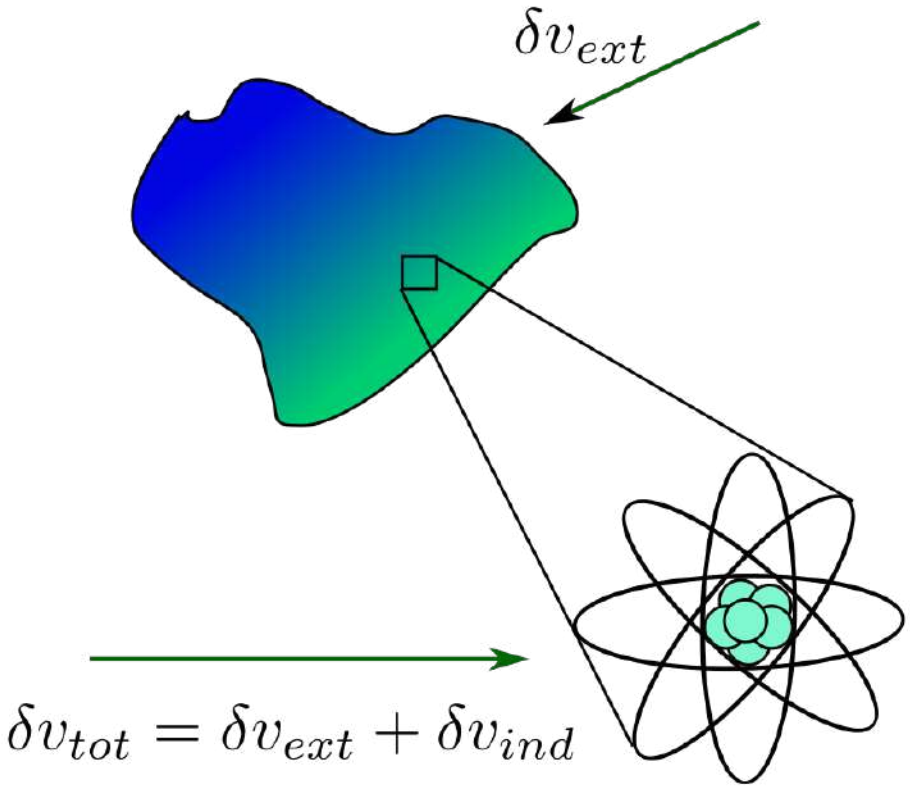
Ω_I excitations energies


what about spectra
(absorption, eels, x-ray, IXS,...)
??

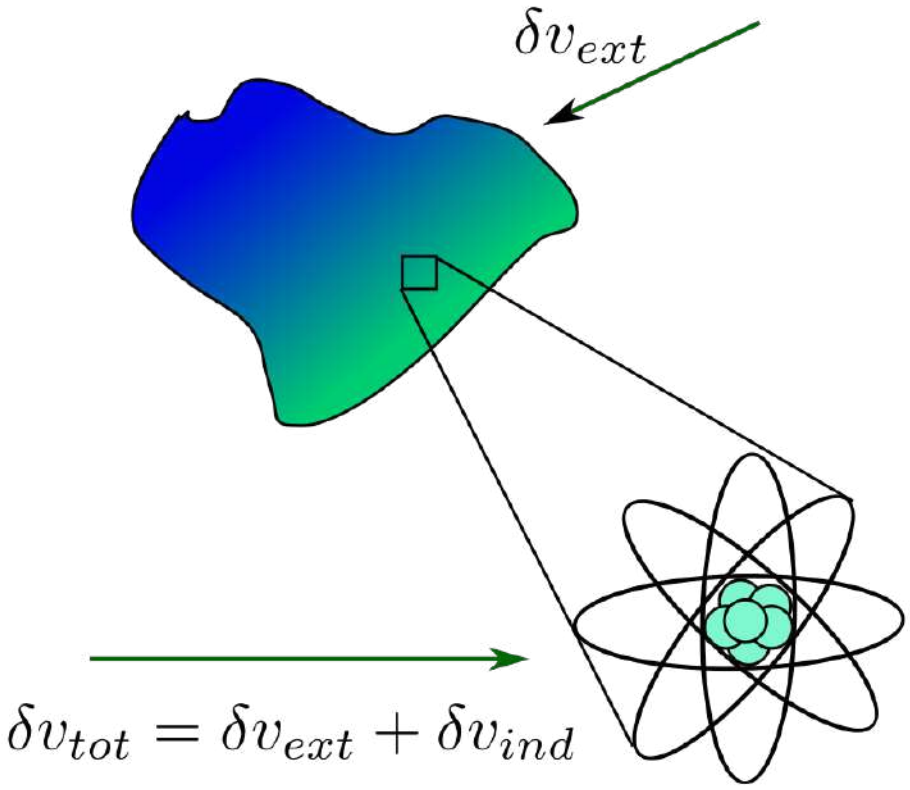
Connection to spectroscopies :: inverse dielectric function



Connection to spectroscopies :: inverse dielectric function



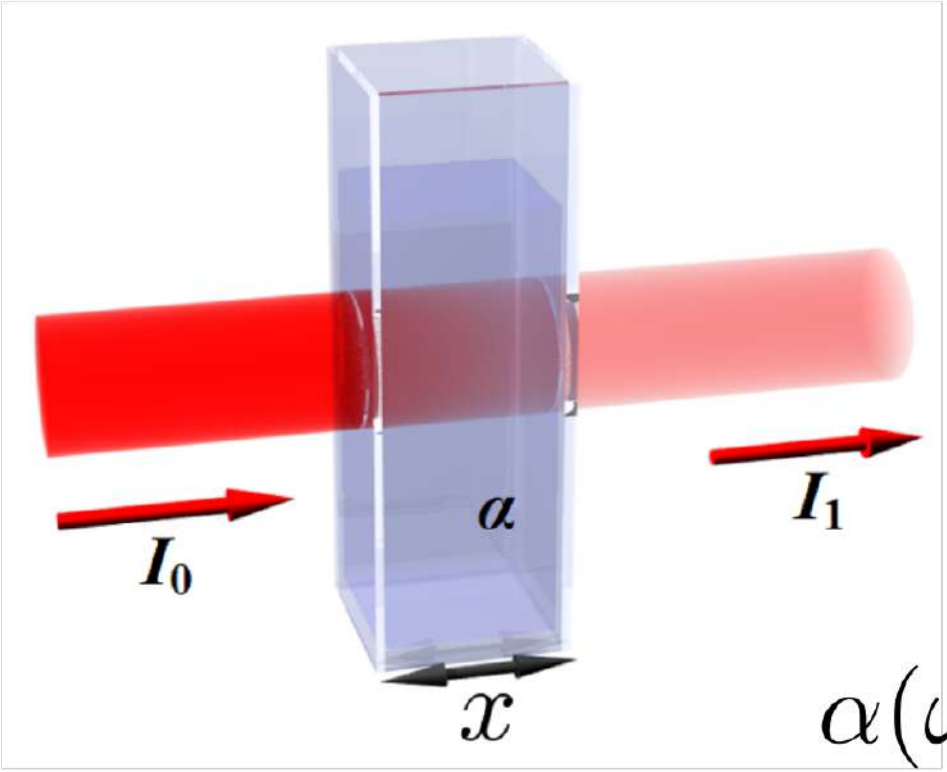
Connection to spectroscopies :: inverse dielectric function



$$\delta v_{tot} = \varepsilon^{-1} \delta v_{ext}$$

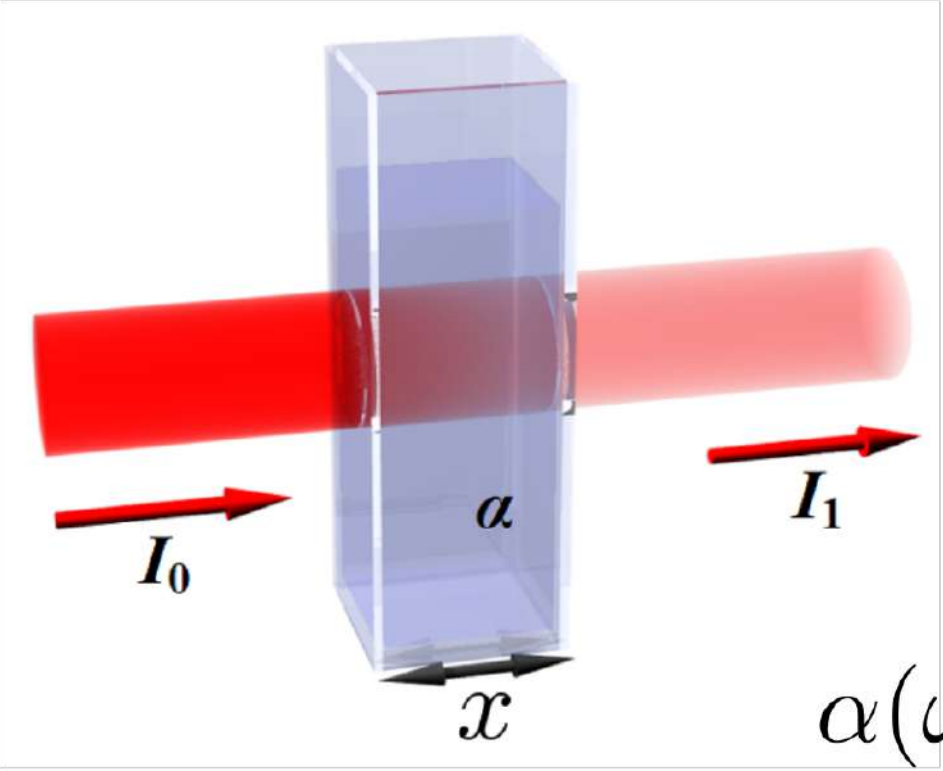
ε dielectric function

Connection to spectroscopies :: optical absorption



$$\alpha(\omega) = \mathrm{Im}\left[\varepsilon_M(\omega)\right]$$

Connection to spectroscopies :: optical and X-ray absorption



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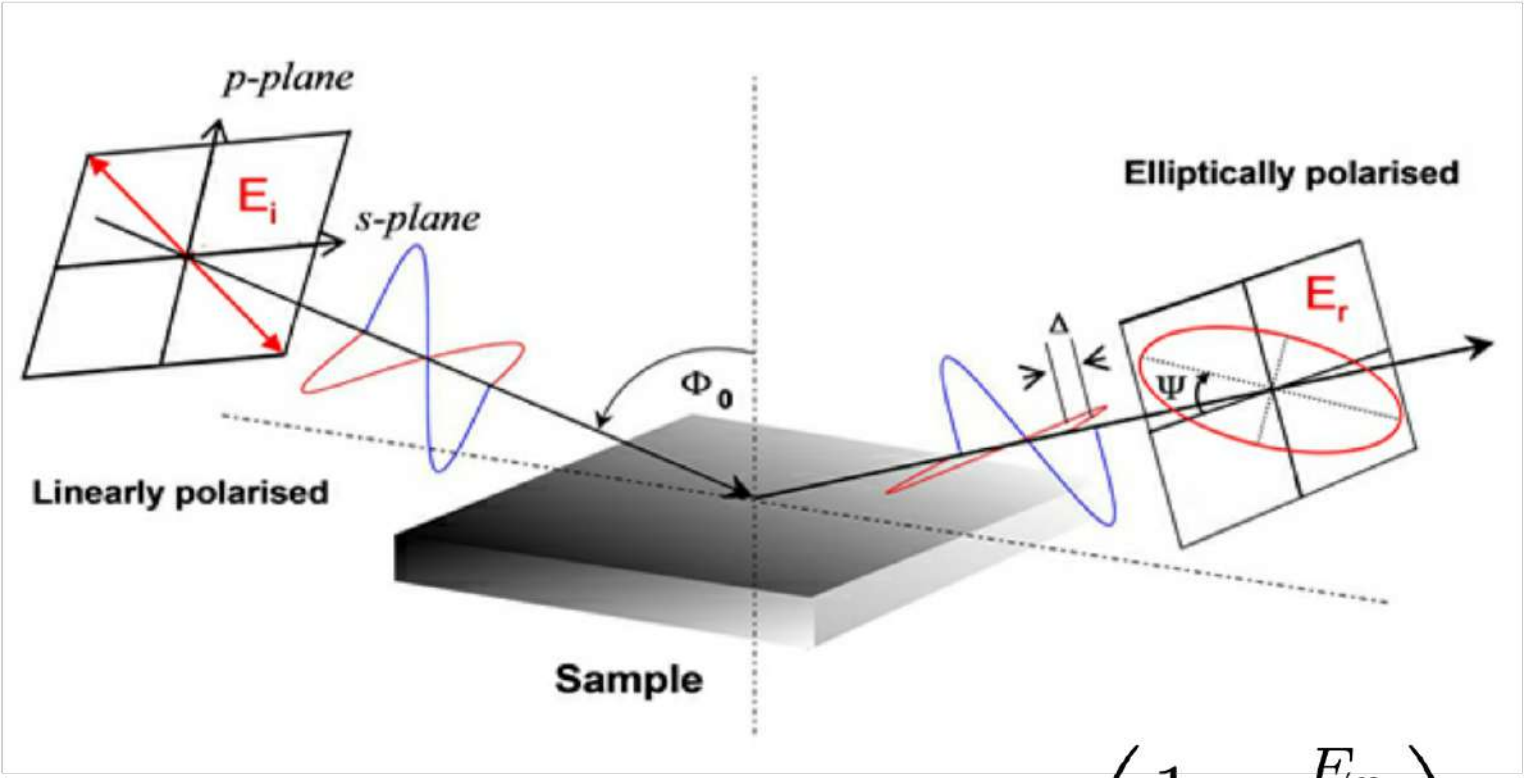
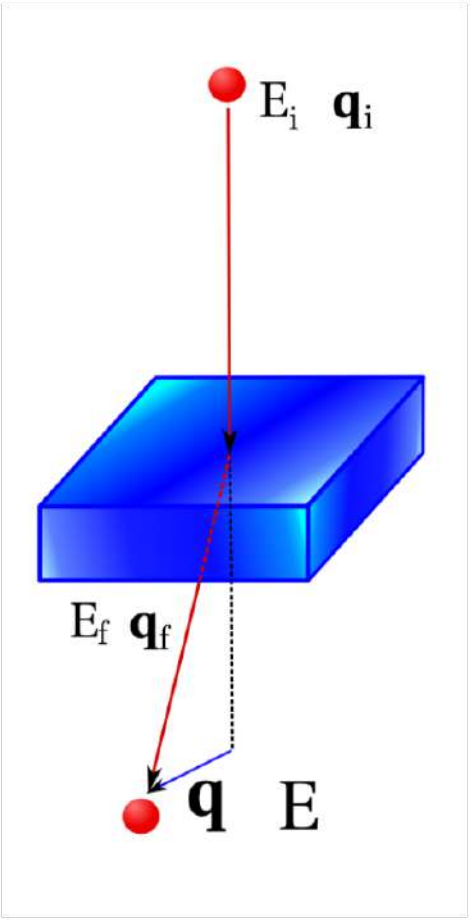
Connection to spectroscopies :: optical absorption



$$\varepsilon_M = \sin^2\Phi + \sin^2\Phi\tan^2\Phi\left(\frac{1-\frac{E_r}{E_i}}{1+\frac{E_r}{E_i}}\right)$$

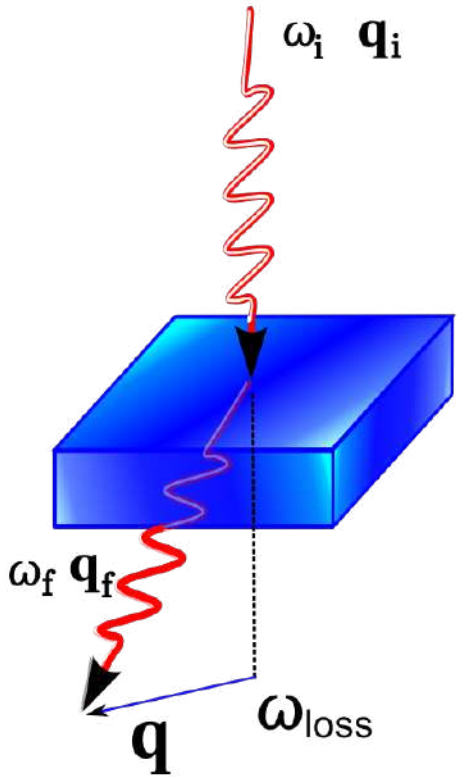
Connection to spectroscopies :: electron energy loss (EELS)

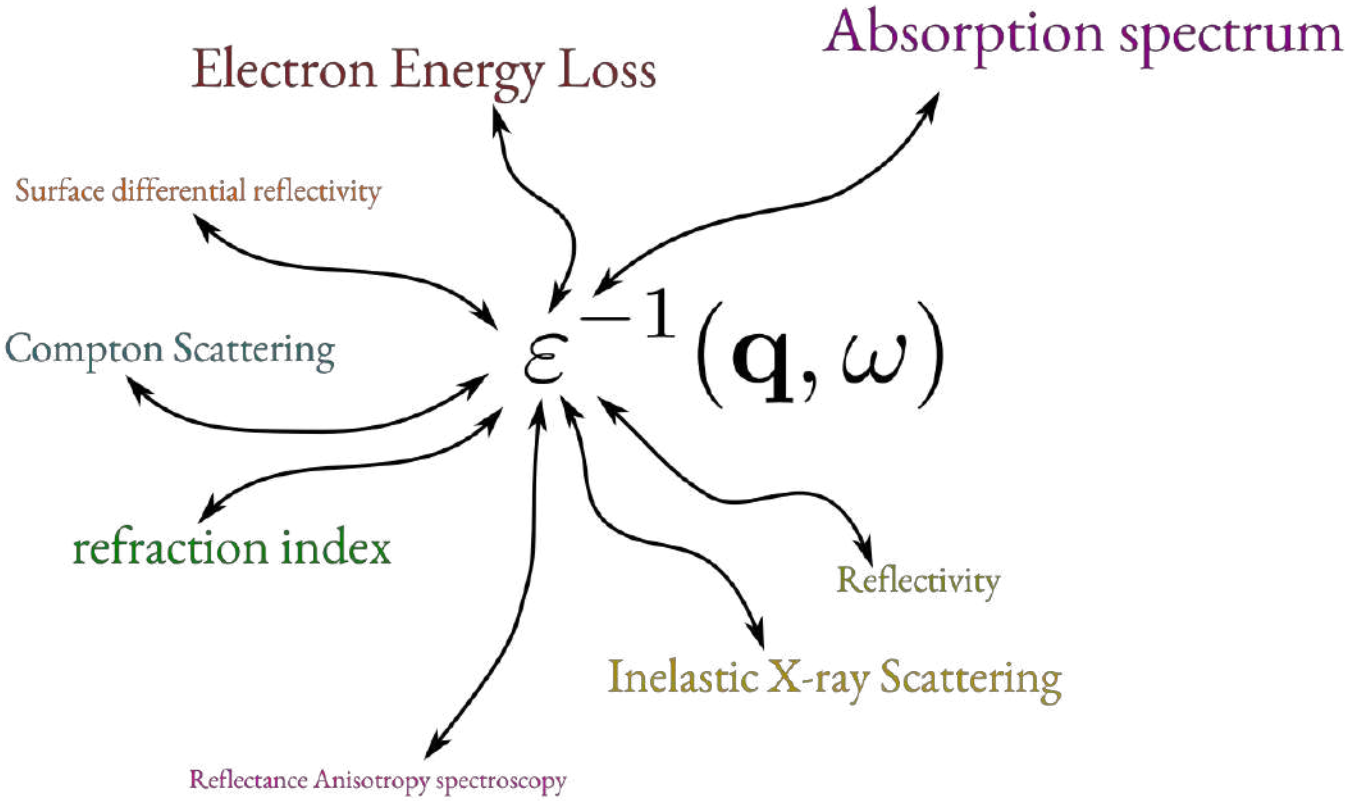
$$\frac{d^2\sigma}{d\Omega d\omega} \propto \mathrm{Im}\left[\varepsilon^{-1}(\mathbf{q},\omega)\right]$$

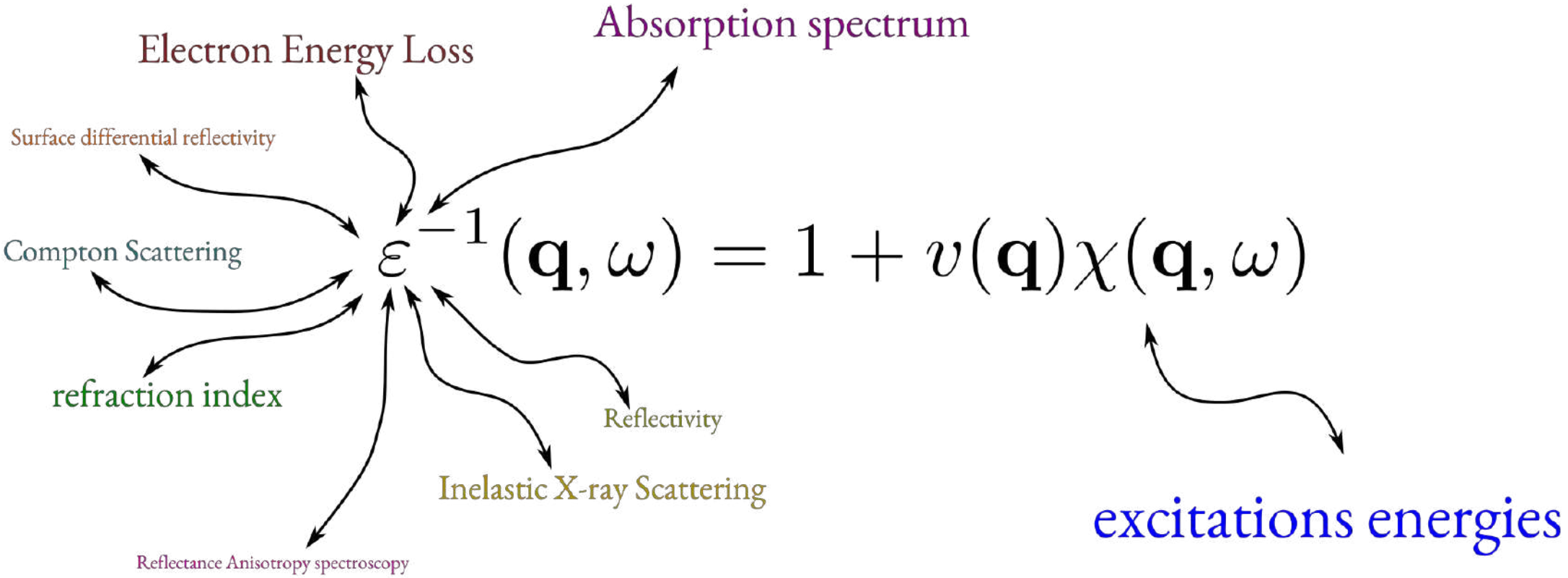


Connection to spectroscopies :: inelastic X-ray scattering (IXS)

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \mathrm{Im}\left[\varepsilon^{-1}(\mathbf{q},\omega)\right]$$




Absorption spectrum
Electron Energy Loss
Surface differential reflectivity
$\varepsilon^{-1}(\mathbf{q},\omega)$
Compton Scattering
refraction index
Reflectivity
Inelastic X-ray Scattering
Reflectance Anisotropy spectroscopy


Electron Energy Loss
Absorption spectrum
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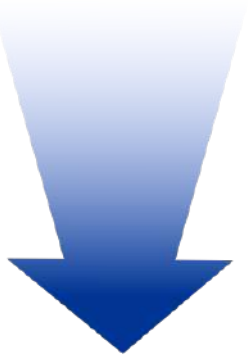
$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v(\mathbf{q})\chi(\mathbf{q},\omega)$
excitations energies

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \left[\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - (E_I - E_0) + i0^+} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega + (E_I - E_0) + i0^+} \right]$$

Polarizability of an independent-particle system

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \left[\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - (E_I - E_0) + i0^+} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega + (E_I - E_0) + i0^+} \right]$$

Ψ_0  single determinant

Polarizability of an independent-particle system

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Ψ_0 single determinant

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{ij} (f_i - f_j) \left[\frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i0^+} - \frac{\psi_i(\mathbf{r})\psi_j^*(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{\omega + (\epsilon_j - \epsilon_i) + i0^+} \right]$$

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Ψ_0 single determinant

Exercise

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$$\delta n = \chi \delta v_{ext}$$

$$\delta n = \chi^0 \delta v_{eff} \qquad \delta n = \chi \delta v_{ext}$$

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$$\chi \delta v_{ext} \overset{\text{DFT}}{=} \chi^0 \delta v_{eff}$$

$$\delta v_{eff} = \delta v_{ext} + \delta v_H + \delta v_{xc}$$

Dyson equation for the polarizability

$$\chi = \chi^0 + \chi^0 \left[v + f_{xc} \right] \chi$$

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$$f_{xc} = \frac{\delta v_{xc}}{\delta n}$$ exchange-correlation kernel

- evaluation of χ knowing (χ^0 ground state calculation)
- f_{xc} functional of the ground-state density
- approximations for f_{xc}

  - $f_{xc} = 0$ RPA
  - $f_{xc} = \dfrac{\delta v_{xc}^{gs}}{\delta n}$
  - any other f_{xc}

  } *coherence vs freedom*

Practical procedure for χ and ε^{-1}

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- DFT-KS calculation ψ_i, ϵ_i (approx ::)v_{xc}, V_{ion}^{ps}

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- evaluation of $\varepsilon^{-1} = 1 + v\chi$

Absorption spectrum Inelastic X-ray Scattering refraction index Surface differential reflectivity
Compton Scattering Reflectivity Electron Energy Loss Reflectance Anisotropy spectroscopy

Practical procedure for χ and ε^{-1}

Scaling (with N_{atoms})

- DFT-KS calculation ψ_i, ϵ_i (approx ::)v_{xc}, V_{ion}^{ps} — $o(N^{1\div 3})$
- creation of $\chi^0 = \sum_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i0^+}$ — $o(N^4)$
- determination of $\chi = \chi^0 + \chi^0 \left[v + f_{xc}\right] \chi$ (approx ::)f_{xc} — $o(N^{2\div 3})$
- evaluation of $\varepsilon^{-1} = 1 + v\chi$

Absorption spectrum Inelastic X-ray Scattering refraction index Surface differential reflectivity
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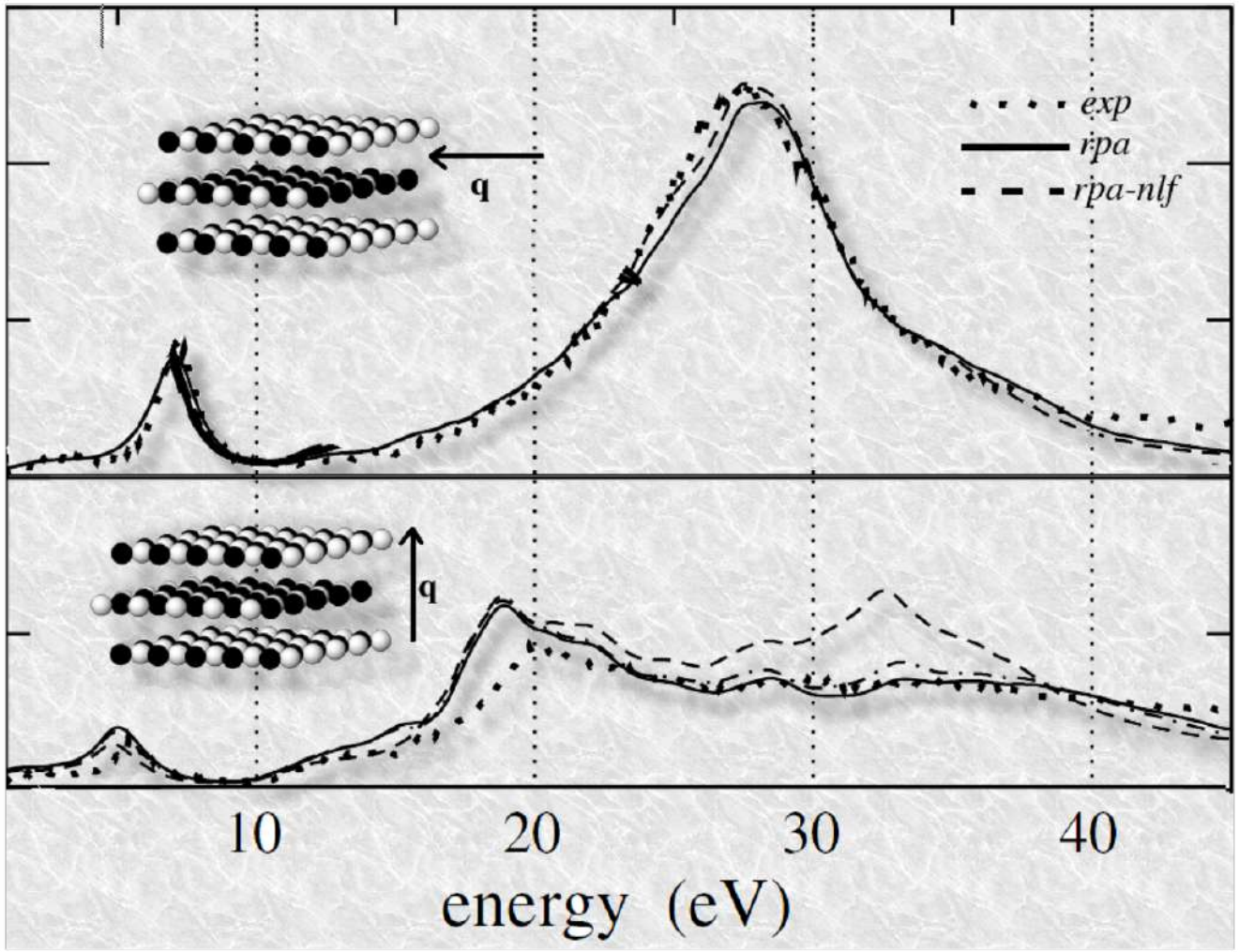
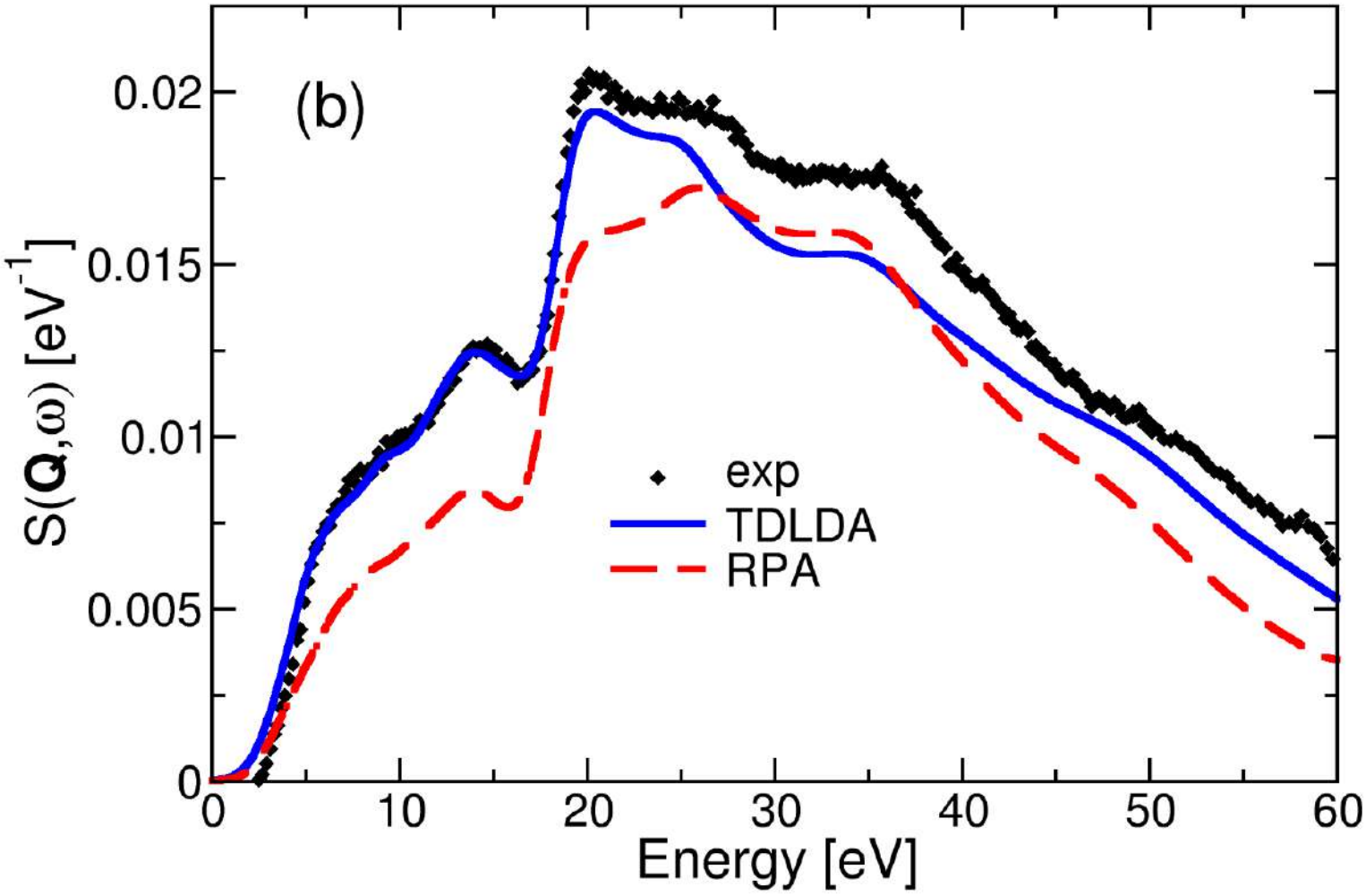
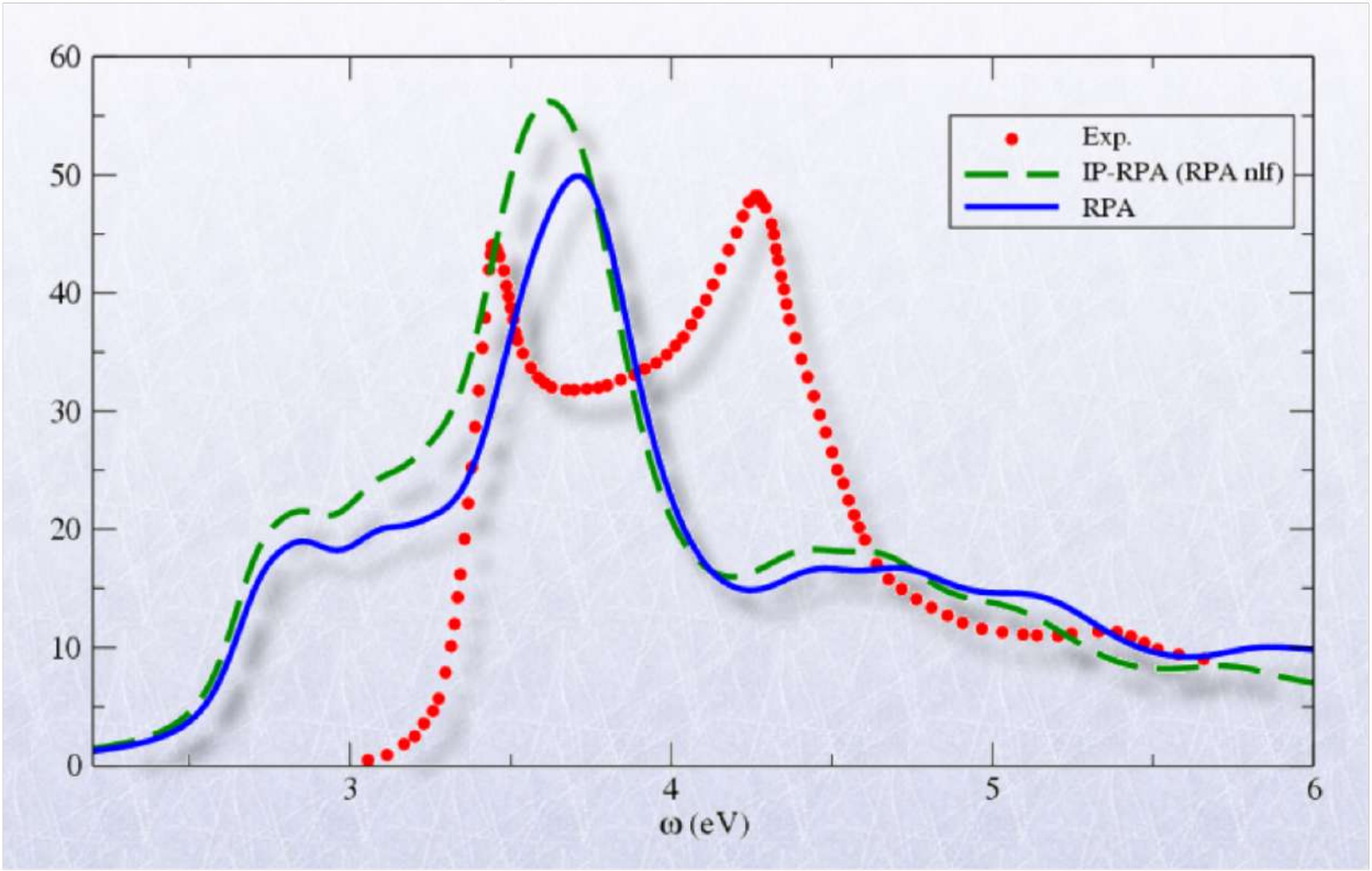
EELS of graphite



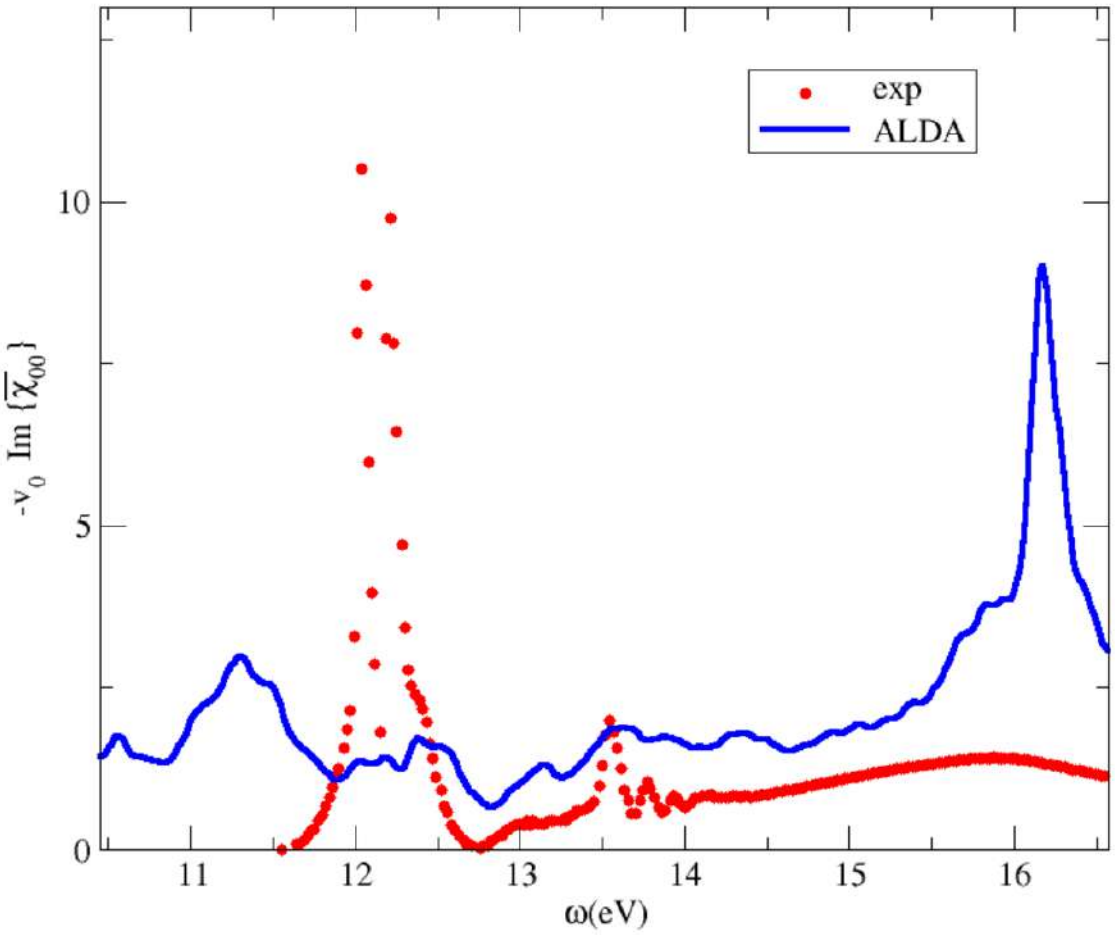
IXS of Silicon



Absorption of Silicon



Absorption of Argon



- Absorption of simple molecules
- EELS and IXS of solids
- Absorption of solids

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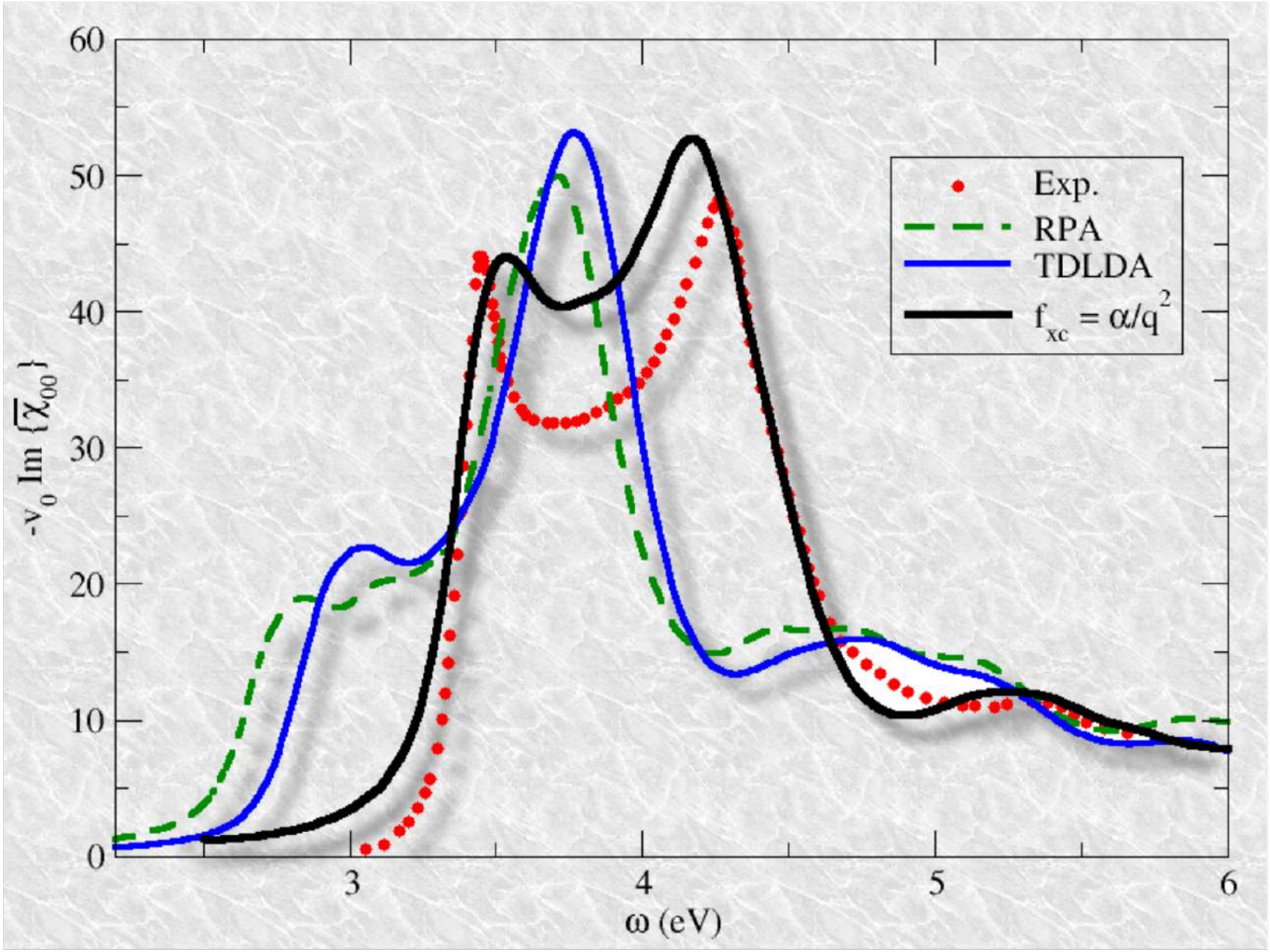
- Absorption of solids

- $f_{xc} = 0$
- $f_{xc} = \dfrac{\delta v_{xc}^{lda}}{\delta n}$
- $f_{xc} = \dfrac{\delta v_{xc}^{gga}}{\delta n}$

$$f_{xc}(\mathbf{q} \to 0) \neq \frac{1}{\mathbf{q}^2}$$

$$f_{xc}(|\mathbf{r} - \mathbf{r}'| = r \to \infty) \neq \frac{1}{r}$$


60
50
40
30
20
10
0
3
4
5
6
ω (eV)
-v0 Im {χ̄00}
Exp.
RPA
TDLDA
fxc = α/q2

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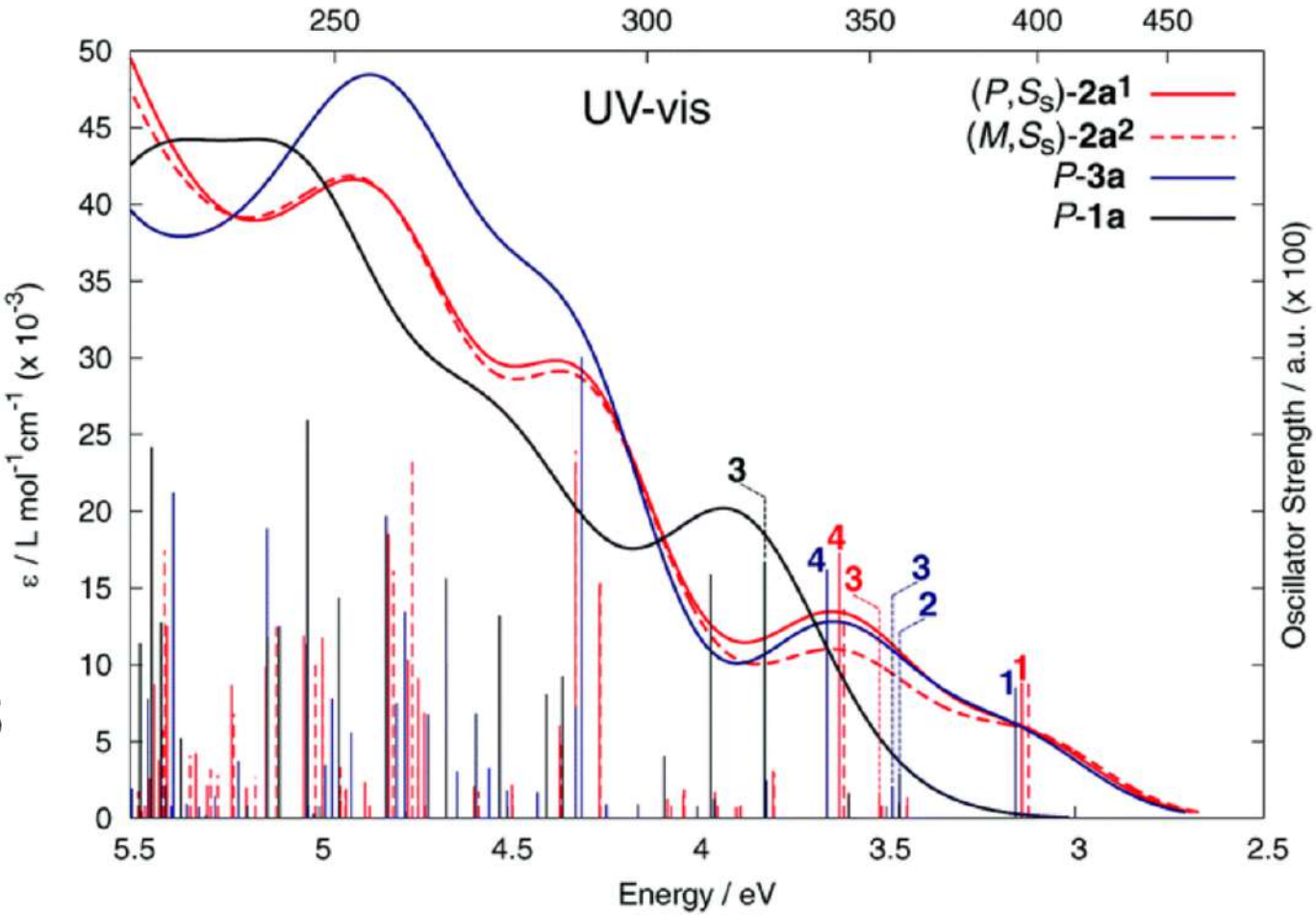
Absorption of cycloplatinated helicenes

excitations energies

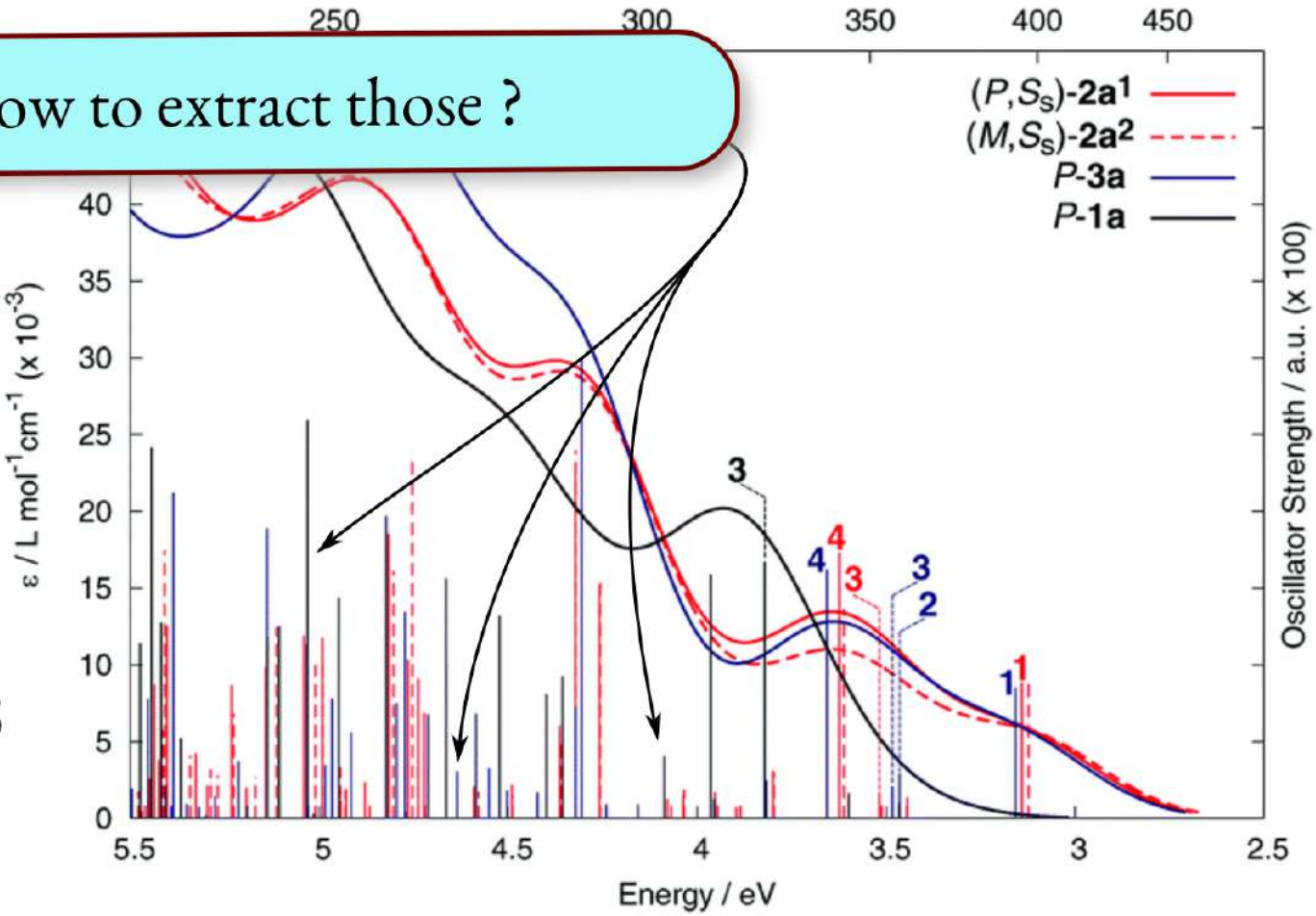


Shen *et al.* Chem. Sci. **5**, 1915 (2014)

Absorption of cycloplatinated helicenes

how to extract those ?

excitations energies



Shen *et al.* Chem. Sci. **5**, 1915 (2014)

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) +$$

$$+ \int d\mathbf{r}_1 d\mathbf{r}_2 \chi^0(\mathbf{r},\mathbf{r}_1,\omega)\left[v(\mathbf{r}_1,\mathbf{r}_2) + f_{xc}(\mathbf{r}_1,\mathbf{r}_2,\omega)\right]\chi(\mathbf{r}_2,\mathbf{r}',\omega)$$

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change of basis

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change of basis

$$f_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_k(\mathbf{r}')\psi_l^*(\mathbf{r}')\, f(\mathbf{r},\mathbf{r}')\; d\mathbf{r}d\mathbf{r}'$$

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$$\chi_{ij}^{kl} = \left[\chi^0\right]_{ij}^{kl} + \sum_{mnop} \left[\chi^0\right]_{ij}^{mn} \left[v_{mn}^{op} + \left[f_{xc}\right]_{mn}^{op}\right]\chi_{op}^{kl}$$

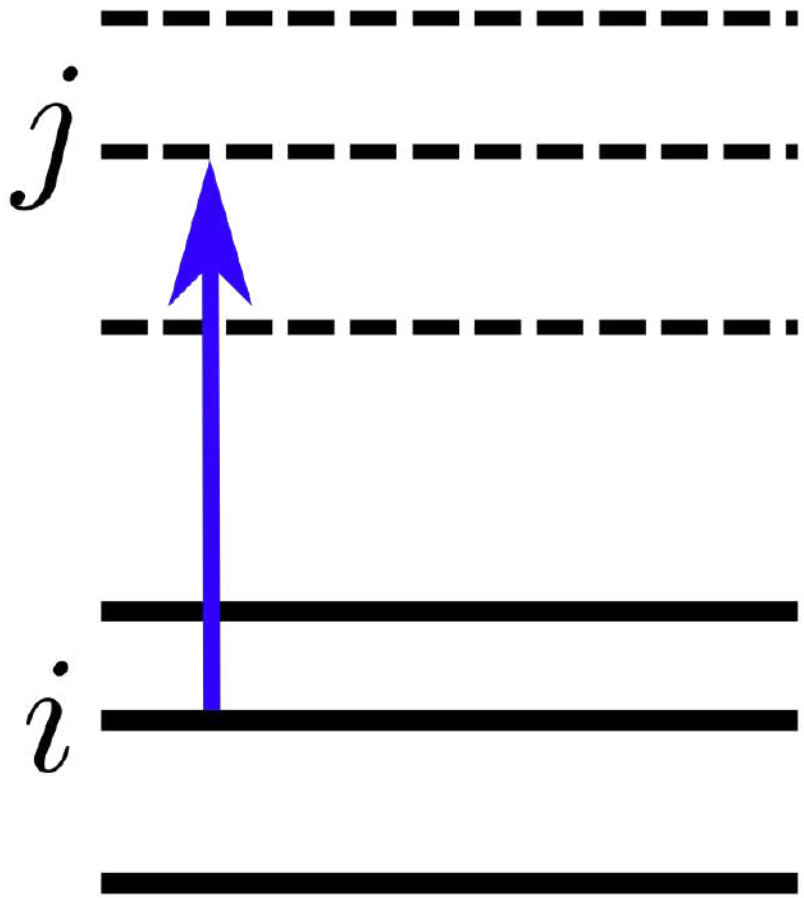
choose $\psi_i(\mathbf{r})$

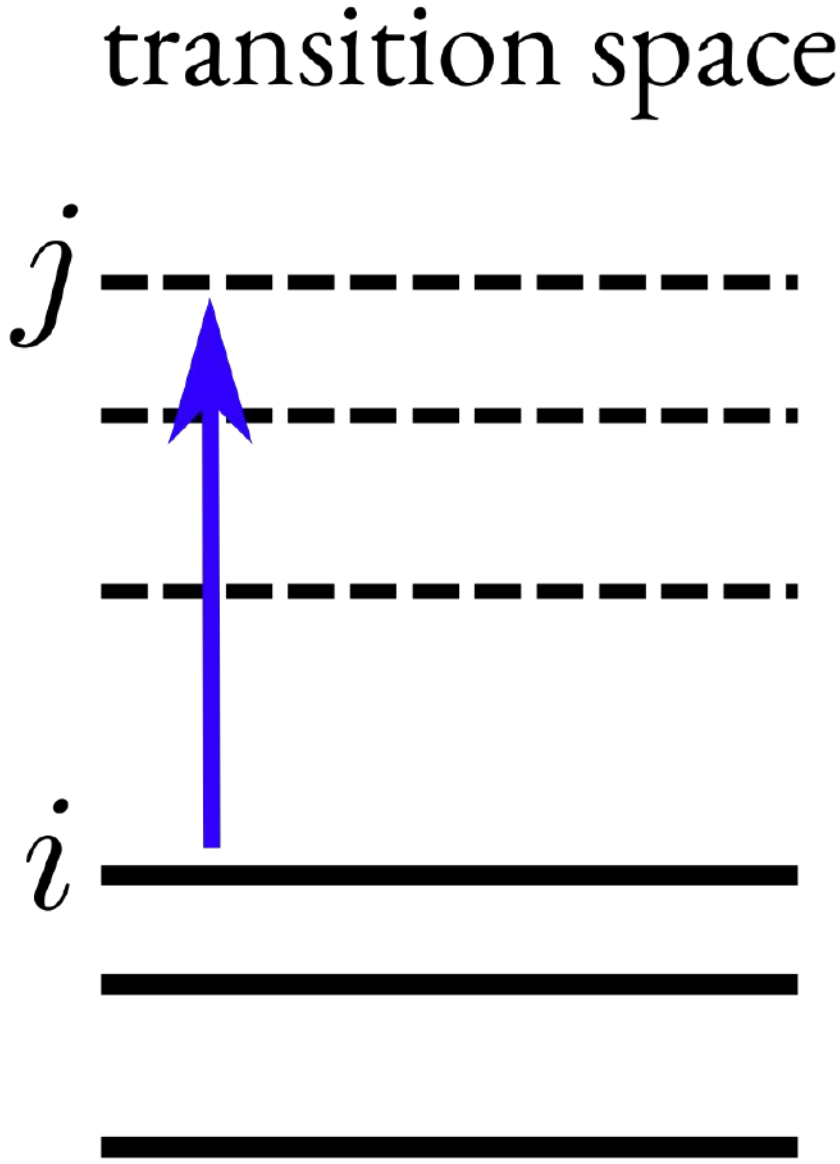
choose $\psi_i(\mathbf{r})$

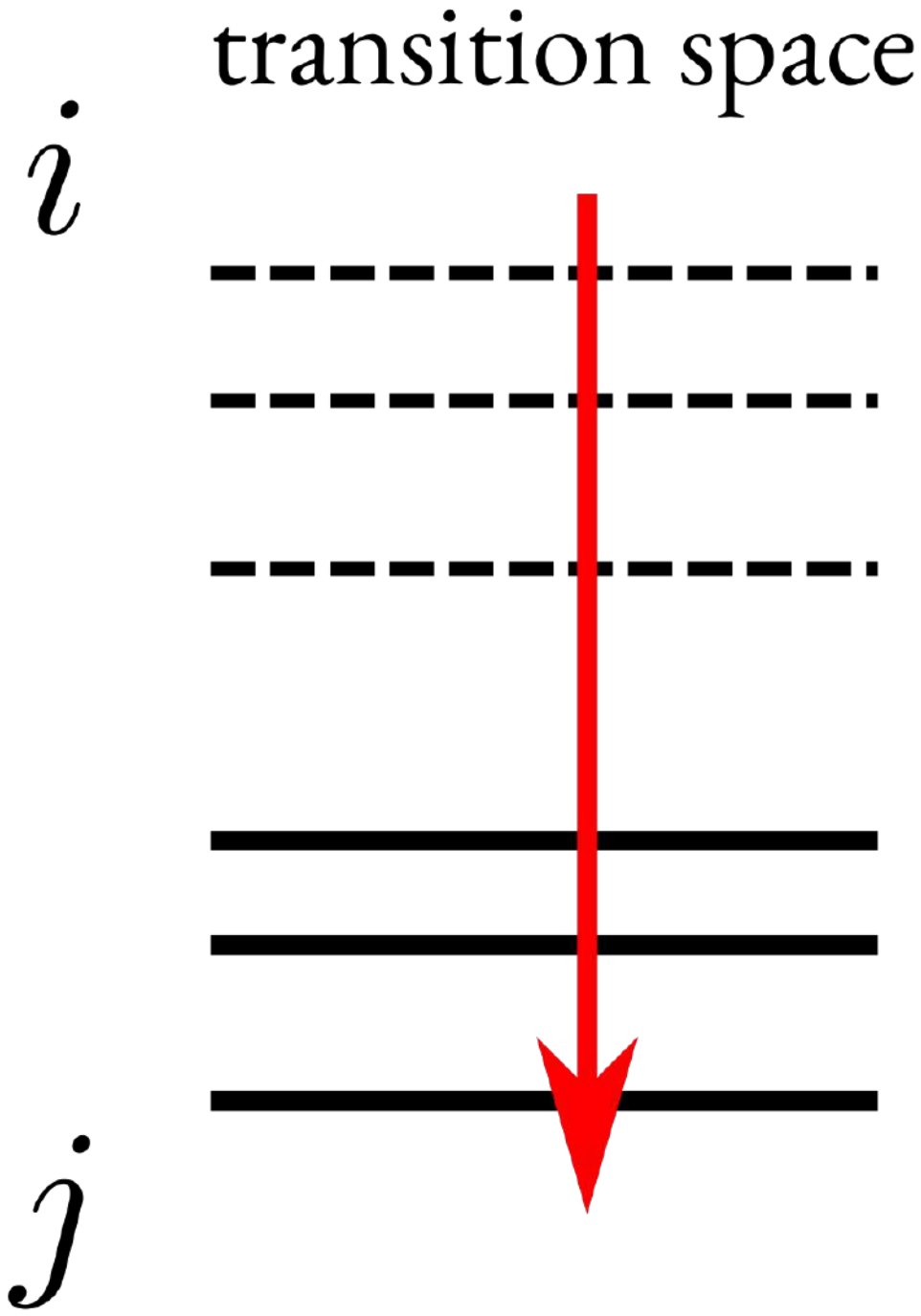
$$\left[\chi^0\right]_{ij}^{kl} = \frac{(f_i - f_j)\delta_{ik}\delta_{jl}}{\omega - (\epsilon_j - \epsilon_i)}$$

diagonal in ij, kl

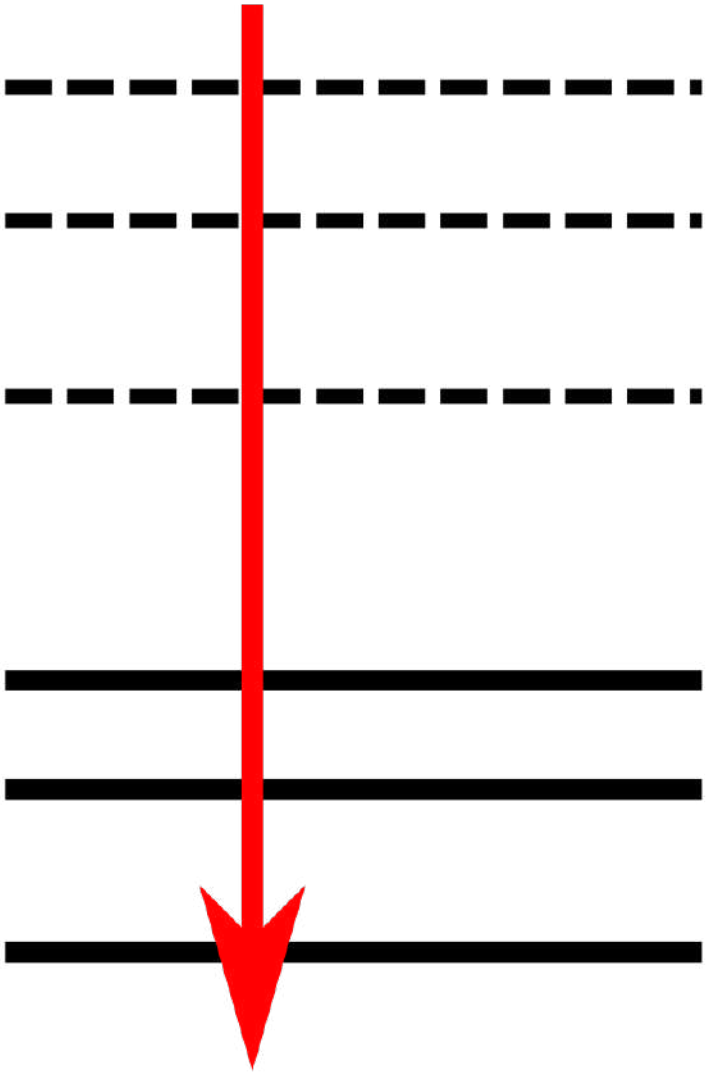
transition space

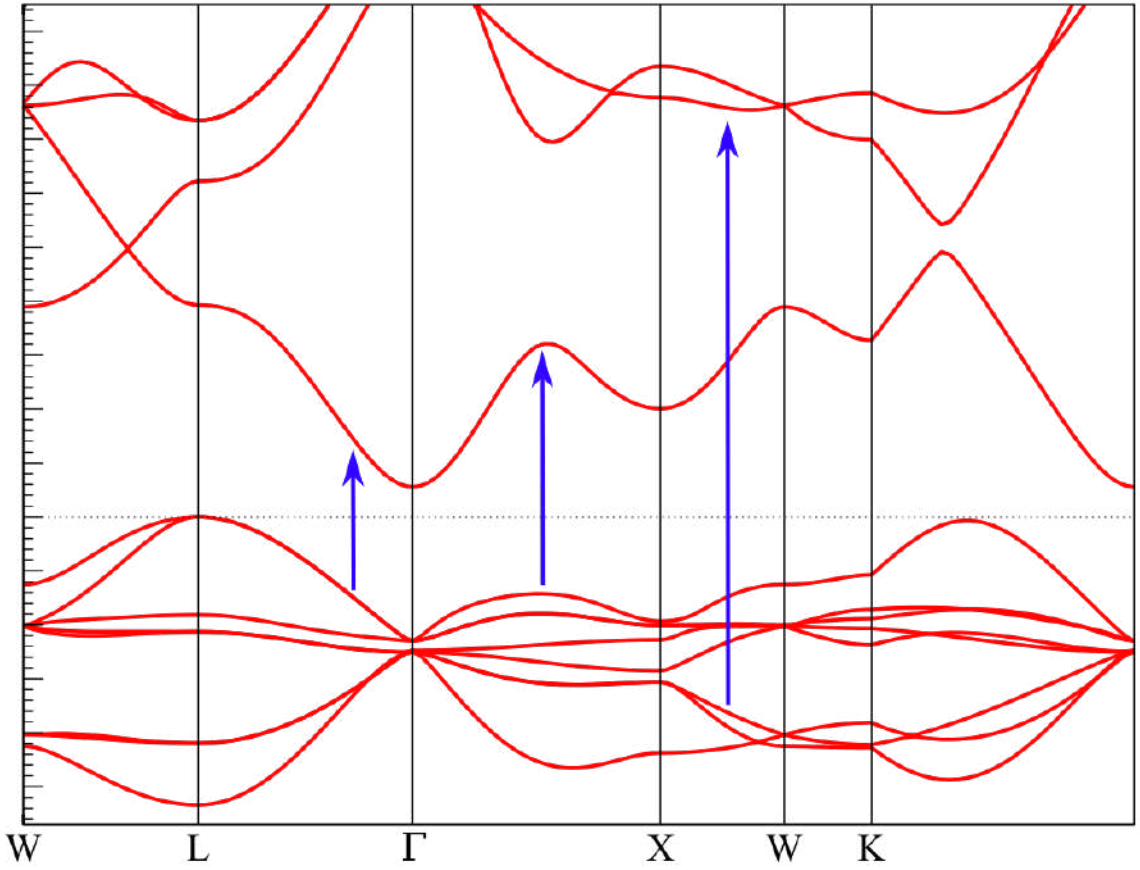



transition space
j
i


transition space
i
j

transition space





$$[\chi^0]^{kl}_{ij} = \begin{bmatrix} \ddots & & & & \\ & \ddots & & & \\ & & \frac{\delta_{ik}\delta_{jl}}{\omega - (\epsilon_j - \epsilon_i) + i0+} & & \\ & & & \ddots & \\ & & & & \ddots \end{bmatrix}$$

$$\chi = \chi^0 + \chi^0 \left[v + f_{xc} \right] \chi$$

$$\chi = \chi^0 + \chi^0 \left[v + f_{xc} \right] \chi$$

$$\chi = \left[\left(\chi^0 \right)^{-1} - \left(v + f_{xc} \right) \right]^{-1}$$

$$\chi = \left[\left(\chi^0 \right)^{-1} - K \right]^{-1}$$

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χ_{ij}^{kl}

$\omega - (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$

$K_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')K(\mathbf{r},\mathbf{r}')\,d\mathbf{r}d\mathbf{r}'$

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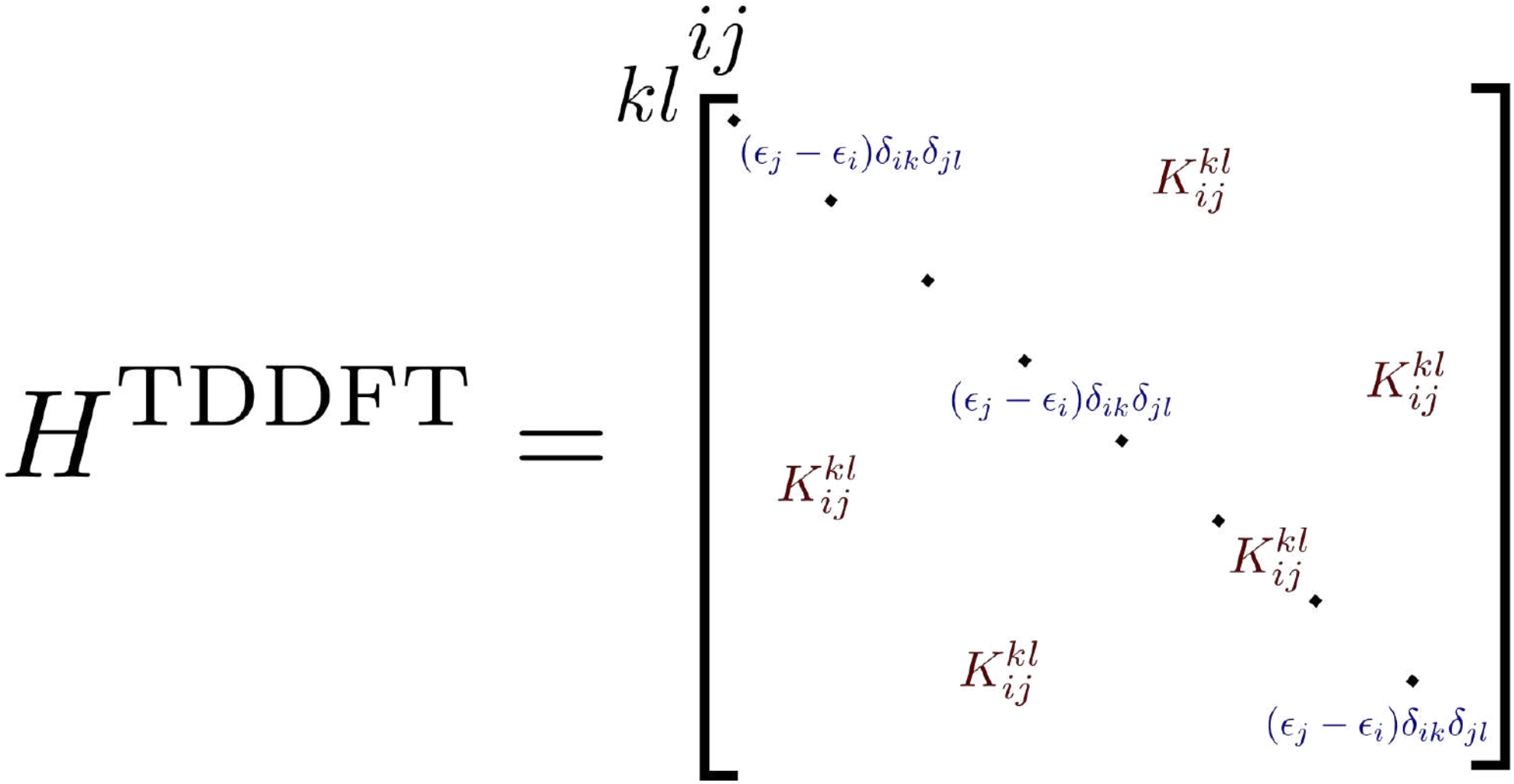
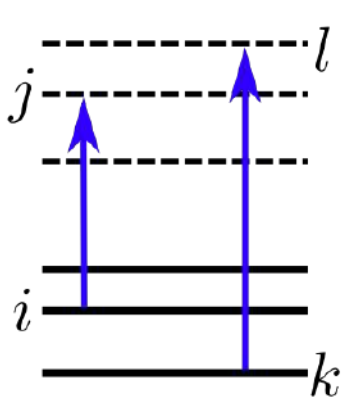
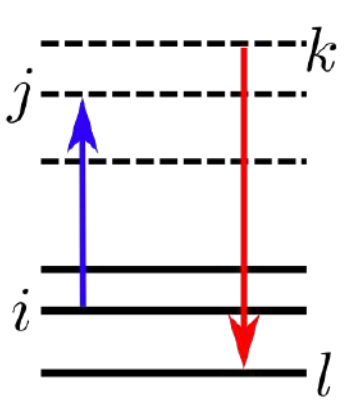
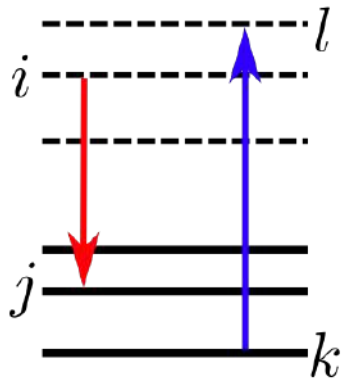
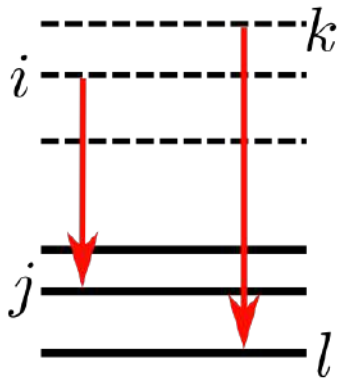
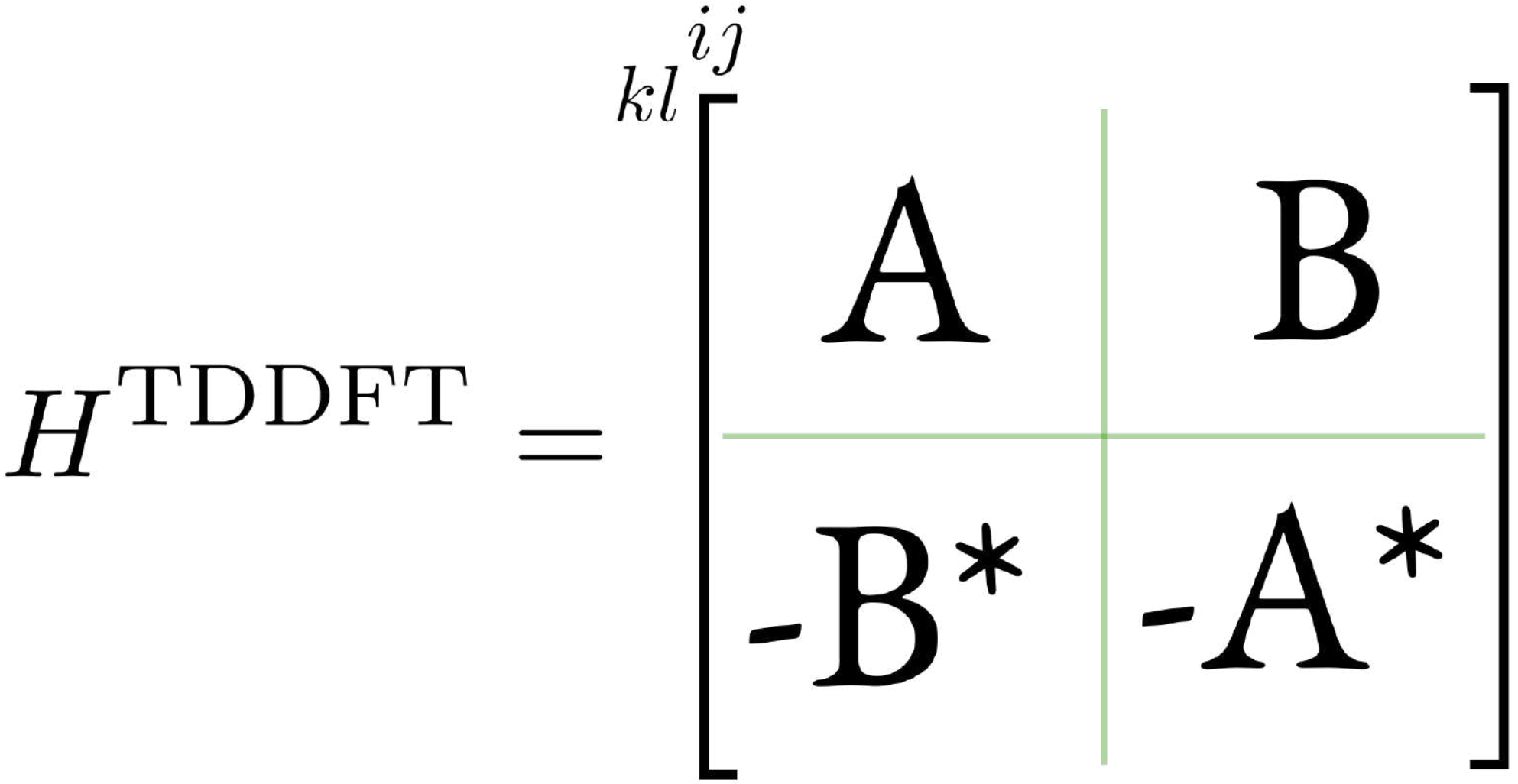
adiabatic approx.

$$\chi = \frac{1}{H^{\mathrm{TDDFT}} - \omega}$$


$H^{\mathrm{TDDFT}} =$
kl
ij
$(\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$
K_{ij}^{kl}
$(\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$
K_{ij}^{kl}
K_{ij}^{kl}
K_{ij}^{kl}
K_{ij}^{kl}
$(\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$

$$\chi = \frac{1}{H^{\mathrm{TDDFT}} - \omega} = \sum_{\lambda\lambda'} \frac{|V_\lambda\rangle\, S_\lambda^{\lambda'}\, \langle V_\lambda|}{E_\lambda - \omega}$$

$$H^{\mathrm{TDDFT}} = {}^{ij}_{kl}\left[\begin{array}{cc} \text{  } & \text{  } \\ \text{  } & \text{  } \end{array}\right]$$

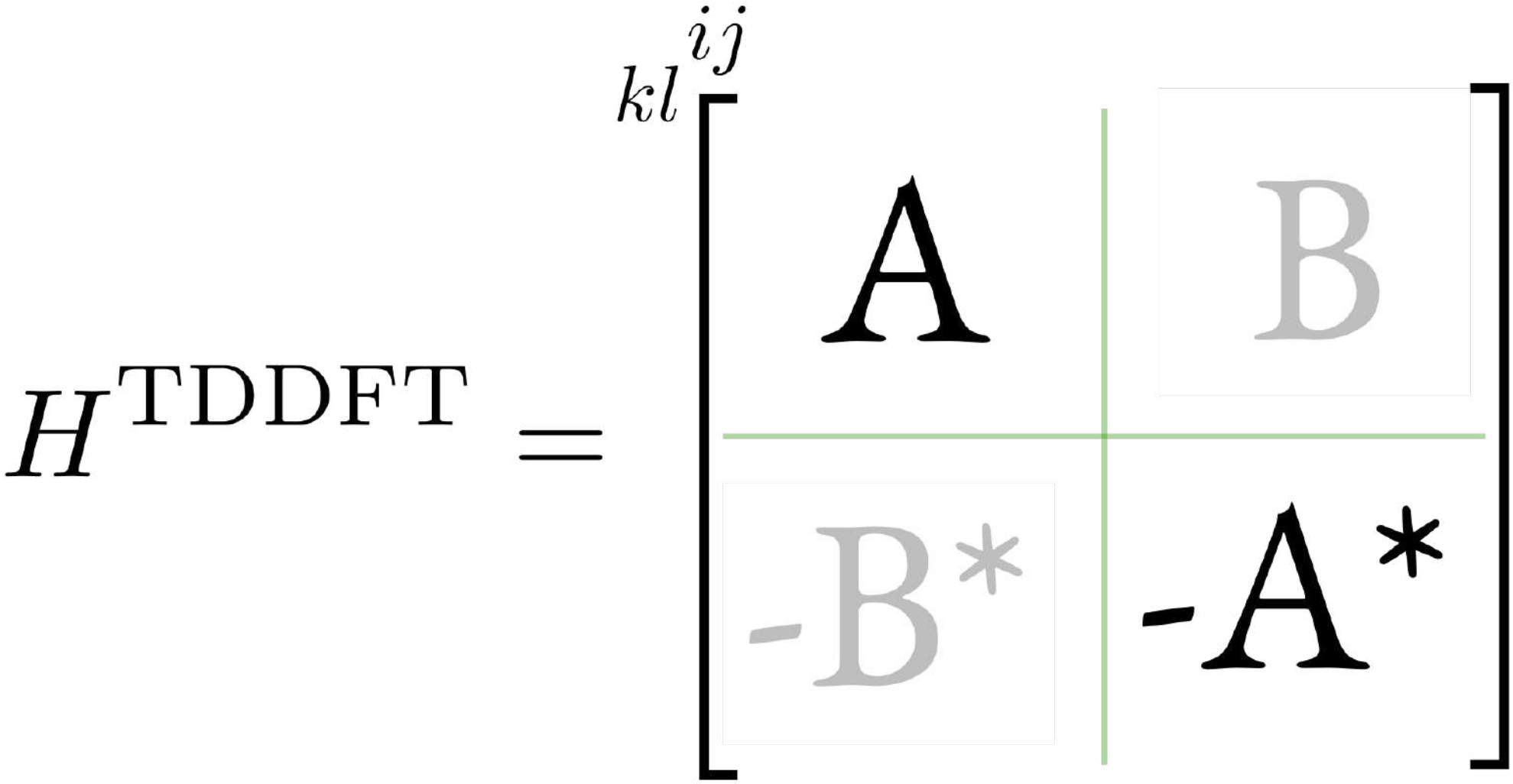

$H^{\mathrm{TDDFT}} =$
kl
ij
A
B
-B*
-A*

$$\begin{bmatrix} \mathrm{A} & \mathrm{B} \\ -\mathrm{B}^* & -\mathrm{A}^* \end{bmatrix} \begin{bmatrix} \mathrm{X} \\ \mathrm{Y} \end{bmatrix} = E_\lambda \begin{bmatrix} \mathrm{X} \\ \mathrm{Y} \end{bmatrix}$$

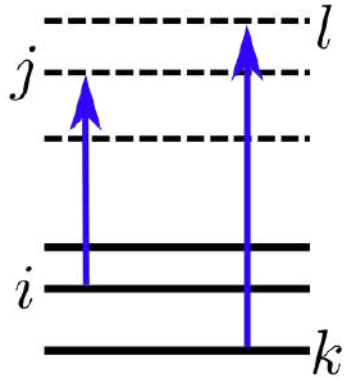
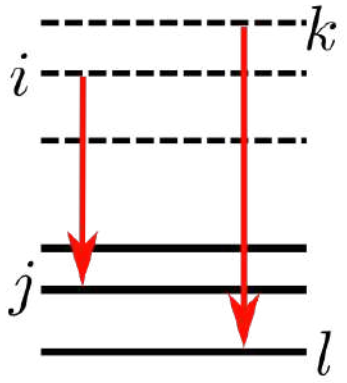
$$|V_\lambda\rangle = \begin{bmatrix} \mathrm{X} \\ \mathrm{Y} \end{bmatrix}$$

$$\left[\begin{array}{c|c} A & B \\ \hline B^* & -A^* \end{array}\right]\left[\begin{array}{c} X \\ Y \end{array}\right] = E_\lambda \left[\begin{array}{c|c} 1 & 0 \\ \hline 0 & -1 \end{array}\right]\left[\begin{array}{c} X \\ Y \end{array}\right]$$

$$|V_\lambda\rangle = \begin{bmatrix} X \\ Y \end{bmatrix}$$



Tamm-Dancoff approx

$$H^{\mathrm{TDDFT}} = {}^{ij}_{kl}\left[\begin{array}{cc} \text{  } & \text{} \\ \text{} & \text{  } \end{array}\right]$$

Tamm-Dancoff approx

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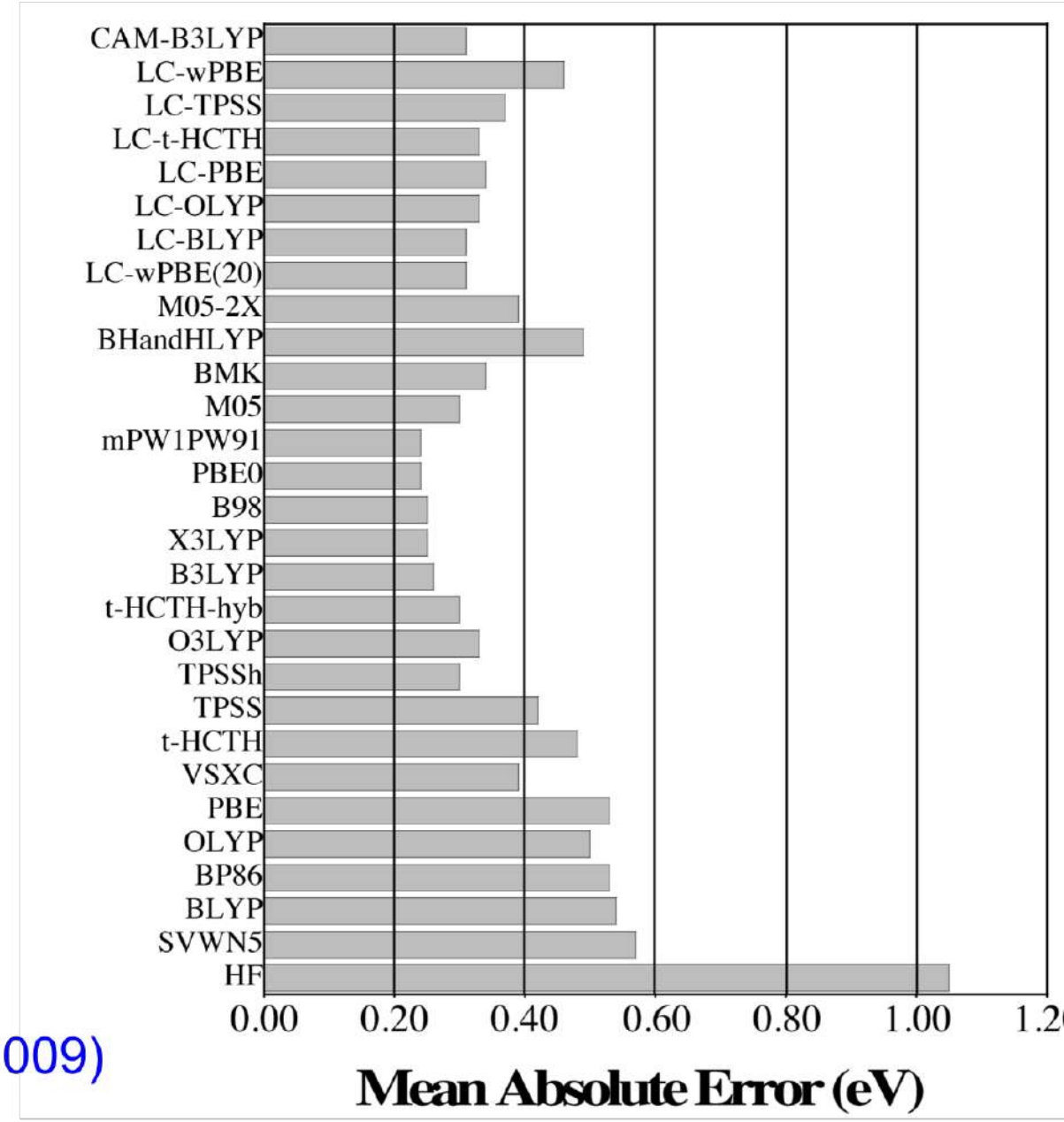
TDDFT excitation energies
500 compounds



J. Chem. Theory Comput. **5**, 2420 (2009)

TDDFT excitation energies
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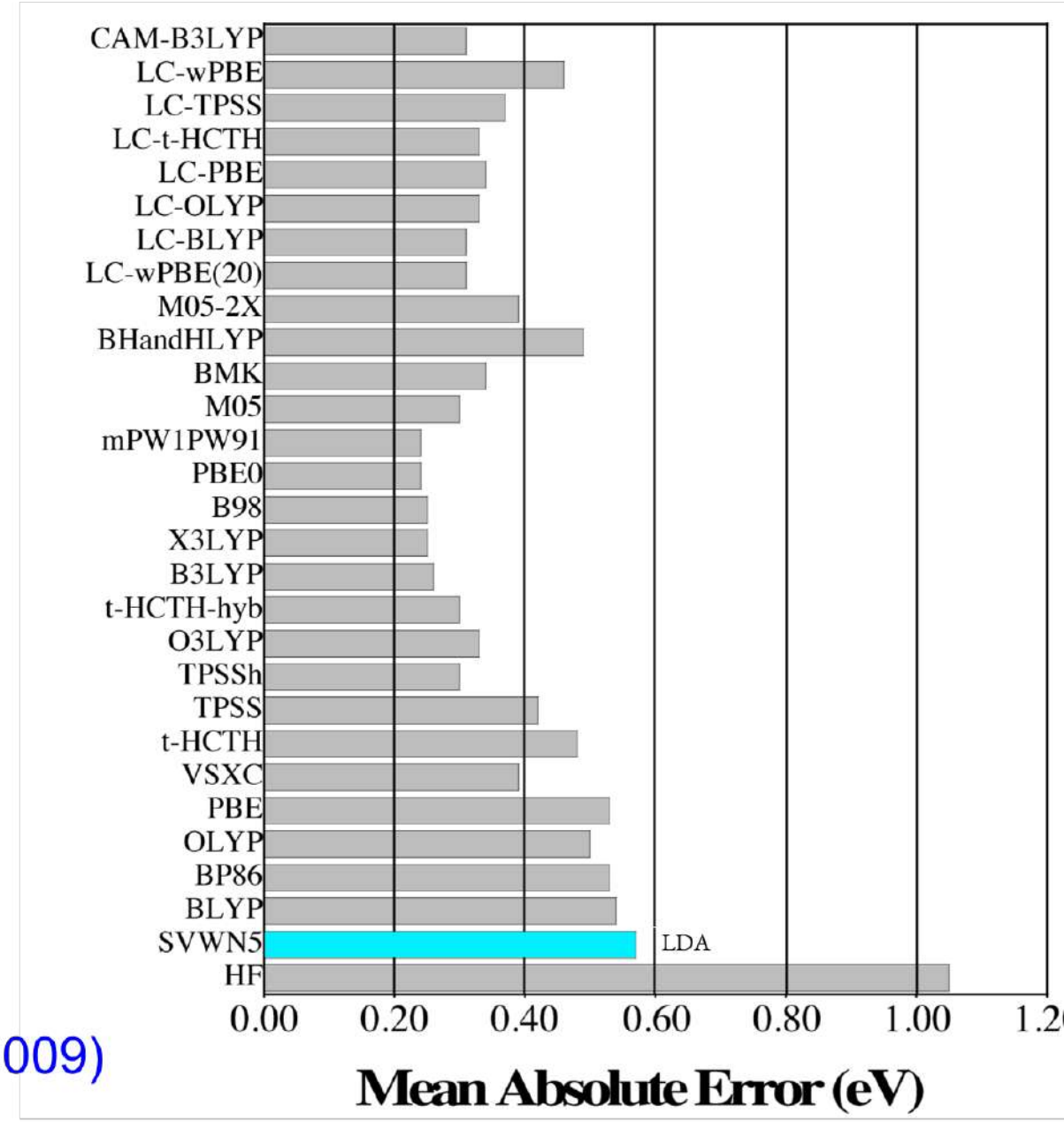

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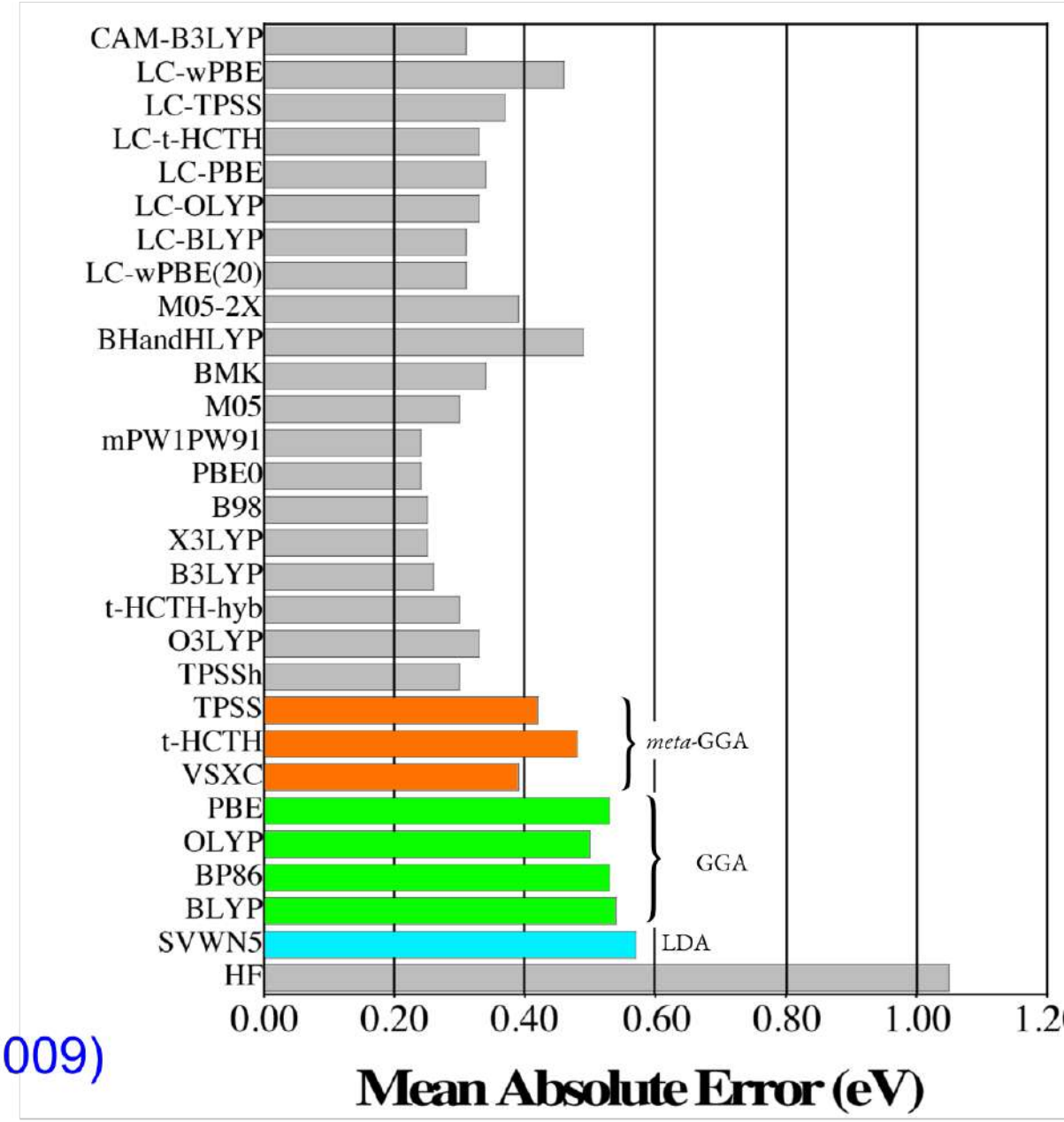

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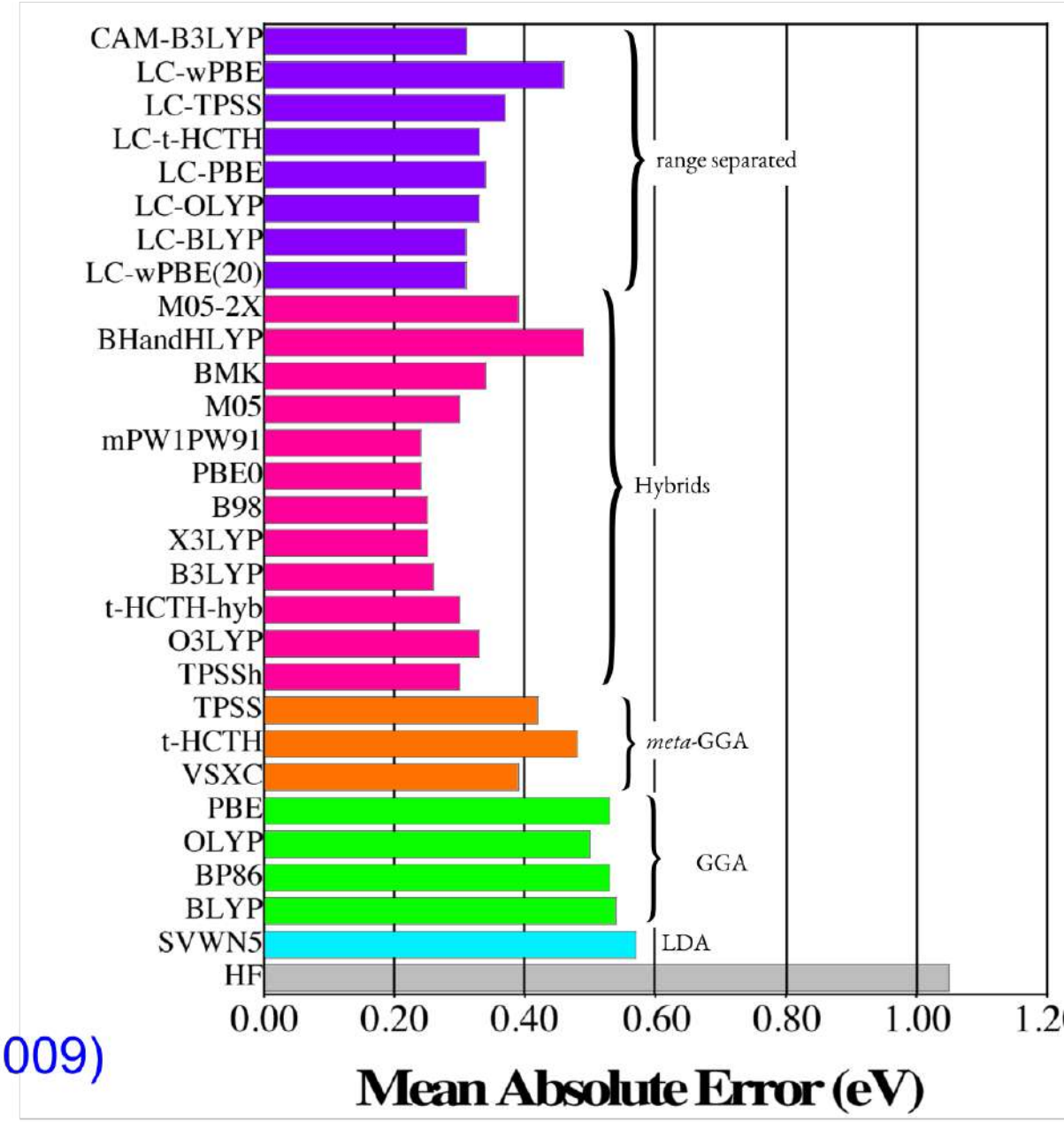

J. Chem. Theory Comput. **5**, 2420 (2009)

- Linear response approach

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  access to excitations energies

$$\chi = \sum_{\lambda} \frac{|V_\lambda\rangle \langle V_\lambda|}{E_\lambda - \omega}$$

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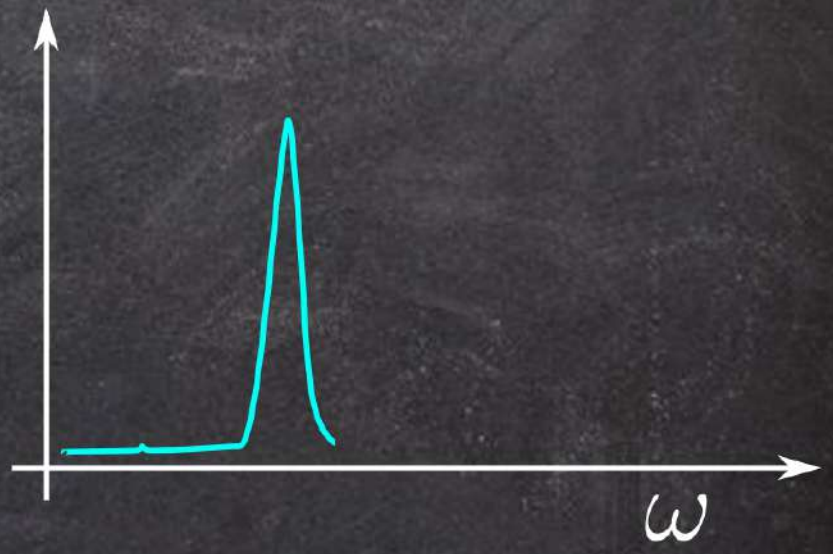
access to excitations energies

build the spectrum by ω



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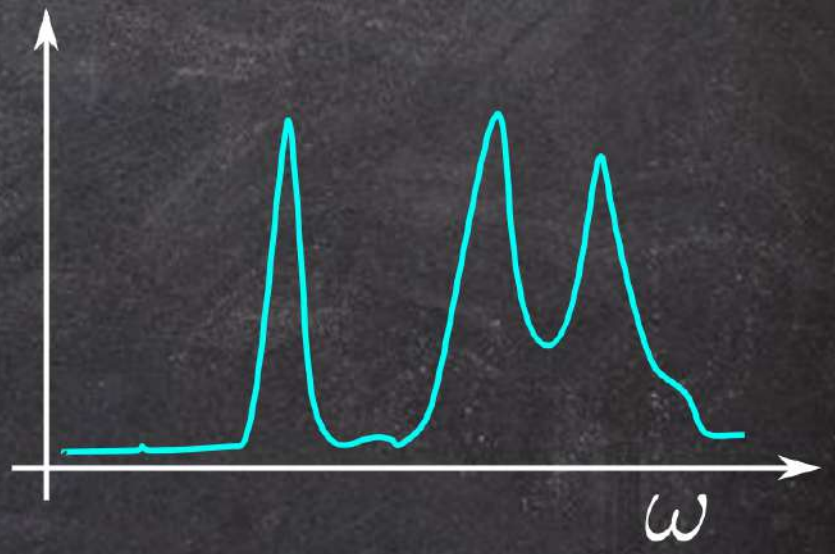

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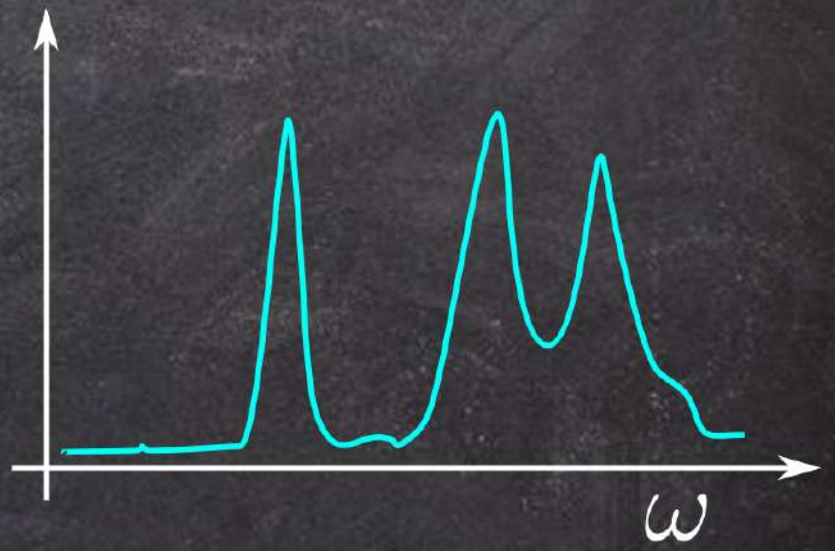
build the spectrum by ω

analysis
- frequency range
- KS excitations contribution
- singlet/triplet
- dark excitations
- ...



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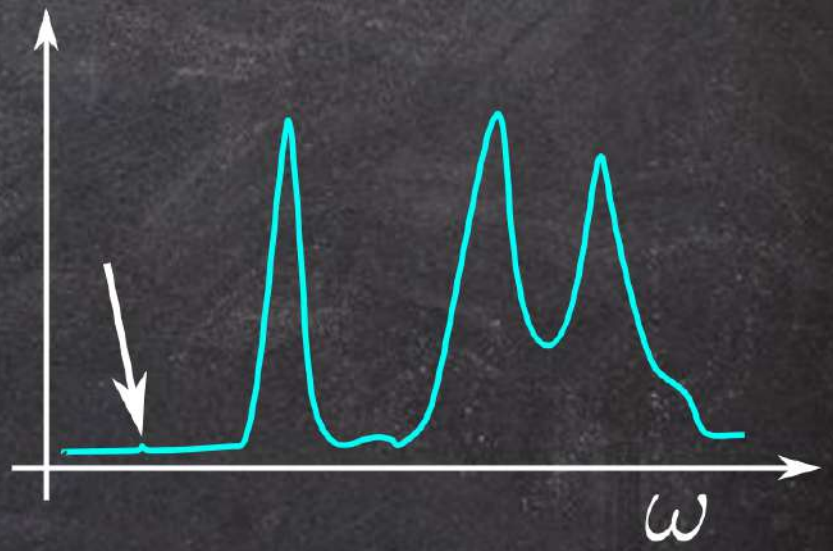

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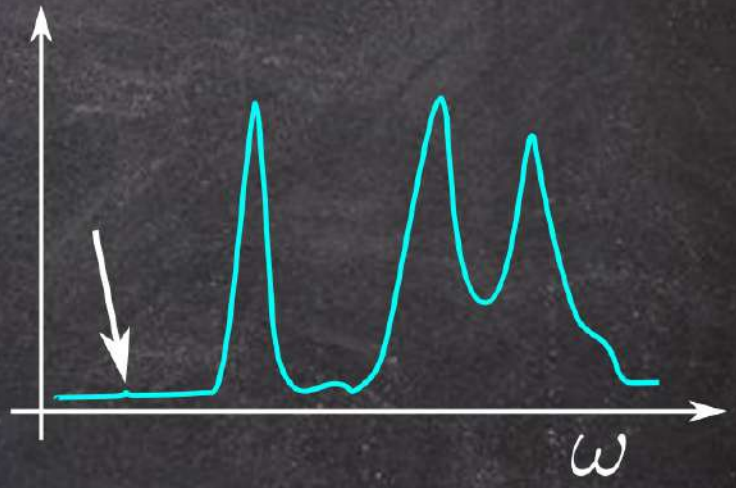

Full Time Dependent KS eqs.

access to full spectrum at once

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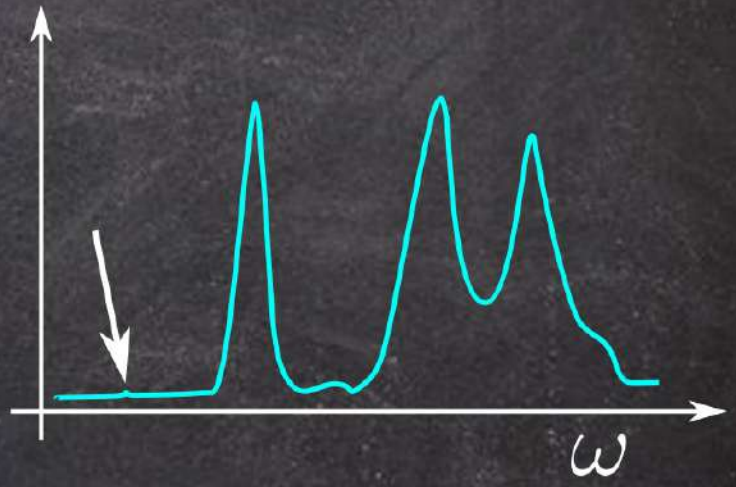

Full Time Dependent KS eqs.

access to full spectrum at once

non-linear effects automatically included

better scaling

TDDFT applications

- Absorption spectra of simple molecules
- Loss function of metals and semiconductors
- Excitations energies

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- Qualitatively first step

  → strong field phenomena

  → open quantum systems

  → superconductivity

  → quantum optimal control

  → beyond BO dynamics

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