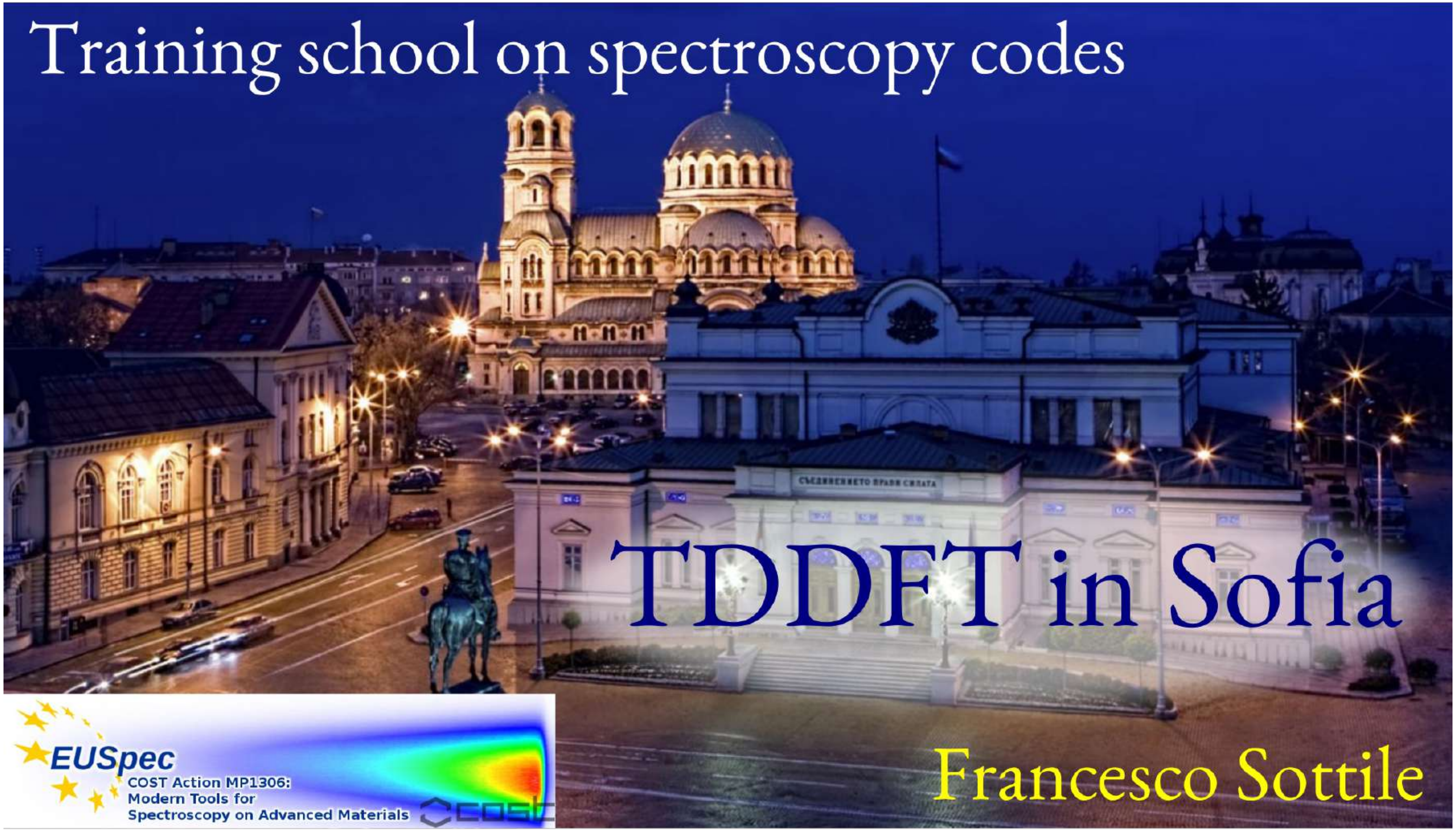
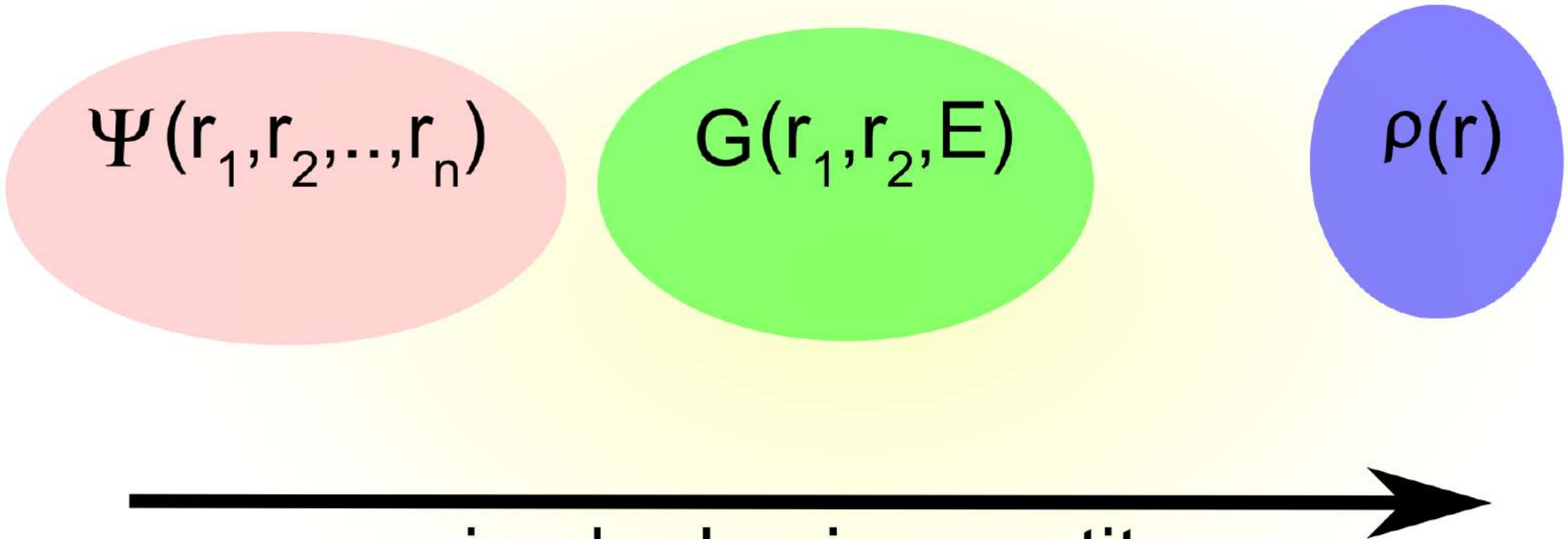
Training school on spectroscopy codes



TDDFT in Sofia

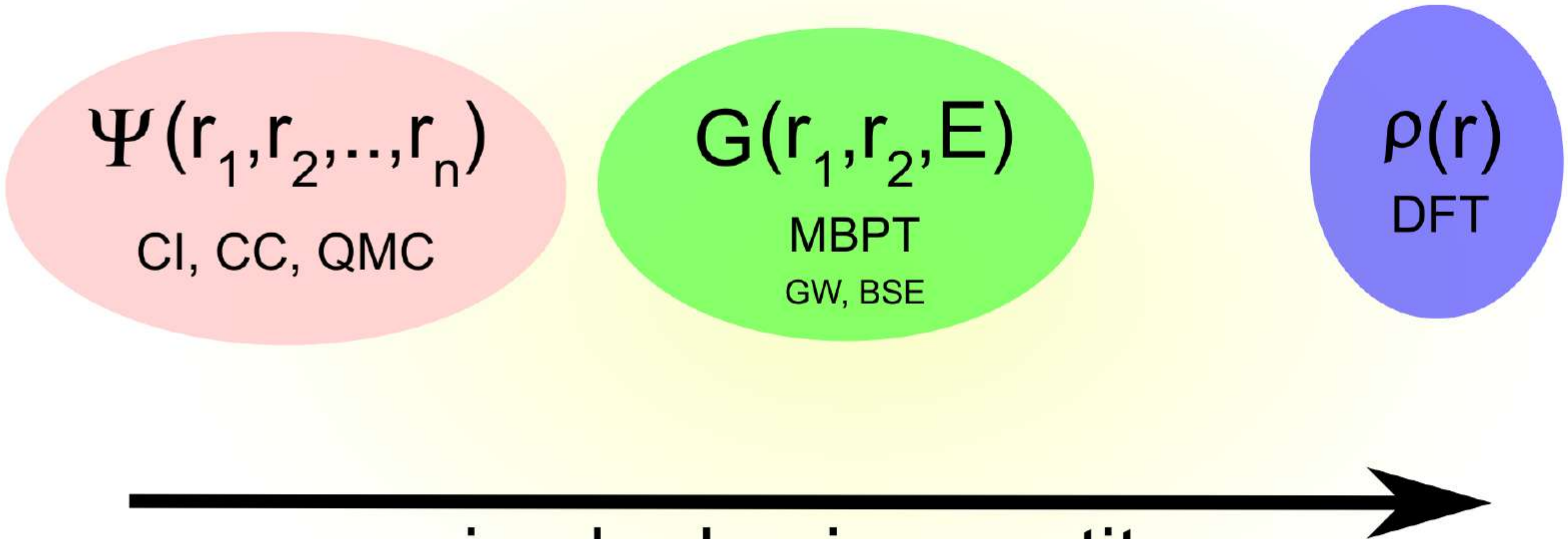
Francesco Sottile

EUSpec
COST Action MP1306:
Modern Tools for
Spectroscopy on Advanced Materials
cost



simpler basic quantity

more complicate approximation



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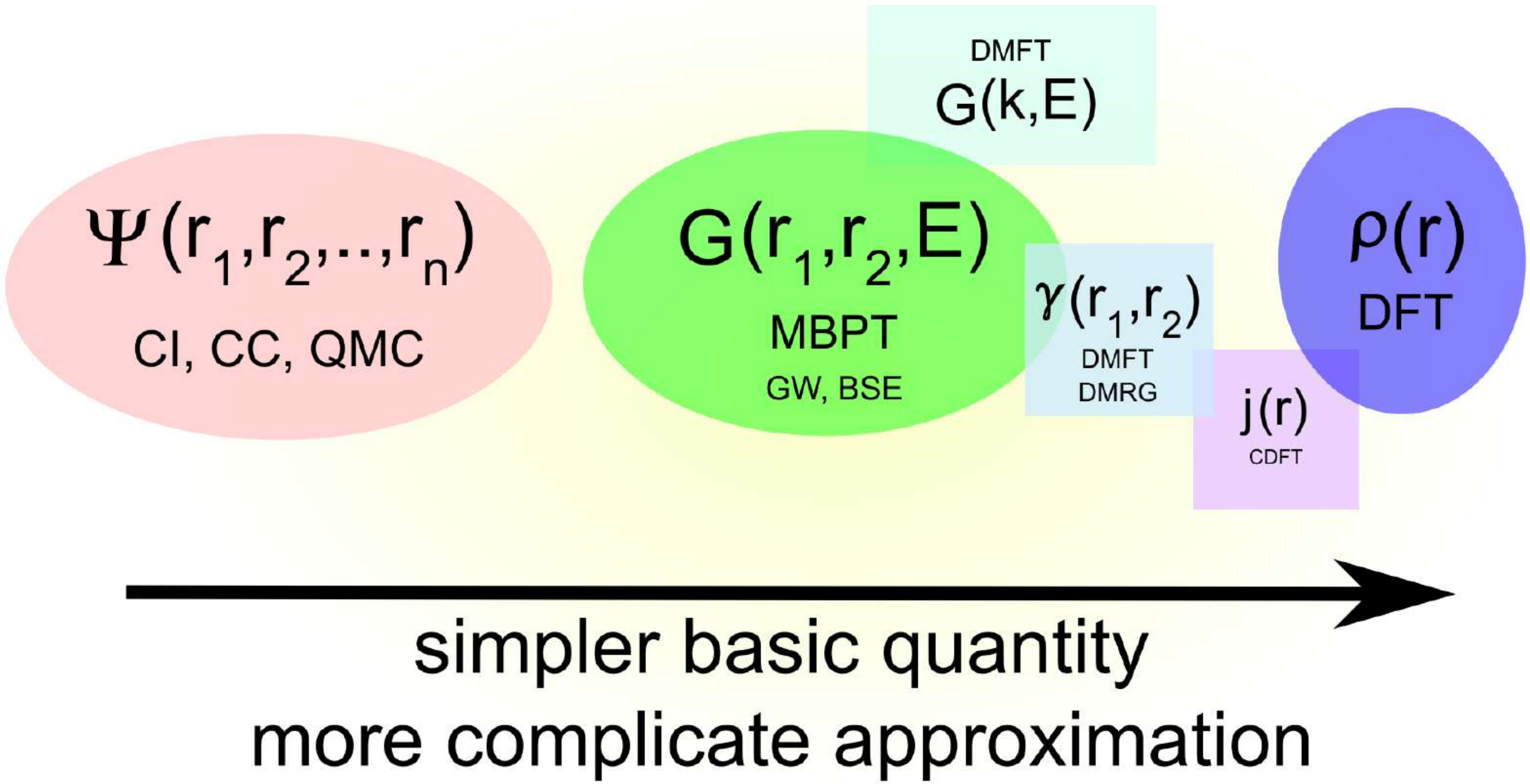
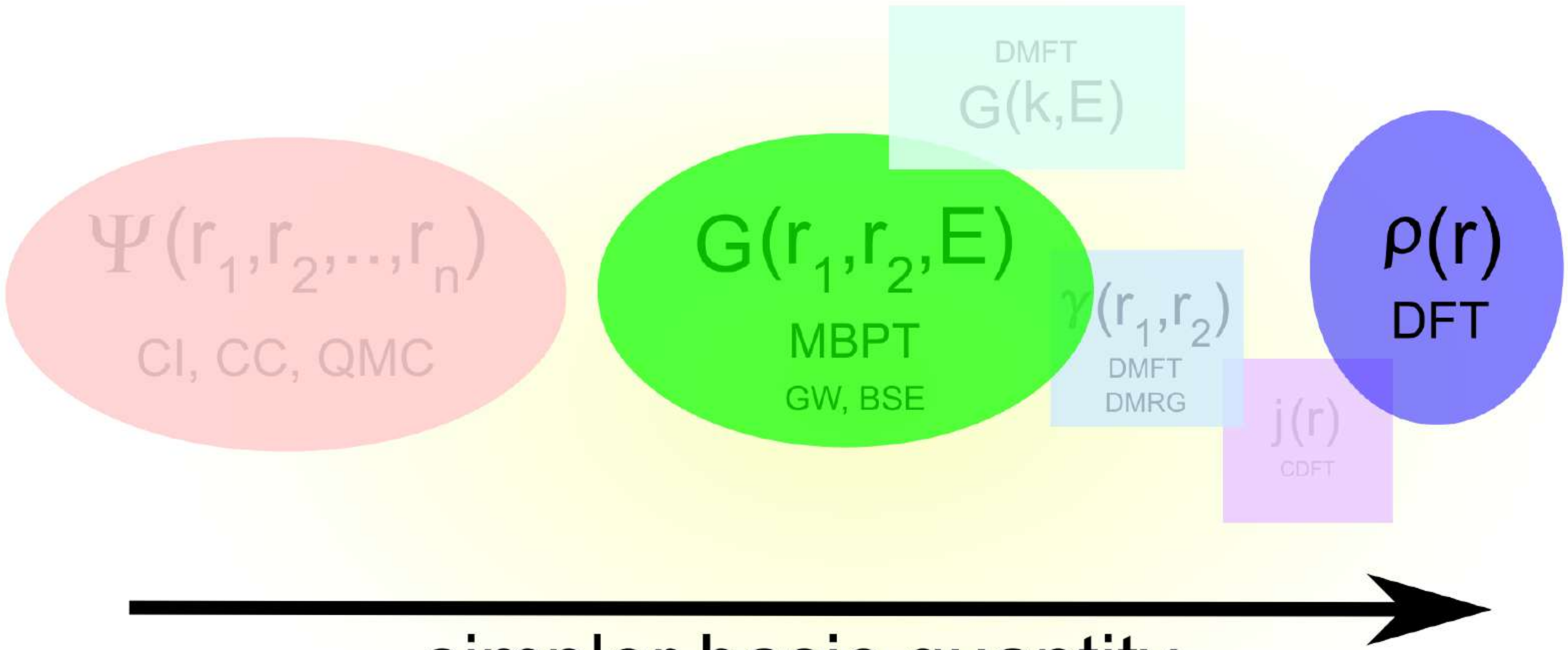

DMFT
G(k,E)
Ψ(r1,r2,..,rn)
CI, CC, QMC
G(r1,r2,E)
MBPT
GW, BSE
γ(r1,r2)
DMFT
DMRG
ρ(r)
DFT
j(r)
CDFT
simpler basic quantity
more complicate approximation



simpler basic quantity

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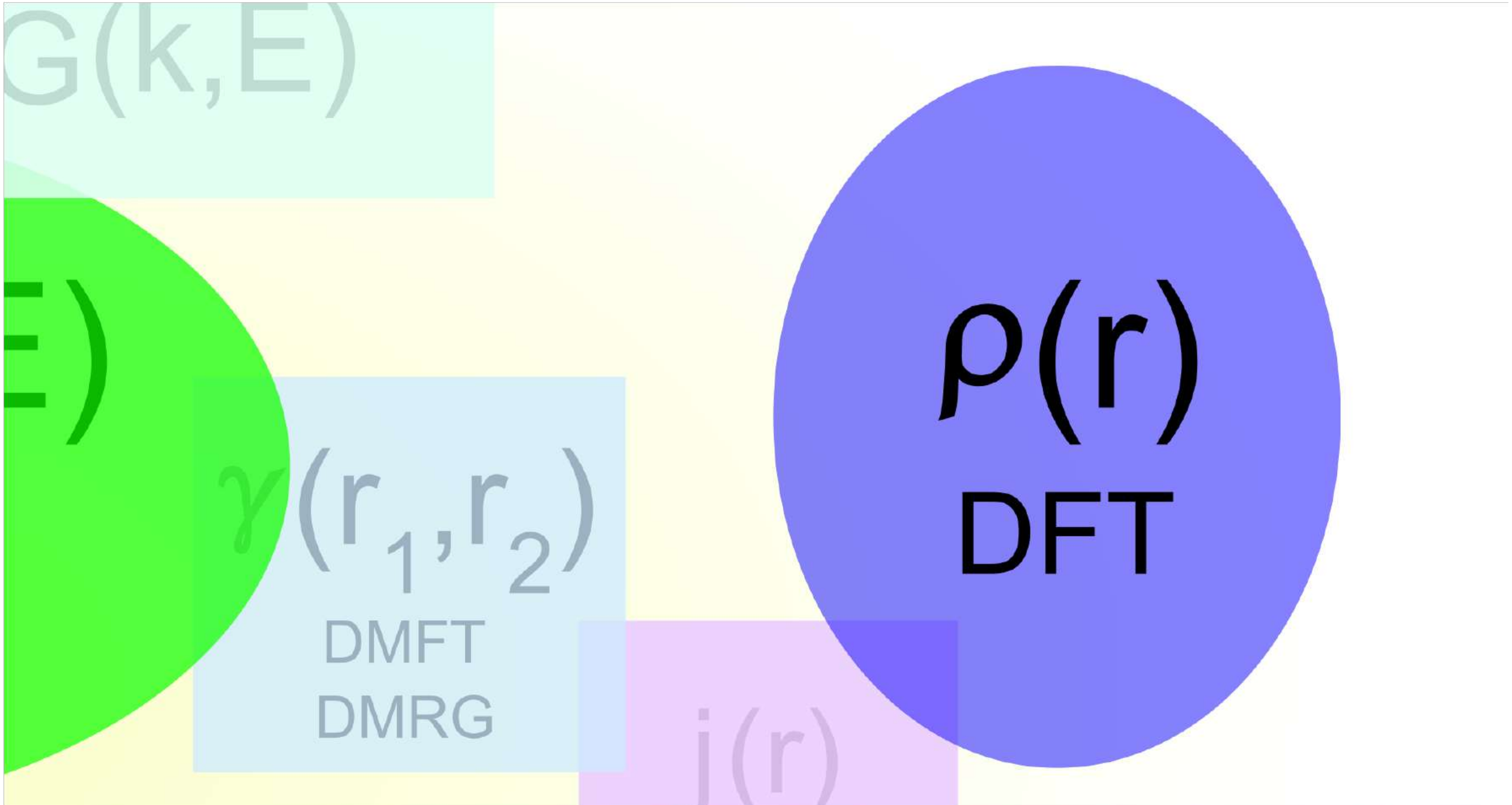
G(k,E)
E)
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DMFT
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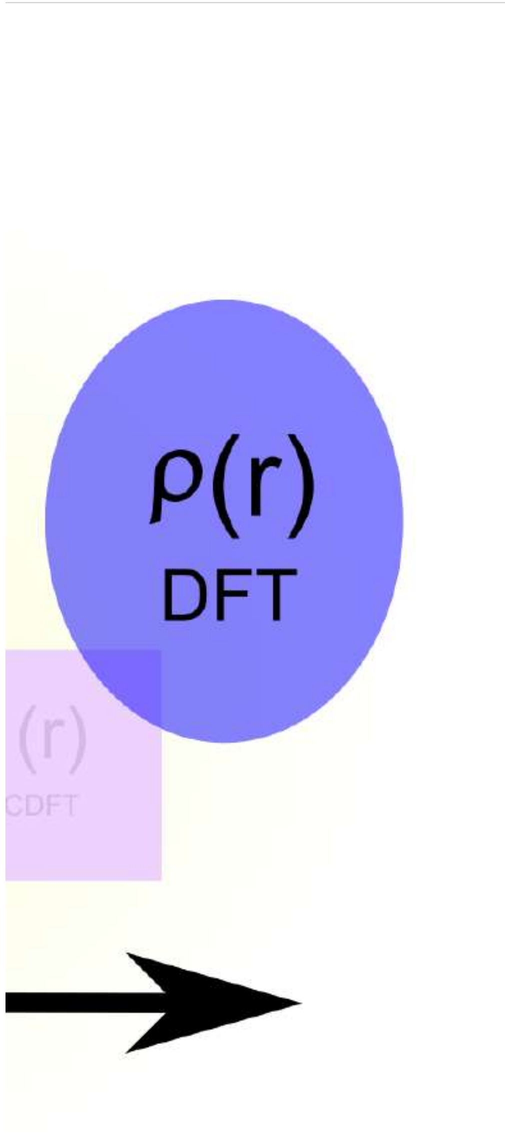
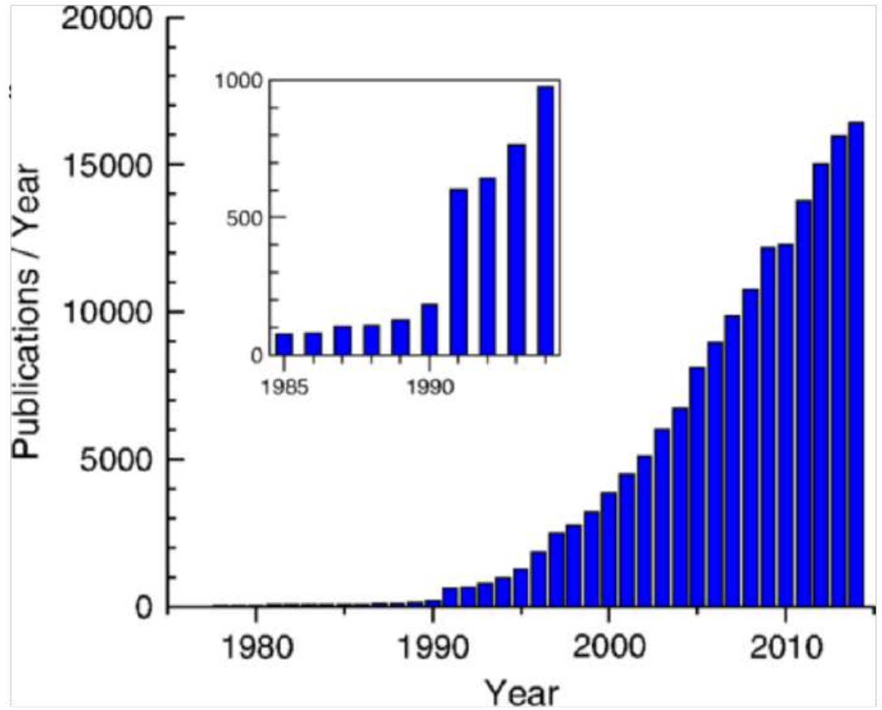
DFT





R. O. Jones Rev. Mod. Phys. 87, 897 (2015)

Success of DFT

Ground-state properties

- lattice parameters
- intermolecular distance
- bulk modulus
- phonons / vibrations spectra
- total energies
- ......

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Excited-state energies

- ΔSCF
- ensemble DFT (Phys. Rev. B **95**, 035120 (201
- Variational Density-Functional Theory (Levy and Nagy PRL **83**, 4361 (1999))
- Adiabatic-connection formalism (Perdew and Levy PRB **31**, 6264 (1985))

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Excitation Spectra

- band structure calculation, via Kohn-Sham → **PES**
- optical properties, via linear response → **Absorption**, **Electron Energy Loss**

Success of DFT

Ground-state properties

- lattice parameters
- intermolecular distance
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- ......

Excited-state energies

- ΔSCF
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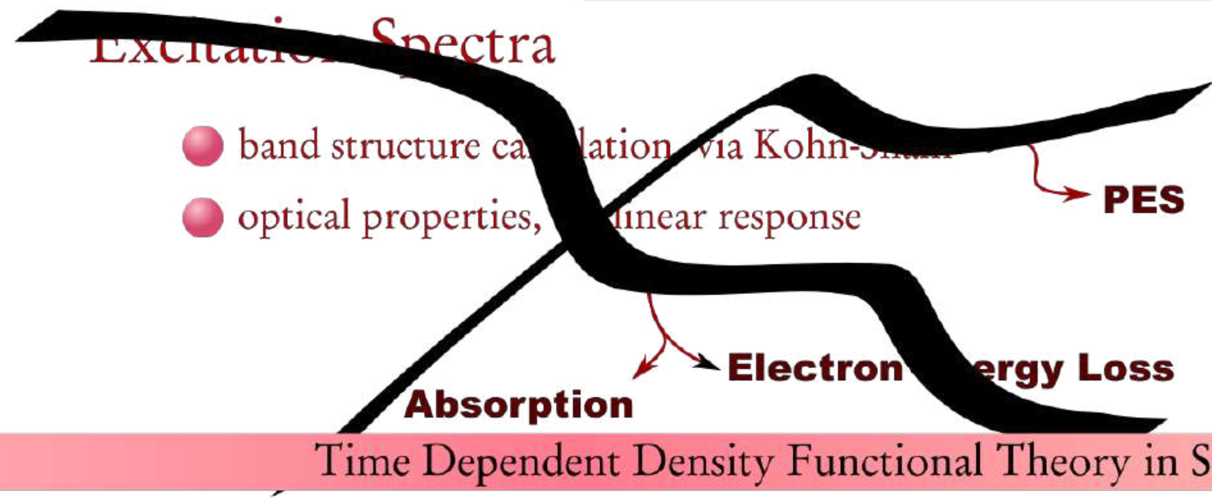

DFT $\longrightarrow$ TDDFT

- Optical/dielectric properties
- system under strong laser impulses
- multiple harmonic generation
- relaxation
- convergence to steady state
- ....

$$[T + V_{e-e} + V_N + V_{\text{ext}}(t)]\,\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t) = i\hbar \frac{\partial \Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, t)}{\partial t}$$

Outline

- Time Dependent Density Functional Theory
  - introduction and derivation
  - thoughts and particularities
  - approximations, applications
- Linear Response approach
  - connection with spectroscopy
  - exchange-correlation kernel
  - beyond linear response
- Micro-macro connection and the DP code

DFT **TDDFT**

DFT

Hohenberg-Kohn theorem

$$V_{\rm ext} \longleftrightarrow n$$

$$\langle\Psi|O|\Psi\rangle = O[n]$$

TDDFT

Runge-Gross theorem

$$V_{\rm ext}(t) \longleftrightarrow n(t)$$

$$\langle\Psi(t)|O(t)|\Psi(t)\rangle = O[n,\Psi^0](t)$$

Hohenberg and Kohn, Phys. Rev. **136**, B864 (1964)

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Runge-Gross theorem

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Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

Runge-Gross theorem

$$V_{\text{ext}}(t) \quad \longleftrightarrow \quad n(t)$$

Demonstration

Runge-Gross theorem

$$V_{\text{ext}}(t) \quad \longleftrightarrow \quad n(t)$$

Demonstration

1) $$V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$$

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2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

DFT

Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2}+v_{\mathrm{KS}}[n](\mathbf{r})\right]\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r})$$

$$v_{\mathrm{KS}}[n](\mathbf{r})=v_{\mathrm{ext}}+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{\mathrm{xc}}[n](\mathbf{r})$$

$$n(\mathbf{r})=\sum_{\mathrm{occ}}|\psi_i(\mathbf{r})|^2$$

Kohn and Sham, Phys. Rev. **140**, A1133 (1965)

TDDFT

Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2}+v_{\mathrm{KS}}[n;\Phi^0](\mathbf{r},t)\right]\psi_i(\mathbf{r},t)=i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t}$$

$$v_{\mathrm{KS}}[n;\Phi^0](\mathbf{r},t)=v_{\mathrm{ext}}[n,\Psi_0](\mathbf{r},t)+\int\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{\mathrm{xc}}[n,\Psi_0,\Phi_0](\mathbf{r},t)$$

$$n(\mathbf{r},t)=\sum_{\mathrm{occ}}|\psi_i(\mathbf{r},t)|^2$$

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

TDDFT

Kohn-Sham equation

$$\left[-\frac{\nabla^2}{2} + v_{\rm KS}[n;\Phi^0](\mathbf{r},t)\right]\psi_i(\mathbf{r},t) = i\frac{\partial \psi_i(\mathbf{r},t)}{\partial t}$$

$$v_{\rm KS}[n;\Phi^0](\mathbf{r},t) = v_{\rm ext}[n,\Psi_0](\mathbf{r},t) + \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\rm xc}[n,\Psi_0,\Phi_0](\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_{\rm occ} |\psi_i(\mathbf{r},t)|^2$$

no self-consistency

local in space and time

functionally non-local

no variational from an energy functional

Runge and Gross, Phys. Rev. Lett. **52**, 997 (1984)

$_0](\mathbf{r}, t)$

no self-consistency

local in space and time
functionally non-local

no variational from an energy functional

no (direct) derivation of the TDKS eqs.
less exact conditions known

Time propagation in practise

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

$$M_{lm}(t) = \int r^l\, Y_{lm}(r)\, n(\mathbf{r},t)\, d\mathbf{r}$$

Multipoles

Time propagation in practise

$$\alpha(t) = \int \mathbf{r}\, n(\mathbf{r},t) d\mathbf{r}$$

$$\sigma(\omega) = \frac{4\pi\omega}{c}\alpha(\omega)$$

Photo-absorption cross section

$$M_{lm}(t) = \int r^l\, Y_{lm}(r)\, n(\mathbf{r},t)\, d\mathbf{r}$$

Multipoles

$$L_z(t) = \sum_i \int \psi_i(\mathbf{r},t) i(\mathbf{r}\times\nabla)_z \psi_i(\mathbf{r},t)\, d\mathbf{r}$$

Angular Momentum

Approximations

- ALDA

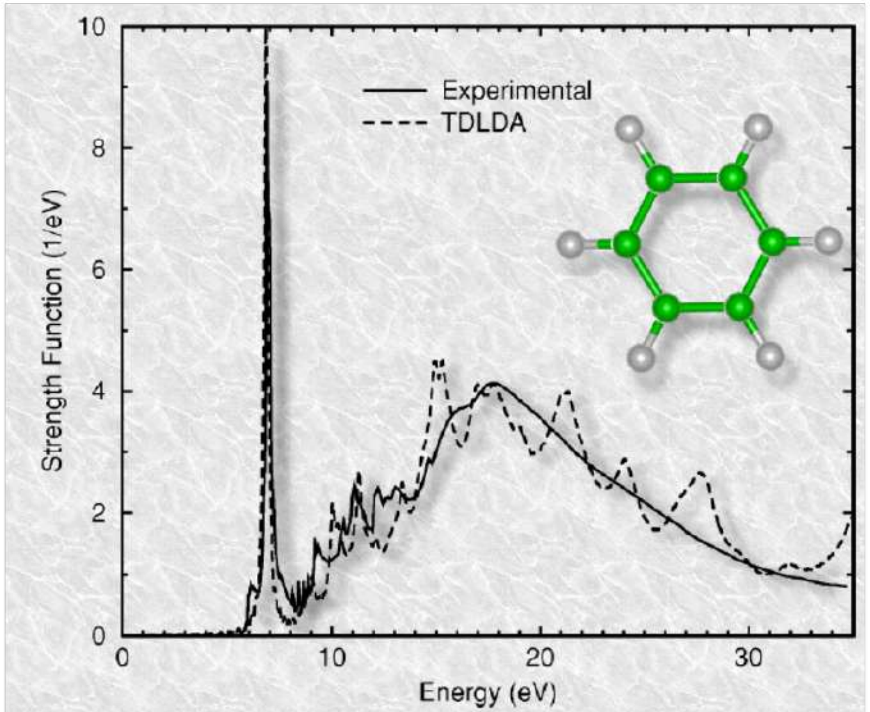
$$v_{xc}^{\text{ALDA}}[n](\mathbf{r},t) = v_{xc}^{\text{heg}}(n(\mathbf{r},t)) = \frac{d}{dn}\left[n e_{xc}^{\text{heg}}(n)\right]\Big|_{n=n(\mathbf{r},t)}$$

- AGGA
- Orbital dependent (OEP, TDEXX, hybrids, BSE-derived)

TDDFT applications

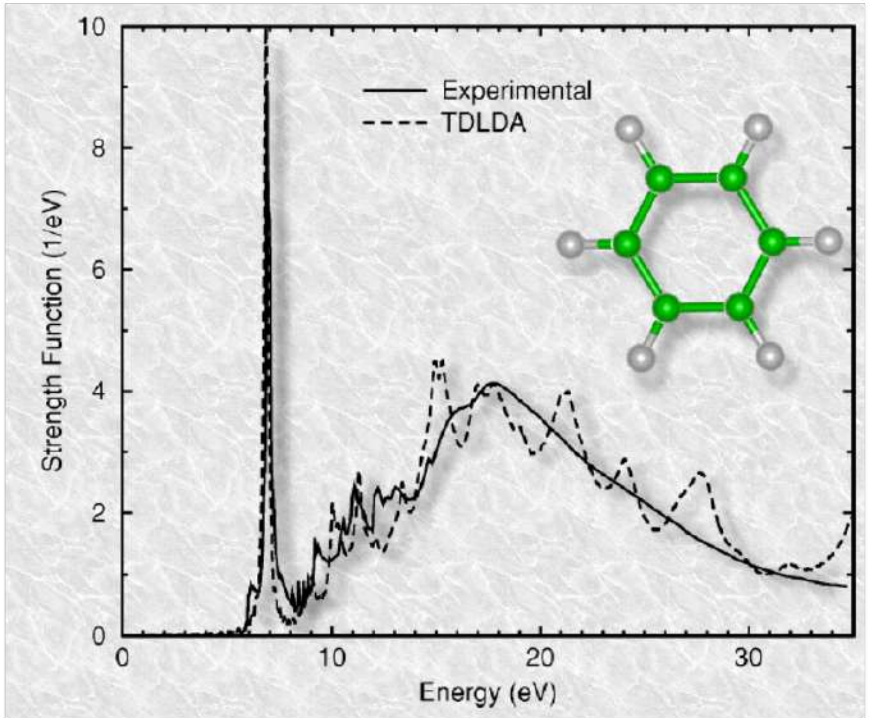
- Absorption spectra of simple molecules
- Loss function of metals and semiconductors

Benzene



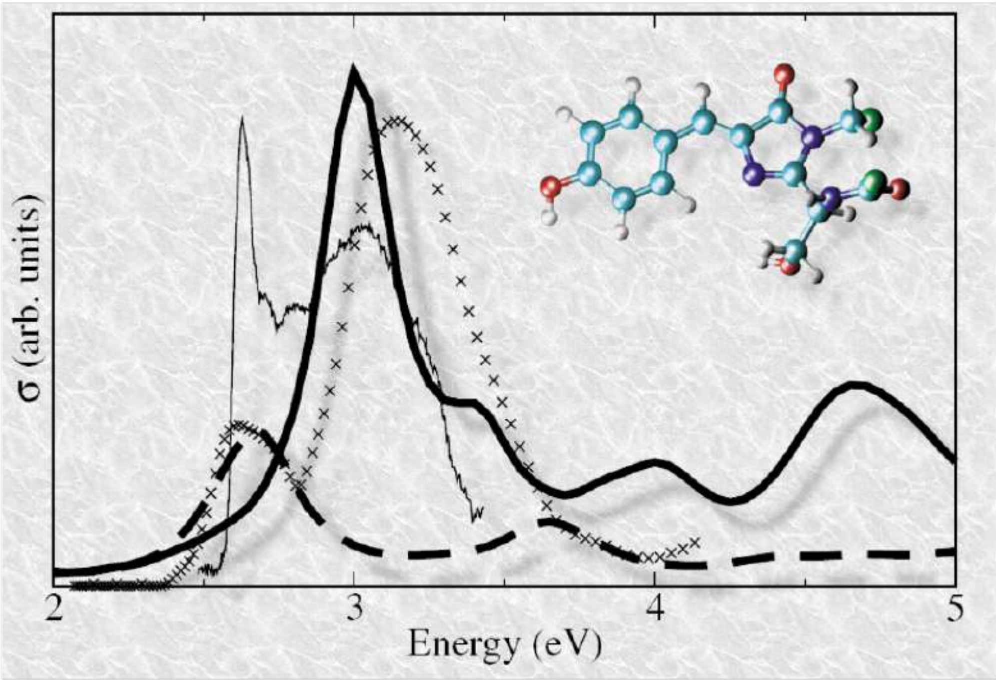
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

Benzene

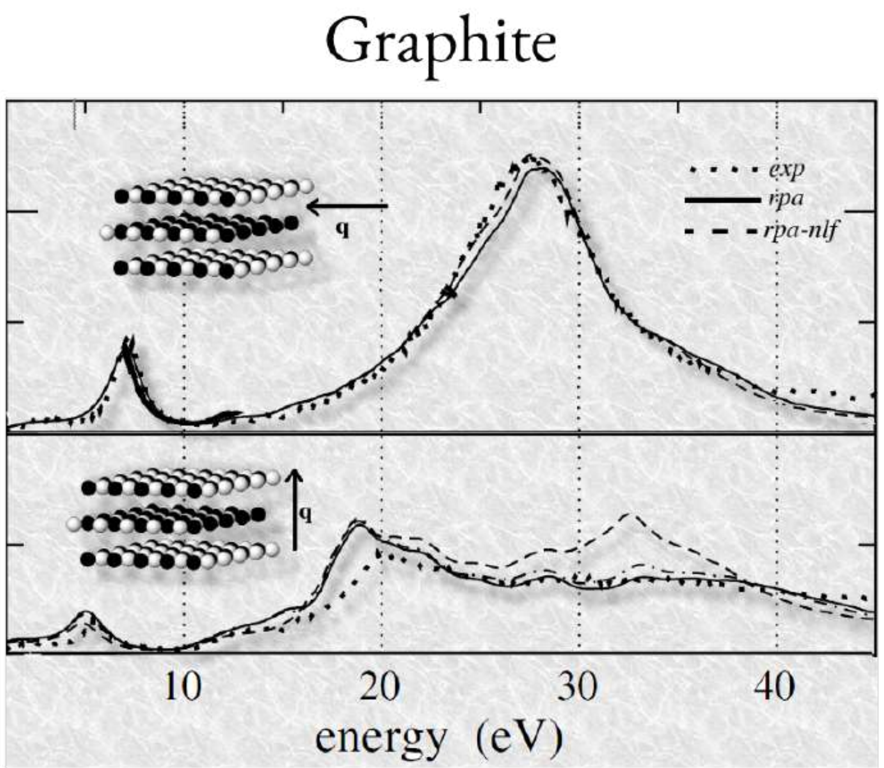


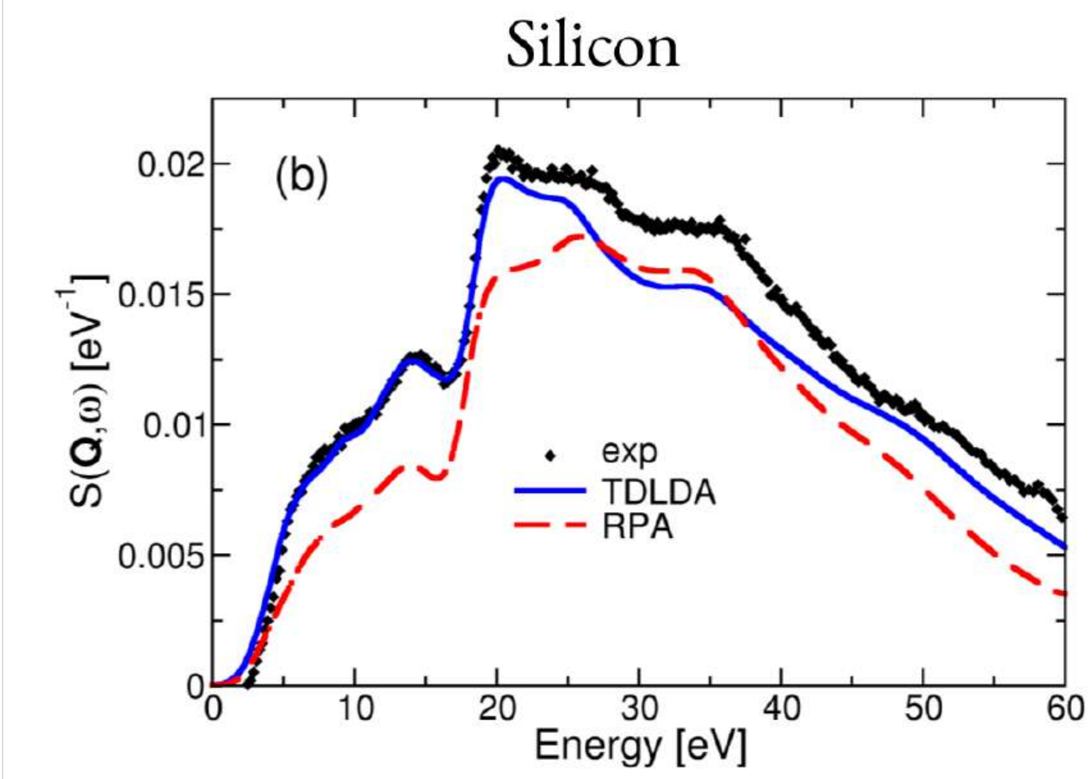
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

GFP



M.Marques *et al.* Phys.Rev.Lett. **90**, 258101 (2003)





A.Marinopoulos et al. Phys.Rev.Lett **89**, 76402 (2002)

Weissker *et al.* Phys. Rev. B **81**, 085104 (2010)

TDDFT applications

- Absorption spectra of simple molecules
- Loss function of metals and semiconductors
- Qualitatively first step

  → strong field phenomena

  → open quantum systems

  → superconductivity

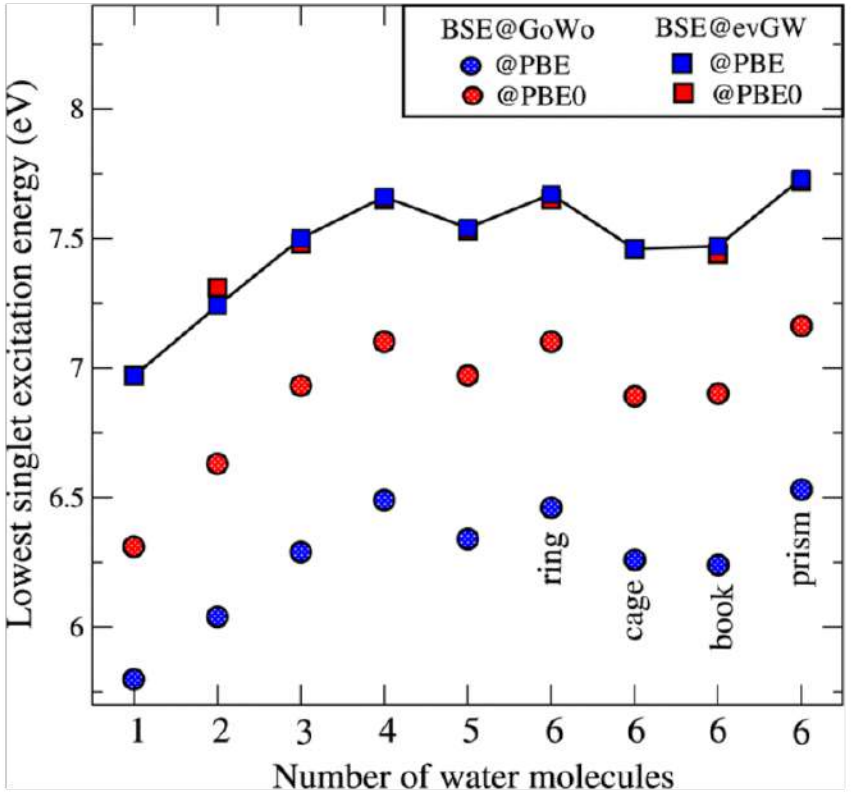
  → quantum optimal control

  → beyond BO dynamics

  → quantum transport

  → .....

Excitation energies of water clusters



Blase *et al.* . Chem. Phys. **144**, 034109 (2016)

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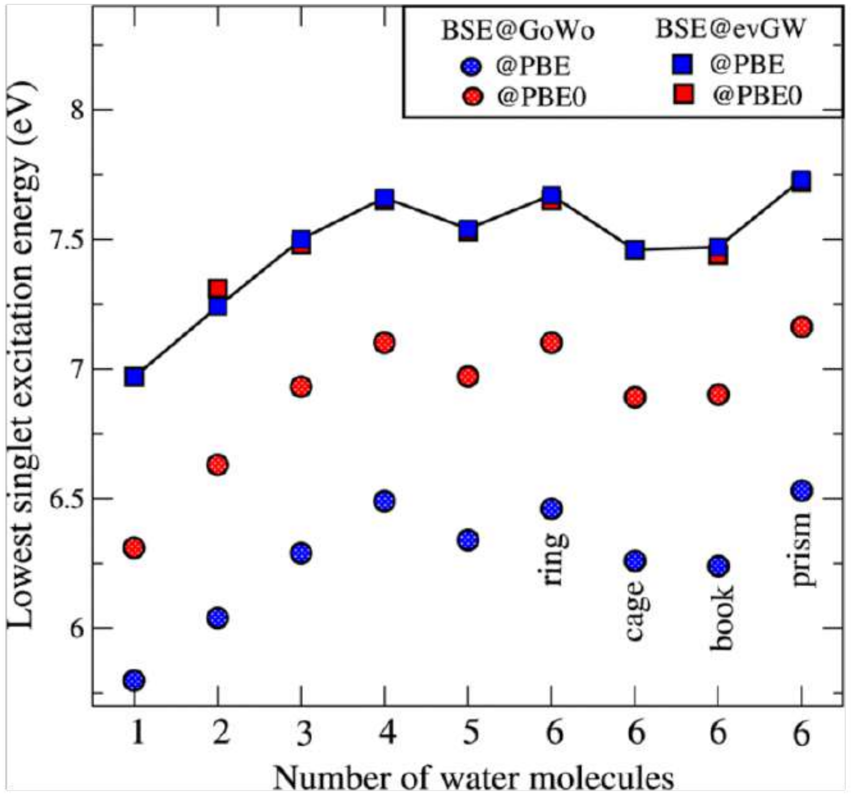
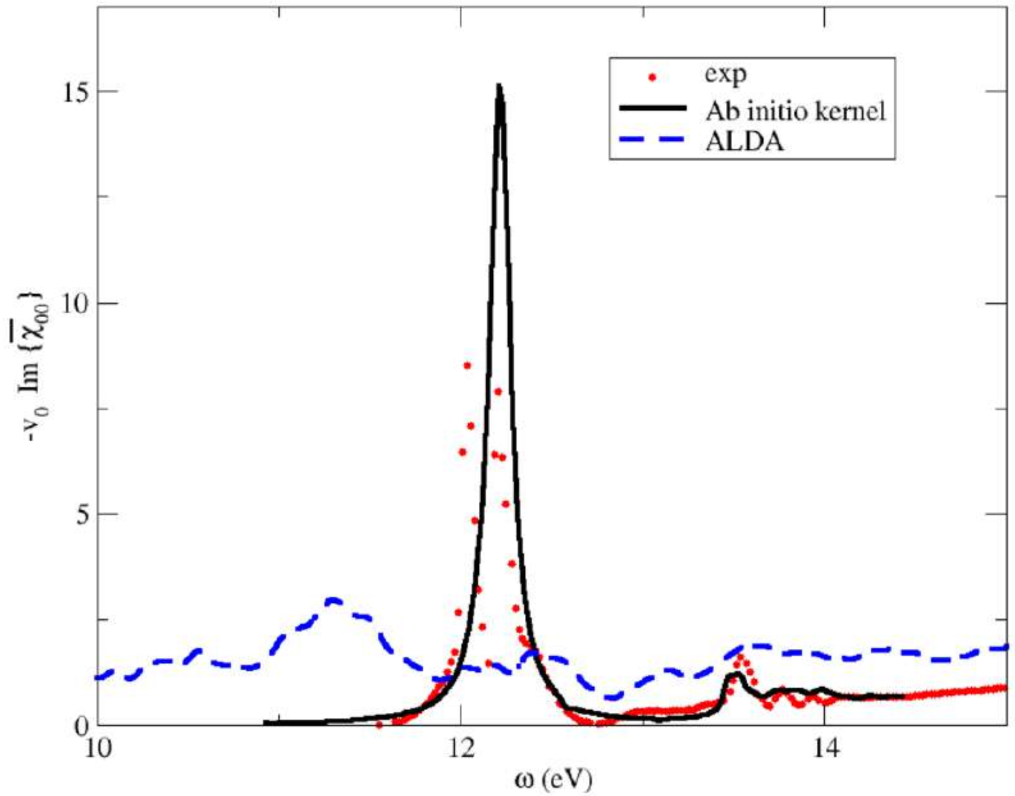


Blase *et al.* . Chem. Phys. **144**, 034109 (2016)

Abs of solid Argon



Marsili *et al.* Phys. Rev. B **76**, 161101(R) (2007)

TDDFT challenges

$\frac{1}{r}$ tail

no memory

TDDFT challenges

burden to v_{xc}, f_{xc}

operator in term of the density

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Demonstration of the Runge Gross theorem

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1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

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$$= n_0(\mathbf{r})\nabla\left[v_{\rm ext}(\mathbf{r},0) - v'_{\rm ext}(\mathbf{r},0)\right]$$

if two potentials differ by more than a constant at t=0, they will generate two different current densities

$$i\frac{\partial\left[\mathbf{j}(\mathbf{r}), H(t)\right]}{\partial t} = \langle\Psi(t)|\left[\left[\mathbf{j}(\mathbf{r}), H(t)\right], H\right]|\Psi(t)\rangle$$

$$i\frac{\partial\,[\mathbf{j}(\mathbf{r}),H(t)]}{\partial t} = \langle\Psi(t)|\big[\,[\mathbf{j}(\mathbf{r}),H(t)]\,,H\big]|\Psi(t)\rangle$$

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v_{ext} ↓ Taylor expandable (in t)

$$i\frac{\partial^2}{\partial t^2}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=t_0} = n_0(\mathbf{r})\nabla\frac{\partial}{\partial t}\left[v_{\mathrm{ext}}(\mathbf{r},t) - v'_{\mathrm{ext}}(\mathbf{r},t)\right]\Big|_{t=0}$$

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⋮

$$i\frac{\partial^{k+1}}{\partial t^{k+1}}\left[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=t_0} = n_0(\mathbf{r})\nabla\,\frac{\partial^k}{\partial t^k}\left[v_{\mathrm{ext}}(\mathbf{r},t)-v'_{\mathrm{ext}}(\mathbf{r},t)\right]\Big|_{t=0}$$

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two different potentials will generate two different current densities

Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r},t)$$

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$$= \nabla \cdot \left[n_0(\mathbf{r})\nabla\left[v_{\text{ext}}(\mathbf{r},0) - v'_{\text{ext}}(\mathbf{r},0)\right]\right]$$

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Demonstration of the Runge Gross theorem

2) $\mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t) \quad \longleftrightarrow \quad n(\mathbf{r},t) \neq n'(\mathbf{r},t)$

$$i\frac{\partial^{k+2}}{\partial t^{k+2}}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right]\Big|_{t=0} = \nabla \cdot \left[n_0(\mathbf{r})\nabla \frac{\partial^k}{\partial t^k}\left[v_{\mathrm{ext}}(\mathbf{r},t) - v'_{\mathrm{ext}}(\mathbf{r},t)\right]\Big|_{t=0}\right.$$

two different potentials will generate two different densities

provided that the surface integral does not vanish

Time evolution operator

$$i\frac{\partial\psi(\mathbf{r},t)}{\partial t} = H(t)\psi(\mathbf{r},t) \quad \longrightarrow \quad i\frac{dU(t,t_0)}{dt} = H(t)U(t,t_0)$$

Time evolution operator

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$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau H(\tau)U(\tau,t_0)$$

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$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_1)H(\tau_2) +$$

$$-i\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_3 H(\tau_1)H(\tau_2)H(\tau_3) + \quad \ldots$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_1)H(\tau_2) +$$

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$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \cdot\cdot \int_{t_0}^{\tau_{n-1}} d\tau_n H(\tau_1)H(\tau_2)\cdot\cdot H(\tau_n)$$

$$U(t,t_0) = 1 + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{t} d\tau_2 \cdot\cdot \int_{t_0}^{t} d\tau_n \mathcal{T}\left[H(\tau_1)H(\tau_2)\cdot\cdot H(\tau_n)\right]$$

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$$U(t,t_0) = \mathcal{T} e^{-i\int_{t_0}^{t} d\tau H(\tau)}$$

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time integrators problem

exponential operator

second-order differencing

Crank-Nicholson implicit midpoint

predictor-corrector

splitting techniques

Magnus expansion

exponential midpoint

$$U(t+\delta t, t) = e^{-i\delta t H(t+\delta t/2)}$$

Taylor expansion

Chebychev polynomials

Lanczos iterative scheme

TDDFT in linear response

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

TDDFT in linear response

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

"small"

TDDFT in linear response

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

"small"

$$\chi(\mathbf{r},\mathbf{r}',\omega)$$

polarizability :: linear response function polarizability :: linear response function

excitations energies

Absorption spectrum

Electron Energy Loss

refraction index

Inelastic X-ray Scattering

Compton Scattering

Reflectivity

Surface differential reflectivity

Reflectance Anisotropy spectroscopy

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

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

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

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

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

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

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

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

polarizability

polarizability :: density-density response function

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

polarizability :: density-density response function

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

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

polarizability :: density-density response function

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

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

Exercise

polarizability :: density-density response function

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

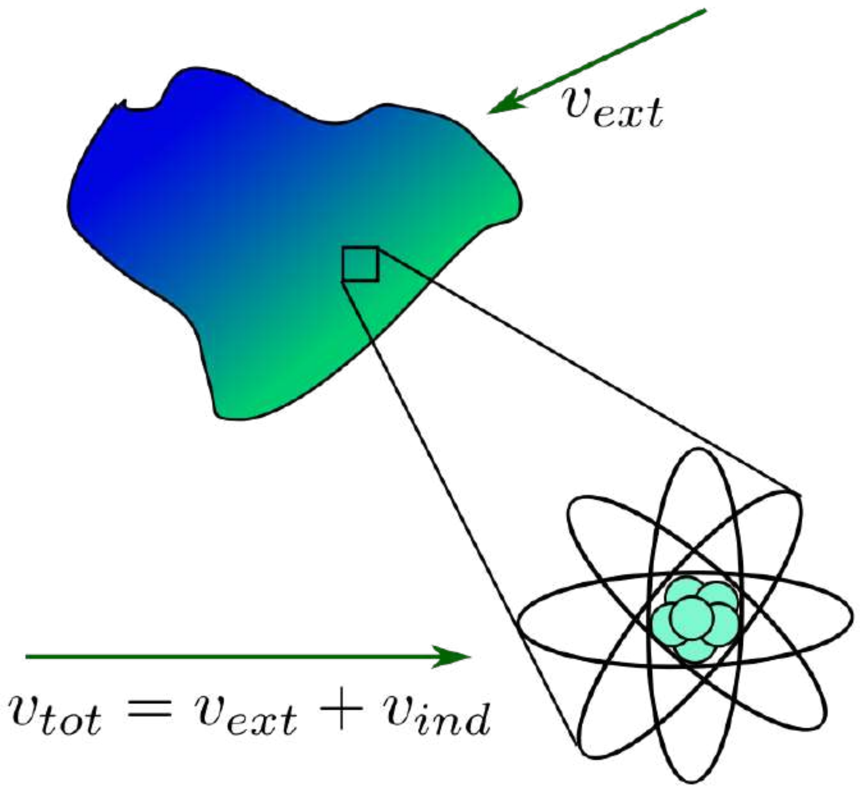
$$\hat{n}(\mathbf{r},t) = e^{-iHt}\hat{n}(\mathbf{r})e^{iHt} \qquad \hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$$

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

Ω_I excitations energies

Exercise

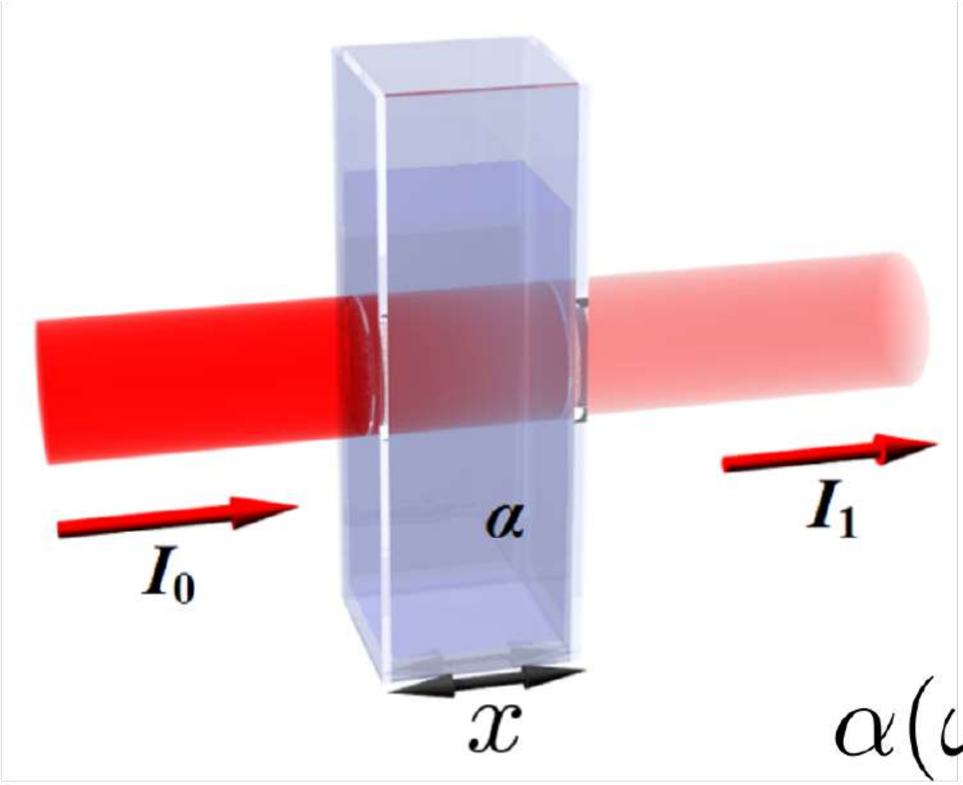
Connection to spectroscopies :: inverse dielectric function



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

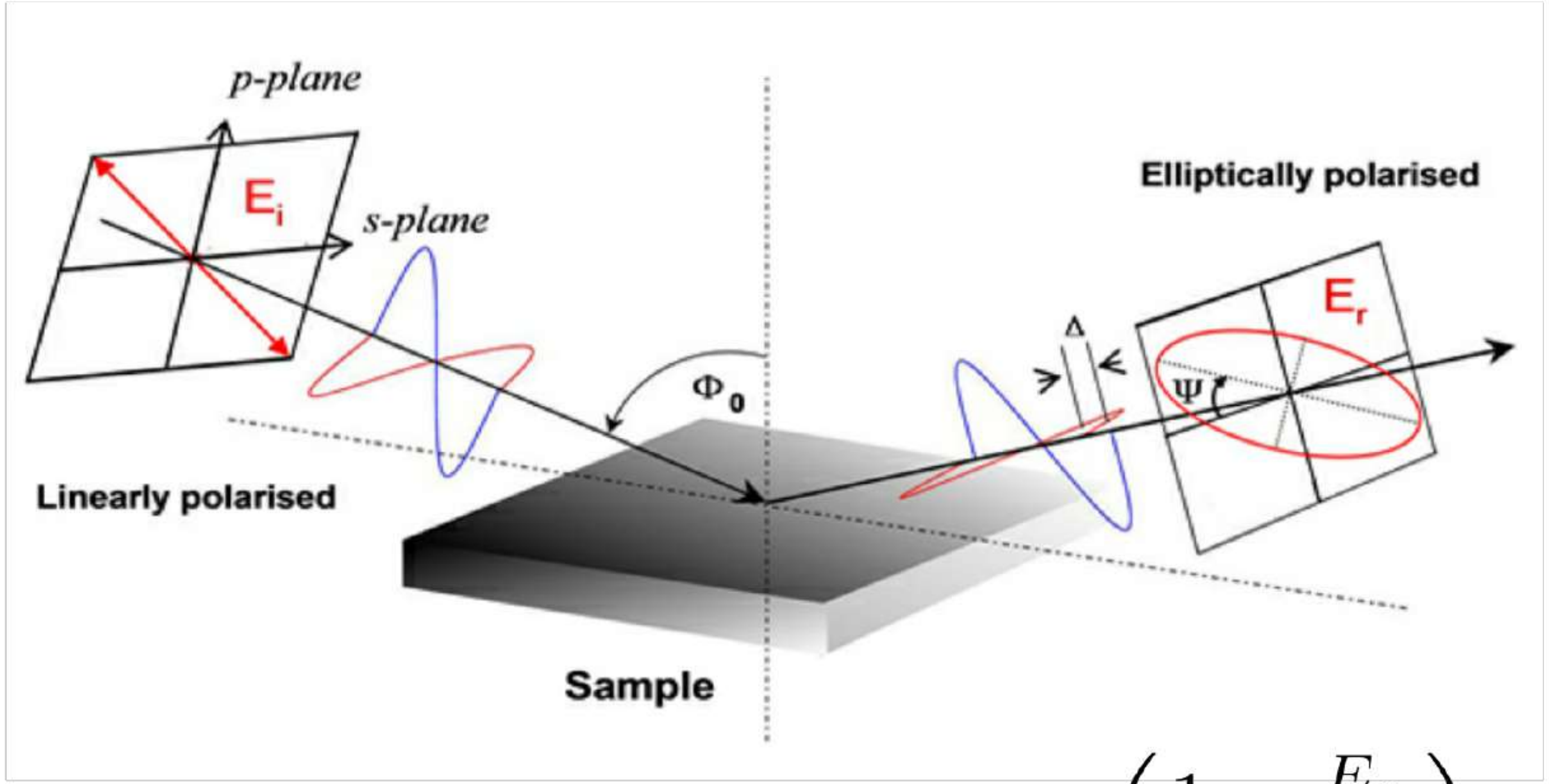
$$\varepsilon^{-1} = 1 + v\chi$$

Connection to spectroscopies :: optical absorption



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

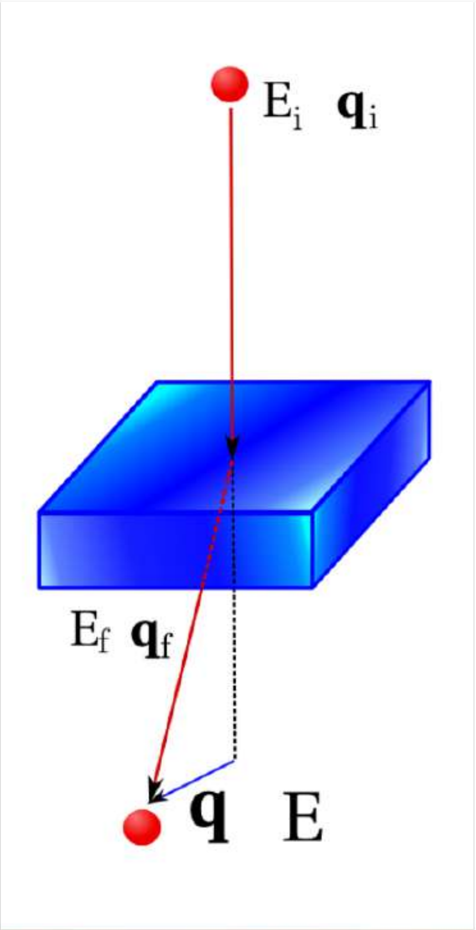
Connection to spectroscopies :: optical absorption



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

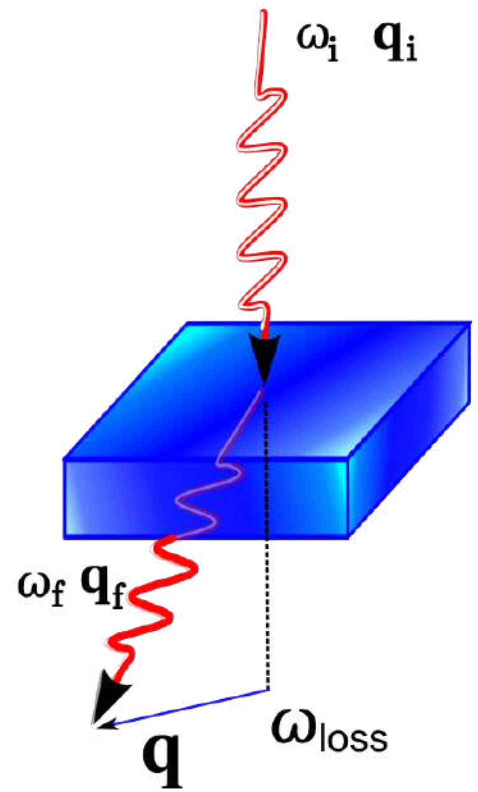
Connection to spectroscopies :: electron energy loss (EELS)

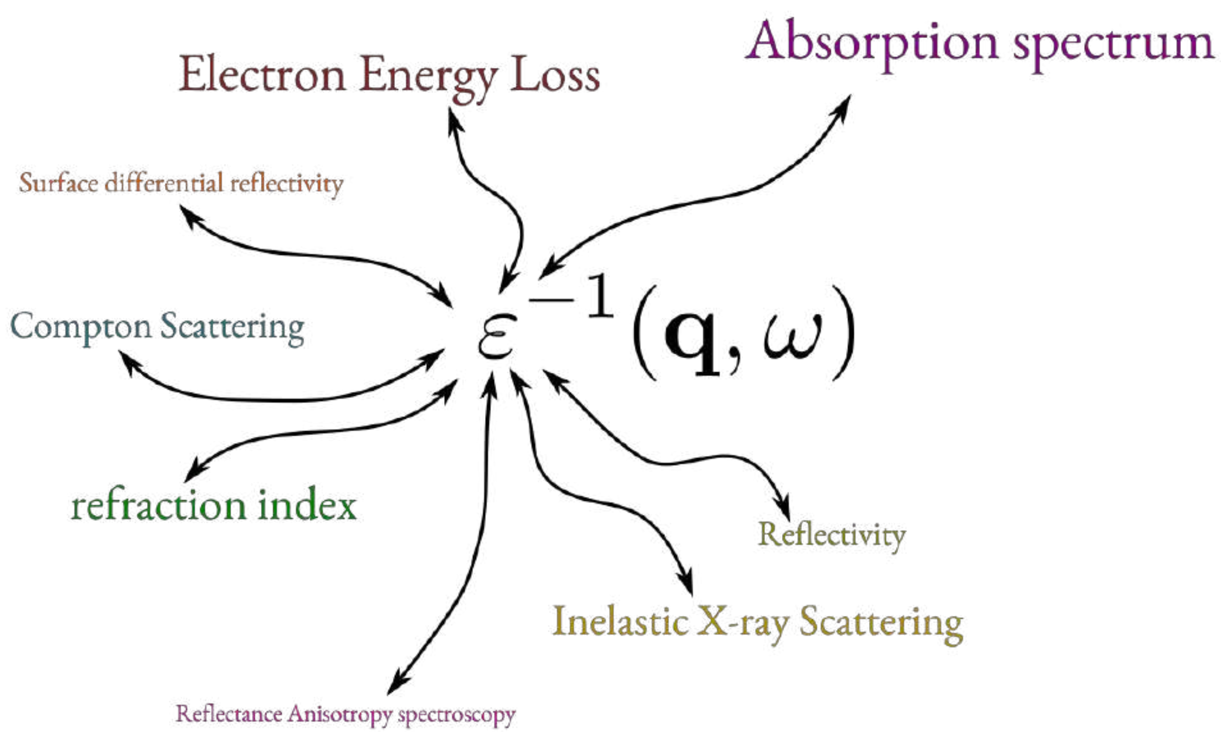
$$\frac{d^2\sigma}{d\Omega d\omega} \propto \mathrm{Im}\left[\varepsilon^{-1}(\mathbf{q},\omega)\right]$$



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

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




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

Electron Energy Loss

Absorption spectrum

Surface differential reflectivity

Compton Scattering

refraction index

Reflectivity

Inelastic X-ray Scattering

Reflectance Anisotropy spectroscopy

$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v(\mathbf{q})\chi(\mathbf{q},\omega)$$

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

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

$\underbrace{\epsilon_j - \epsilon_i}$ one-particle excitations energies

Polarizability of an independent-particle system

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Ψ_0 single determinant

Exercise

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

one-particle excitations energies

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

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

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

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

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

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

Dyson equation for the polarizability

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

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

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

Dyson equation for the polarizability

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

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

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

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

- evaluation of χ knowing χ^0 (ground state calculation)
- f_{xc} functional of the ground-state density
- approximations for f_{xc}
  - $f_{xc} = 0$
  - $f_{xc} = \dfrac{\delta v_{xc}^{gs}}{\delta n}$
  - 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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- determination of $\chi = \chi^0 + \chi^0 \left[v + f_{xc}\right] \chi$ (approx ::) f_{xc}

Practical procedure for χ and ε^{-1}

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- determination of $\chi = \chi^0 + \chi^0 \left[v + f_{xc}\right] \chi$ (approx ::) f_{xc}
- 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

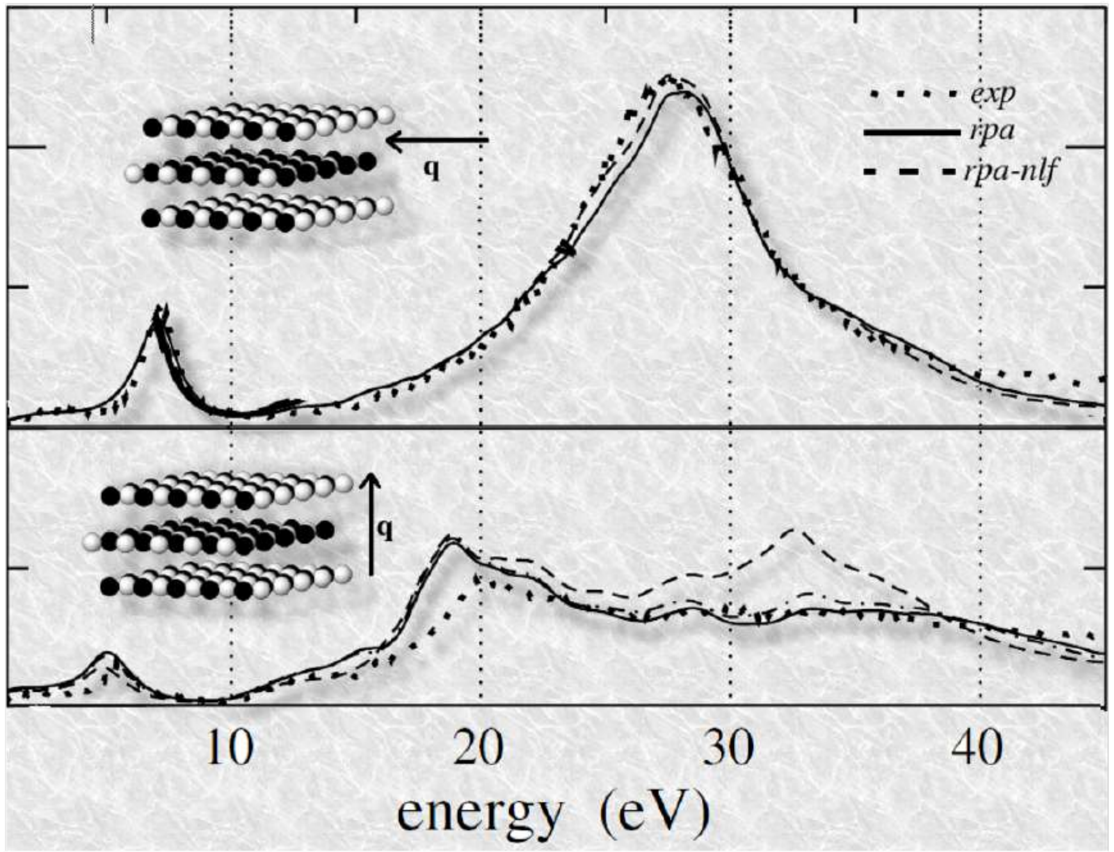
Practical procedure for χ and ε^{-1}

Scaling (with N_{atoms})

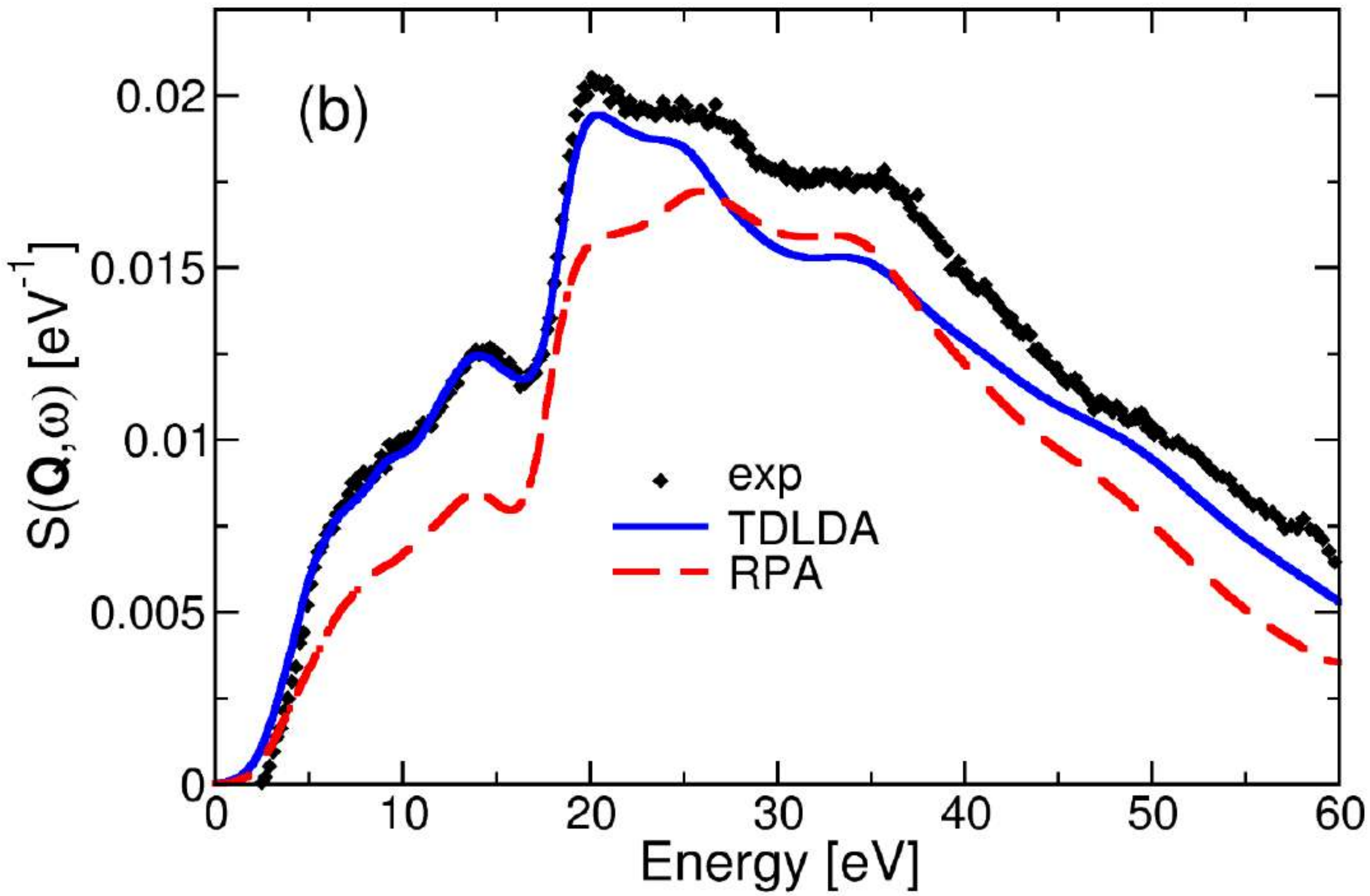
- DFT-KS calculation ψ_i, ϵ_i (approx :: v_{xc}, V_{ion}^{ps}) — $o(N^{1\div3})$
- creation of $\chi^0 = \sum_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i0^+}$ — $o(N^4)$
- determination of $\chi = \chi^0 + \chi^0 [v + f_{xc}] \chi$ (approx :: f_{xc}) — $o(N^{2\div3})$
- 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

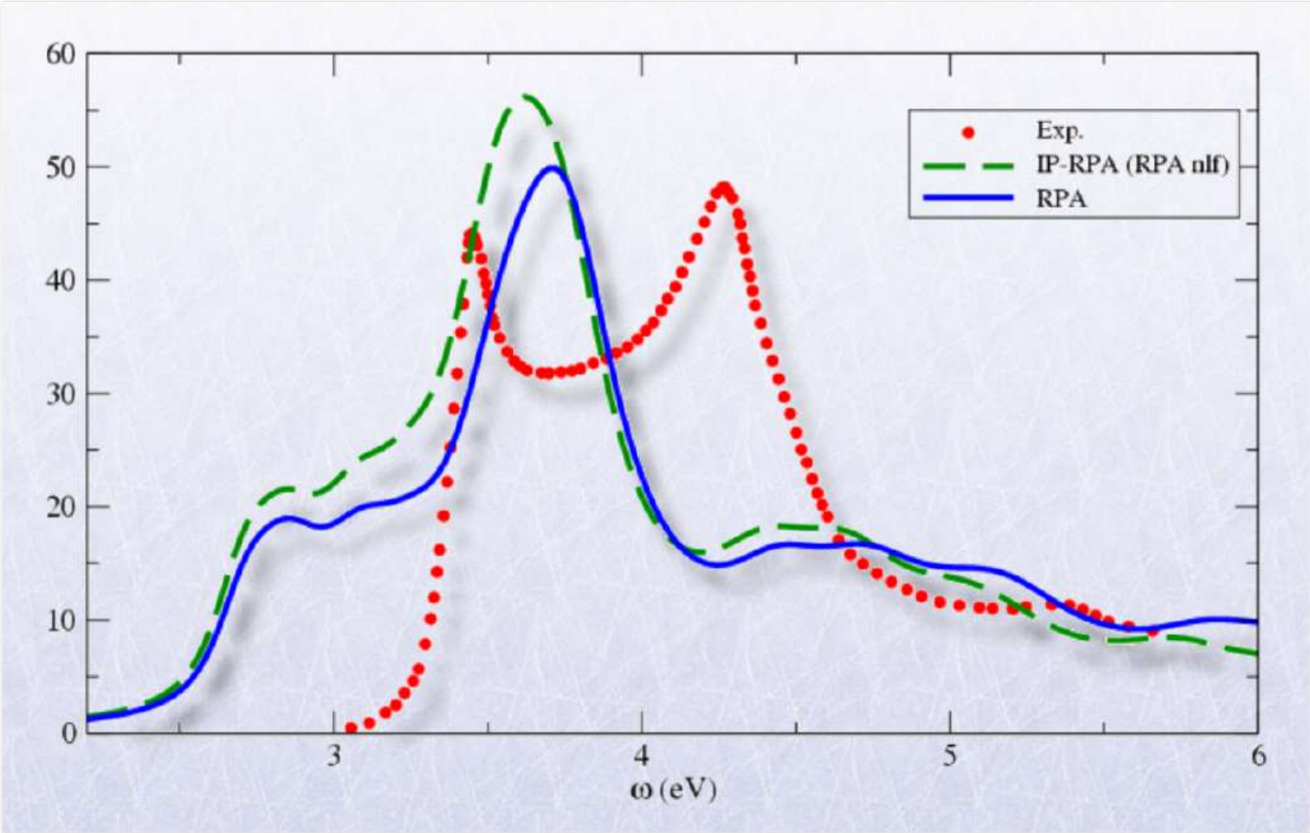
EELS of graphite



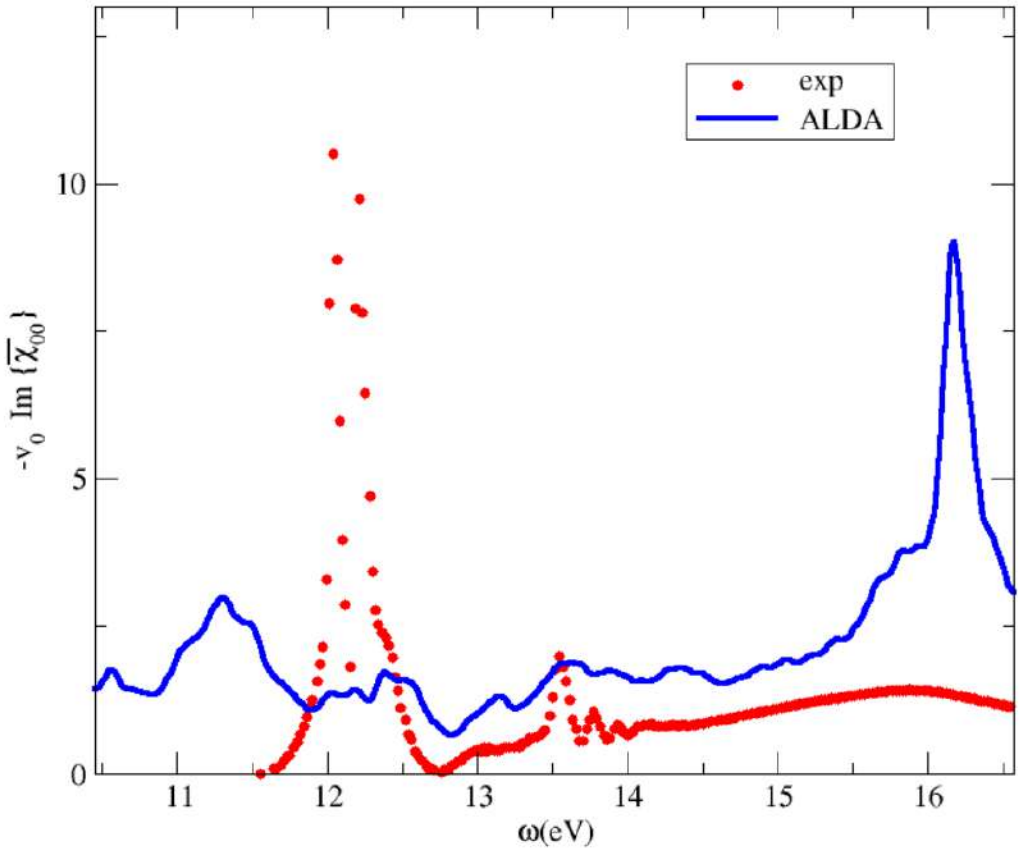
IXS of Silicon

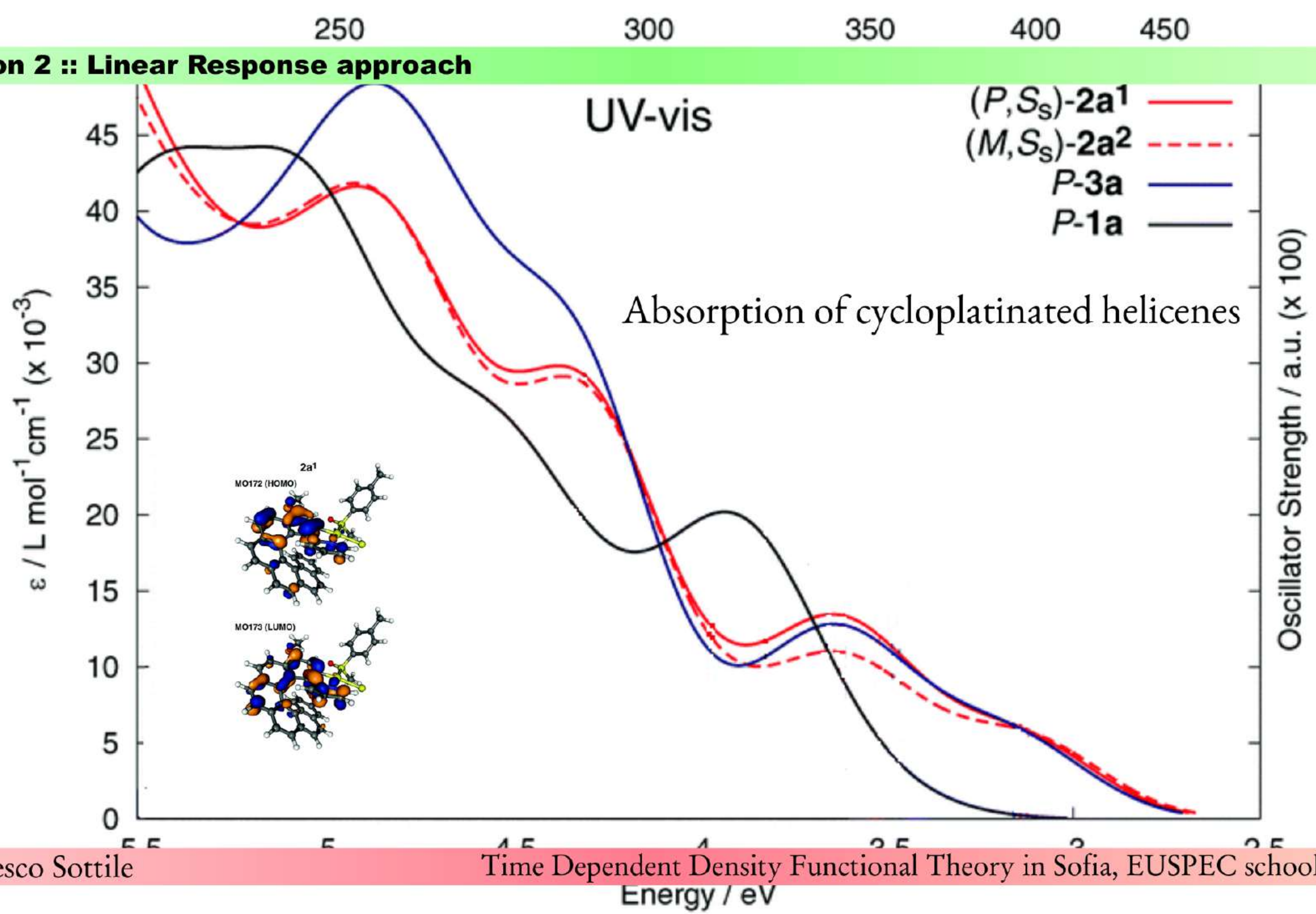


Absorption of Silicon

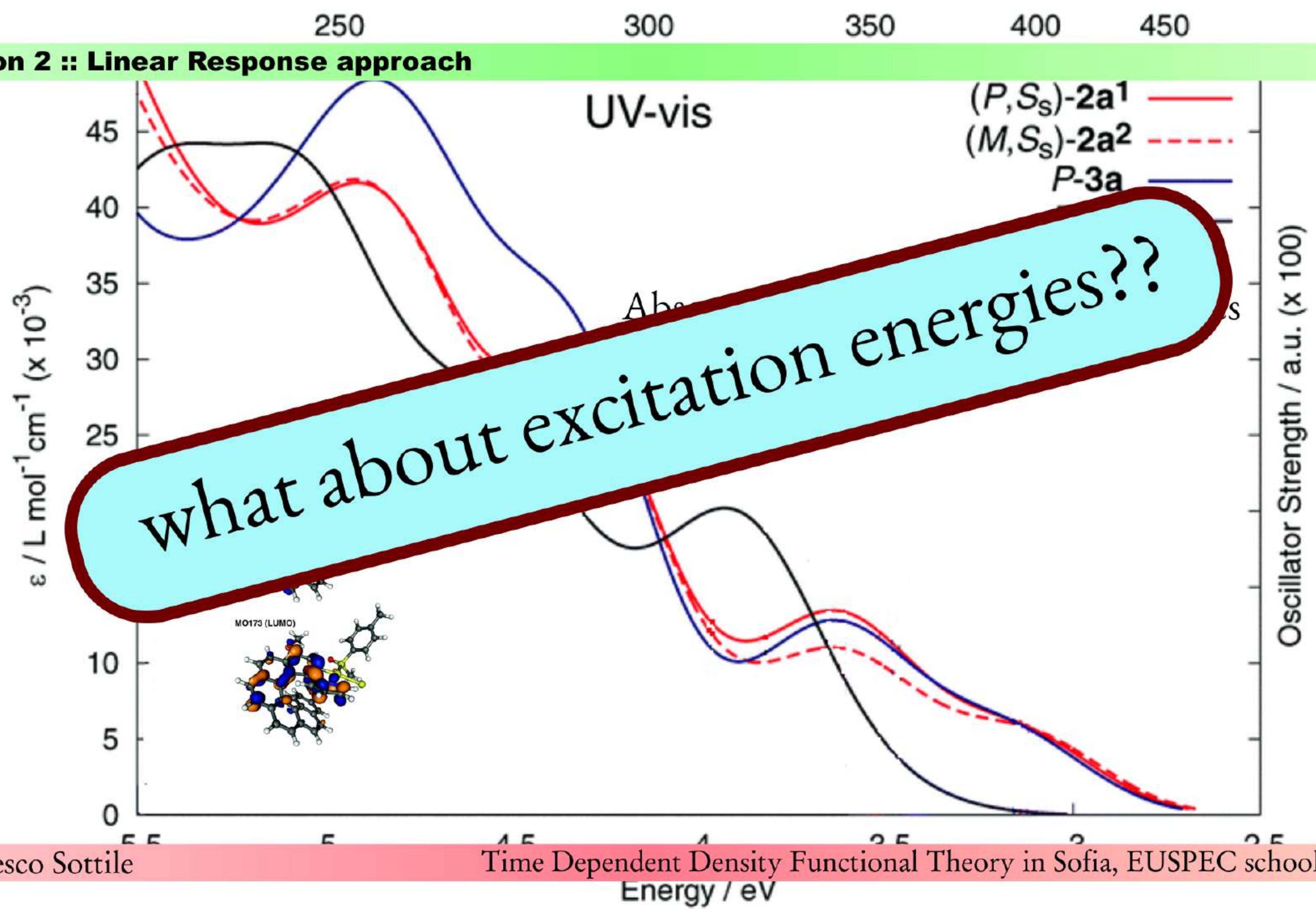


Absorption of Argon

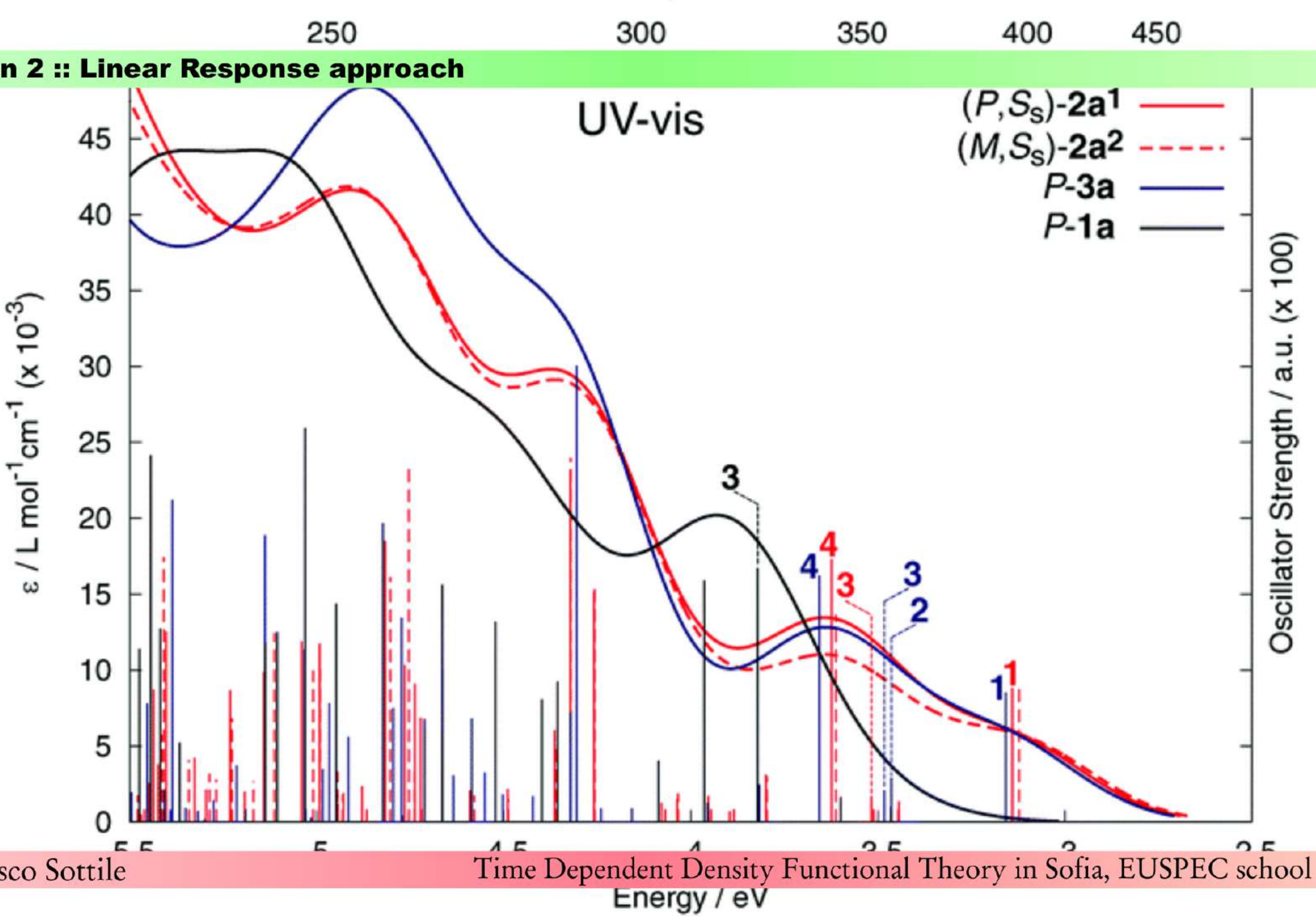




Absorption of cycloplatinated helicenes



what about excitation energies??


UV-vis
(P,S_S)-2a¹
(M,S_S)-2a²
P-3a
P-1a
ε / L mol⁻¹cm⁻¹ (x 10⁻³)
Oscillator Strength / a.u. (x 100)
Energy / eV
250
300
350
400
450
45
40
35
30
25
20
15
10
5
0
5.5
5
4.5
4
3.5
3
2.5

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

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

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

basis change

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

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

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

basis change

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

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

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

diagonal in ij, kl

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

Exercise

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

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

Exercise

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

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

$$\chi =$$

$$\chi_{ij}^{kl}$$

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

$$\chi_{ij}^{kl} \qquad \omega - (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$$

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

χ_{ij}^{kl}

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

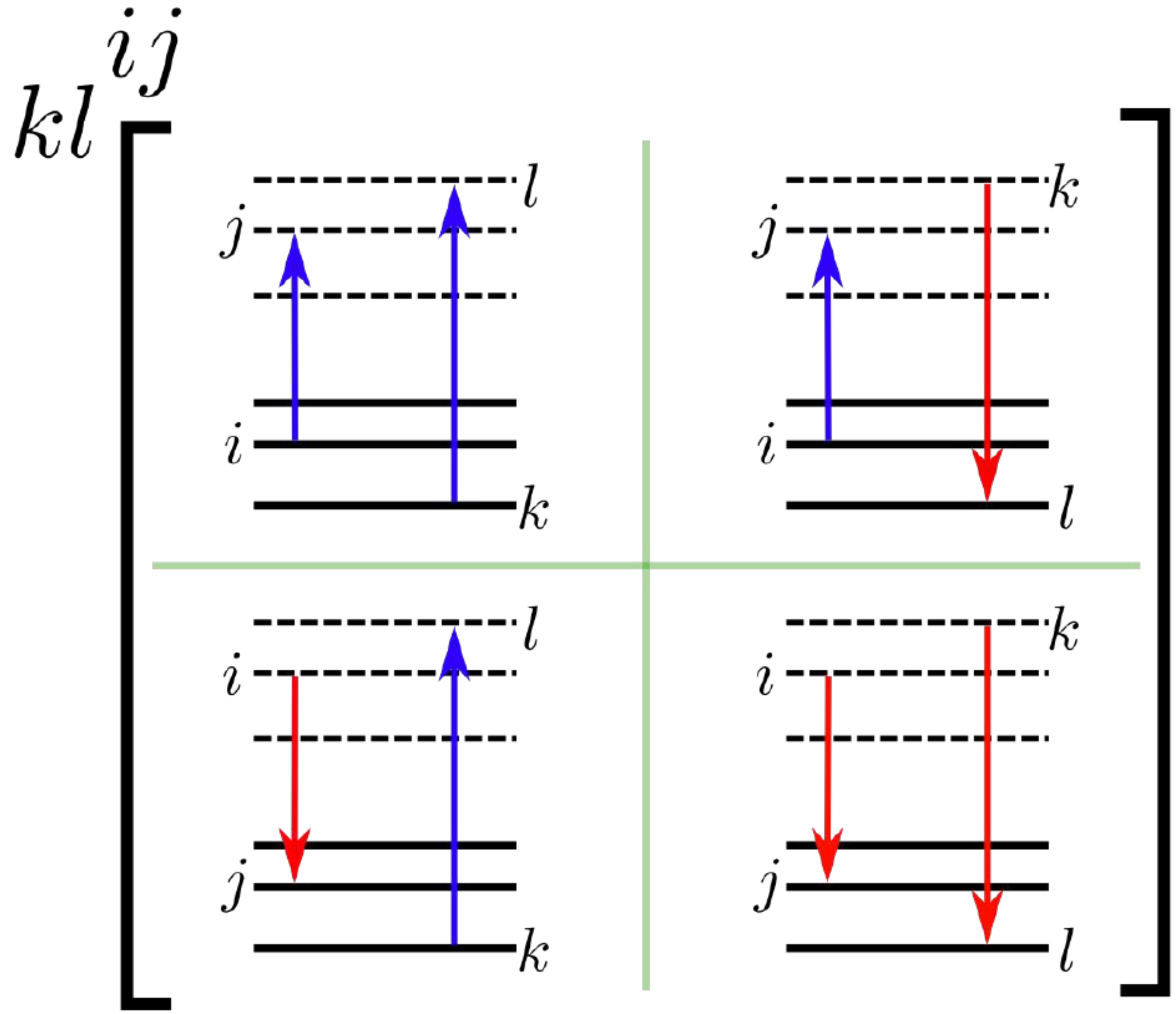
$K_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')K(\mathbf{r},\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$

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

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

$$H^{\mathrm{EXC}} = {}_{kl}\overset{ij}{\begin{bmatrix} (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl} & & K_{ij}^{kl} \\ & (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl} & K_{ij}^{kl} \\ K_{ij}^{kl} & & K_{ij}^{kl} \\ & K_{ij}^{kl} & (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl} \end{bmatrix}}$$

$$H^{\mathrm{EXC}} =$$



$$H^{\mathrm{EXC}} = {}_{kl}^{\;\;ij}\left[\begin{array}{c|c} \mathrm{A} & \mathrm{B} \\ \hline \text{-}\mathrm{B}^* & \text{-}\mathrm{A}^* \end{array}\right]$$

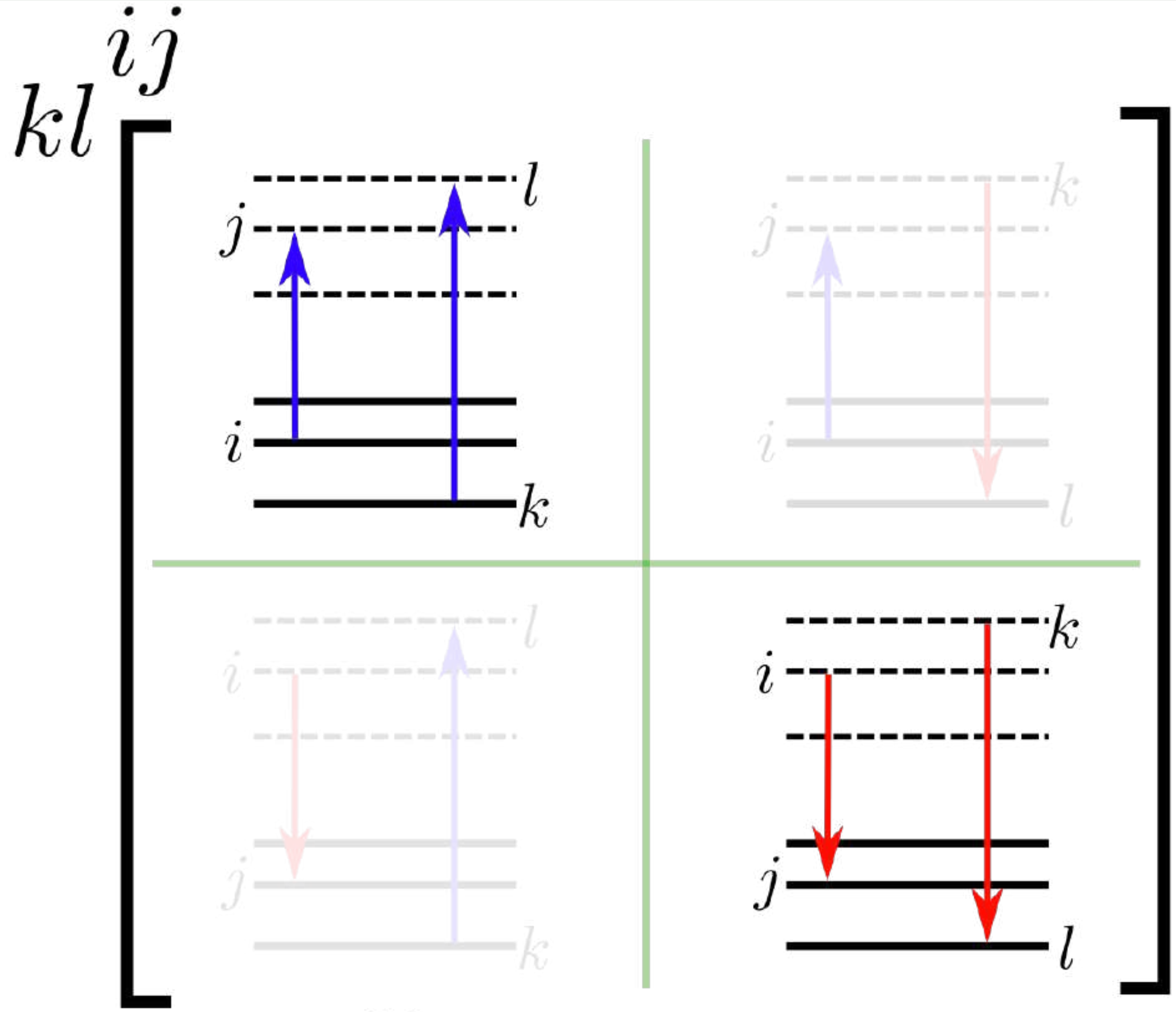
$$\left[\begin{array}{c|c} A & B \\ \hline -B^* & -A^* \end{array}\right]\begin{bmatrix} X \\ Y \end{bmatrix} = E_\lambda \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = E_\lambda \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$H^{\mathrm{EXC}} = {}_{kl}^{\;\;ij}\left[\begin{array}{c|c} A & B \\ \hline -B^* & -A^* \end{array}\right]$$

Tamm-Dancoff approx

$$H^{\mathrm{EXC}} = $$



Tamm-Dancoff approx

		
$\chi = \chi^0 + \chi^0 \left[v + f_{xc} \right] \chi$	full spectrum N^4 scaling	excitations energies
$\begin{bmatrix} A & B \\ -B^* & -A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = E_\lambda \begin{bmatrix} X \\ Y \end{bmatrix}$	few excitations energies iterative techniques analysis	N^6 scaling