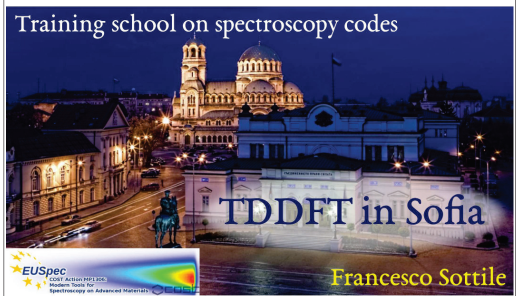

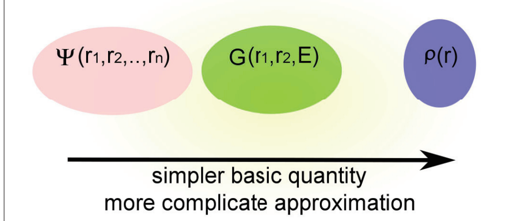

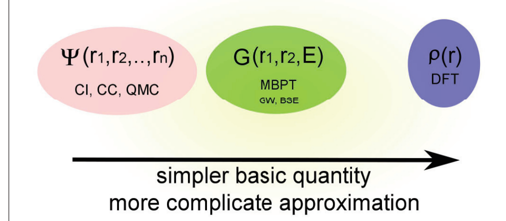

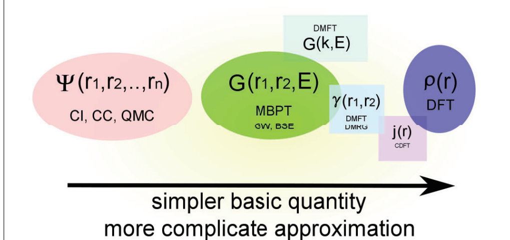

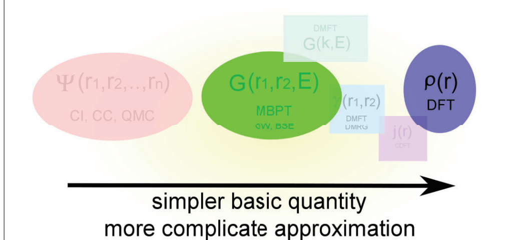

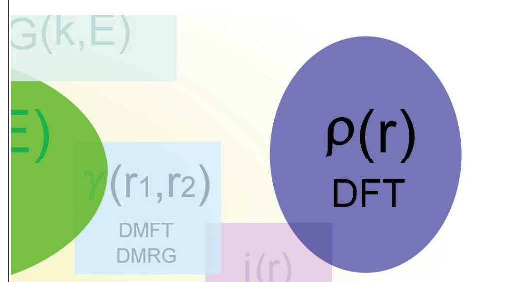

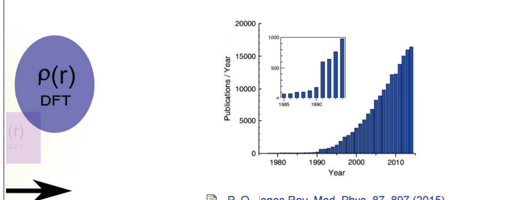

R. O. Jones Rev. Mod. Phys. 87, 897 (2015)

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**

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Excitatio[redacted]Spectra

- band structure ca[redacted]lation, via Kohn[redacted] → **PES**
- optical properties,[redacted]linear response → **Absorption**, **Electron[redacted]ergy Loss**

DFT ⟶ 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
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  - beyond linear response
- Micro-macro connection and the DP code

DFT **TDDFT**

DFT

Hohenberg-Kohn theorem

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

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

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

TDDFT

Runge-Gross theorem

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

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

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

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Demonstration

Runge-Gross theorem

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

Demonstration

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

Runge-Gross theorem

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

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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

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

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

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

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

TDDFT

Kohn-Sham equation

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

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

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TDDFT

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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)

]

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

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

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

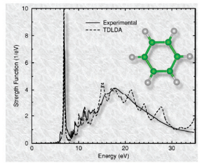
$$v_{xc}^{\rm ALDA}[n](\mathbf{r},t) = v_{xc}^{\rm heg}(n(\mathbf{r},t)) = \frac{d}{dn}\left[n e_{xc}^{\rm heg}(n)\right]\Big|_{n=n(\mathbf{r},t)}$$

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

TDDFT applications

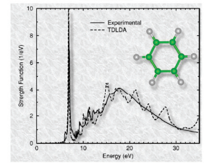
- Absorption spectra of simple molecules
- Loss function of metals and semiconductors

Benzene



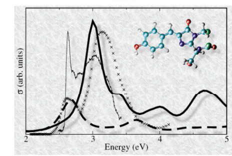
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

Benzene



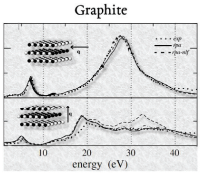
Yabana and Bertsch Int.J.Mod.Phys.**75**, 55 (1999)

GFP



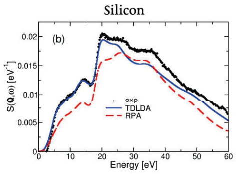
M.Marques *et al.* Phys.Rev.Lett. **90**, 258101 (2003)

Graphite



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

Silicon

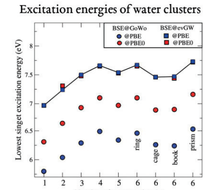


Weissker *et al.* Phys. Rev. B **81**, 085104 (2010)

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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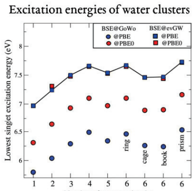
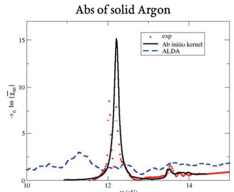


Blase *et al.* . Chem. Phys. **144**, 034109 (2016)

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

Outline

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

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

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

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$v_{\rm ext}$ ↓ Taylor expandable (in t)

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⋮

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

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two different potentials will generate two different current densities

Demonstration of the Runge Gross theorem

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

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two different potentials will generate two different densities

provided that the surface integral does not vanish

Time evolution operator

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

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

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

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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

- second-order differencing
- Crank-Nicholson implicit midpoint
- predictor-corrector
- splitting techniques
- Magnus expansion
- exponential midpoint

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

exponential operator

- 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

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"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

Refectivity

Surface differential reflectivity

Reflectance Anisotropy spectroscopy

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

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

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

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

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

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

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

polarizability

polarizability :: density-density response function

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

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

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

polarizability :: density-density response function

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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

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

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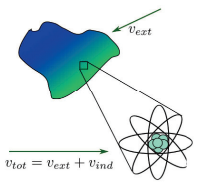
Ω_I excitations energies

Exercise

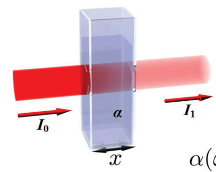
Connection to spectroscopies :: inverse dielectric function



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

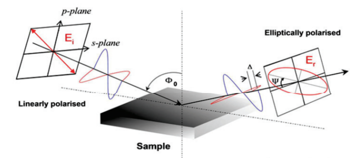
$$\varepsilon^{-1} = 1 + v\chi$$

Connection to spectroscopies :: optical absorption



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

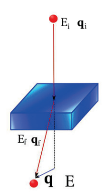
Connection to spectroscopies :: optical absorption



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

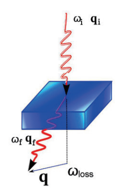
Connection to spectroscopies :: electron energy loss (EELS)

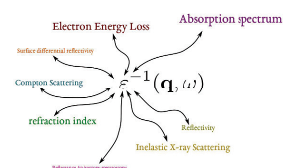
$$\frac{d^2\sigma}{d\Omega d\omega} \propto \mathrm{Im}\left[\varepsilon^{-1}(\mathbf{q},\omega)\right]$$

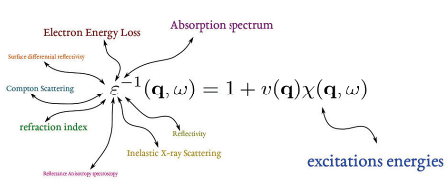


Connection to spectroscopies :: inelastic X-ray scattering (IXS)

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







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

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

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

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

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

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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}
  - $f_{xc}=0$
  - $f_{xc}=\frac{\delta v_{xc}^{gs}}{\delta n}$
  - 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

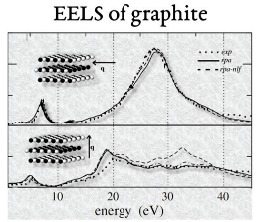
Practical procedure for χ and ε^{-1}

Scaling (with N_{atoms})

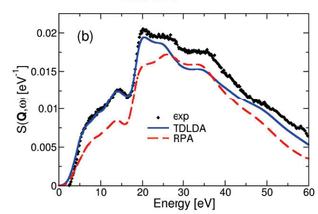
- DFT-KS calculation ψ_i, ϵ_i (approx :: v_{xc} V_{ion}^{ps}) $o(N^{1\div3})$
- creation of $\chi^0 = \sum_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i0^+}$ $o(N^4)$
- determination of $\chi = \chi^0 + \chi^0 \left[v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

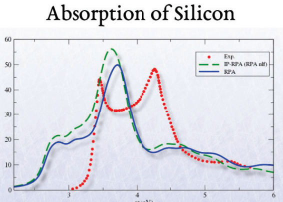
EELS of graphite



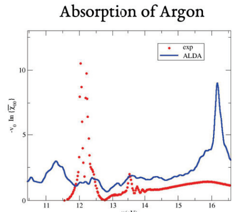
IXS of Silicon

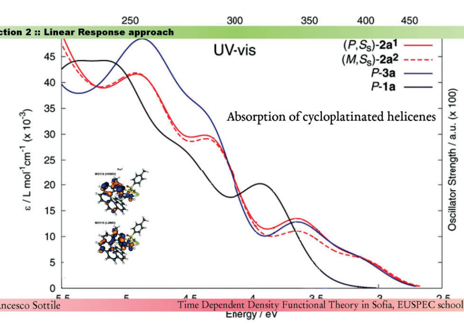


Absorption of Silicon

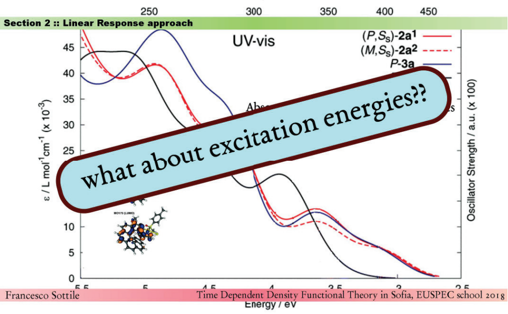


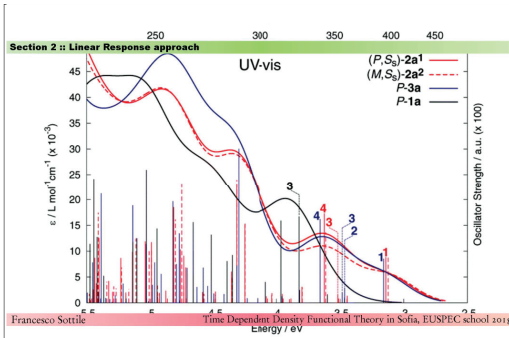
Absorption of Argon





Absorption of cycloplatinated helicenes





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

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basis change

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

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) +$$
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$$f_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_k(\mathbf{r}')\psi_l^*(\mathbf{r}')\, f(\mathbf{r},\mathbf{r}')\ d\mathbf{r}d\mathbf{r}'$$

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

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

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

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

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

$$\chi =$$

χ_{ij}^{kl}

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

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

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

χ_{ij}^{kl} $\omega - (\epsilon_j - \epsilon_i)\delta_{ik}\delta_{jl}$ $K_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')K(\mathbf{r},\mathbf{r}')\, d\mathbf{r}d\mathbf{r}'$

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

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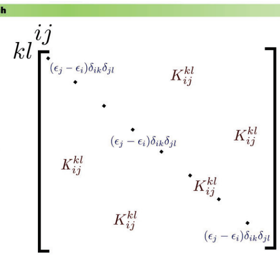
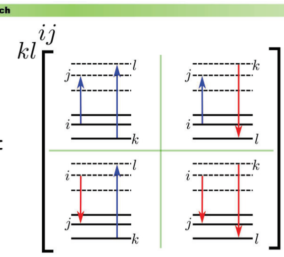
$H^{\text{EXC}} =$



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



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

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

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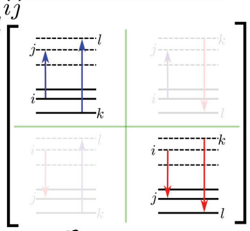
$$H^{\mathrm{EXC}} = {}^{ij}_{kl}\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{-B^*} & \mathbf{-A^*} \end{bmatrix}$$

Tamm-Dancoff approx

$$H^{\mathrm{EXC}} = {}^{ij}_{kl}\Big[$$

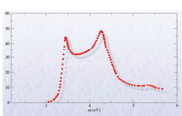


Tamm-Dancoff approx

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

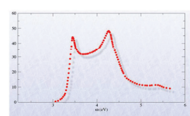
microscopic ⟷ Macroscopic

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$$



microscopic ⟷ (average procedure) Macroscopic

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$$



$$f(\mathbf{r}) \longrightarrow f_{\mathbf{G}}(\mathbf{q}) = \frac{1}{\Omega}\int d\mathbf{r} f(\mathbf{r}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}$$

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$$\varepsilon_M^{-1}(\mathbf{q}, \omega) = \varepsilon_{00}^{-1}(\mathbf{q}, \omega)$$

$$\chi^0_{\mathbf{GG}'}(\mathbf{q},\omega)=\sum_{vc\mathbf{k}}\frac{\left\langle\phi_{v\mathbf{k}}|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}\,\phi^*_{c\mathbf{k}+\mathbf{q}}\right\rangle\left\langle\phi_{c\mathbf{k}+\mathbf{q}}|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\phi^*_{v\mathbf{k}}\right\rangle}{\omega-(\epsilon_{c\mathbf{k}+\mathbf{q}}-\epsilon_{v\mathbf{k}})+i\eta}$$

$$\chi_{\mathbf{GG}'}(\mathbf{q},\omega)=\left[1-\chi^0(v+f_{xc})\right]^{-1}_{\mathbf{GG}''}\chi^0_{\mathbf{G}''\mathbf{G}'}$$

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$$\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega)=\delta_{\mathbf{GG}'}+v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{GG}'}(\mathbf{q},\omega)$$

$$\mathrm{ELS}(\mathbf{q},\omega)=-Im\{\varepsilon^{-1}_{\mathrm{M}}(\mathbf{q},\omega)\}=-Im\{\varepsilon^{-1}_{00}(\mathbf{q},\omega)\}$$

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$$\alpha\;\propto\;Im\Big[\varepsilon_M(\mathbf{q},\omega)\Big]$$

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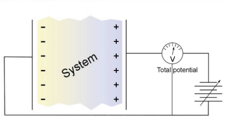
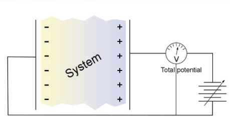
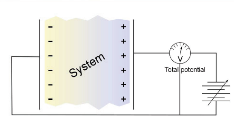


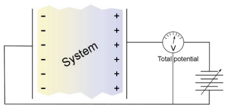


$$\mathsf{D}(\mathbf{q},\omega)=\varepsilon_M(\mathbf{q},\omega)\mathsf{E}(\mathbf{q},\omega)$$



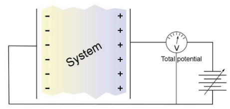
$$\mathsf{D}(\mathbf{q},\omega)=\varepsilon_M(\mathbf{q},\omega)\mathsf{E}(\mathbf{q},\omega)$$

$$\mathsf{E}_{\mathbf{G}}(\mathbf{q},\omega)=\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)\mathsf{D}_{\mathbf{G}'}(\mathbf{q},\omega)$$



$$\mathsf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\mathsf{E}(\mathbf{q},\omega)$$

$$\mathsf{E}_0(\mathbf{q},\omega) = \varepsilon_{00}^{-1}(\mathbf{q},\omega)\mathsf{D}_0(\mathbf{q},\omega)$$



$$\mathsf{D}(\mathbf{q},\omega) = \varepsilon_M(\mathbf{q},\omega)\mathsf{E}(\mathbf{q},\omega)$$

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$$\varepsilon_M(\mathbf{q},\omega) = \frac{1}{\varepsilon_{00}^{-1}(\mathbf{q},\omega)}$$

? $\varepsilon_{00}(\mathbf{q},\omega)$?

? $\varepsilon_{00}(\mathbf{q},\omega)$?

$\varepsilon_{00}(\mathbf{q},\omega)$ is a 'macroscopic quantity' without local fields

TDDFT linear response

Pseudopotential, plane waves, frequency domain

`http://etsf.polytechnique.fr/Software/Ab_Initio`

Fortran (C,Perl,Python), LAPACK/BLAS (MKL, DXML, ASL, ESSL), FFTW3

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Relies on ground state calculation (Abinit, Quantum Espresso)

$$\chi = \chi^0 + \chi^0 \Big[v + f_{\mathrm{xc}} \Big] \chi$$

$$\chi^0\left(\mathbf{r},\mathbf{r}',\omega\right) = \sum_{vc\mathbf{k}} \frac{\phi^*_{v\mathbf{k}}(\mathbf{r})\phi_{c\mathbf{k}}(\mathbf{r})\phi^*_{c\mathbf{k}}(\mathbf{r}')\phi_{v\mathbf{k}}(\mathbf{r}')}{\omega - (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}) + i\eta}$$

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$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{\texttt{npwwfn}} c_{n,\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

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$$\phi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}}^{\texttt{npwwfn}} c_{n,\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\tilde{\rho}_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}) = \int d\mathbf{r}\, \phi_{v,\mathbf{k}}(\mathbf{r}) e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \phi_{c,\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

$$\chi^0(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{2}{N_{\mathbf{k}}}\sum_{v,c,\mathbf{k}} \frac{\tilde\rho_{vc\mathbf{k}}(\mathbf{q},\mathbf{G})\,\tilde\rho^*_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega-(\varepsilon_{c,\mathbf{k}+\mathbf{q}}-\varepsilon_{v,\mathbf{k}})+i\eta}$$

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npwmat

q polarization vector

$$\chi^0(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{2}{N_{\mathbf{k}}}\sum_{v,c,\mathbf{k}} \frac{\tilde\rho_{vc\mathbf{k}}(\mathbf{q},\mathbf{G})\,\tilde\rho^*_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega-(\varepsilon_{c,\mathbf{k}+\mathbf{q}}-\varepsilon_{v,\mathbf{k}})+i\eta}$$

npwmat

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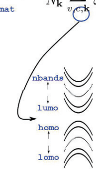
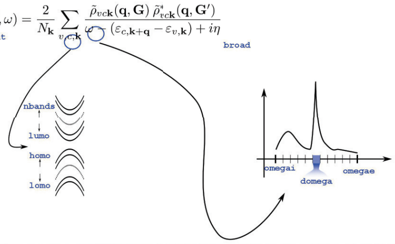


$$\chi^0(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{2}{N_{\mathbf{k}}}\sum_{v,c,\mathbf{k}} \frac{\tilde\rho_{vc\mathbf{k}}(\mathbf{q},\mathbf{G})\,\tilde\rho^*_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}')}{\omega-(\varepsilon_{c,\mathbf{k}+\mathbf{q}}-\varepsilon_{v,\mathbf{k}})+i\eta}$$

npwmat

broad

q polarization vector



input file

```
npwwfn  120
npwmat  12
rpa
q 0.0 0.0 0.0
lomo 1
nbands 7
omegai  0.0
omegae  10.0
domega 0.5
broad  0.5
```



```
~/bin/dp -i <inputfile> -k <kssfile> -r prefix > dp_prefix.log
```