Time Dependent Density Functional Theory

Francesco Sottile

International summer School in electronic structure Theory: electron correlation in Physics and Chemistry (ISTPC)

27 June

ISTPC

2024

REST

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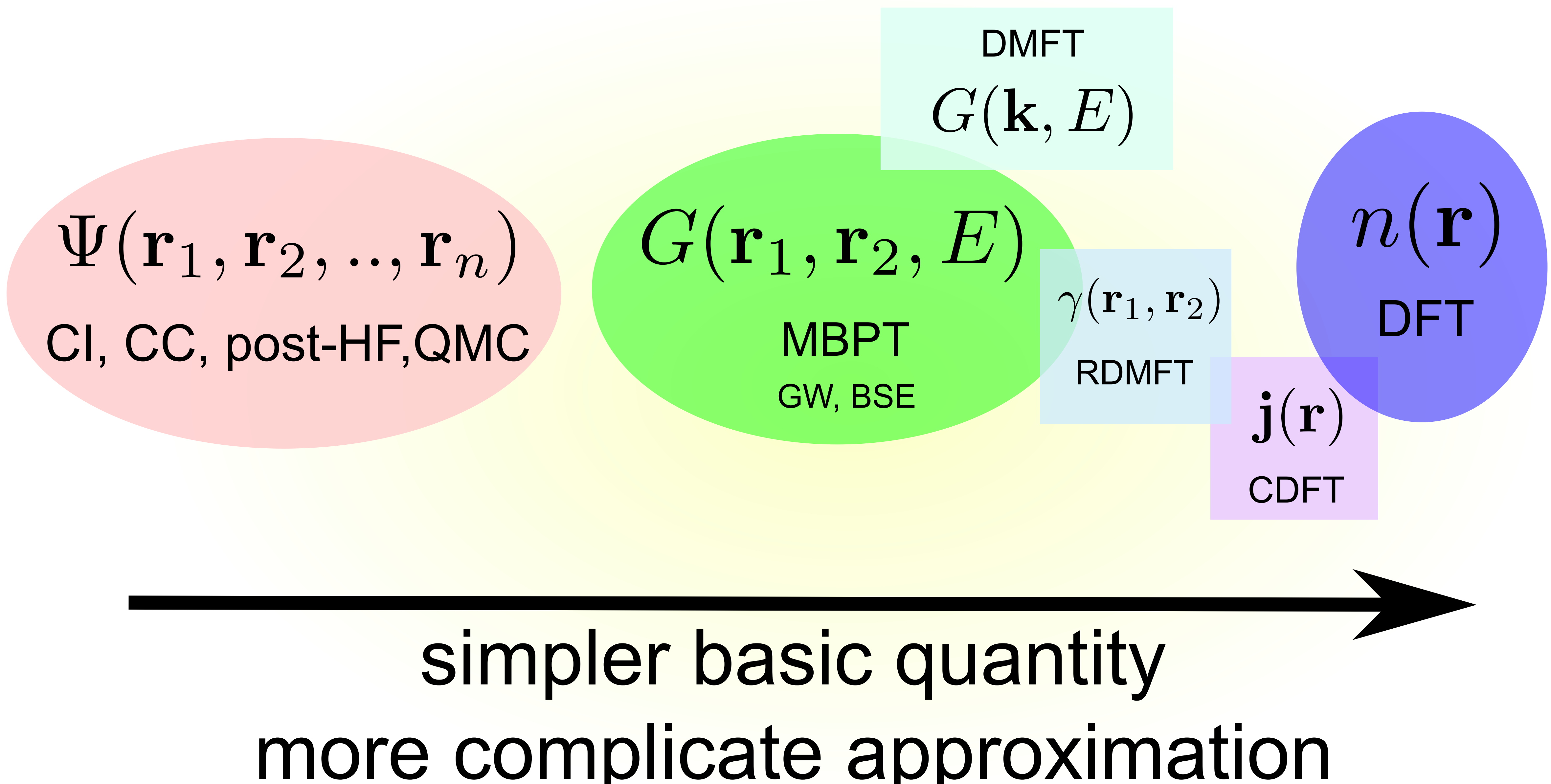
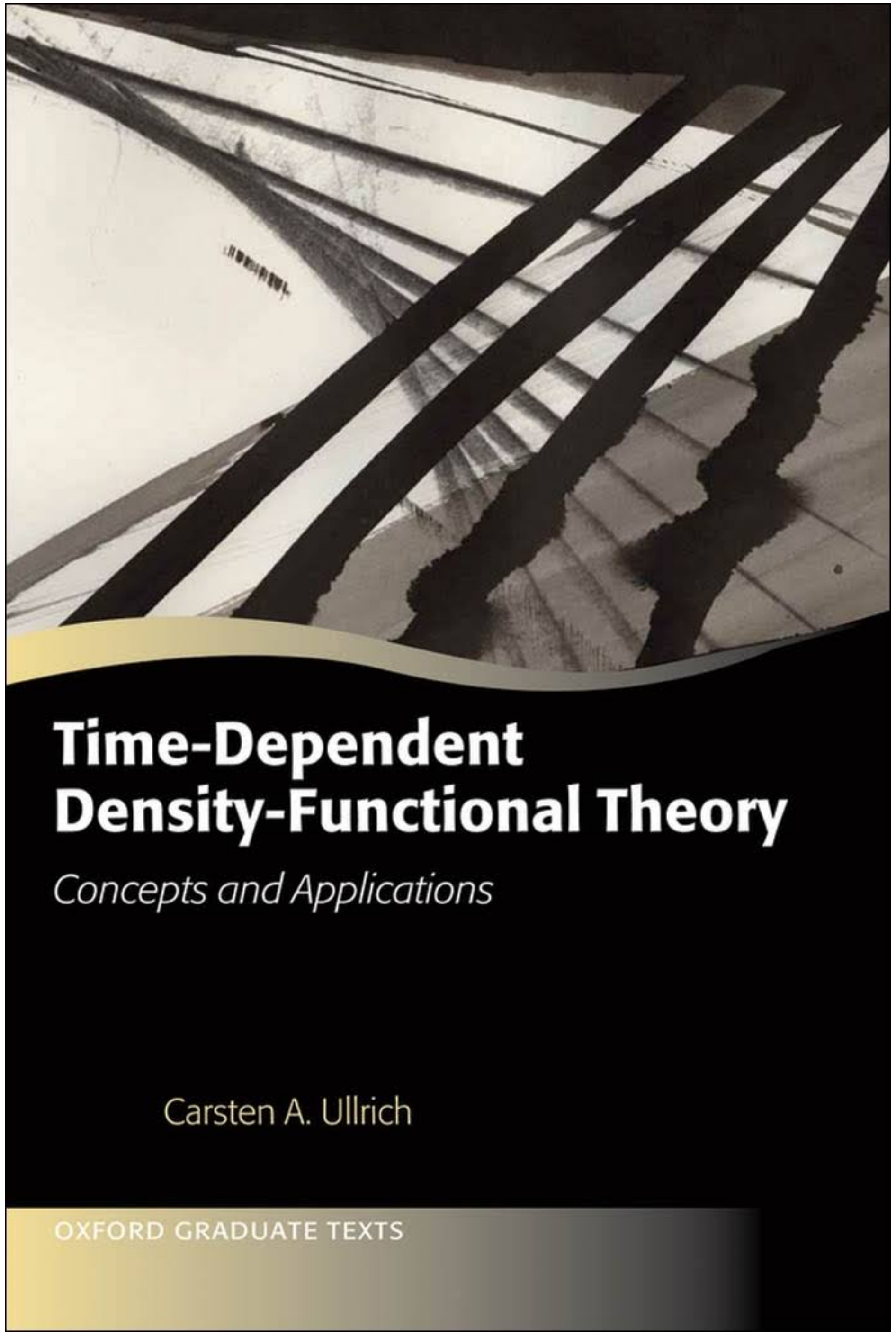
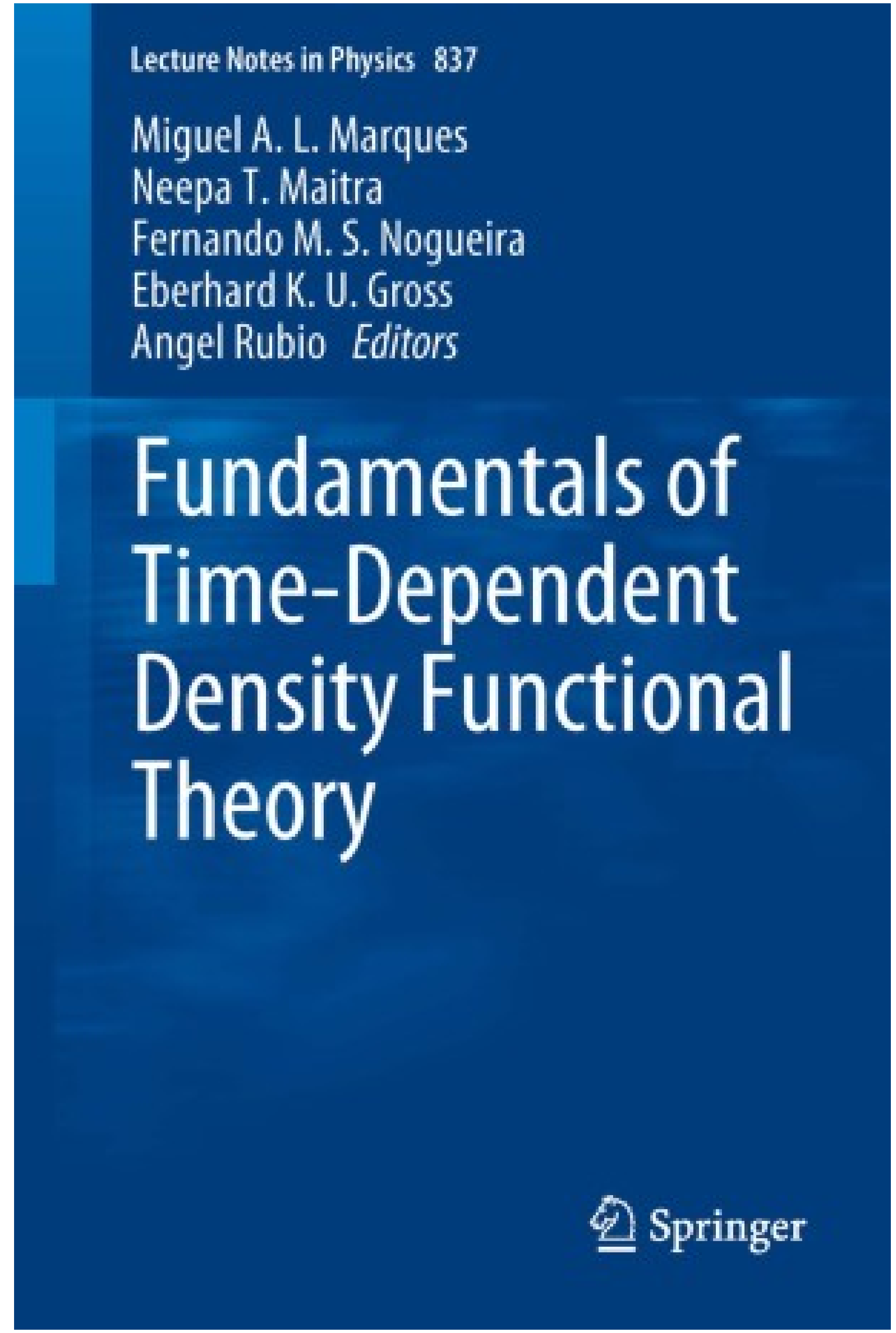


DMFT
$G(\mathbf{k}, E)$
$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n)$
CI, CC, post-HF,QMC
$G(\mathbf{r}_1, \mathbf{r}_2, E)$
MBPT
GW, BSE
$\gamma(\mathbf{r}_1, \mathbf{r}_2)$
RDMFT
$\mathbf{j}(\mathbf{r})$
CDFT
$n(\mathbf{r})$
DFT
simpler basic quantity
more complicate approximation

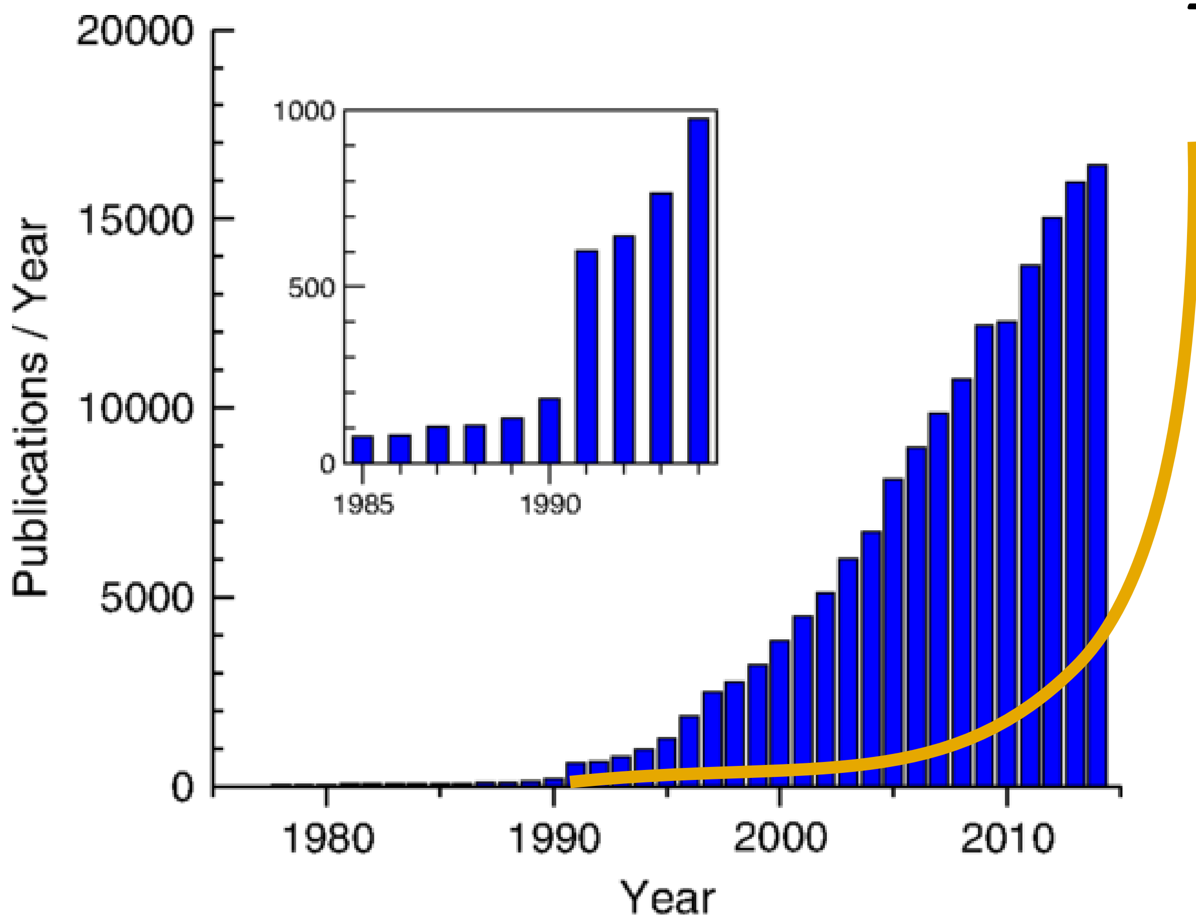

Time-Dependent
Density-Functional Theory
Concepts and Applications
Carsten A. Ullrich
OXFORD GRADUATE TEXTS


Lecture Notes in Physics 837
Miguel A. L. Marques
Neepa T. Maitra
Fernando M. S. Nogueira
Eberhard K. U. Gross
Angel Rubio Editors
Fundamentals of Time-Dependent Density Functional Theory
Springer

Success of DFT

+ Machine Learning

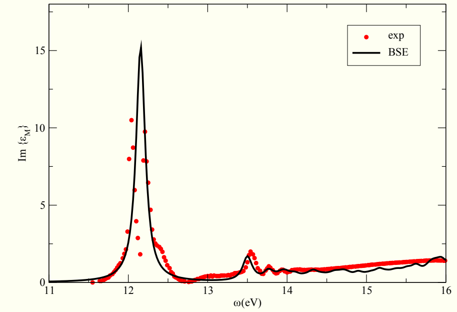
J. Phys. Mater. **2** 032001 (2019)



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

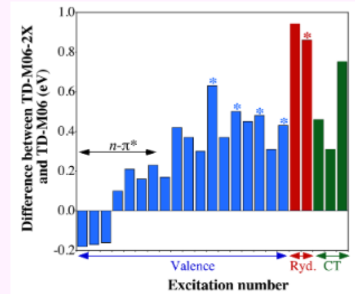
Serious applications

Optical Spectra



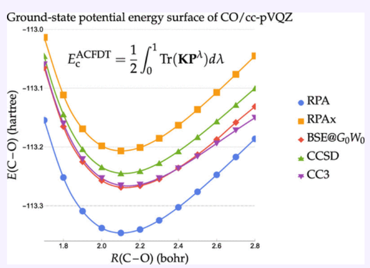
Phys. Rev. B **76**, 161103 (2007)

Excitation energies



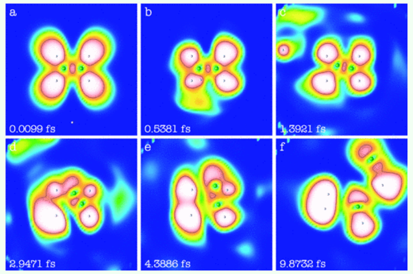
J.Phys.Chem.Lett. **8**, 1524 (2017)

Ground-state total energy



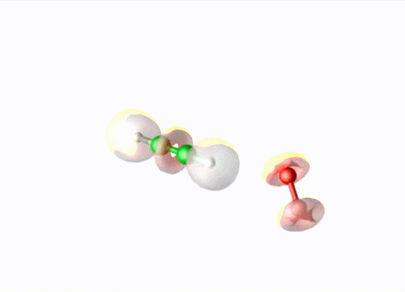
Phys. Rev. Lett. **98**, 157404 (2007)

Electrons in intense laser fields



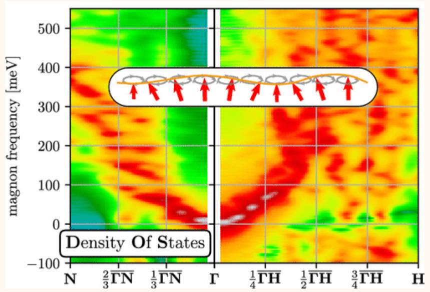
Phys. Rev. A **71**, 010501 (2004)

Electron-ion dynamics



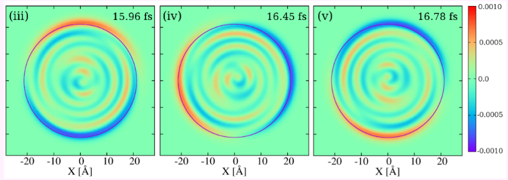
A. Castro - https://youtu.be/VixOLFubxBw

Magnetic excitations



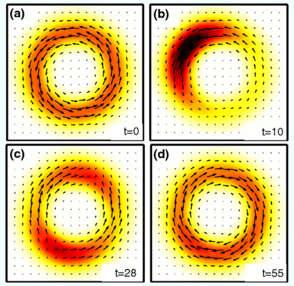
J. Chem. Theory Comput. **16**, 1007 (2020)

Quantum plasmonics



ACS photonics, **7**, 2429 (2020)

Optimal control theory



Phys. Rev. Lett. **98**, 157404 (2007)

TDDFT in linear response

- Different (easier) theoretical approach

- Practical scheme for spectroscopy
  and excitation energies

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

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

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

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

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

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

polarizability

polarizability :: density-density response function

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

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

Exercise

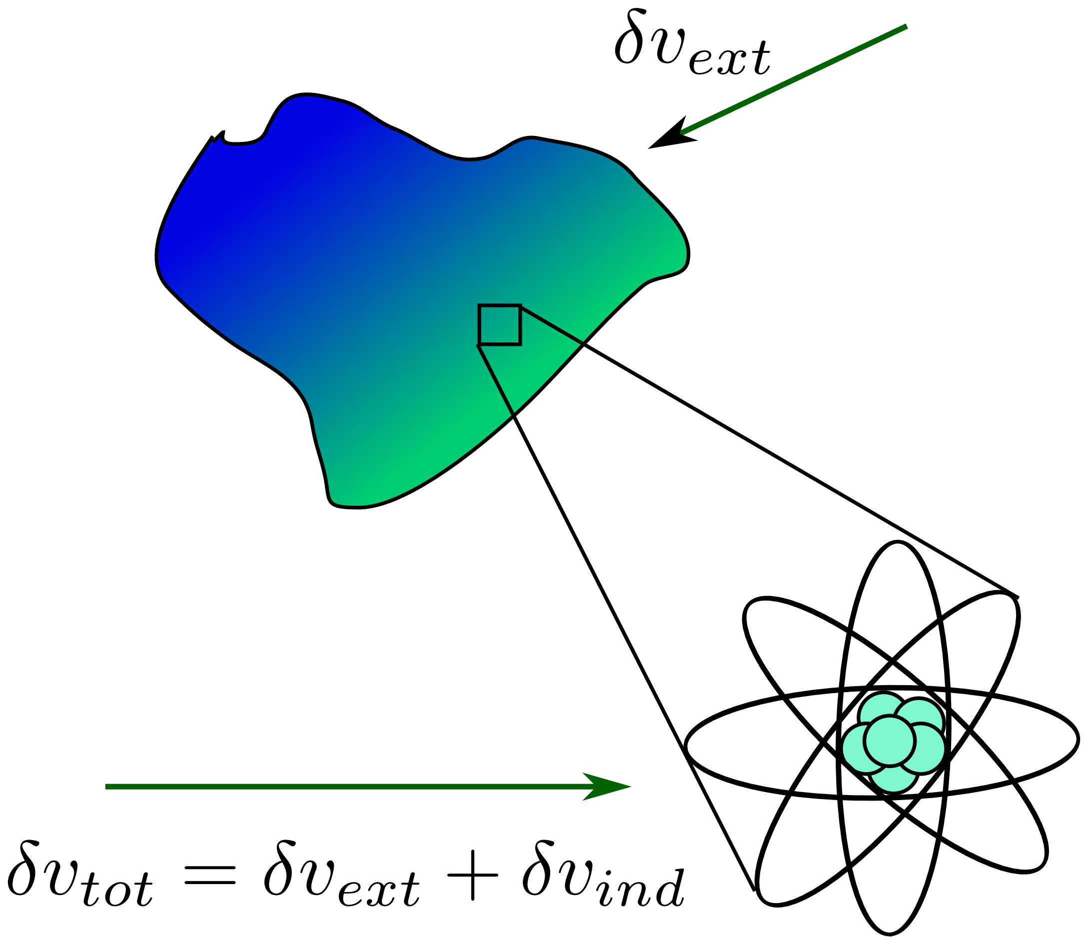
$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_I \left[\frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega-\underbrace{(E_I-E_0)}_{\Omega_I}+i\eta} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_I\rangle\ \langle\Psi_I|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega+(E_I-E_0)+i\eta}\right]$$

Ω_I excitations energies

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

??

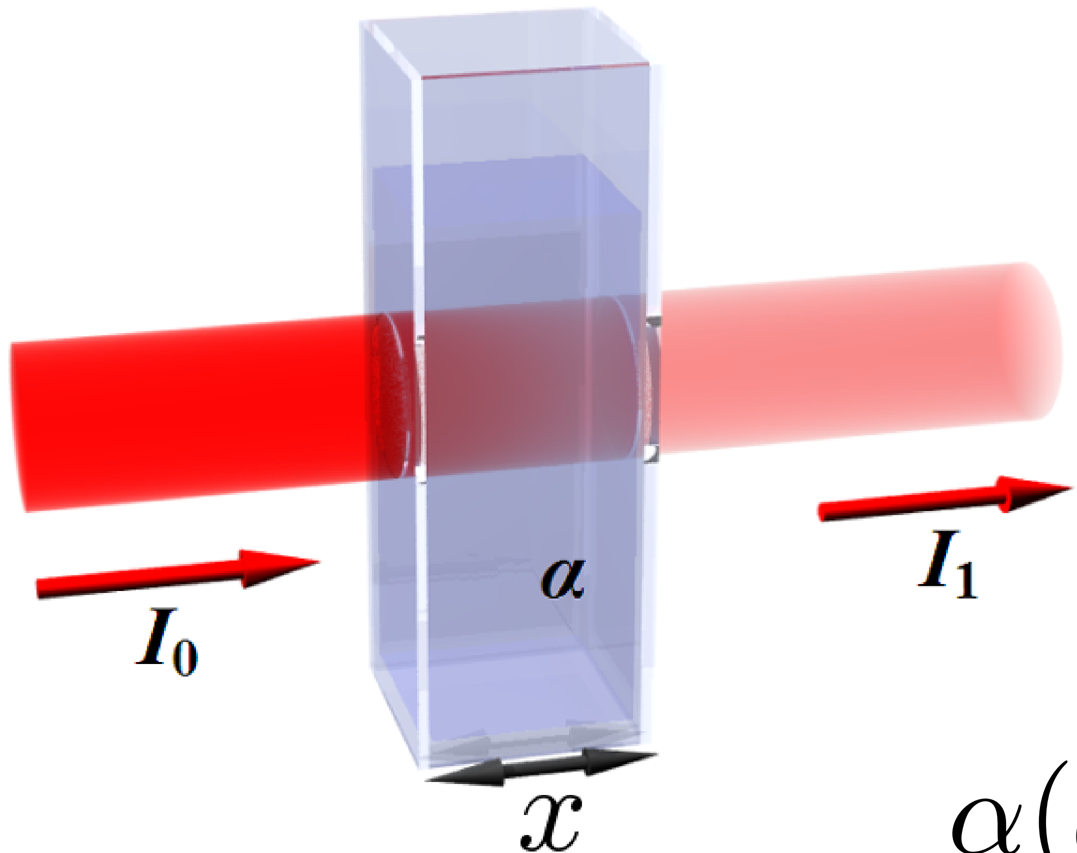
Connection to spectroscopies :: inverse dielectric function



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

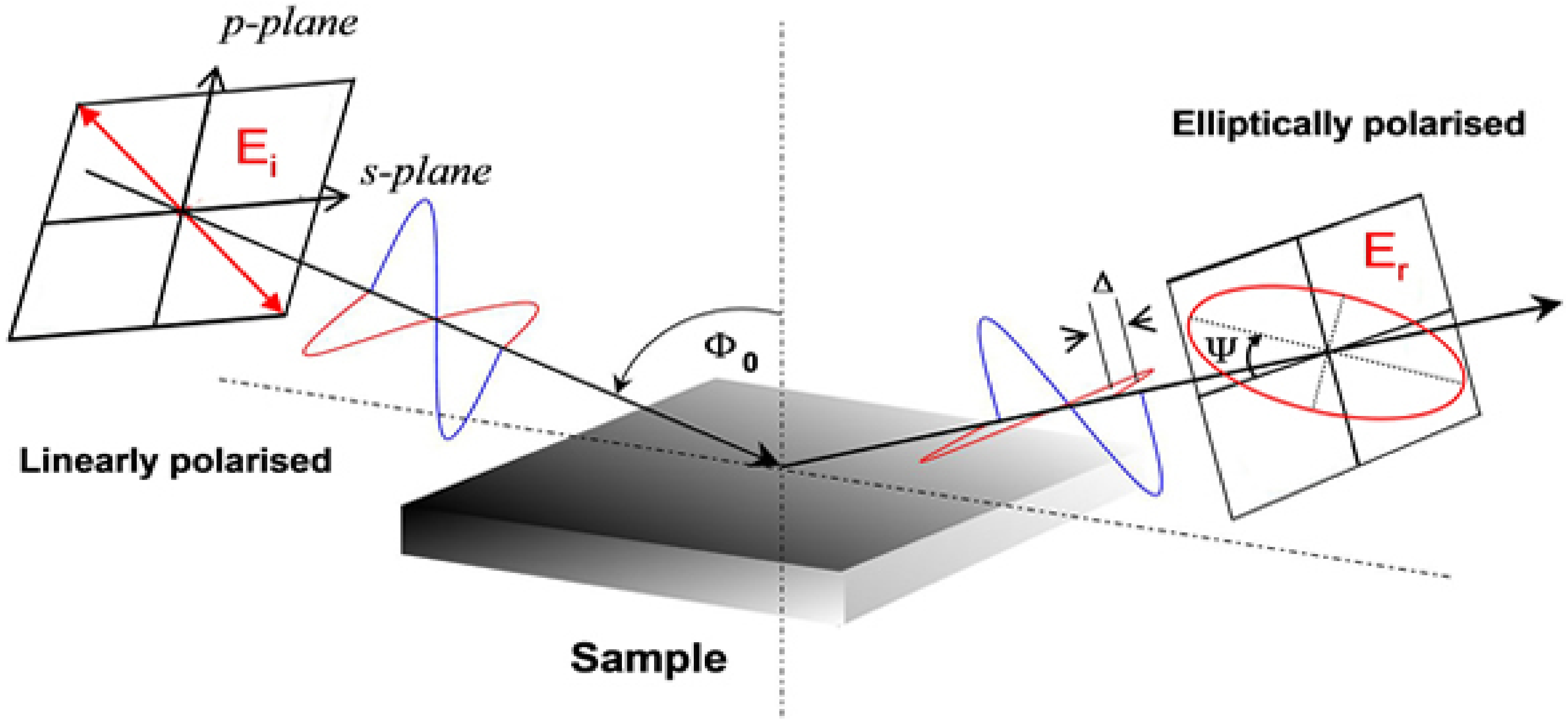
ε dielectric function

Connection to spectroscopies :: optical [and X-ray] absorption



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

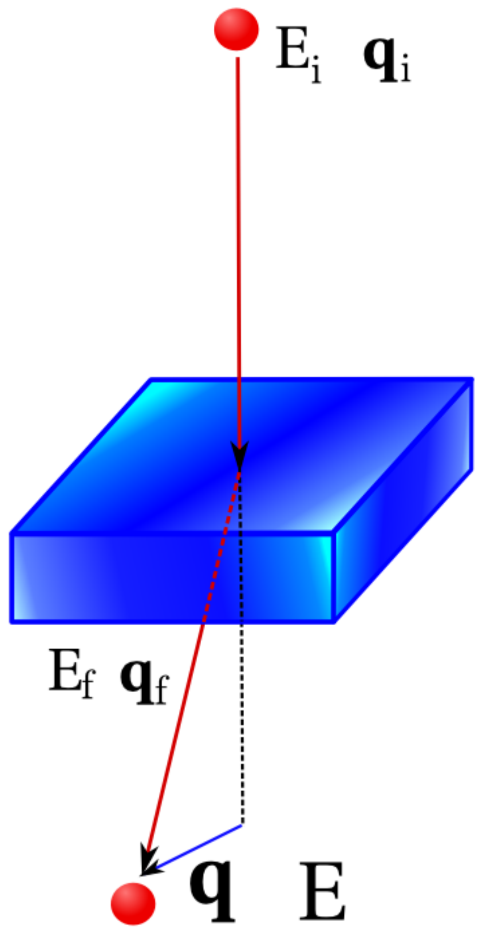
Connection to spectroscopies :: optical absorption



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

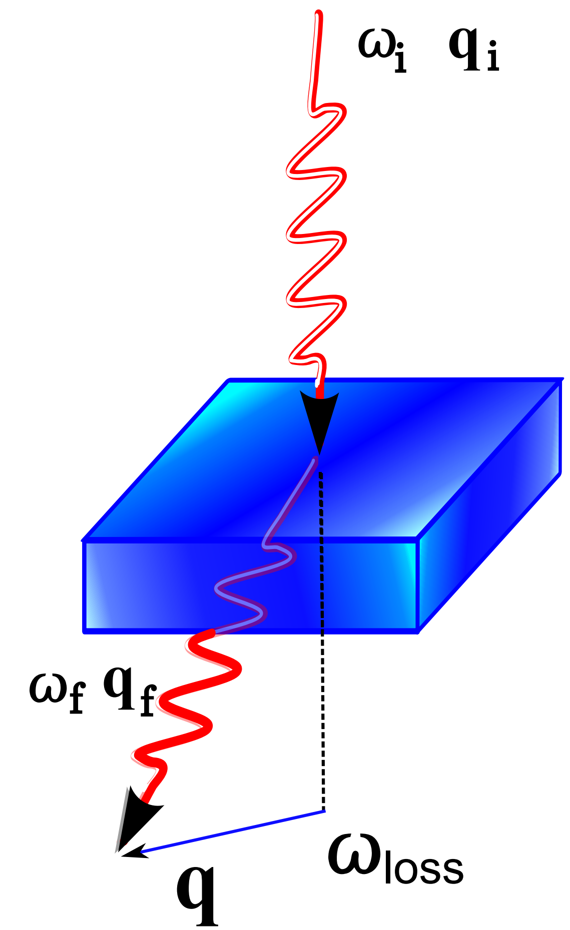
Connection to spectroscopies :: electron energy loss (EELS)

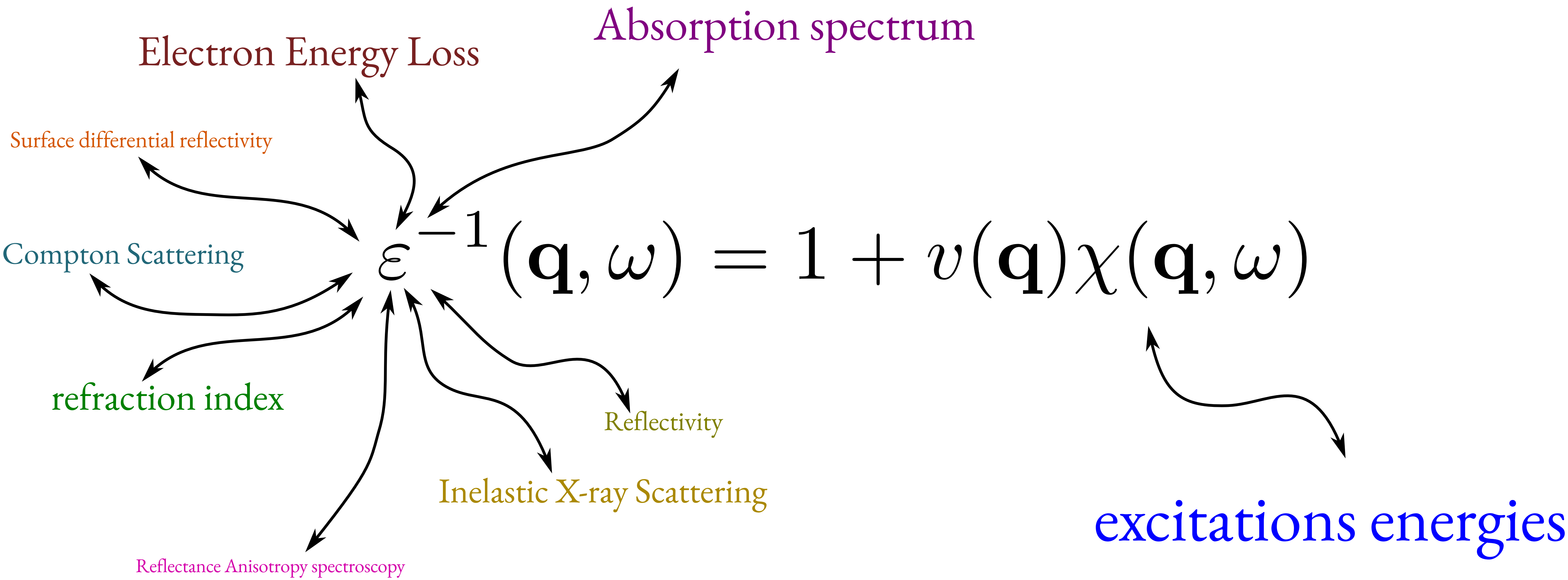
$$\frac{d^2\sigma}{d\Omega d\omega} \propto \mathrm{Im}\left[\varepsilon^{-1}(\mathbf{q},\omega)\right]$$



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
refraction index
$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v(\mathbf{q})\chi(\mathbf{q},\omega)$
Reflectivity
Inelastic X-ray Scattering
Reflectance Anisotropy spectroscopy
excitations energies

Polarizability of an independent-particle system

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

Ψ_0 ↓ single determinant

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

$(\epsilon_j - \epsilon_i)$: one-particle excitations energies

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

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

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

Dyson equation for the polarizability

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

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

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

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

- evaluation of χ knowing χ^0 (ground state calculation)
- f_{xc} functional of the ground-state density
- approximations for f_{xc}
  - $f_{xc} = 0$ RPA
  - $f_{xc} = \dfrac{\delta v_{xc}^{gs}}{\delta n}$
  - any other f_{xc}

coherence vs freedom

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 $\chi^0 = \sum_{ij} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$ — $o(N^4)$
- 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

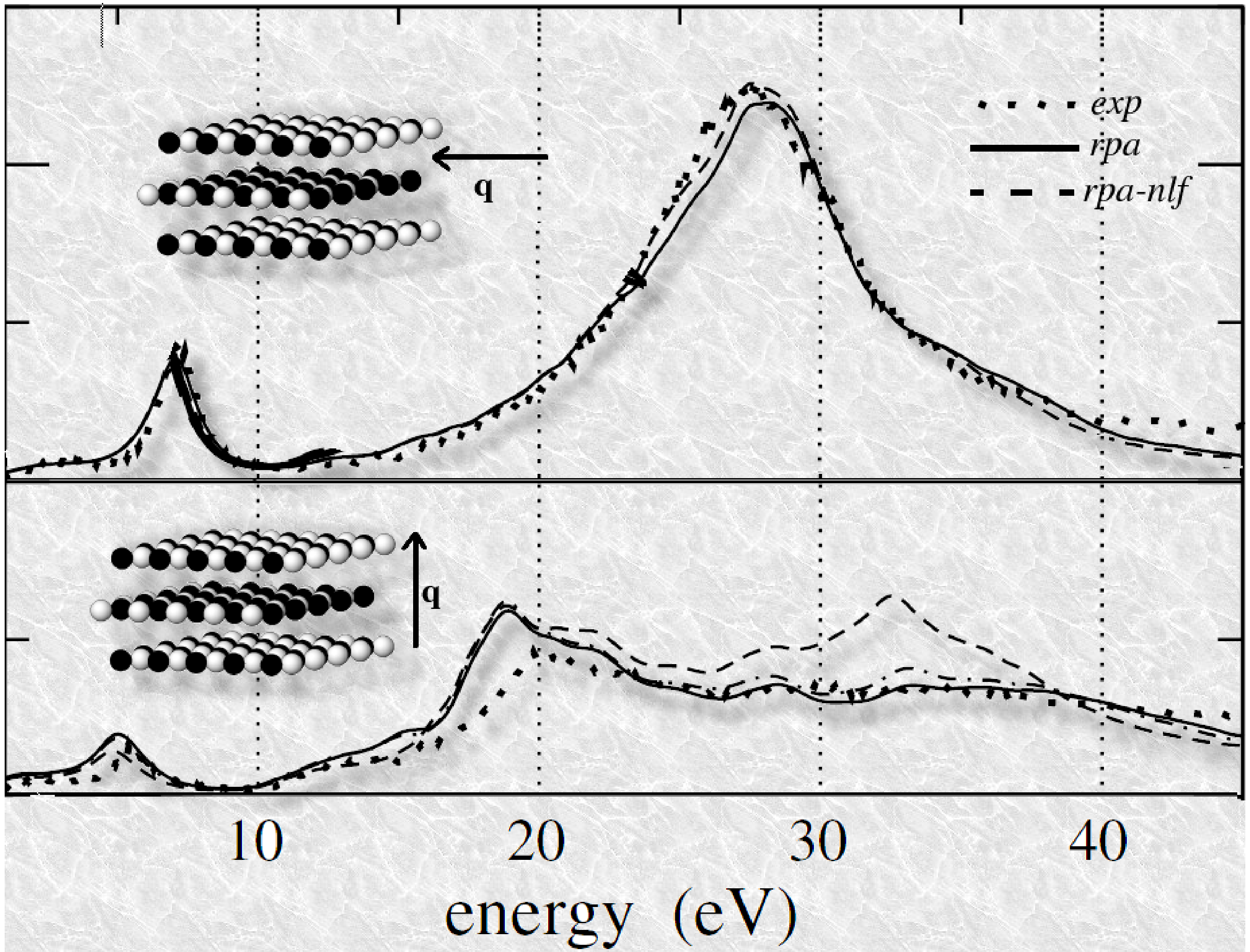
Dyson equation for the polarizability

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

local field effects
(local inhomogeneities)

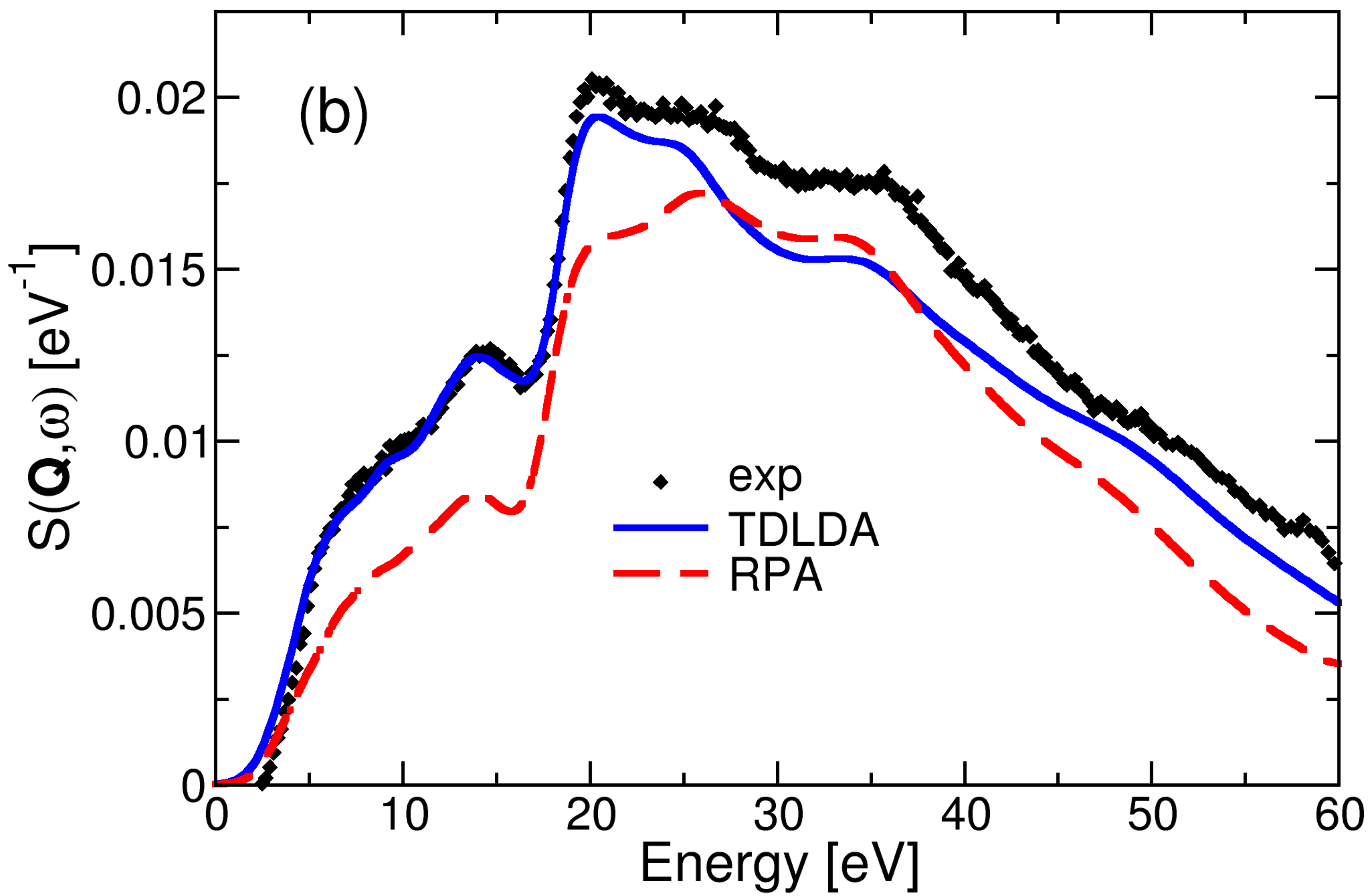
exchange-correlation
(quantum) effects

EELS of graphite



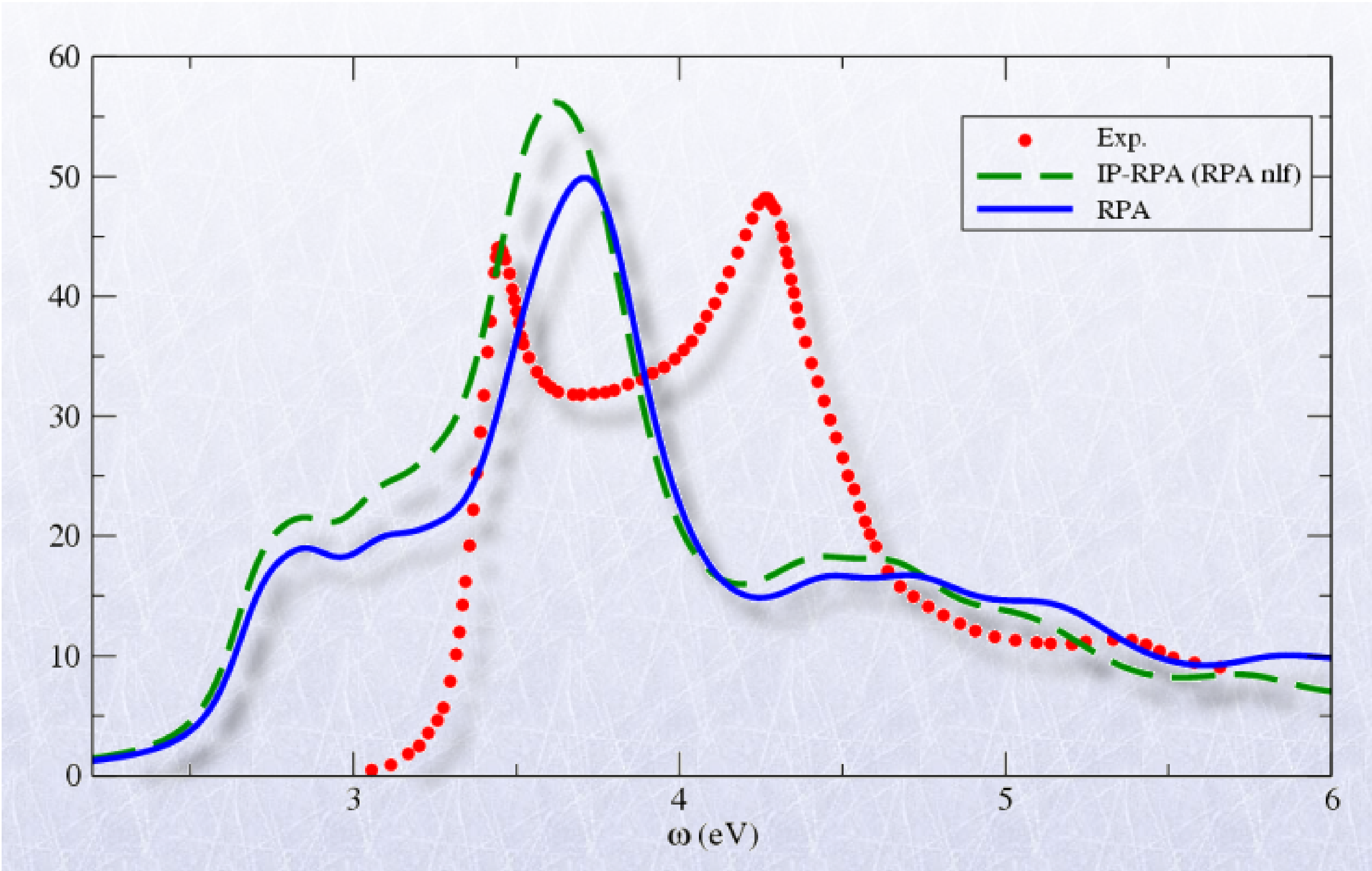
Marinopoulos *et al.* Phys. Rev. Lett. **89**, 076402 (2002)

IXS of Silicon



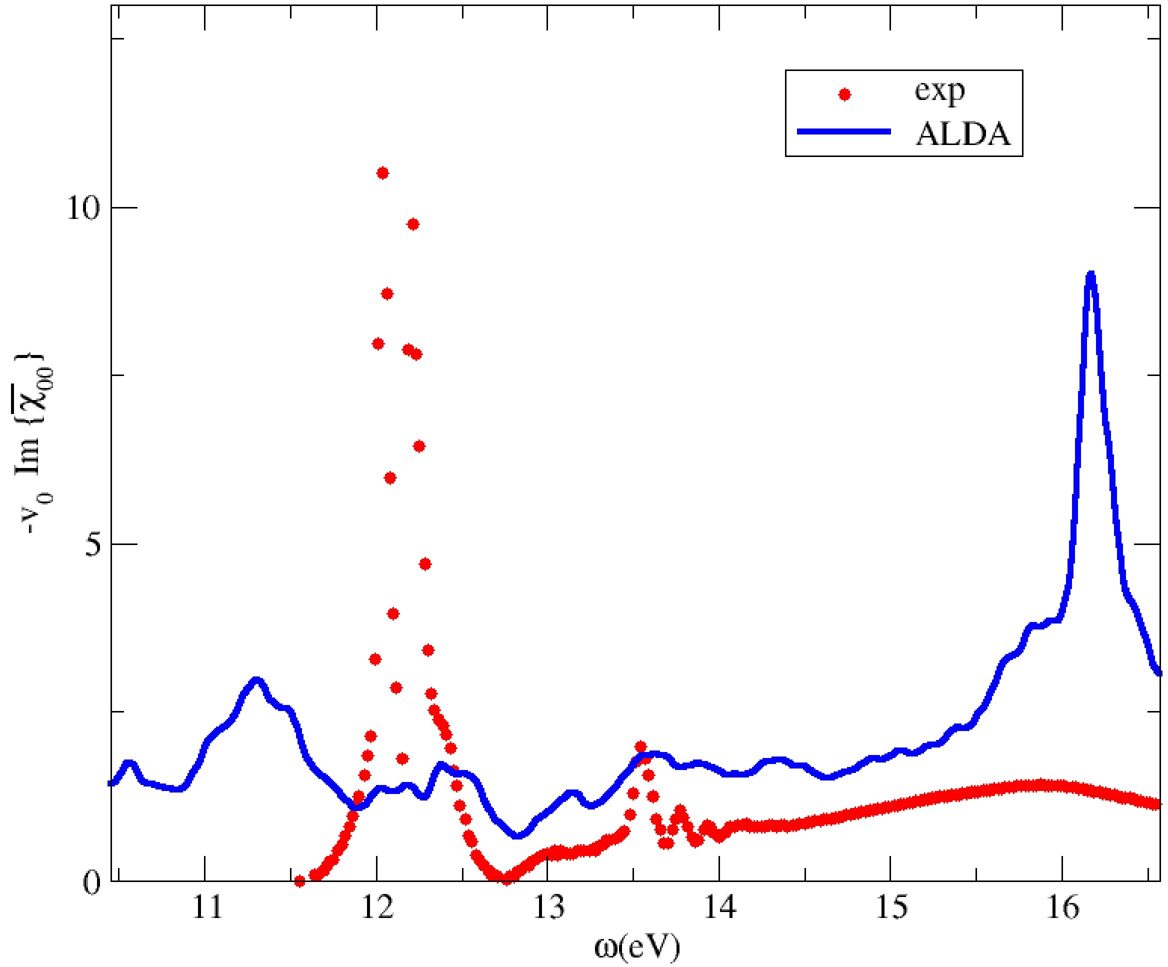
Weissker *et al.* Phys. Rev. Lett. **97**, 237602 (2006)

Absorption of Silicon



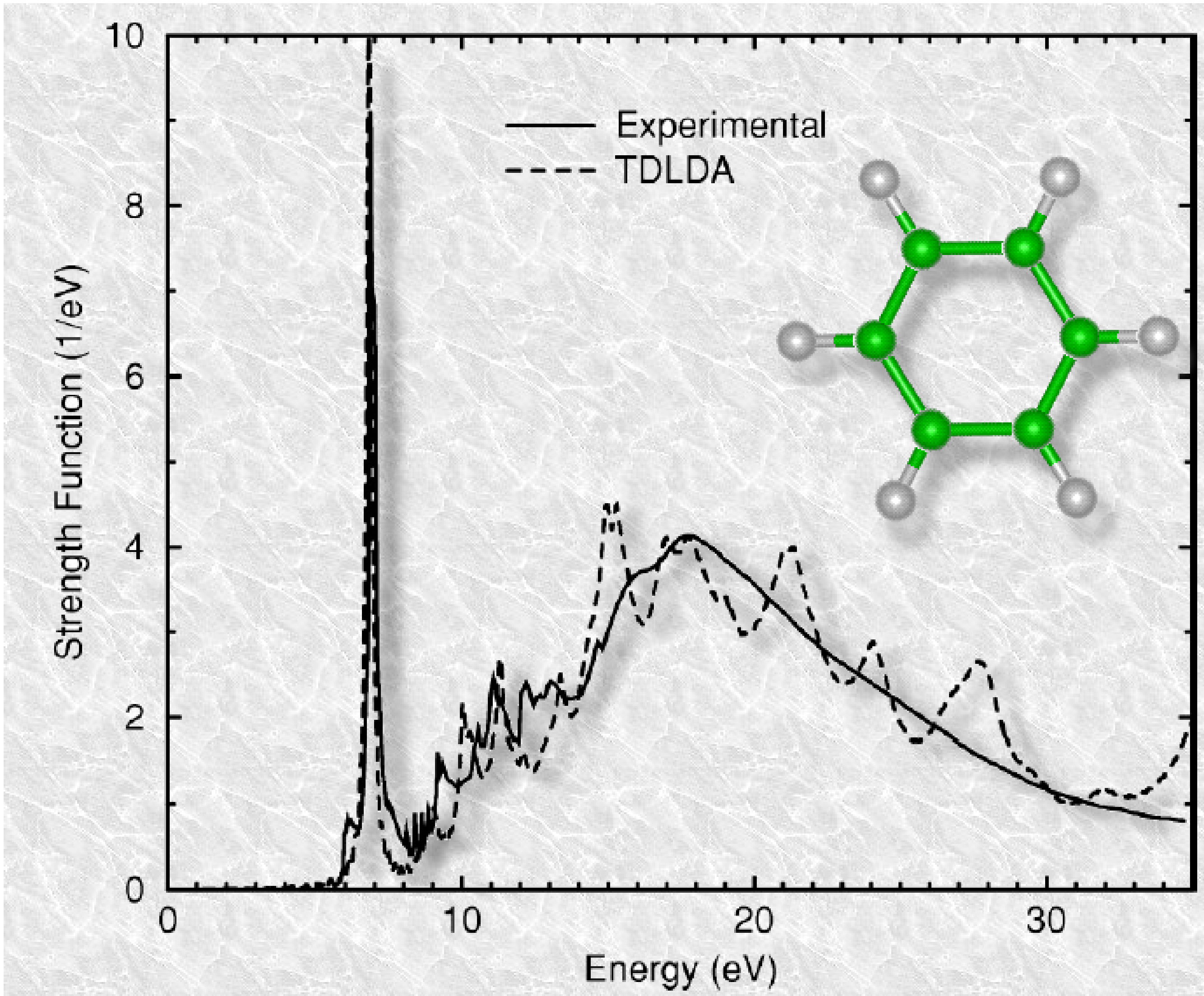
Albrecht *et al.* Phys. Rev. Lett. **80**, 4510 (1998)

Absorption of Argon



Sottile *et al.* Phys. Rev. B **76**, 161103(R) (2007)

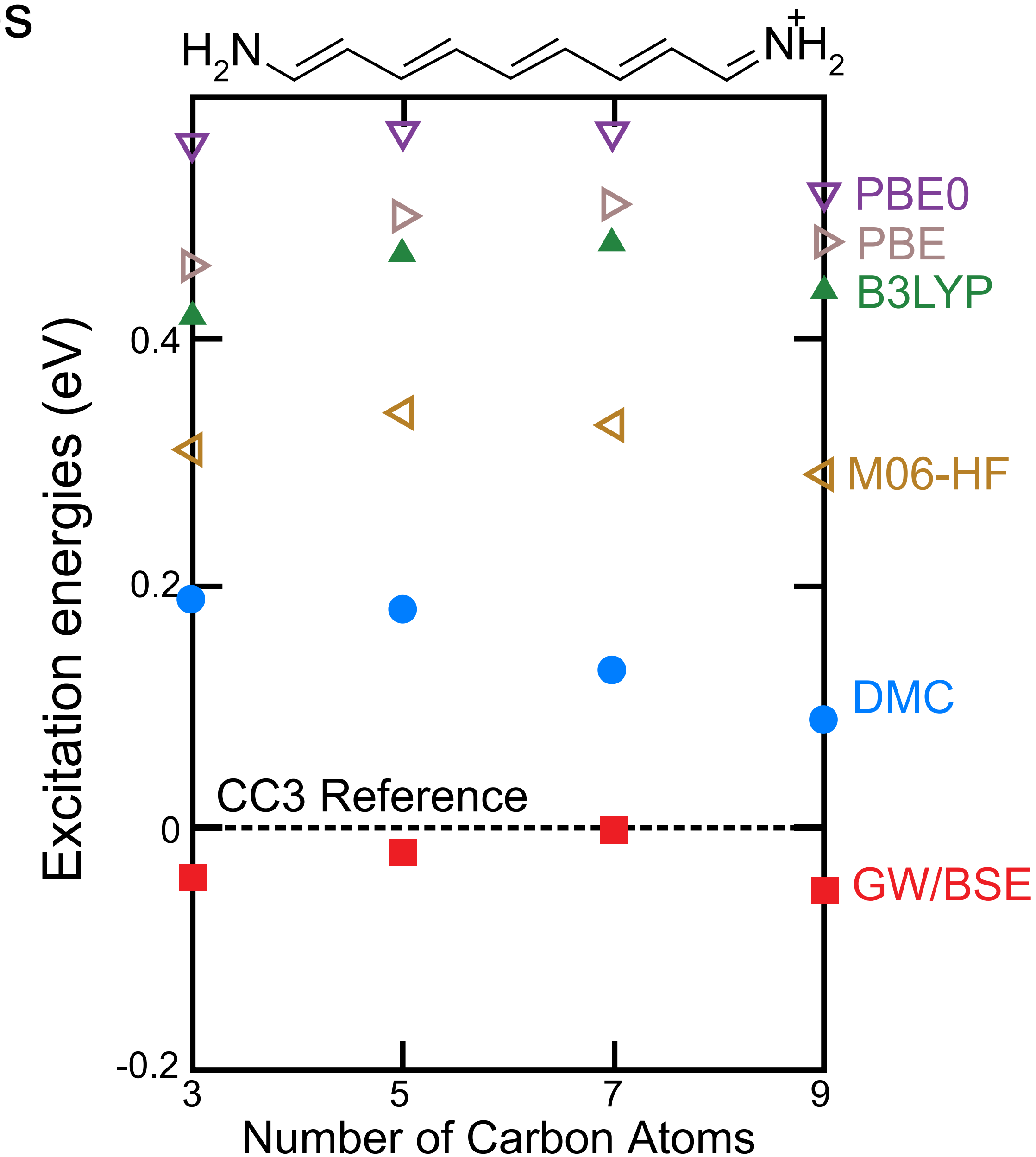
Benzene



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

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

Transition energies of streptocyanine chains



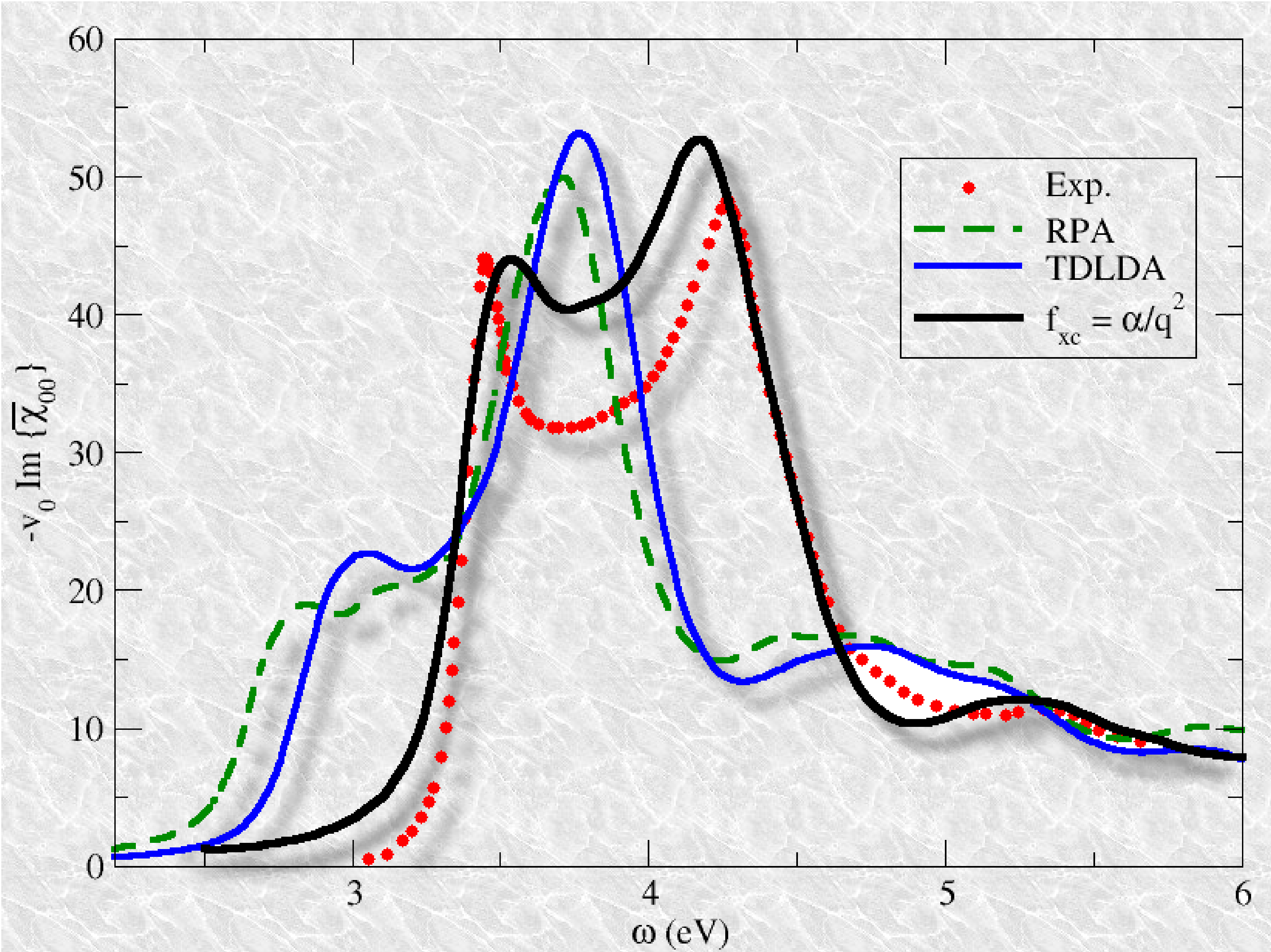
Blase *et al.* Chem. Soc. Rev. **47**, 1022 (2018)

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

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

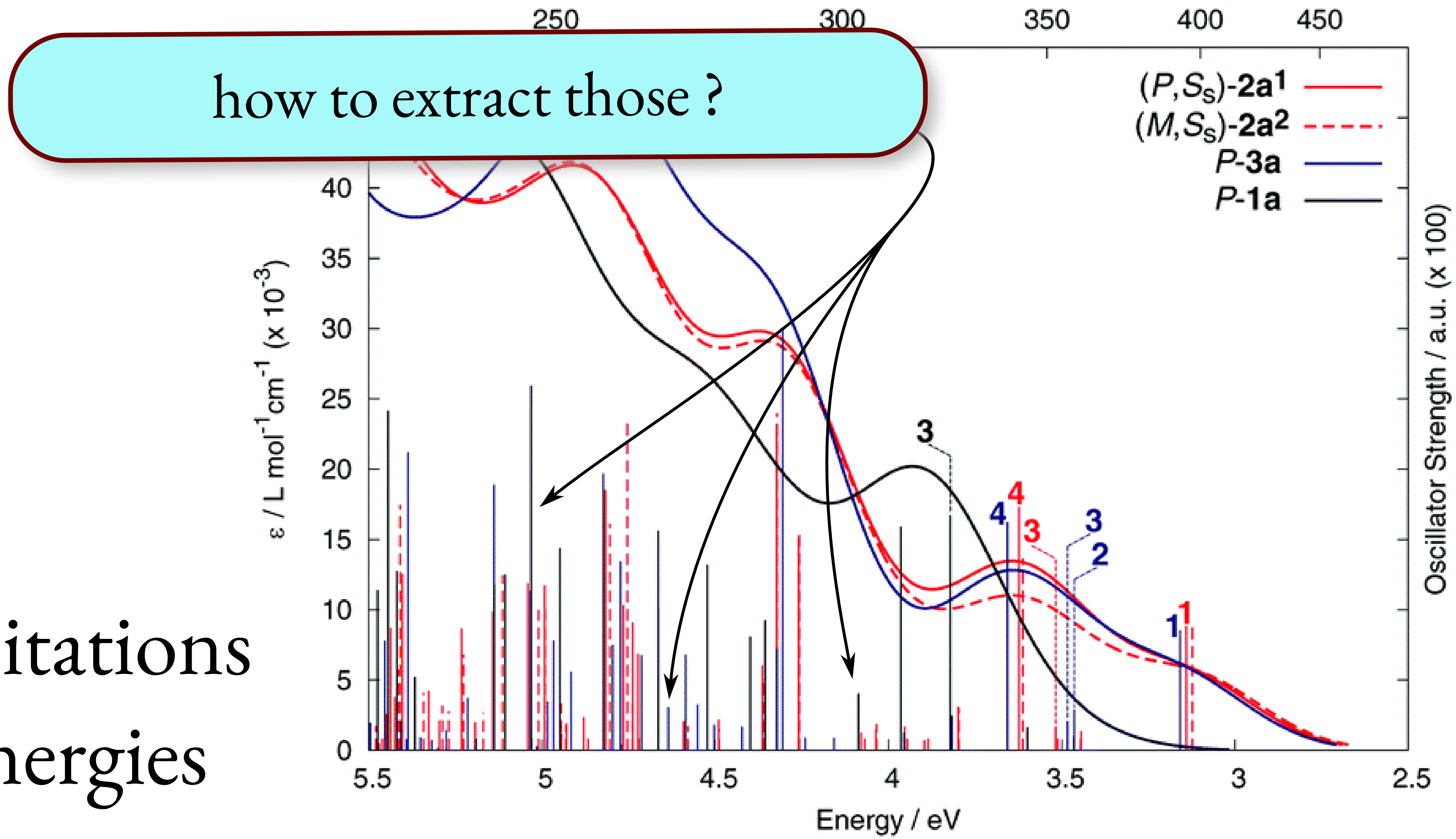
$$f_{xc}(\mathbf{q} \to 0) \neq \frac{1}{\mathbf{q}^2}$$

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



Exp.
RPA
TDLDA
$f_{xc} = \alpha/q^2$
$-v_0 \, \mathrm{Im}\,\{\overline{\chi}_{00}\}$
ω (eV)
0
10
20
30
40
50
60
3
4
5
6

Absorption of cycloplatinated helicenes



excitations energies

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

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

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

change of basis

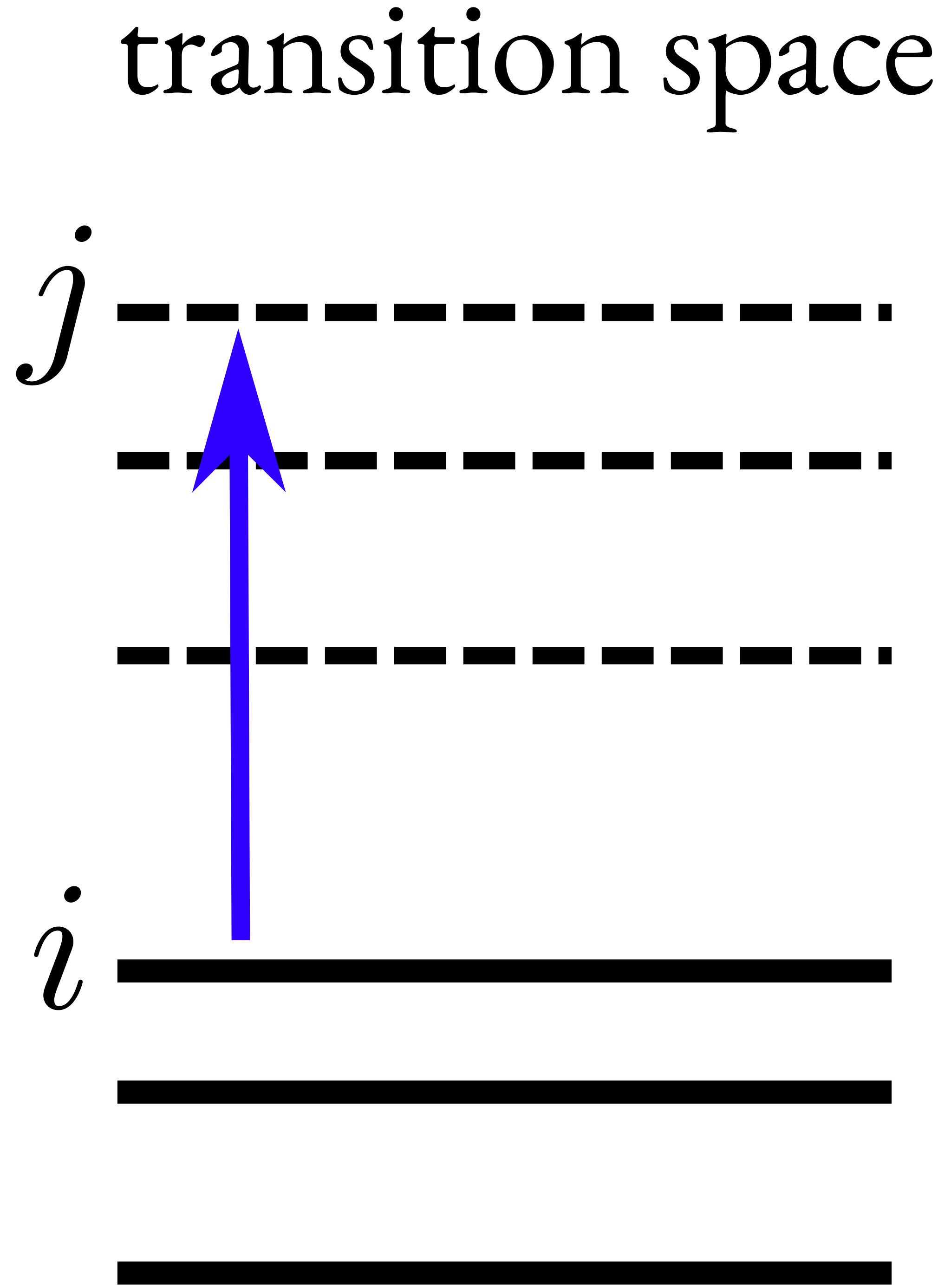
$$f_{ij}^{kl} = \iint \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_k(\mathbf{r}')\psi_l^*(\mathbf{r}')\, f(\mathbf{r},\mathbf{r}')\; d\mathbf{r} d\mathbf{r}'$$

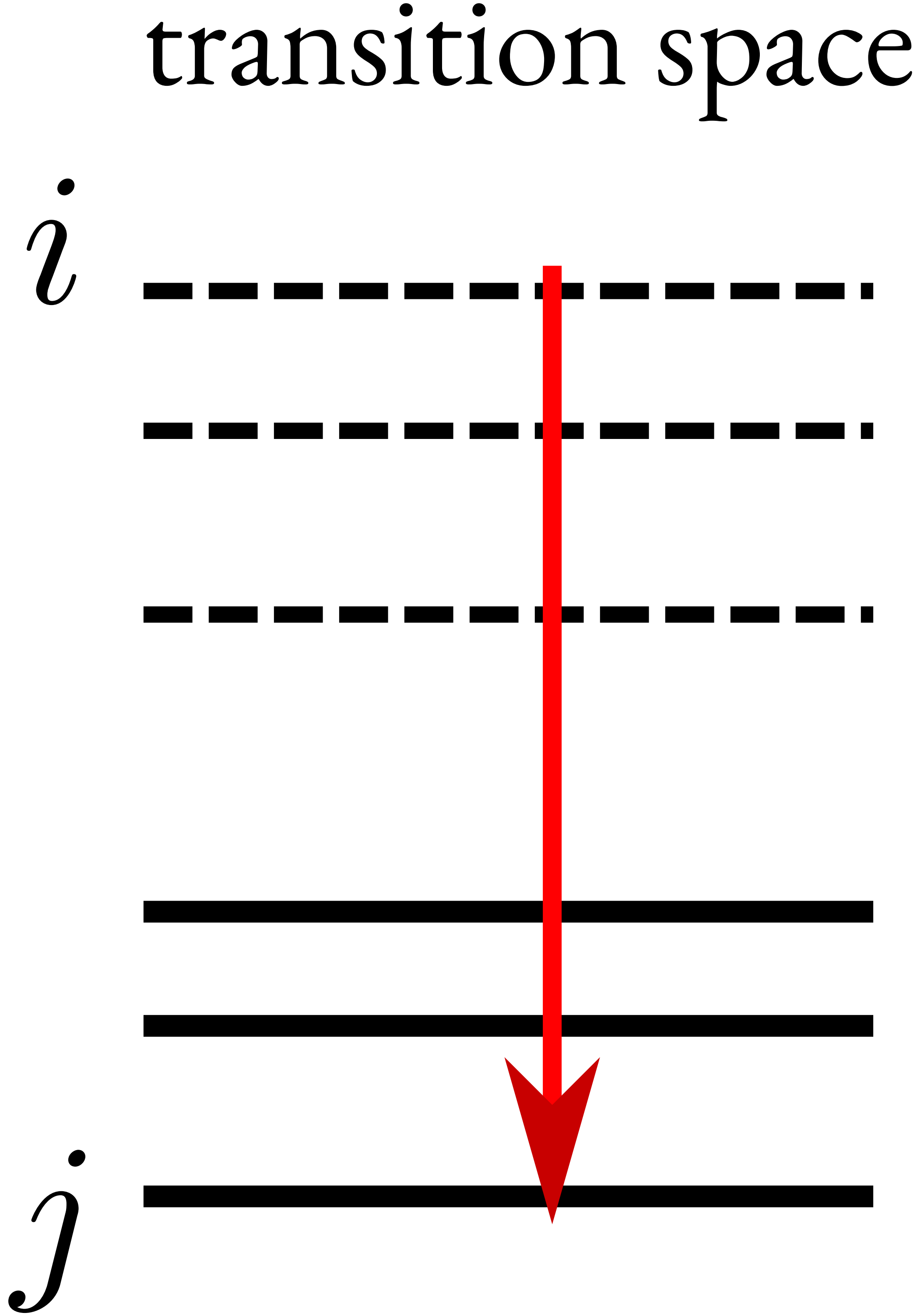
$$\chi_{ij}^{kl} = \left[\chi^0\right]_{ij}^{kl} + \sum_{mnop}\left[\chi^0\right]_{ij}^{mn}\left[v_{mn}^{op} + \left[f_{xc}\right]_{mn}^{op}\right]\chi_{op}^{kl}$$

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

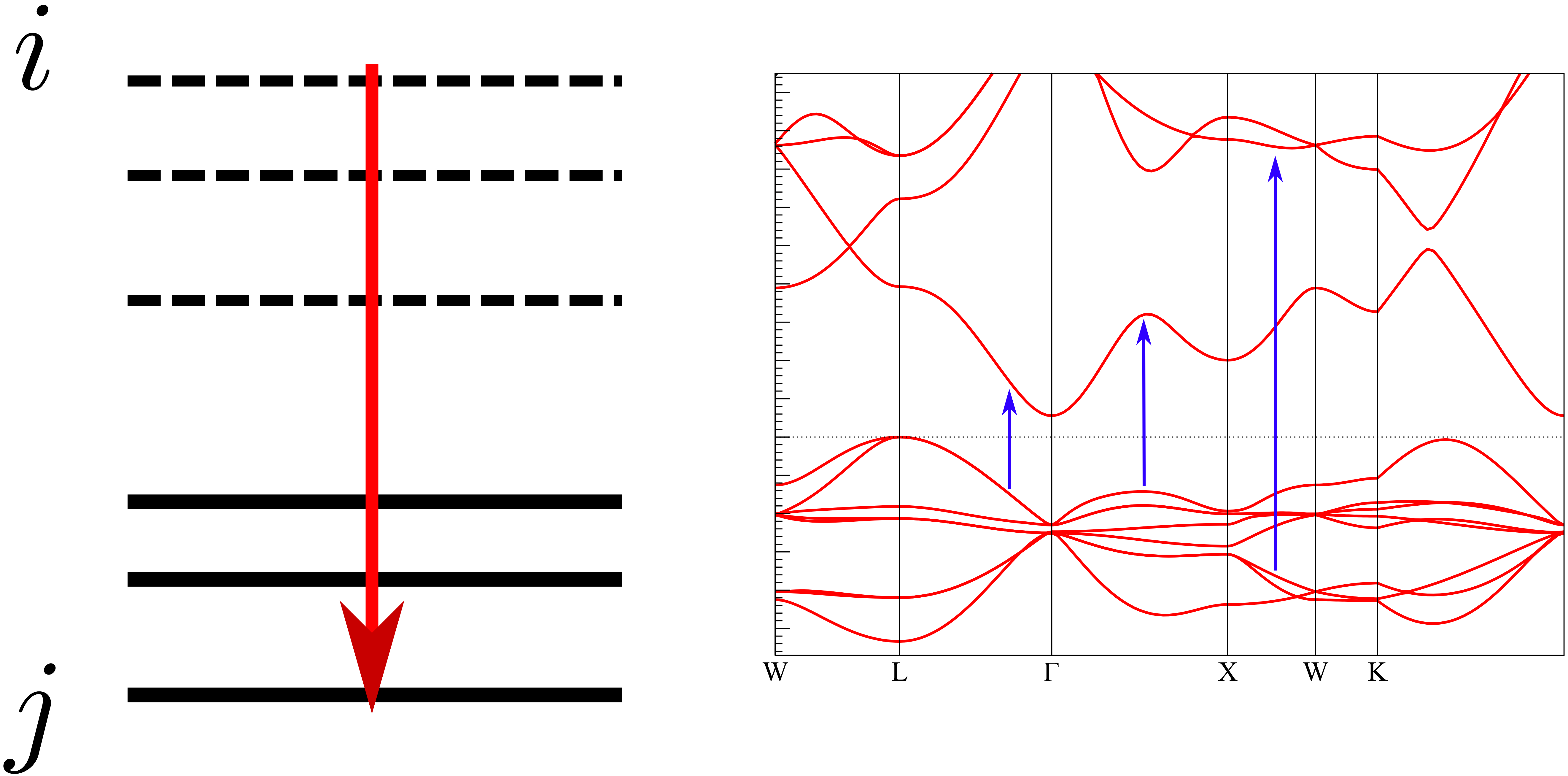
$$[\chi^0]_{ij}^{kl} = \frac{(f_i - f_j)\delta_{ik}\delta_{jl}}{\omega - (\epsilon_j - \epsilon_i)}$$

diagonal in ij, kl


transition space
j
i


transition space
i
j

transition space



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

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

Exercise

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

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

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

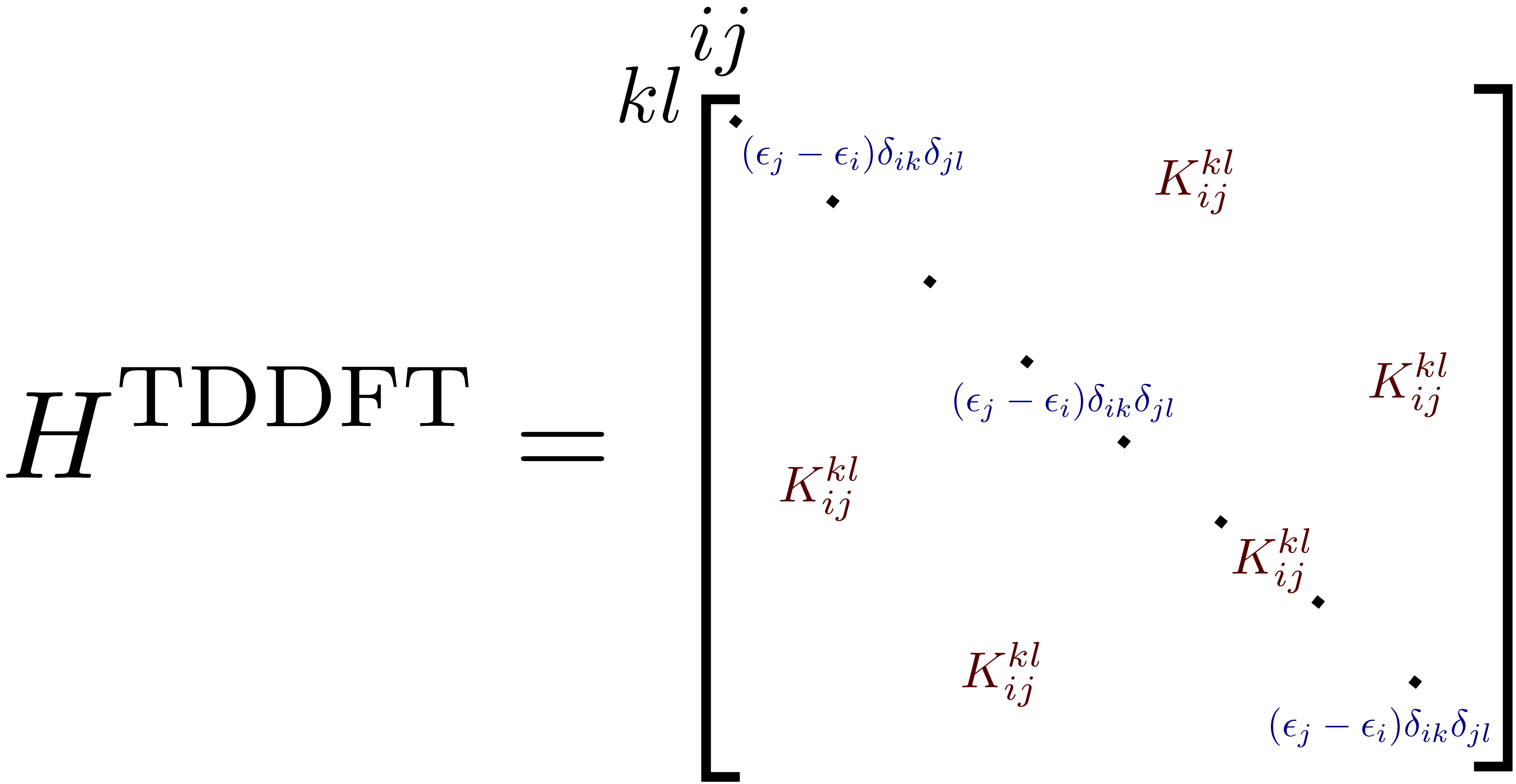
χ_{ij}^{kl}

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

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

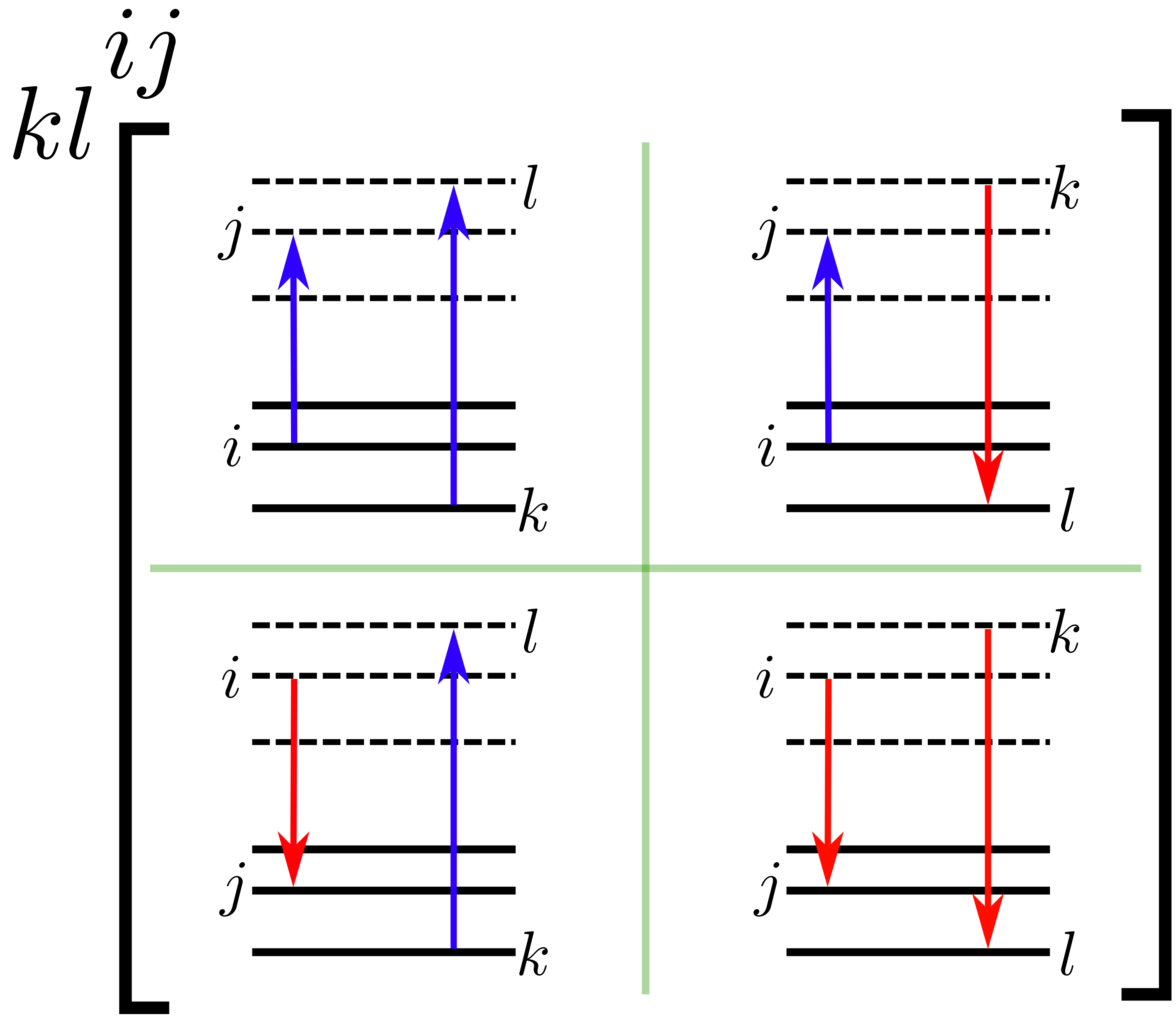
adiabatic approx.

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


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

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

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



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

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

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

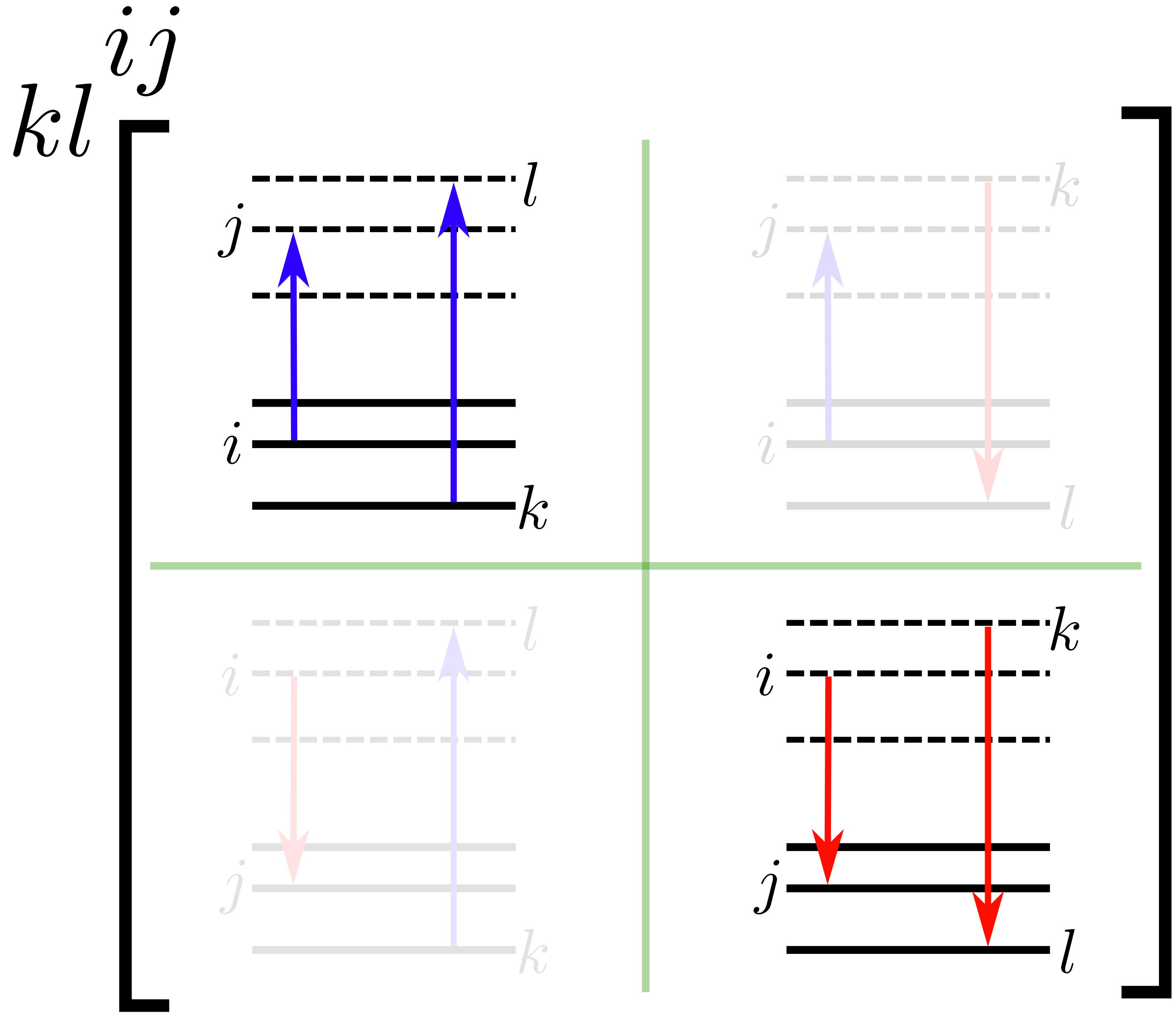
$$\begin{bmatrix} A & B \\ B^* & -A^* \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = E_\lambda \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

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

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

Tamm-Dancoff approx

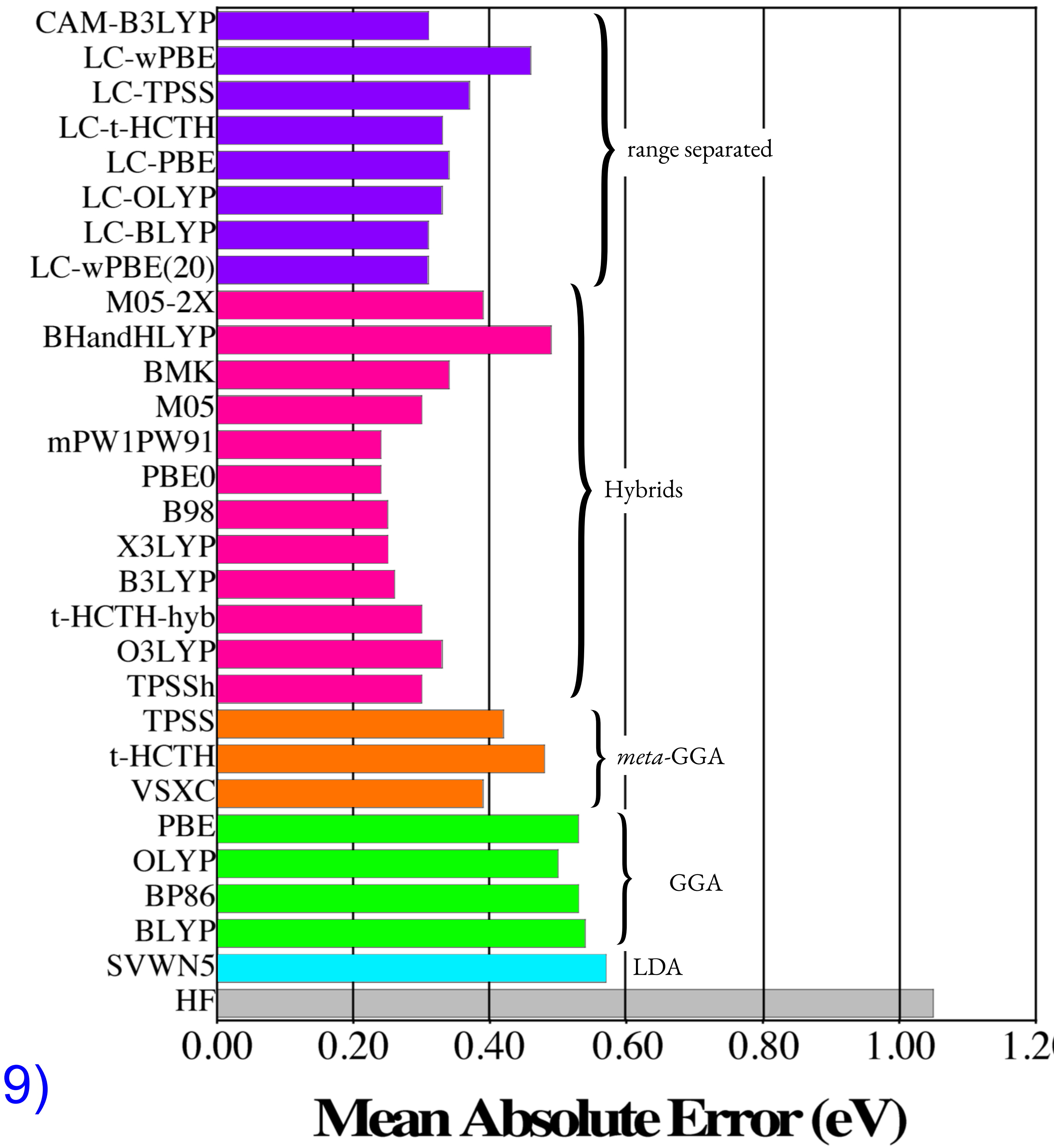
$$H^{\text{TDDFT}} =$$



Tamm-Dancoff approx

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

TDDFT excitation energies
500 compounds



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

Name of the game

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

given $\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n, 0)$

DFT world

Name of the game

DFT

Hohenberg-Kohn theorem

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

$$\left\langle \Psi^0 \middle| O \middle| \Psi^0 \right\rangle = O[n]$$

TDDFT

Runge-Gross theorem

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

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

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

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

Name of the game

TDDFT

Runge-Gross theorem

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

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

is it true?

Demonstration

but in practice?

KS equations

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

Runge-Gross theorem

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

Demonstration

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

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

Demonstration of the Runge Gross theorem

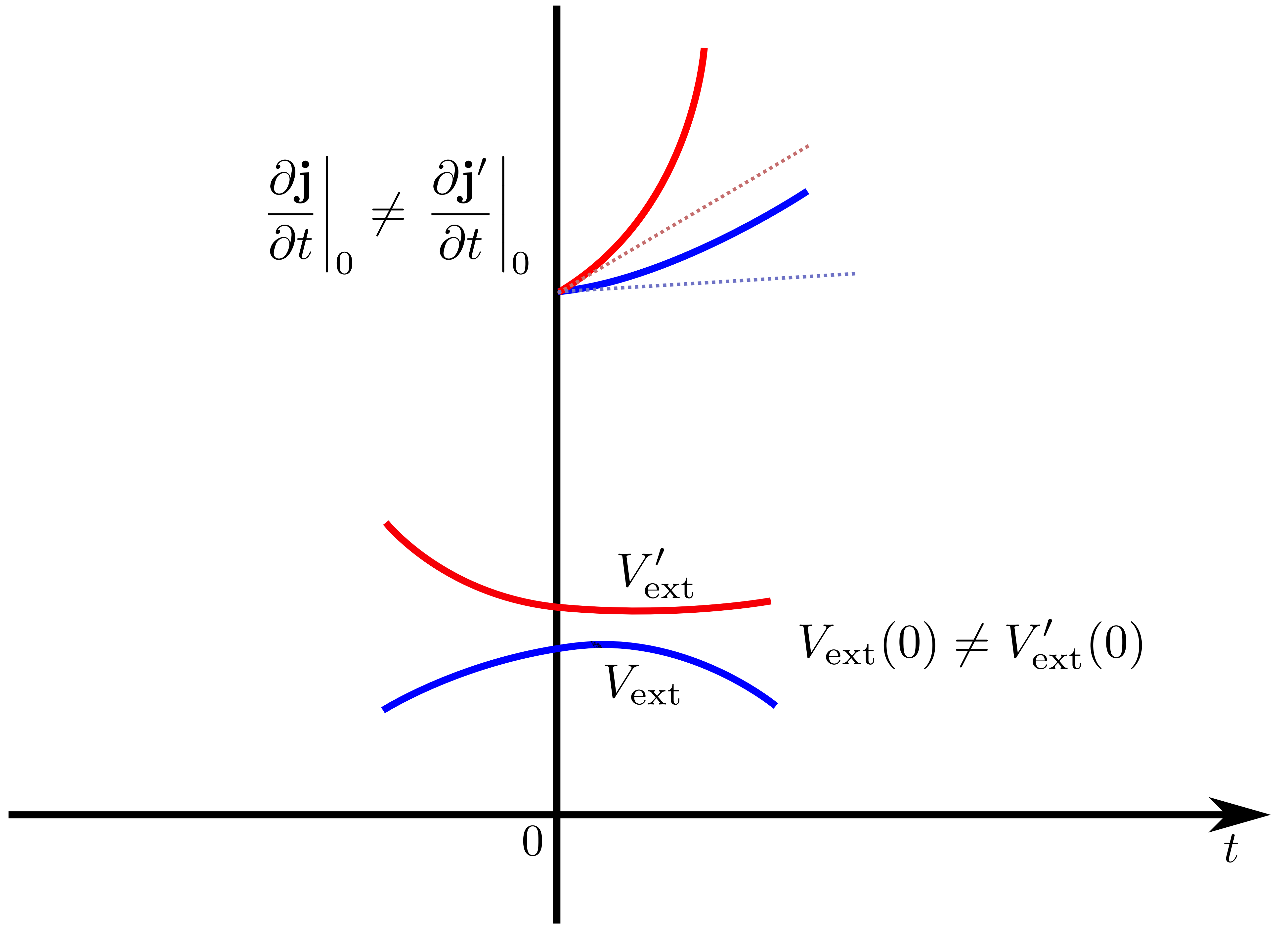
1) $V_{\text{ext}}(\mathbf{r},t) \neq V'_{\text{ext}}(\mathbf{r},t) + c(t) \quad \longleftrightarrow \quad \mathbf{j}(\mathbf{r},t) \neq \mathbf{j}'(\mathbf{r},t)$

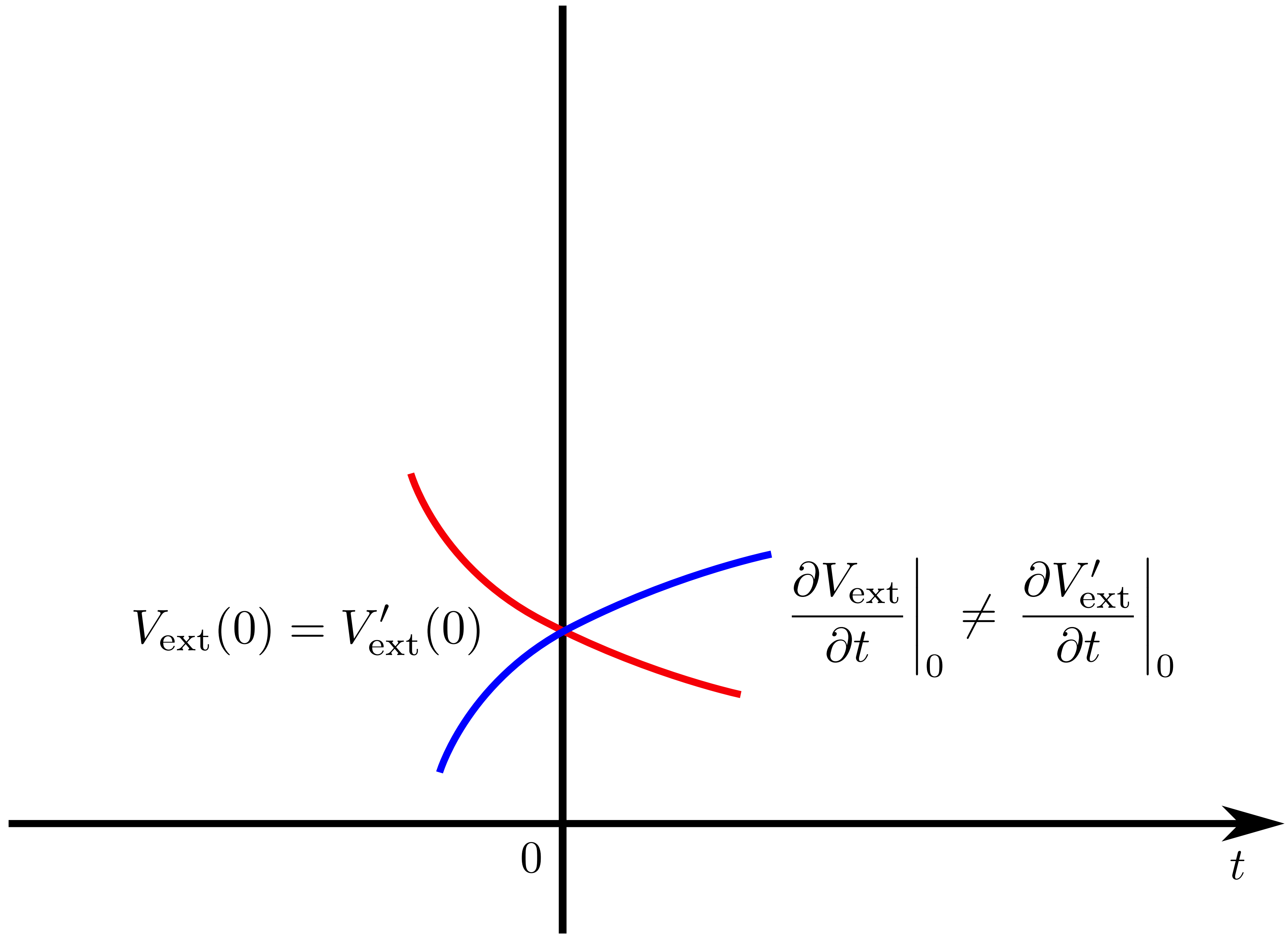
$$i\frac{\partial \mathbf{j}(\mathbf{r},t)}{\partial t} = \langle \Psi(t)|[\mathbf{j}(\mathbf{r}), H(t)]|\Psi(t)\rangle$$

$$i\frac{\partial \mathbf{j}'(\mathbf{r},t)}{\partial t} = \langle \Psi'(t)|[\mathbf{j}(\mathbf{r}), H'(t)]|\Psi'(t)\rangle$$

$$\begin{aligned} i\frac{\partial}{\partial t}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=0} &= \langle \Psi_0|[\mathbf{j}(\mathbf{r}), H(0) - H'(0)]|\Psi_0\rangle \\ &= -i\, n_0(\mathbf{r})\nabla\left[V_{\text{ext}}(\mathbf{r},0) - V'_{\text{ext}}(\mathbf{r},0)\right] \end{aligned}$$

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


$\frac{\partial \mathbf{j}}{\partial t}\Big|_0 \neq \frac{\partial \mathbf{j}'}{\partial t}\Big|_0$
V'_{ext}
$V_{\mathrm{ext}}(0) \neq V'_{\mathrm{ext}}(0)$
V_{ext}
0
t

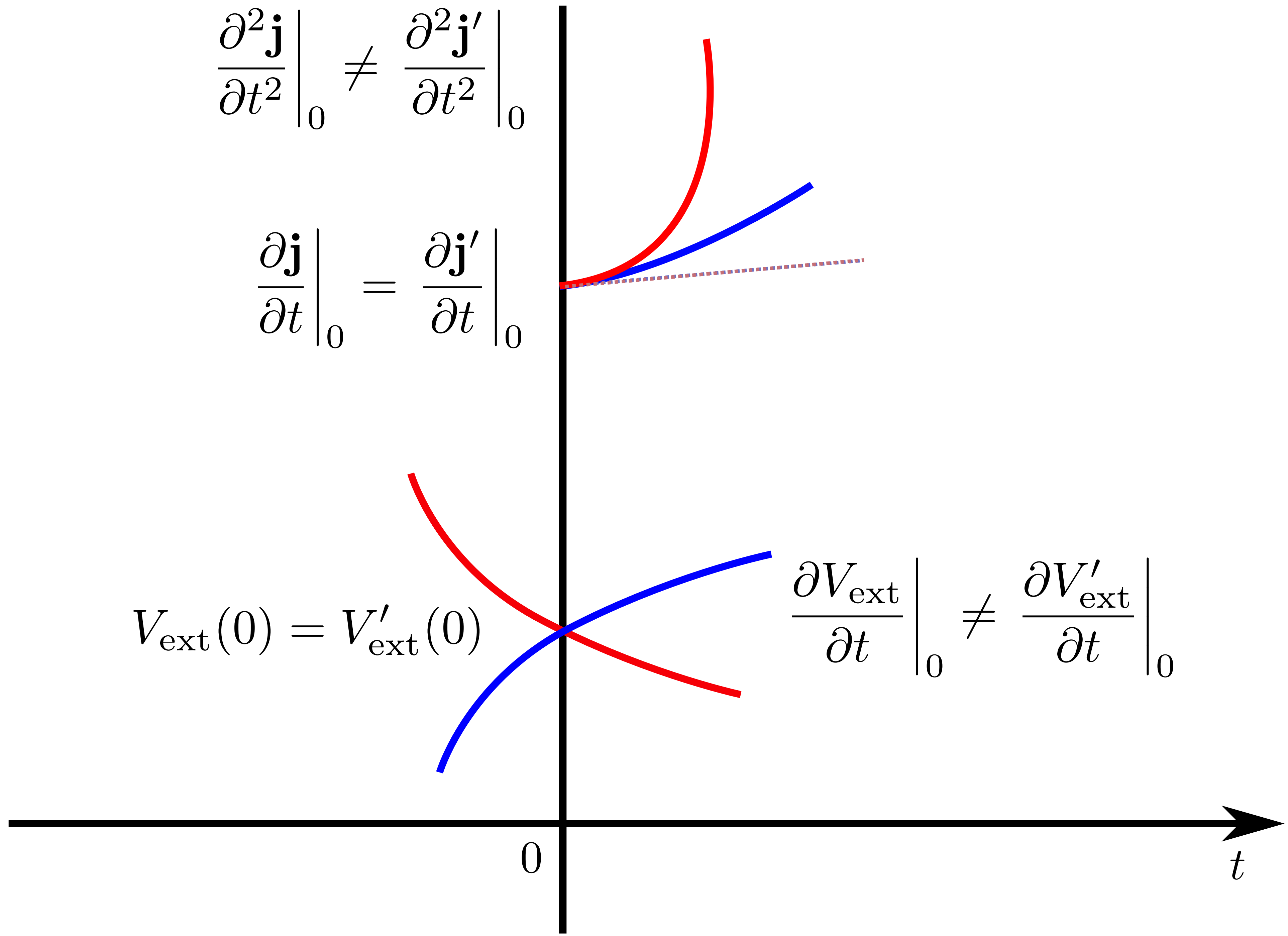


$V_{\rm ext}(0) = V'_{\rm ext}(0)$
$\left.\frac{\partial V_{\rm ext}}{\partial t}\right|_0 \neq \left.\frac{\partial V'_{\rm ext}}{\partial t}\right|_0$
0
t

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

$$i\frac{\partial \langle | [\mathbf{j}'(\mathbf{r}), H'(t)] | \rangle}{\partial t} = \langle \Psi(t) | \Big[[\mathbf{j}'(\mathbf{r}), H'(t)] , H'(t) \Big] | \Psi(t) \rangle$$

$$\frac{\partial^2}{\partial t^2} [\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)] \Big|_{t=t_0} = -n_0(\mathbf{r}) \nabla \, \frac{\partial}{\partial t} [V_{\text{ext}}(\mathbf{r},t) - V'_{\text{ext}}(\mathbf{r},t)] \Big|_{t=0}$$



$\left.\frac{\partial^2 \mathbf{j}}{\partial t^2}\right|_0 \neq \left.\frac{\partial^2 \mathbf{j}'}{\partial t^2}\right|_0$
$\left.\frac{\partial \mathbf{j}}{\partial t}\right|_0 = \left.\frac{\partial \mathbf{j}'}{\partial t}\right|_0$
$V_{\mathrm{ext}}(0) = V'_{\mathrm{ext}}(0)$
$\left.\frac{\partial V_{\mathrm{ext}}}{\partial t}\right|_0 \neq \left.\frac{\partial V'_{\mathrm{ext}}}{\partial t}\right|_0$
0
t

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

$$i\frac{\partial \langle |[\mathbf{j}'(\mathbf{r}), H'(t)]| \rangle}{\partial t} = \langle \Psi(t) | \left[[\mathbf{j}'(\mathbf{r}), H'(t)], H'(t) \right] | \Psi(t) \rangle$$

v_{ext}

Taylor expandable

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

$$\vdots$$

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

two different potentials will generate two different current densities

Runge-Gross theorem

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

Demonstration

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

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

Demonstration of the Runge Gross theorem

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

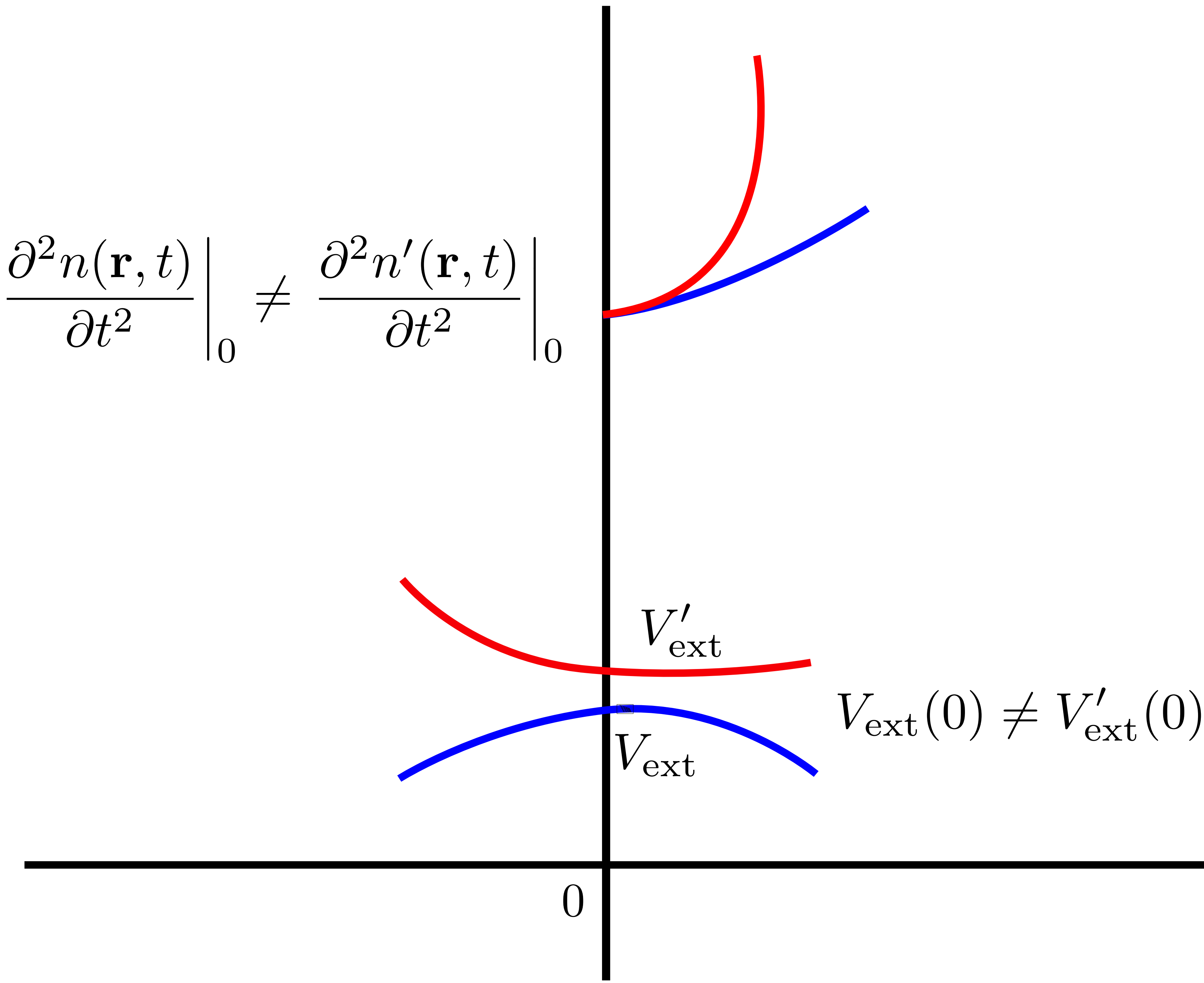
$$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r},t)$$

$$\frac{\partial n'(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{j}'(\mathbf{r},t)$$

$$i\frac{\partial}{\partial t}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=0} = \langle \Psi_0 | [\mathbf{j}(\mathbf{r}), H(0) - H'(0)] | \Psi_0 \rangle$$
$$= n_0(\mathbf{r}) \nabla \left[v_{\text{ext}}(\mathbf{r},0) - v'_{\text{ext}}(\mathbf{r},0) \right]$$

$$i\frac{\partial^2}{\partial t^2}\left[n(\mathbf{r},t) - n'(\mathbf{r},t)\right]\Big|_{t=0} = \nabla \cdot \frac{\partial}{\partial t}\left[\mathbf{j}(\mathbf{r},t) - \mathbf{j}'(\mathbf{r},t)\right]\Big|_{t=0}$$

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



$\left.\frac{\partial^2 n(\mathbf{r},t)}{\partial t^2}\right|_0 \neq \left.\frac{\partial^2 n'(\mathbf{r},t)}{\partial t^2}\right|_0$
V'_{ext}
$V_{\text{ext}}(0) \neq V'_{\text{ext}}(0)$
V_{ext}
0
t

Demonstration of the Runge Gross theorem

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

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

two different potentials will generate two different densities

provided that the divergence does not vanish

Runge-Gross Theorem

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

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

- Functional of the TD density $n(\mathbf{r}, t)$ **and** of the initial state Ψ^0
- V_{ext} Taylor expandable
- $\nabla \cdot \left[n_0(\mathbf{r}) \nabla V_k \right] \neq 0$ non-vanishing divergence

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

Name of the game

TDDFT

Runge-Gross theorem

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

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

is it true?

✓ Demonstration

but in practice?

KS equations

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

$$V_{\text{ext}}(\mathbf{r}, t) \quad \longleftrightarrow \quad n(\mathbf{r}, t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t = 0)$$

$$V_{ee} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V_{\text{ext}}(\mathbf{r},t) \longleftrightarrow n(\mathbf{r},t) \qquad \text{given} \;\; \Psi^0(\mathbf{r}_1,\mathbf{r}_2,..,\mathbf{r}_N,t=0)$$

$$V_{ee}=0$$

$$V_{\text{KS}}([n,\Phi^0],\mathbf{r},t) \longleftrightarrow n(\mathbf{r},t) \;\text{given}\;\; \Phi^0(\{\mathbf{r}_i\},t=0)=\frac{1}{\sqrt{N}}\begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & .. & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & .. & \psi_2(\mathbf{r}_N) \\ .. & .. & .. & .. \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & .. & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

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

$$V_{\text{KS}}[n,\Phi^0](\mathbf{r},t)=V_{\text{ext}}[n,\Psi^0](\mathbf{r},t)+\int\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+V_{\text{xc}}[n,\Psi^0,\Phi^0](\mathbf{r},t)$$

Kohn-Sham potential

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

Kohn-Sham equations

Kohn-Sham Equations

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

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

- No self-consistency
- No variational principle
- $V_{\mathrm{xc}}[n,\Psi^0,\Phi^0](\mathbf{r},t)$

(local in space and time) functionally non-local

non-interacting v-representability

non-interacting v-representability

van Leeuwen theorem

conditions for the existence of $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

R.van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999)

Name of the game

TDDFT

Runge-Gross theorem

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

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

is it true?

✓ Demonstration

but in practice?

✓ KS equations

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

1 approximate $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

2 solve the TD Kohn-Sham equations

C look at some observables

Approximations

$$V_{\mathrm{xc}}[n(\mathbf{r}', t' < t), \Psi^0, \Phi^0](\mathbf{r}, t)$$

Live in the present or *no grudge* approximation

Approximations

- Adiabatic $V_{\mathrm{xc}}^{A}[n(\mathbf{r}',t)](\mathbf{r},t)$
  - ALDA $v_{xc}^{\mathrm{ALDA}}[n](\mathbf{r},t) = v_{xc}^{\mathrm{heg}}(n(\mathbf{r},t)) = \frac{d}{dn}\left[n e_{xc}^{\mathrm{heg}}(n)\right]\Big|_{n=n(\mathbf{r},t)}$
  - AGGA
  - Orbital dependent
- non-adiabatic (few examples like Vignale Kohn)

✓ approximate $V_{\mathrm{xc}}[n, \Psi^0, \Phi^0](\mathbf{r}, t)$

2 solve the TD Kohn-Sham equations

C look at some observables

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{KS}}[n](\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad \Rightarrow \quad n(\mathbf{r})$$

KS equations

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

TD KS equations

Time evolution operator

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

$$i\frac{d\,U(t,t_0)}{dt} = H(t)U(t,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1)U(\tau_1,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_2)U(\tau_2,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_1)H(\tau_2) +$$

$$(-i)^3\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_3 H(\tau_1)H(\tau_2)H(\tau_3) + \quad \cdots$$

Time evolution operator

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

$$i\frac{dU(t,t_0)}{dt} = H(t)U(t,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1)U(\tau_1,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_2)U(\tau_2,t_0)$$

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

Time evolution operator

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

$$i\frac{d\,U(t,t_0)}{dt} = H(t)U(t,t_0)$$

$$U(t,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1)U(\tau_1,t_0) = 1 - i\int_{t_0}^{t} d\tau_1 H(\tau_1) + (-i)^2 \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_2)U(\tau_2,t_0)$$

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

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

Time evolution operator

$$i\frac{\partial\psi(t)}{\partial t} = H(t)\psi(t) \longrightarrow \psi(t) = U(t,t_0)\psi(t_0)$$

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

time integrators problem

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

exponential operator

- Taylor expansion
- Chebychev polynomials
- Lanczos iterative scheme

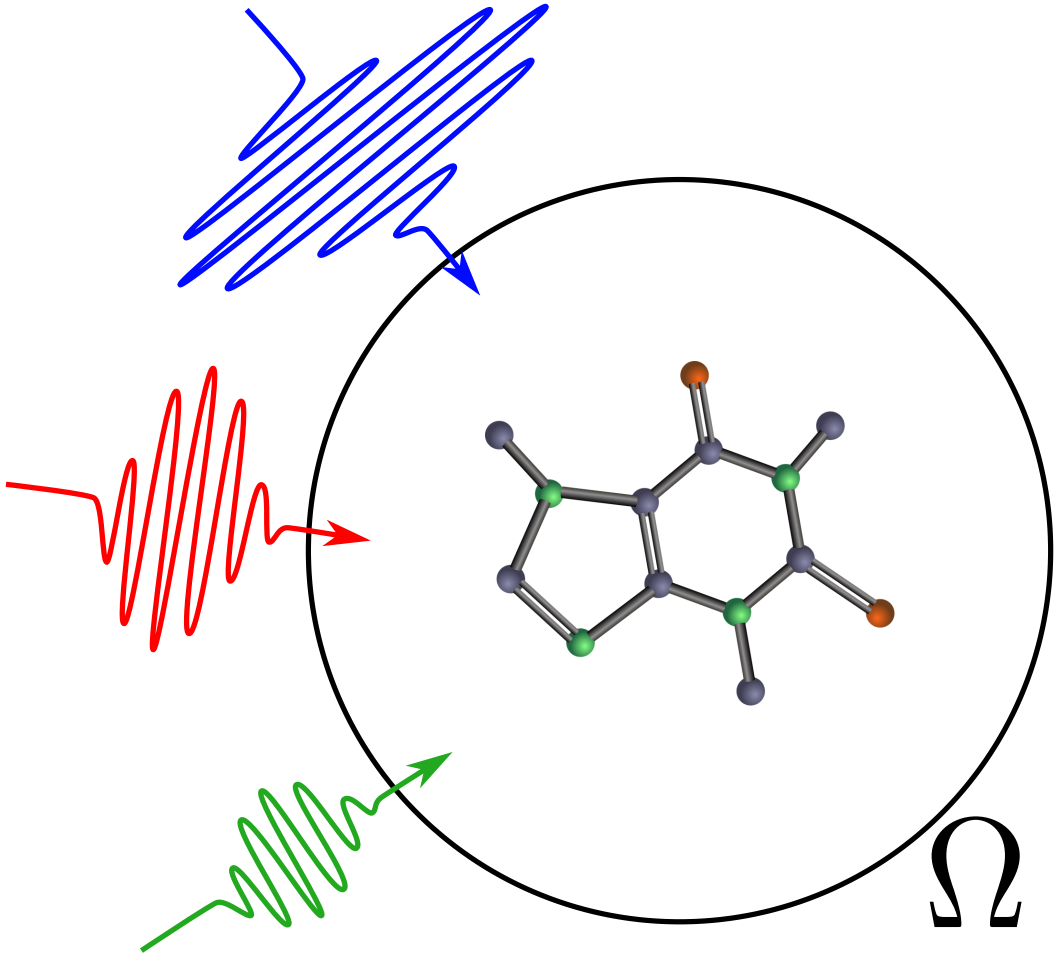
Castro *et al.* Lect. Notes Phys. **706**, 197 (2004)

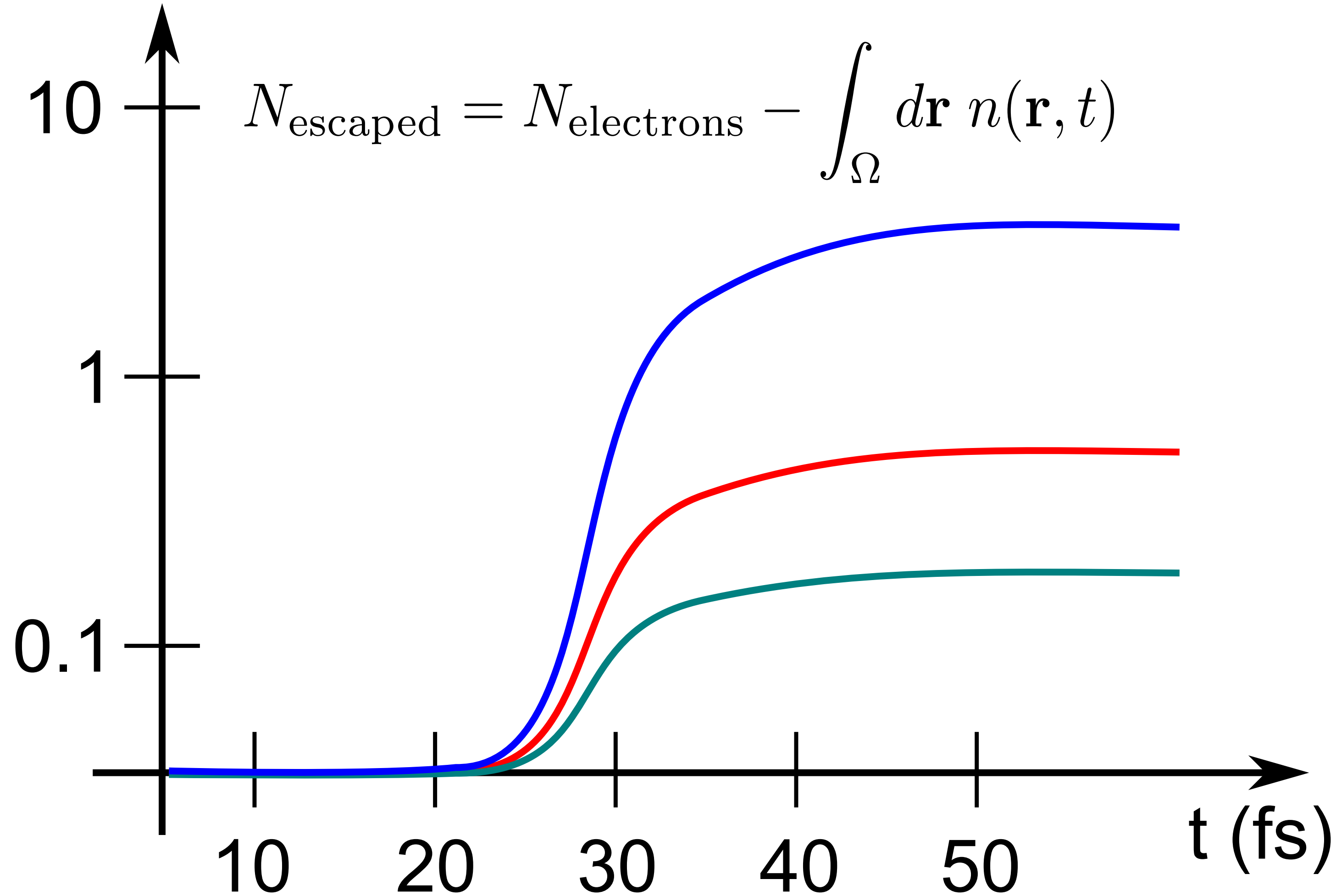
C look at some observables

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

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

$$\int d\mathbf{r}\; n(\mathbf{r}, t) = N_{\text{electrons}}$$





C.Ullrich *et al.*, J. Phys. B: At. Mol. Opt. Phys. **30**, 5043 (1997)

Time Dependent ELF

$$ELF(\mathbf{r},t) = \left[1 + D^0\left(\sum_i |\nabla\psi_i(\mathbf{r},t)| - \frac{1}{4}\frac{[\nabla n(\mathbf{r},t)]^2}{n(\mathbf{r},t)} - \frac{1}{2}\frac{j^2(\mathbf{r},t)}{n(\mathbf{r},t)}\right)^2\right]^{-1}$$

T. Burnus, M. A. L. Marques, and E. K. U. Gross, Phys. Rev. A **71**, 010501(R) (2005)

One-particle operator

$$\langle \Psi(t)|\hat{O}|\Psi(t)\rangle = \int O(\mathbf{r})\, n(\mathbf{r},t)d\mathbf{r}$$

Some observables

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

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

Photo-absorption cross section

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

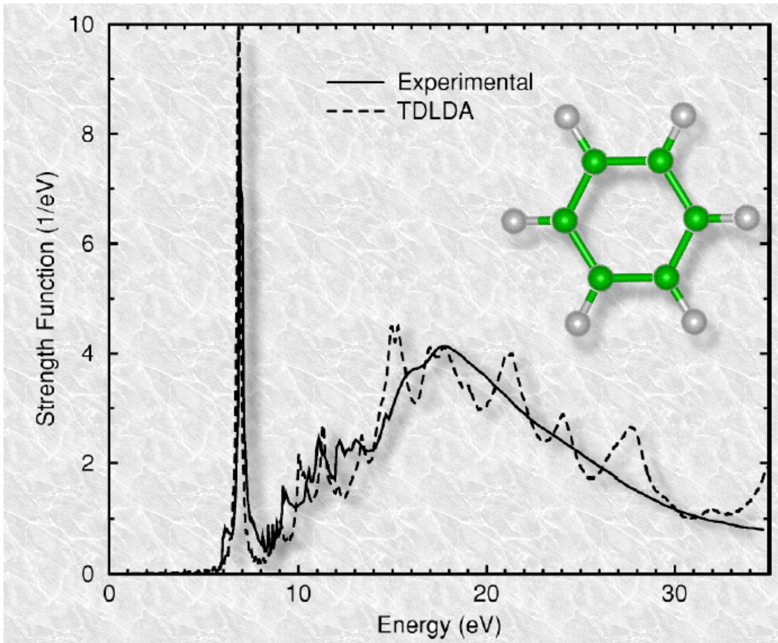
Multipoles

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

Angular Momentum

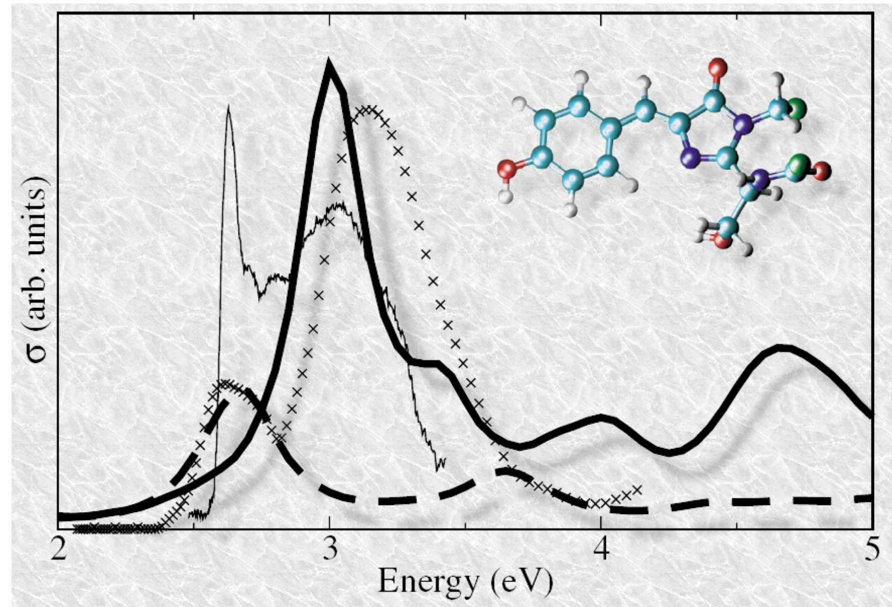
Photo-absorption cross section

Benzene



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

GFP



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

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

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

$$\left[-\frac{\nabla^2}{2} + V_H(\mathbf{r},t) + V_{\rm xc}^{ALDA}(\mathbf{r},t) + V_{\rm ext}(\mathbf{r},t)\right]\psi_i(\mathbf{r},t) = i\frac{\partial\psi_i(\mathbf{r},t)}{\partial t}$$

$$V_{\rm ext}(\mathbf{r},t) = V_{\rm ext}^{nucl}(\mathbf{r}) + \delta(t=0)\eta$$

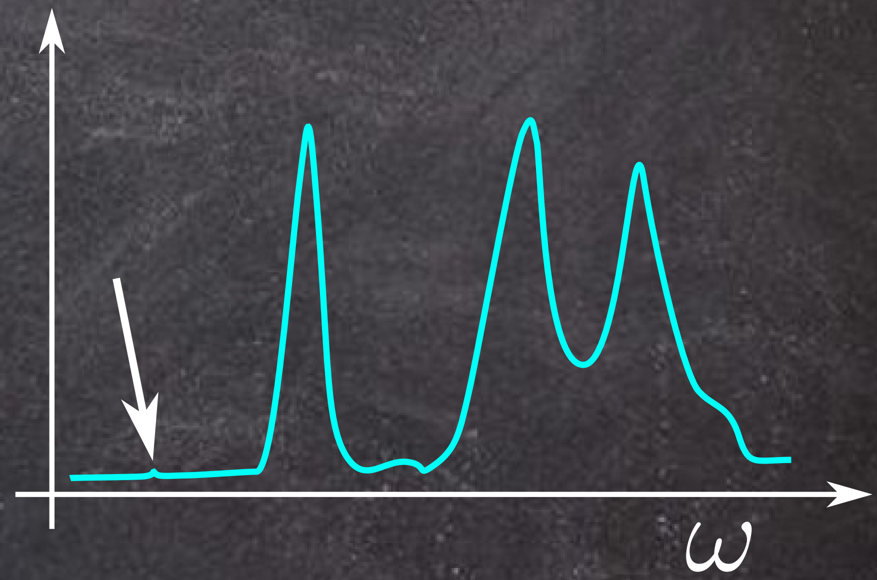
Linear response approach

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

access to excitations energies

build the spectrum ω by ω

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



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
- Qualitatively first step

  → strong field phenomena
  → open quantum systems
  → superconductivity
  → quantum optimal control
  → beyond BO dynamics
  → quantum transport
  → .....