Introduction to TDDFT in extended systems

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<u>and you all present here</u>

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Outline

References

M. A. L. Marques *et al.*
Fundamentals of Time-Dependent Density Functional Theory

C. A. Ullrich
Time-Dependent Density-Functional Theory Concepts and Applications

S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining
Rep. Progr. Phys. **70**, 357 (2007).

Outline

What is TDDFT?

What is TDDFT?

- TDDFT is an extension of DFT: it is a DFT with time-dependent external potential
- The fundamental degree of freedom is the time-dependent electronic density $\rho(\mathbf{r}, t)$

Basic theorems

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

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

G. Vignale, Phys. Rev. A **77**, 062511 (2008).

DFT

- There exists a one-to-one correspondence (up to an additive constant) between the ground-state density $\rho(\mathbf{r})$ and the static external potential $V_{ext}(\mathbf{r})$.

TDDFT

- For a given initial state $\Phi(t=0)=\Phi_0$, time-dependent potentials $V_{ext}(\mathbf{r},t)$ and time-dependent densities $\rho(\mathbf{r},t)$ are in a one-to-one correspondence (up to a purely time-dependent function).

DFT

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- The expectation value of any physical observable of a many-electron system is a unique functional of the ground-state electron density $\rho(\mathbf{r})$.

TDDFT

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- The expectation value of any physical time-dependent observable is a unique functional of the electron density $\rho(\mathbf{r},t)$ and of the initial state $\Phi(t=0)=\Phi_0$ (in our case: always the ground state).

DFT

- There exists a one-to-one correspondence (up to an additive constant) between the ground-state density $\rho(\mathbf{r})$ and the static external potential $V_{ext}(\mathbf{r})$.
- The expectation value of any physical observable of a many-electron system is a unique functional of the ground-state electron density $\rho(\mathbf{r})$.
- The minimum of the total energy functional gives the ground-state density $\rho(\mathbf{r})$.

TDDFT

- For a given initial state $\Phi(t = 0) = \Phi_0$, time-dependent potentials $V_{ext}(\mathbf{r}, t)$ and time-dependent densities $\rho(\mathbf{r}, t)$ are in a one-to-one correspondence (up to a purely time-dependent function).
- The expectation value of any physical time-dependent observable is a unique functional of the electron density $\rho(\mathbf{r}, t)$ and of the initial state $\Phi(t = 0) = \Phi_0$ (in our case: always the ground state).
- The stationary point of the action (plus a boundary condition) gives the density $\rho(\mathbf{r}, t)$.

Action functional

Quantum mechanics

$$A[\Psi] = \int_0^T \langle \Psi(t) | i\partial_t - H | \Psi(t) \rangle$$

$\delta A[\Psi]/\delta\Psi = 0$ with $|\delta\Psi(0)\rangle = |\delta\Psi(T)\rangle = 0$ is equivalent to the time-dependent Schrödinger equation:

$$(i\partial_t - H)|\Psi(t)\rangle = 0$$

Action functional

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TDDFT

Runge Gross theorem $\Rightarrow \Psi(t) = \Psi(t)[\rho]$.

$$A[\rho] = \int_0^T \langle \Psi(t)[\rho]|i\partial_t - H|\Psi(t)[\rho]\rangle$$

But $\delta A[\rho]/\delta\rho = 0$ is wrong!

Action functional

Quantum mechanics

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TDDFT

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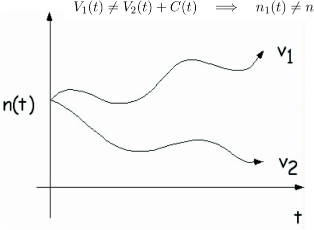
$$A[\rho] = \int_0^T \langle \Psi(t)[\rho] | i\partial_t - H | \Psi(t)[\rho] \rangle$$

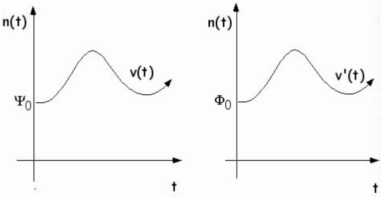
But $\delta A[\rho]/\delta\rho = 0$ is wrong!
The variation of the density at any time $t < T$ causes a variation of the wavefunction: we cannot set $|\delta\Psi(T)\rangle = 0$. So the correct variational principle in TDDFT is:

$$\delta A[\rho]/\delta\rho = i\langle \Psi(T)[\rho] | \delta\Psi(T)[\rho]/\delta\rho \rangle$$

TDDFT summary

$$\hat{V}_1(t) \neq \hat{V}_2(t) + C(t) \quad \Longrightarrow \quad n_1(t) \neq n_2(t)$$



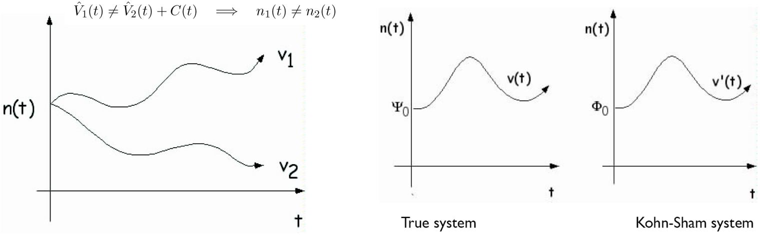


True system

Kohn-Sham system

- (Runge-Gross) Given an initial state, if two time-dependent external potentials v_1 and v_2 differ more than a time-dependent constant, then the corresponding time-dependent densities ρ_1 and ρ_2 are different

TDDFT summary



$\hat{V}_1(t) \neq \hat{V}_2(t) + C(t) \quad \Longrightarrow \quad n_1(t) \neq n_2(t)$

True system

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- (Runge-Gross) Given an initial state, if two time-dependent external potentials v_1 and v_2 differ more than a time-dependent constant, then the corresponding time-dependent densities ρ_1 and ρ_2 are different
- (van Leeuwen) If the density ρ_1 is produced by a time-dependent external potential v_1 in system 1 (starting from a given initial state), then one can uniquely construct the potential v_2 that produces the same density in system 2 (the choice of initial state in system 2 is also unique) - “v-representability in TDDFT”

Kohn-Sham equations

DFT

$$\Big[-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r})\Big)\Big]\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r})$$

$$V_{KS}(\mathbf{r}) = V_H(\mathbf{r}) + V_{ext}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

Unknown exchange-correlation potential $V_{xc}(\mathbf{r})$: functional of the density $\rho(\mathbf{r})$.

$$V_{xc}^{LDA}(\mathbf{r}) = V_{xc}^{HEG}(\rho(\mathbf{r}))$$

TDDFT

$$\Big[-\frac{\nabla^2}{2} + V_{KS}(\mathbf{r},t)\Big]\varphi_i(\mathbf{r},t) = i\frac{\partial}{\partial t}\varphi_i(\mathbf{r},t)$$

$$V_{KS}(\mathbf{r},t) = V_H(\mathbf{r},t) + V_{ext}(\mathbf{r},t) + V_{xc}(\mathbf{r},t)$$

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r},t)|^2$$

Unknown exchange-correlation time-dependent potential $V_{xc}(\mathbf{r},t)$: functional of the density at all past times $\rho(\mathbf{r},t')$ with $t' < t$ (and of the initial states).

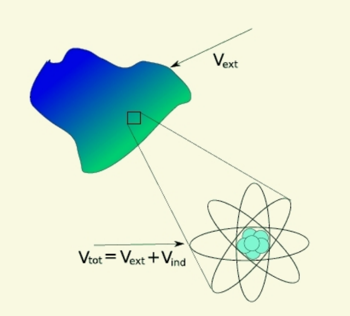
$$V_{xc}^{ALDA}(\mathbf{r},t) = V_{xc}^{HEG}(\rho(\mathbf{r},t))$$

Outline

1. TDDFT: Basic theorems
2. Linear response in TDDFT
3. Approximations

Response functions

External perturbation V_{ext} applied on the sample
$\rightarrow$ V_{tot} acting on the electronic system



Potentials

$$\delta V_{tot} = \delta V_{ext} + \delta V_{ind}$$

$$\delta V_{ind} = v \delta \rho$$

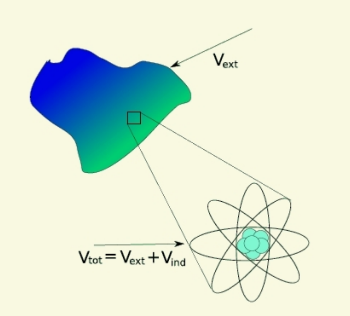
Dielectric function

$$\epsilon = \frac{\delta V_{ext}}{\delta V_{tot}} = 1 - v \frac{\delta \rho}{\delta V_{tot}}$$

$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}} = 1 + v \frac{\delta \rho}{\delta V_{ext}}$$

Response functions

External perturbation V_{ext} applied on the sample
$\rightarrow$ V_{tot} acting on the electronic system



Dielectric function

$$\epsilon = \frac{\delta V_{ext}}{\delta V_{tot}} = 1 - vP$$
$$\epsilon^{-1} = \frac{\delta V_{tot}}{\delta V_{ext}} = 1 + v\chi$$

$$P = \frac{\delta \rho}{\delta V_{tot}} \qquad \chi = \frac{\delta \rho}{\delta V_{ext}}$$

$$\chi = P + Pv\chi$$

Spectra

Spectra

$$\mathrm{Abs}(\omega) = \lim_{\mathbf{q}\to 0} \mathrm{Im}\,\varepsilon_M(\mathbf{q},\omega)$$

$$\mathrm{Eels}(\mathbf{q},\omega) = -\mathrm{Im}\left\{\frac{1}{\varepsilon_M(\mathbf{q},\omega)}\right\}$$

$$\mathrm{Eels}(\mathbf{q},\omega) = \frac{\mathrm{Im}\,\varepsilon_M(\mathbf{q},\omega)}{[\mathrm{Re}\,\varepsilon_M(\mathbf{q},\omega)]^2 + [\mathrm{Im}\,\varepsilon_M(\mathbf{q},\omega)]^2}$$

Linear response TDDFT

Linear response TDDFT

$$\delta\rho(1) = \int d2\chi(1,2)\delta V_{ext}(2) \quad \text{and} \quad \delta\rho(1) = \int d2\chi^0(1,2)\delta V_{KS}(2)$$

Linear response TDDFT

Linear response TDDFT

$$\delta\rho(1) = \int d2\chi(1,2)\delta V_{ext}(2) \quad \text{and} \quad \delta\rho(1) = \int d2\chi^0(1,2)\delta V_{KS}(2)$$

Using:

$$\frac{\delta V_{KS}(1)}{\delta V_{ext}(2)} = \delta(1,2) + \frac{\delta V_H(1)}{\delta V_{ext}(2)} + \frac{\delta V_{xc}(1)}{\delta V_{ext}(2)}$$

one obtains the Dyson equation of linear response TDDFT :

$$\chi(1,2) = \chi^0(1,2) + \int d34\chi^0(1,3)[v(3,4) + f_{xc}(3,4)]\chi(4,2)$$

where the exchange-correlation kernel f_{xc} has been defined as:

$$f_{xc}(1,2) = \frac{\delta V_{xc}(1)}{\delta\rho(2)}$$

$$f_{xc}^{ALDA}(\mathbf{r},\mathbf{r}',t,t') = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\frac{\partial V_{xc}^{LDA}(\rho(\mathbf{r}))}{\partial\rho(\mathbf{r})}$$

Linear response TDDFT

Exercise: derivation of TDDFT Dyson equation

$$\delta\rho(1) = \int d2\chi(1,2)\delta V_{ext}(2) = \int d2\chi^0(1,2)\delta V_{KS}(2)$$

$$\int d2\chi(1,2)\frac{\delta V_{ext}(2)}{\delta V_{ext}(3)} = \int d2\chi^0(1,2)\frac{\delta V_{KS}(2)}{\delta V_{ext}(3)}$$

$$\chi(1,3) = \int d2\chi^0(1,2)\frac{\delta V_{ext}(2) + \delta V_H(2) + \delta V_{xc}(2)}{\delta V_{ext}(3)}$$

$$\chi(1,3) = \chi^0(1,3) + \int d2\chi^0(1,2)\left[\frac{\delta V_H(2)}{\delta V_{ext}(3)} + \frac{\delta V_{xc}(2)}{\delta V_{ext}(3)}\right]$$

$$\chi(1,3) = \chi^0(1,3) + \int d24\chi^0(1,2)\left[\frac{\delta V_H(2)}{\delta\rho(4)}\frac{\delta\rho(4)}{\delta V_{ext}(3)} + \frac{\delta V_{xc}(2)}{\delta\rho(4)}\frac{\delta\rho(4)}{\delta V_{ext}(3)}\right]$$

$$\delta V_H(2) = \int d5v(2,5)\delta\rho(5)$$

$$\chi(1,3) = \chi^0(1,3) + \int d24\chi^0(1,2)[v(2,4) + f_{xc}(2,4)]\chi(4,3)$$

Linear response TDDFT

One equation...

$$\chi(1,2) = \chi^0(1,2) + \int d34\,\chi^0(1,3)[v(3,4) + f_{xc}(3,4)]\chi(4,2)$$

...many algorithms

- Dyson equation in transition space (aka “Casida equation”): finite systems
- Dyson equation in Fourier space: extended systems
- Lanczos algorithm - see B. Walker *et al.*, PRL **96** (2006); D. Rocca *et al.*, J. Chem. Phys. **128** (2008).
- Sternheimer equation - see X. Andrade *et al.*, J. Chem. Phys. **126** (2007).

Linear response TDDFT

Dyson equation

$$\chi(1,2) = \chi^0(1,2) + \int d34\, \chi^0(1,3)[v(3,4) + f_{xc}(3,4)]\chi(4,2)$$

Kohn-Sham response function

$$\chi^0\left(\mathbf{r},\mathbf{r}',\omega\right) = \sum_{ij}(f_i - f_j)\frac{\varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_i) + i\eta}$$

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{\Omega}\sum_{v c \mathbf{k}}(f_{v\mathbf{k}} - f_{c\mathbf{k}+\mathbf{q}})\frac{\langle u_{v\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|u_{c\mathbf{k}+\mathbf{q}}\rangle\langle u_{c\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|u_{v\mathbf{k}}\rangle}{\omega - (\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}}) + i\eta}$$

where we use $\varphi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$

TDDFT flow chart

Ground state calculation : ε_i, φ_i $\Rightarrow$ construction of χ^0

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1,\mathbf{G}_2} \chi^0_{\mathbf{G},\mathbf{G}_1}(\mathbf{q},\omega)[v_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1,\mathbf{G}_2} + f^{xc}_{\mathbf{G}_1,\mathbf{G}_2}]\chi_{\mathbf{G}_2,\mathbf{G}'}(\mathbf{q},\omega)$$

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

$$\epsilon_M(\omega) = \lim_{\mathbf{q}\to 0} \frac{1}{\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

$$\mathrm{Abs}(\omega) = \mathrm{Im}\{\varepsilon_M(\omega)\} \qquad \mathrm{Eels}(\omega) = -\mathrm{Im}\left\{\frac{1}{\varepsilon_M(\omega)}\right\}$$

Outline

1. TDDFT: Basic theorems
2. Linear response in TDDFT
3. Approximations

Approximations

Dyson equation

$$\chi = \chi^0 + \chi^0(v + f_{xc})\chi$$

Approximations

- Independent-particle approximation (IPA): $v = f_{xc} = 0$
- Random-phase approximation (RPA): $f_{xc} = 0$
- TDLDA: $f_{xc} = f_{xc}^{ALDA}$

Independent particles

$$\mathrm{Im}\epsilon_M(\omega) = -\lim_{\mathbf{q}\to 0} v_{\mathbf{G}=0}(\mathbf{q})\mathrm{Im}\chi^0_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)$$

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{\Omega}\sum_{vc\mathbf{k}}(f_{v\mathbf{k}} - f_{c\mathbf{k}+\mathbf{q}})\frac{\langle u_{v\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|u_{c\mathbf{k}+\mathbf{q}}\rangle\langle u_{c\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|u_{v\mathbf{k}}\rangle}{\omega - (\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}}) + i\eta}$$

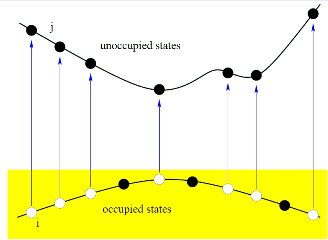
Independent particles

$$\mathrm{Im}\epsilon_M(\omega) = -\lim_{\mathbf{q}\to 0} v_{\mathbf{G}=0}(\mathbf{q})\mathrm{Im}\chi^0_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)$$

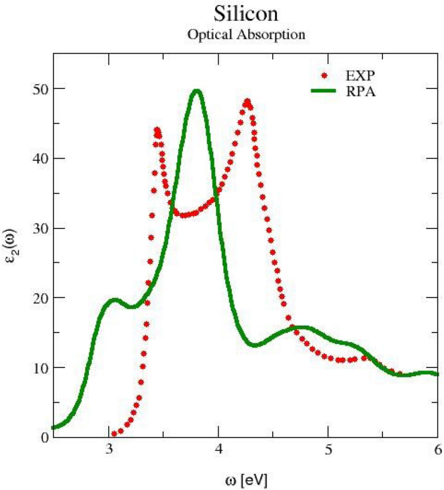
$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{\Omega}\sum_{v c \mathbf{k}}(f_{v\mathbf{k}} - f_{c\mathbf{k}+\mathbf{q}})\frac{\langle u_{v\mathbf{k}}|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|u_{c\mathbf{k}+\mathbf{q}}\rangle\langle u_{c\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|u_{v\mathbf{k}}\rangle}{\omega - (\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}}) + i\eta}$$

Fermi's golden rule

$$\mathrm{Im}\epsilon_M(\omega) = \lim_{\mathbf{q}\to 0}\frac{8\pi^2}{\Omega q^2}\sum_{v c \mathbf{k}}|\langle u_{c\mathbf{k}+\mathbf{q}}|e^{i\mathbf{q}\mathbf{r}}|u_{v\mathbf{k}}\rangle|^2\delta(\omega - (\varepsilon_{c\mathbf{k}+\mathbf{q}} - \varepsilon_{v\mathbf{k}}))$$



Independent particles



Approximations

Dyson equation

$$\chi = \chi^0 + \chi^0 (v + f_{xc}) \chi$$

can be equivalently be written as:

$$\chi = \chi^0 + \chi^0 (v_0 + \bar{v} + f_{xc}) \chi$$

Coulomb interaction

$$v \equiv v_0 + \bar{v}$$

$$v_0 = v_{\mathbf{G}}(\mathbf{q}) \quad \text{for } \mathbf{G} = 0$$

$$\bar{v}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{for } \mathbf{G} = 0 \\ v_{\mathbf{G}}(\mathbf{q}) & \text{for } \mathbf{G} \neq 0 \end{cases}$$

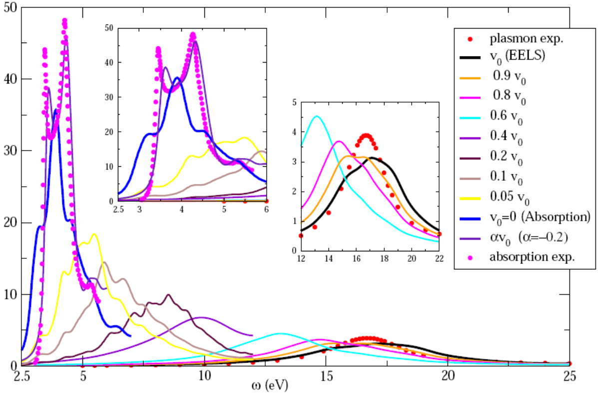
The Coulomb term v

The Coulomb term

$$v = v_0 + \bar{v}$$

long-range $v_0 \Rightarrow$ difference between Abs and Eels

Coulomb term v_0: Abs vs. Eels



F. Sottile, PhD thesis (2003) - Bulk silicon: absorption vs. EELS.

The Coulomb term v

The Coulomb term

$$v = v_0 + \bar{v}$$

long-range $v_0 \Rightarrow$ difference between Abs and Eels

what about $\bar{v}$?

The Coulomb term v

The Coulomb term

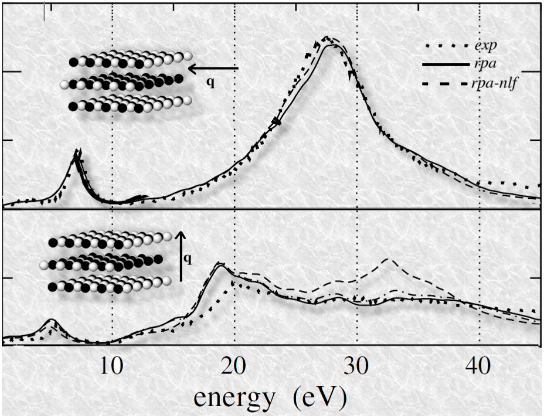
$$v = v_0 + \bar{v}$$

long-range $v_0 \Rightarrow$ difference between Abs and Eels

what about $\bar{v}$?

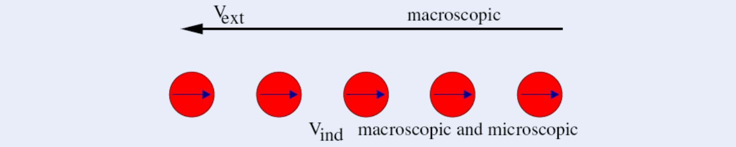
$\bar{v}$ is responsible for crystal local-field effects

Coulomb term $\bar{v}$: local fields



A. G. Marinopoulos *et al.*, PRL **89** (2002) - Graphite EELS

What are local fields?



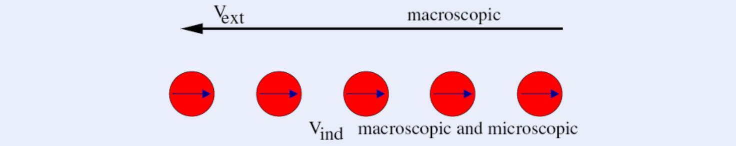
Effective medium theory

Uniform field E_0 applied to a dielectric sphere with dielectric constant ϵ in vacuum. From continuity conditions at the interface:

$$P = \frac{3}{4\pi}\frac{\epsilon - 1}{\epsilon + 2}E_0$$

Jackson, Classical electrodynamics, Sec. 4.4.

What are local fields?



Effective medium theory

Regular lattice of objects dimensionality *d* of material ϵ_1 in vacuum
Maxwell-Garnett formulas

- dot (O D system)

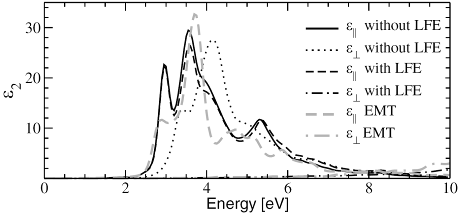
$$\mathrm{Im}\epsilon_M(\omega) \propto 9\frac{\mathrm{Im}\epsilon_1(\omega)}{[\mathrm{Re}\epsilon_1(\omega)+2]^2+[\mathrm{Im}\epsilon_1(\omega)]^2}$$

- wire (1D system)

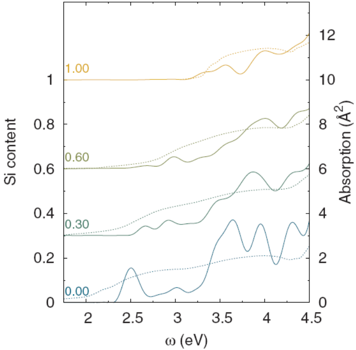
$$\mathrm{Im}\epsilon_M^{\|}(\omega) \propto \mathrm{Im}\epsilon_1(\omega)$$

$$\mathrm{Im}\epsilon_M^{\perp}(\omega) \propto 4\frac{\mathrm{Im}\epsilon_1(\omega)}{[\mathrm{Re}\epsilon_1(\omega)+1]^2+[\mathrm{Im}\epsilon_1(\omega)]^2}$$

What are local fields?



F. Bruneval *et al.*, PRL **94** (2005) - Si nanowires

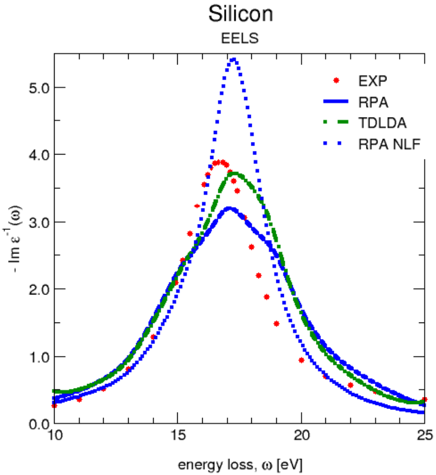


S. Botti *et al.*, PRB **79** (2009) - SiGe nanodots

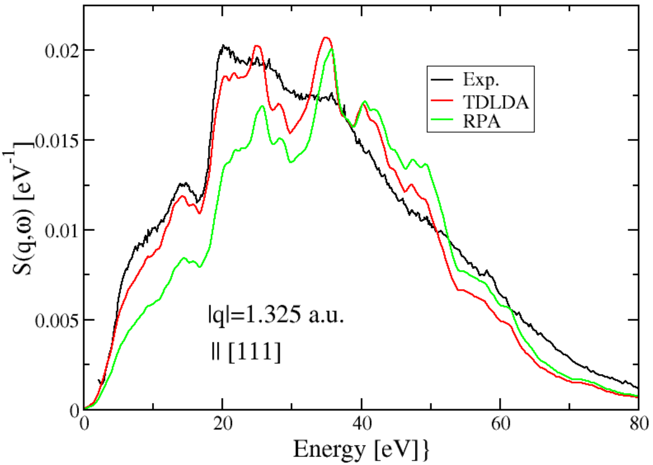
f_{xc} kernel: TDLDA

Up to now $f_{xc} = 0$ (RPA).
What about the kernel f_{xc}?

f_{xc} kernel: TDLDA

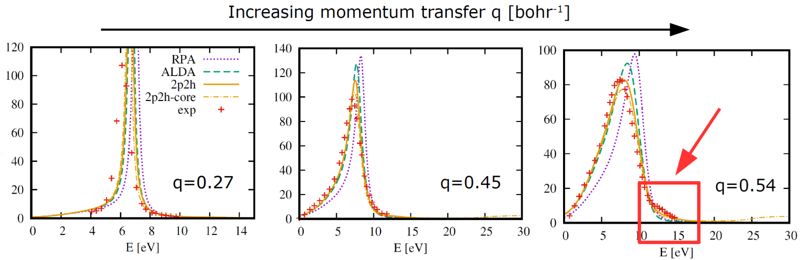


f_{xc} kernel: TDLDA



H. Weissker *et al*, PRL **97** (2006) - Bulk Si - IXS

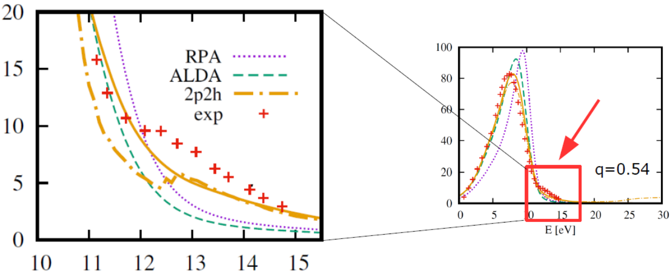
f_{xc} kernel: TDLDA



Sodium - IXS

Exp. M. Cazzaniga, et al, PRB 84 (2011);
Theo: M. Panholzer et al, PRL 120 (2018).

f_{xc} kernel: TDLDA



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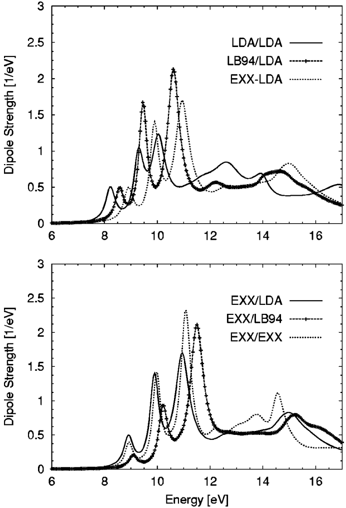
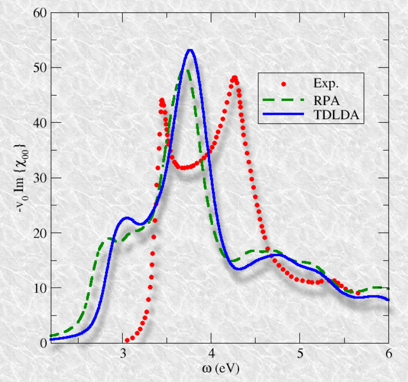


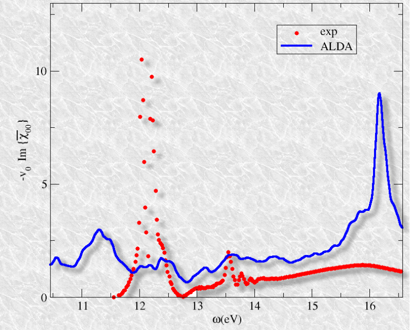
M. Marques *et al.*, J. Chem. Phys. **115** (2001) - SiH_4: V_{xc} vs. f_{xc}

f_{xc} kernel: TDLDA



Bulk silicon: absorption

f_{xc} kernel: TDLDA



Solid argon: absorption

f_{xc} kernel: TDLDA

Summary

TDLDA:

- YES for EELS of solids and absorption of finite systems
- NO for absorption of solids

What is missing?