Time-dependent density-functional theory for excitations in finite and extended systems

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Acknowledgments

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Outline

- Introduction
- TDDFT in a nutshell
- TDDFT for excitation energies: how it works
- Extended systems
- Multiple and charge-transfer excitations

DFT and excitation energies

$$\left[-\frac{\nabla^2}{2}+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\varphi_j(\mathbf{r})=\varepsilon_j\varphi_j(\mathbf{r})$$

- ► Only highest occupied KS eigenvalue has rigorous meaning:

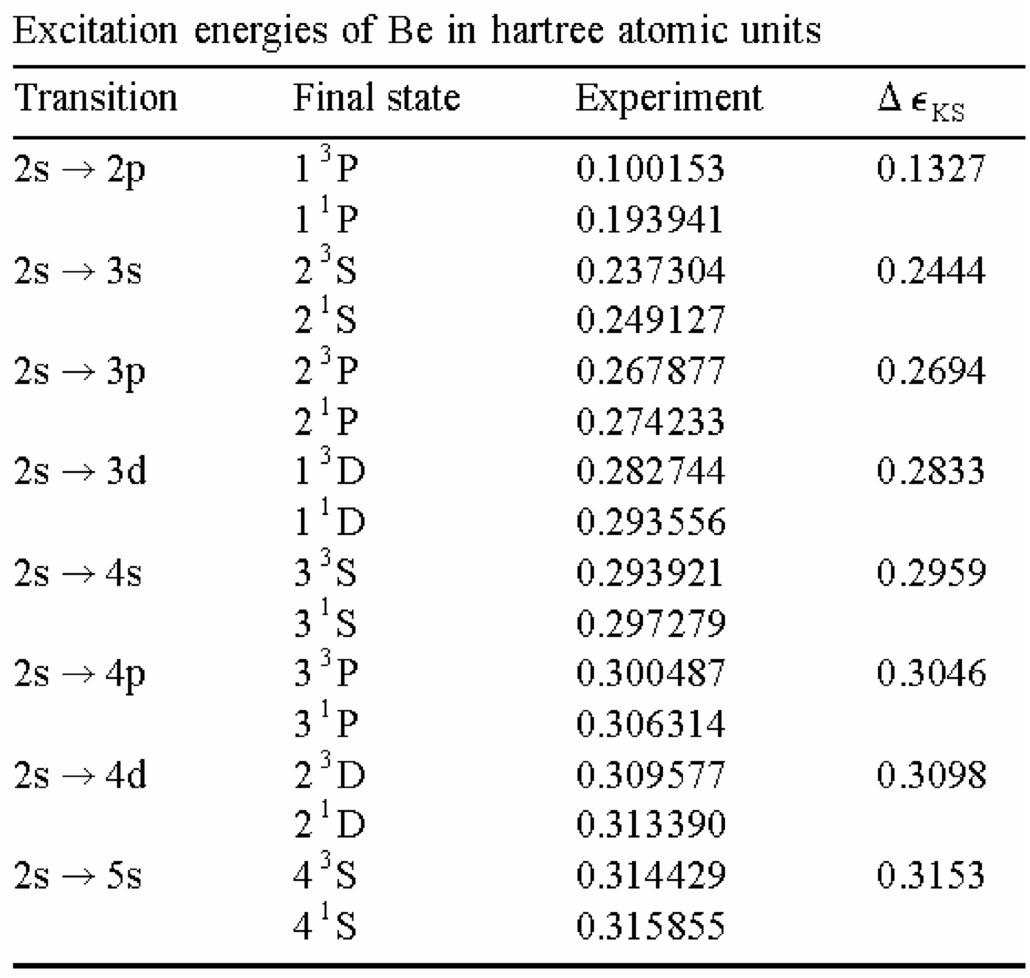
$$\varepsilon_{HOMO}=-I$$

- ► There is no rigorous basis to interpret KS eigenvalue differences as excitation energies of the N-particle system:

$$\omega_{ia}=\varepsilon_a-\varepsilon_i \quad \neq \quad \Omega_j=E_j-E_0$$

(i=occupied, a=unoccupied)

How good are the Kohn-Sham eigenvalues really?



Excitation energies of Be in hartree atomic units

Transition	Final state	Experiment	$\Delta\epsilon_{\mathrm{KS}}$
$2s \to 2p$	$1\,^3\mathrm{P}$	0.100153	0.1327
	$1\,^1\mathrm{P}$	0.193941	
$2s \to 3s$	$2\,^3\mathrm{S}$	0.237304	0.2444
	$2\,^1\mathrm{S}$	0.249127	
$2s \to 3p$	$2\,^3\mathrm{P}$	0.267877	0.2694
	$2\,^1\mathrm{P}$	0.274233	
$2s \to 3d$	$1\,^3\mathrm{D}$	0.282744	0.2833
	$1\,^1\mathrm{D}$	0.293556	
$2s \to 4s$	$3\,^3\mathrm{S}$	0.293921	0.2959
	$3\,^1\mathrm{S}$	0.297279	
$2s \to 4p$	$3\,^3\mathrm{P}$	0.300487	0.3046
	$3\,^1\mathrm{P}$	0.306314	
$2s \to 4d$	$2\,^3\mathrm{D}$	0.309577	0.3098
	$2\,^1\mathrm{D}$	0.313390	
$2s \to 5s$	$4\,^3\mathrm{S}$	0.314429	0.3153
	$4\,^1\mathrm{S}$	0.315855	

Savin, Umrigar and Gonze, CPL **288**, 391 (1998): using the exact xc potential from QMC

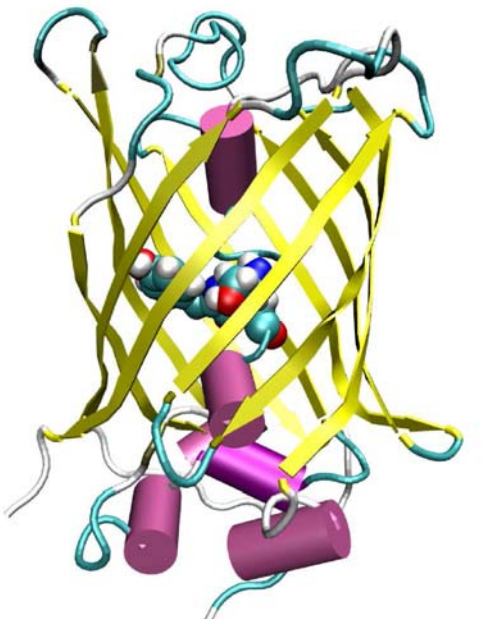
► exact KS eigenvalues are not the exact quasiparticle energies, but come close.

►Goerling (1996):
KS eigenvalue differences are zero-order excitation energies in an effective series expansion.

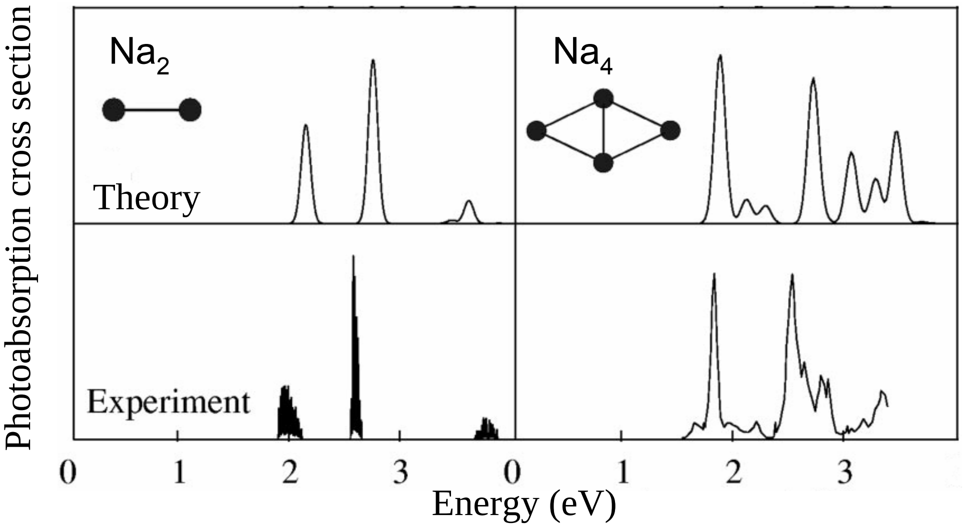
►Strongly depends on the quality of the xc potential: LDA/GGA KS excitation energies are very poor.

Optical spectroscopy

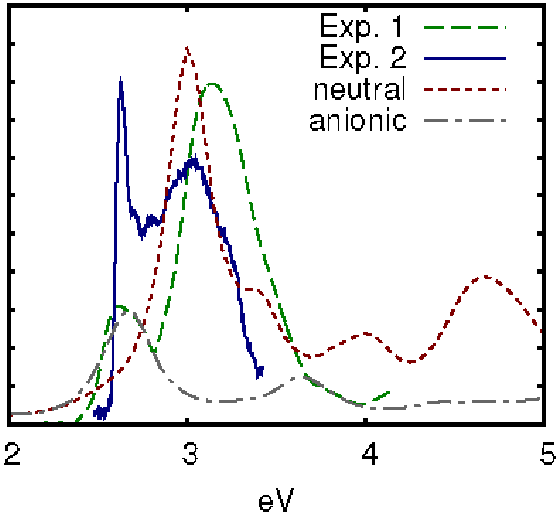
- Uses weak CW laser as Probe
- System Response has peaks at electronic excitation energies



Green fluorescent protein



Vasiliev et al., PRB **65**, 115416 (2002)



Marques et al., PRL **90**, 258101 (2003)

Why use TDDFT for excitations?

Instead of treating an excitation energy as just the energy difference of two eigenstates, consider the **excitation process.**

TDDFT captures the **intrinsically dynamical nature** of an excitation process:

- ►A transition between ground and excited state is accompanied by **charge-density fluctuations.**
- ►This causes corrections to the static KS eigenvalue differences due to **mixing of KS single-particle levels** in combination with **dynamical many-body effects.**

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Static and time-dependent density-functional theory

Hohenberg and Kohn (1964): $n(\mathbf{r}) \Longleftrightarrow V(\mathbf{r})$

All physical observables of a static many-body system are, in principle, functionals of the ground-state density $n(\mathbf{r})$.

➡ most modern electronic-structure calculations use DFT.

Runge and Gross (1984): $n(\mathbf{r},t) \Longleftrightarrow V(\mathbf{r},t)$

Time-dependent density $n(\mathbf{r},t)$ determines, in principle, all time-dependent observables.

➡ TDDFT: universal approach for electron dynamics.

Time-dependent Kohn-Sham equations (1)

Instead of the full N-electron TDSE,

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)=\left(\hat{T}+\hat{V}_{ext}(t)+\hat{W}_{e-e}\right)\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$$

one can solve
N single-electron
TDSE's:

$$\boxed{i\hbar\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t)=\left(-\frac{\hbar^2\nabla^2}{2m}+V_{KS}(\mathbf{r},t)\right)\varphi_j(\mathbf{r},t)}$$

such that the time-dependent densities agree:

$$\int dr_2\ldots\int dr_N\left|\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N,t)\right|^2 = n(\mathbf{r},t) = \sum_{j=1}^{N}\left|\varphi_j(\mathbf{r},t)\right|^2$$

The TDKS equations give the exact **density**, but not the **wave function**!

$$\boxed{\Phi_{KS}(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)=\frac{1}{\sqrt{N}}\det\{\varphi_j(\mathbf{r}_j,t)\}\neq\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)}$$

Time-dependent Kohn-Sham equations (2)

$$V_{KS}(\mathbf{r},t)=V_{ext}(\mathbf{r},t)+\underbrace{\int dr'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Hartree}}+\underbrace{V_{xc}[n](\mathbf{r},t)}_{\text{exchange-correlation}}$$

- ► The TDKS equations require an approximation for the xc potential. Almost everyone uses the adiabatic approximation (e.g. ALDA)

$$V_{xc}^{adia}(\mathbf{r},t)=V_{xc}^{static}\left[n(\mathbf{r},t)\right]$$

- ► The relevant observables must be expressed as functionals of the density n(**r**,t). This may require additional approximations.

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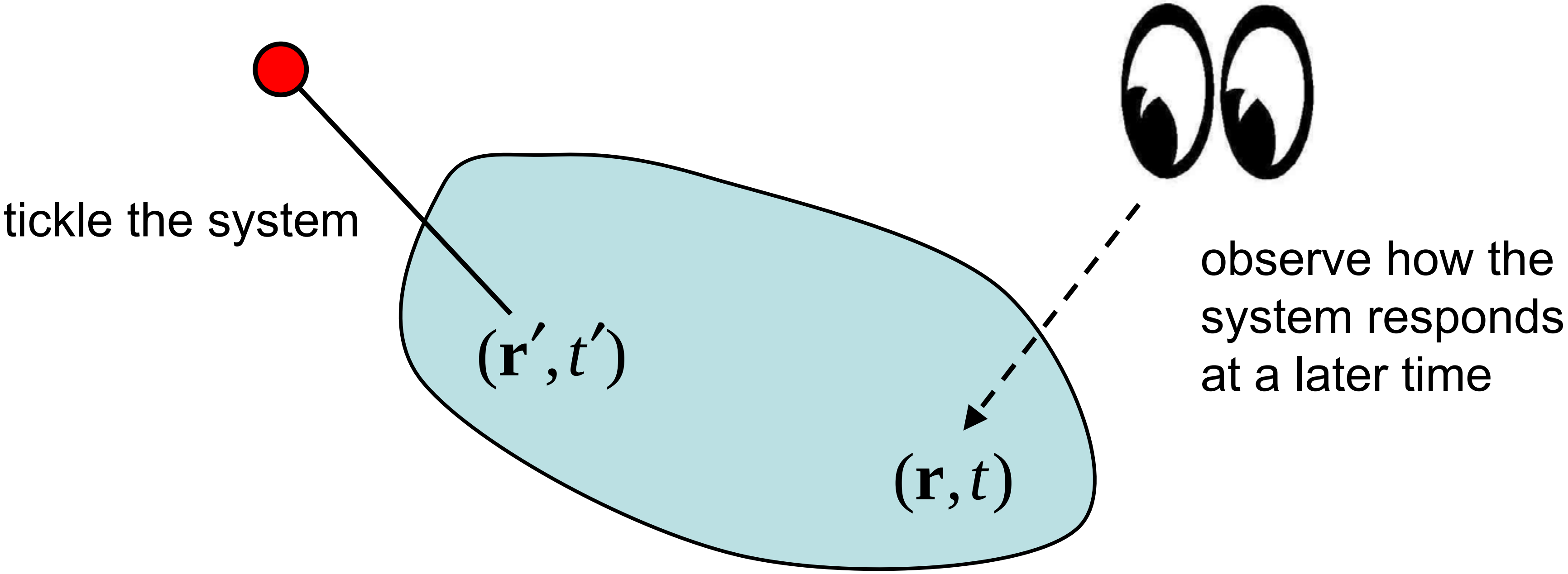
Linear response



$$\boxed{n_1(\mathbf{r},t) = \int d^3r' \int dt' \, \chi(\mathbf{r},t,\mathbf{r}',t') V_1(\mathbf{r}',t')}$$

density response

density-density response function

perturbation

TDDFT for linear response

Gross and Kohn, 1985:

$$n_1(\mathbf{r},t) = \int d^3r' \int dt' \, \chi(\mathbf{r},t,\mathbf{r}',t') V_1(\mathbf{r}',t')$$
$$= \int d^3r' \int dt' \, \chi_0(\mathbf{r},t,\mathbf{r}',t') V_{1,s}(\mathbf{r}',t')$$

Exact density response can be calculated as the response of a noninteracting system to an effective perturbation:

$$V_{1,s}(\mathbf{r},t) = V_1(\mathbf{r},t) + \int dt' \int d^3r' \left[\frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},t,\mathbf{r}',t') \right] n_1(\mathbf{r}',t')$$

xc kernel: $$f_{xc}(\mathbf{r},t,\mathbf{r},t') = \left. \frac{\delta V_{xc}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')} \right|_{n_0(\mathbf{r})}$$

Frequency-dependent linear response

$$\boxed{\begin{aligned} n_1(\mathbf{r},\omega) &= \int d^3r'\,\chi(\mathbf{r},\mathbf{r}',\omega)\,V_1(\mathbf{r}',\omega) \\ &= \int d^3r'\,\chi_0(\mathbf{r},\mathbf{r}',\omega)\,V_{1,s}(\mathbf{r}',\omega) \end{aligned}}$$

many-body response function:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_m \frac{\langle 0|\hat{n}(\mathbf{r})|m\rangle\langle m|\hat{n}(\mathbf{r}')|0\rangle}{\omega - \boxed{(E_m - E_0)} + i\delta} + c.c.(-\omega)$$

exact excitations Ω

noninteracting response function:

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = \sum_{p,q} (f_p - f_q) \frac{\varphi_p^*(\mathbf{r})\varphi_q(\mathbf{r})\varphi_q^*(\mathbf{r}')\varphi_p(\mathbf{r}')}{\omega - \boxed{(\varepsilon_p - \varepsilon_q)} + i\delta}$$

KS excitations ω_{KS}

$$\boxed{V_{1,s} = V_1 + \int d^3r' \left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r},\mathbf{r}',\omega) \right] n_1(\mathbf{r}',\omega)}$$

Warm-up exercise: 2-level system

Consider perturbation $\lambda H'(r,t)$ acting on KS orbital $\varphi_1(r)$:

$$\varphi(r,t) = c_1(t)\varphi_1(r) + \lambda c_2(t)\varphi_2(r)$$

Time-dependent density matrix:

$$\rho(t) = \begin{pmatrix} \rho_{11} & \lambda\rho_{12} \\ \lambda\rho_{21} & \lambda^2\rho_{22} \end{pmatrix} = \begin{pmatrix} |c_1|^2 & \lambda c_1 c_2^* \\ \lambda c_1^* c_2 & \lambda^2 |c_2|^2 \end{pmatrix}$$

Equation of motion:

$$\dot{\rho} = -i[H^0 + \lambda H', \rho]$$

2-level system

Time evolution of the off-diagonal elements to first order in λ:

$$\boxed{\begin{aligned}\dot{\rho}_{12} &= i\left(\omega_{21}\rho_{12} + H'_{12}\right)\\ \dot{\rho}_{21} &= -i\left(\omega_{21}\rho_{21} + H'_{21}\right)\end{aligned}}$$

$$\omega_{21} = \varepsilon_2 - \varepsilon_1$$

(bare KS excitation energy)

Perturbing Hamiltonian:

adiabatic approximation

$$H'(r,t) = \cancel{V_{ext}(r,t)} + \int d^2r' \left[\frac{1}{|r-r'|} + f_{xc}(r,r',\cancel{\omega})\right]\delta n(r',t)$$

no external perturbation → eigenmode

so that $H'_{12}(t) = H'_{21}(t) = \langle 12|\, f_{Hxc}\, |12\rangle \{\rho_{12}(t) + \rho_{21}(t)\}$

2-level system

Let $\rho_{12}(t)=\tilde{\rho}_{12}(\omega)e^{-i\omega t}+\tilde{\rho}_{12}(-\omega)e^{i\omega t}$ so that

$$\tilde{\rho}_{12}(\omega)\cancel{+\tilde{\rho}_{21}(\omega)}=-\frac{\tilde{H}'_{12}}{\omega_{21}+\omega}-\frac{\tilde{H}'_{21}}{\omega_{21}-\omega}$$

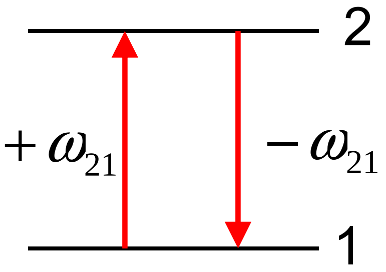
$$=-\langle 12|f_{Hxc}|12\rangle\{\tilde{\rho}_{12}\cancel{+\tilde{\rho}_{21}}\}\left[\frac{1}{\omega_{21}+\omega}+\frac{1}{\omega_{21}-\omega}\right]$$

$$\Rightarrow\quad 1=-\frac{2\omega_{21}}{\omega_{21}^{2}-\omega^{2}}\langle 12|f_{Hxc}|12\rangle$$

$$\Rightarrow\quad \omega^{2}=\omega_{21}^{2}+2\omega_{21}\langle 12|f_{Hxc}|12\rangle$$

2-level system

$$\omega^2 = \omega_{21}^2 + 2\omega_{21}\langle 12 | f_{Hxc} | 12 \rangle$$



“Small-matrix approximation”: KS poles at $\pm\omega_{21}$

1→2: absorption, 2→1: stimulated emission

$$\omega = \omega_{21} + \langle 12 | f_{Hxc} | 12 \rangle$$

“Single-pole approximation”: only 1→2 transition
(Tamm-Dancoff approximation)

M. Petersilka, U.J. Gossmann, E.K.U. Gross, PRL **76**, 1212 (1996)
H. Appel, E.K.U. Gross, K. Burke, PRL **90**, 043005 (2003)

The Casida formalism for excitation energies

Excitation energies follow from eigenvalue problem (Casida 1995):

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia\sigma,i'a'\sigma'} = \delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}\left(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}\right) + K_{ia\sigma,i'a'\sigma'}$$

$$K_{ia\sigma,i'a'\sigma'} = \int d^3r \int d^3r' \varphi^*_{i\sigma}(\mathbf{r})\varphi_{a\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\omega)\right]\varphi_{i'\sigma'}(\mathbf{r}')\varphi_{a'\sigma'}(\mathbf{r}')$$

For real orbitals and frequency-independent xc kernel, can rewrite this as

$$\sum_{i'a'\sigma'}\left[\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}\omega^2_{ai\sigma} + 2\sqrt{\omega_{ai\sigma}\omega_{a'i'\sigma'}}\,K_{ia\sigma,i'a'\sigma'}\right] Z_{i'a'\sigma'} = \Omega^2 Z_{i'a'\sigma'}$$

The Casida formalism for excitation energies

The Casida formalism gives, in principle, the exact excitation energies and oscillator strengths. In practice, three approximations are required:

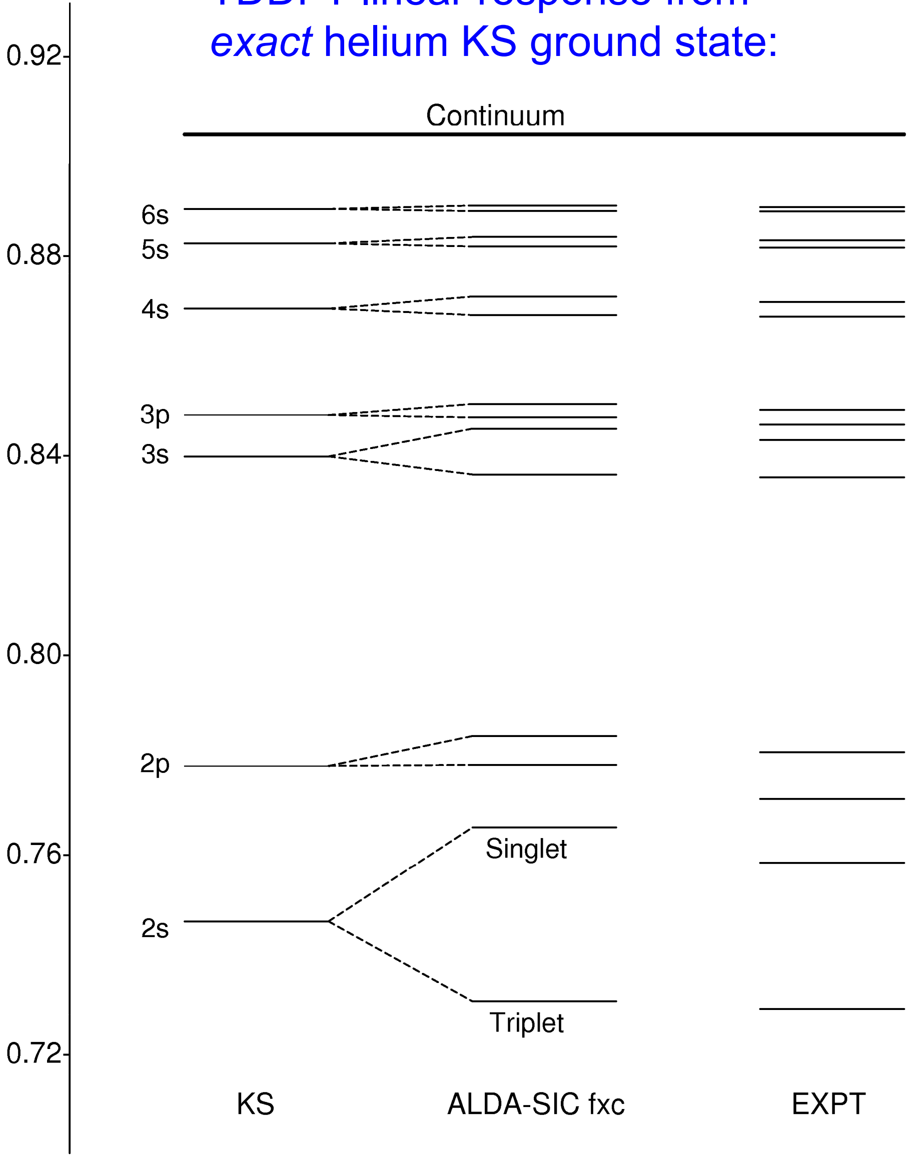
- ► KS ground state with approximate xc potential
- ► The inifinite-dimensional matrix needs to be truncated
- ► Approximate xc kernel (usually adiabatic):

$$f_{xc}^{adia}(\mathbf{r},\mathbf{r}') = \frac{\delta V_{xc}^{stat}(\mathbf{r})}{\delta n(\mathbf{r}')}$$

advantage: can use any xc functional from static DFT ("plug and play")
disadvantage: no frequency dependence, no memory
→ missing physics (see later)

How it works: atomic excitation energies

TDDFT linear response from *exact* helium KS ground state:



From Burke & Gross, (1998); Burke, Petersilka &Gross (2000)

LDA + ALDA lowest excitations

Atom	Exp.	full matrix	SMA	SPA	ω^{KS}
Be	5.28	4.94	5.07	5.43	3.50
Mg	4.34	4.34	4.56	4.76	3.39
Ca	2.94	3.22	3.36	3.56	2.39
Sr	2.69	2.96	3.10	3.28	2.22
Zn	5.79	5.71	6.30	6.54	4.79
Cd	5.41	5.10	5.60	5.86	4.12

Vasiliev, Ogut, Chelikowsky, PRL **82**, 1919 (1999)

Look at other functional approxs (ALDA, EXX), and also with SPA. All quite similar for He.

General trends

- Energies typically to within about “0.4 eV”
- Bonds to within about 1%
- Dipoles good to about 5%
- Vibrational frequencies good to 5%
- Cost scales as N^2-N^3, vs N^5 for wavefunction methods of comparable accuracy (eg CCSD, CASSCF)
- Available now in many electronic structure codes

challenges/open issues:

● complex excitations (multiple, charge-transfer)
● optical response/excitons in bulk insulators

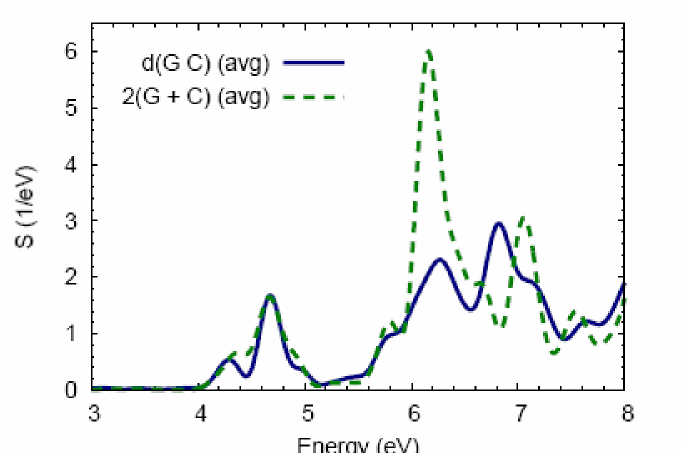
Elliott, Burke, Furche, Reviews in Computational Chemistry **26**, 91 (2009)

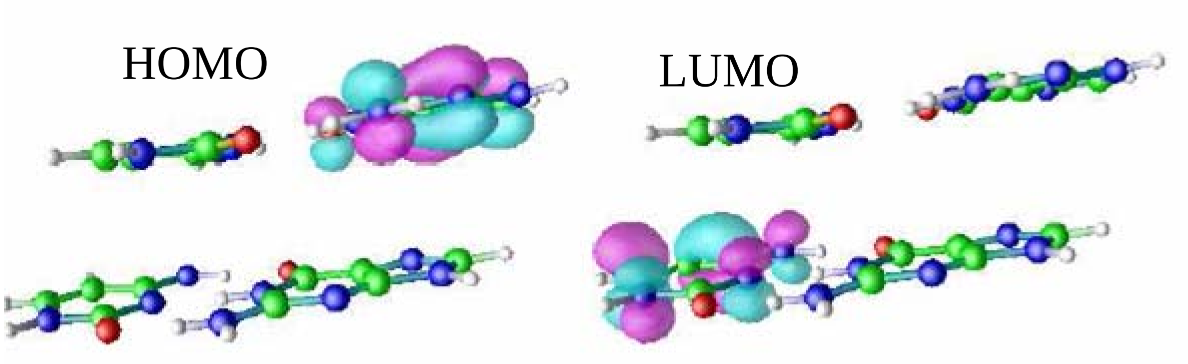
Examples

Can study big molecules with TDDFT !

Optical Spectrum of DNA fragments

d(GC) π-stacked pair

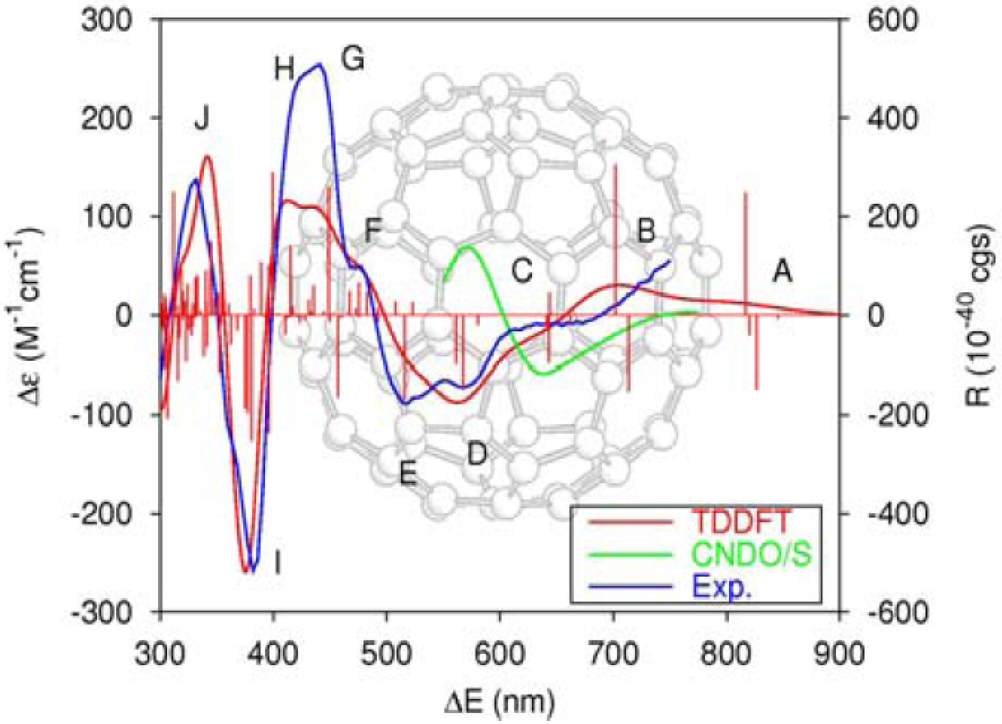




D. Varsano, R. Di Felice, M.A.L. Marques, A. Rubio, J. Phys. Chem. B ***110****, 7129 (2006).*

Examples

Circular dichroism spectra of chiral fullerenes: D_2C_{84}



*F. Furche and R. Ahlrichs, JACS **124**, 3804 (2002).*

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- **Extended systems**
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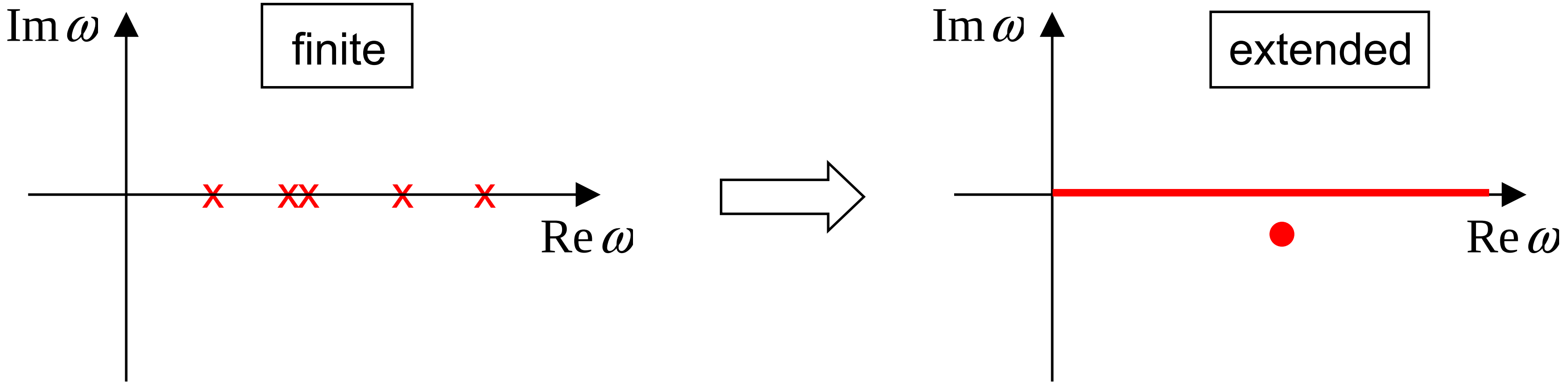
Excitations in finite and extended systems

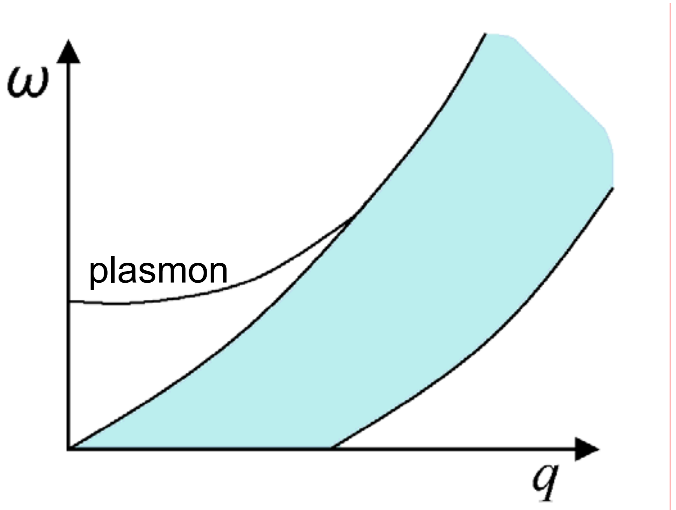
$$\chi(\mathbf{r},\mathbf{r}',\omega)=\lim_{\eta\to0^+}\left[\sum_j \frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_j\rangle\langle\Psi_j|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega-\underbrace{E_j+E_0}_{\Omega_j}+i\eta}+c.c.(\omega\to-\omega)\right]$$

The full many-body response function has poles at the exact excitation energies



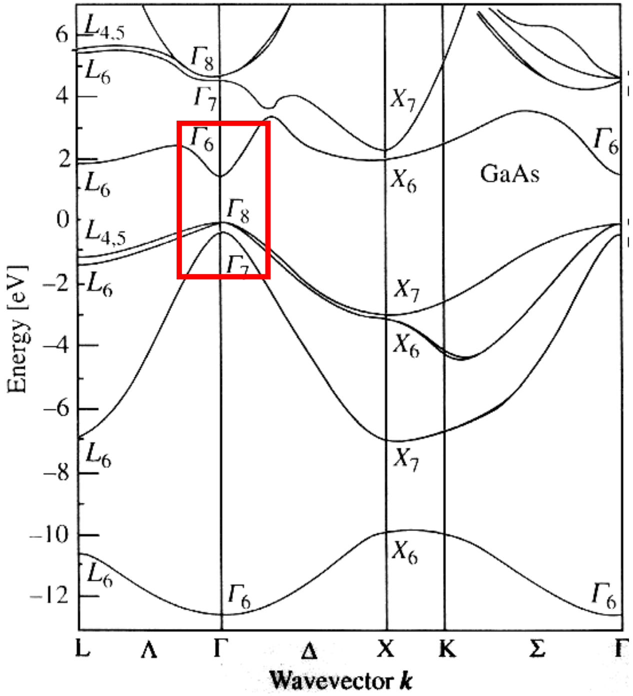
- ► Discrete single-particle excitations merge into a continuum (branch cut in frequency plane)
- ► New types of **collective excitations** appear off the real axis (finite lifetimes)

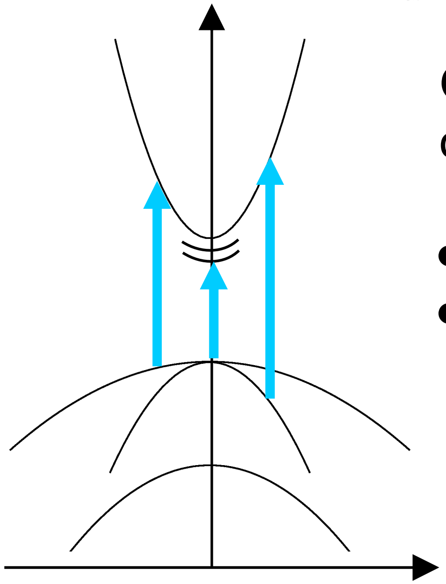
Metals vs. Insulators



Excitation spectrum of simple metals:

- single particle-hole continuum (incoherent)
- collective plasmon mode
- RPA already gives dominant contribution, f_{xc} typically small corrections.

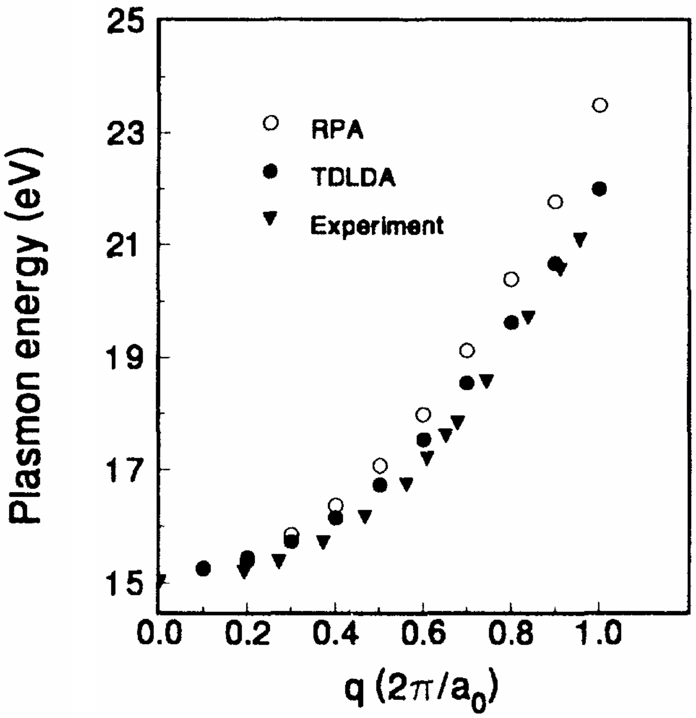




Optical excitations of insulators:

- interband transitions
- <u>excitons</u> (bound electron-hole pairs)

Excitations in bulk metals



Plasmon dispersion of Al

Quong and Eguiluz, PRL **70**, 3955 (1993)

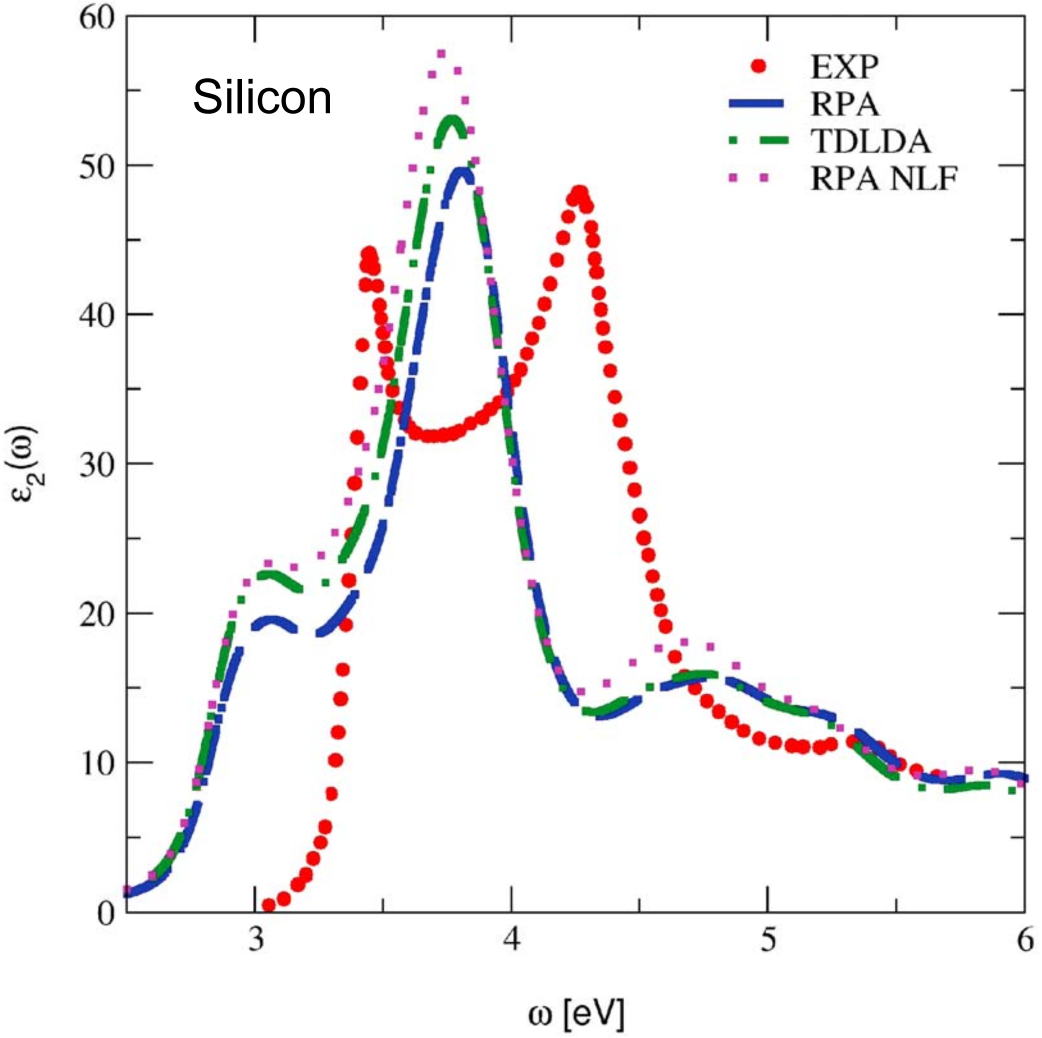
- ►RPA (i.e., Hartree) gives already reasonably good agreement
- ►ALDA agrees very well with exp.

In general, (optical) excitation processes in (simple) metals are very well described by TDDFT within ALDA.

Time-dependent Hartree already gives the dominant contribution, and f_{xc} typically gives some (minor) corrections.

This is also the case for 2DEGs in doped semiconductor heterostructures

Optical absorption of insulators



RPA and ALDA both bad!

- ►absorption edge red shifted (electron self-interaction)
- ►first excitonic peak missing (electron-hole interaction)

Why does the ALDA fail??

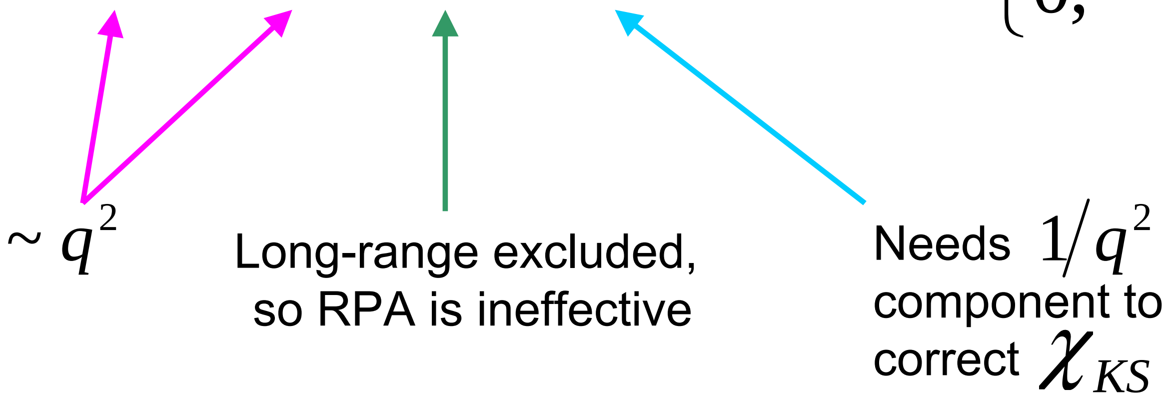
G. Onida, L. Reining, A. Rubio, RMP **74**, 601 (2002)
S. Botti, A. Schindlmayr, R. Del Sole, L. Reining, Rep. Prog. Phys. **70**, 357 (2007)

Optical absorption of insulators: failure of ALDA

Optical absorption requires imaginary part of macroscopic dielectric function:

$$\mathrm{Im}\{\varepsilon_{mac}\} = -\lim_{\mathbf{q}\to 0} V_{\mathbf{G}}(\mathbf{q})\,\mathrm{Im}\{\bar{\chi}_{\mathbf{GG}'}\}\Big|_{G,G'=0}$$

where $$\bar{\chi} = \chi_{KS} + \chi_{KS}\left(\bar{V} + f_{xc}\right)\bar{\chi}\,, \qquad \bar{V}_{\mathbf{G}} = \begin{cases} V_{\mathbf{G}}\,, & \mathbf{G} \neq 0 \\ 0, & \mathbf{G} = 0 \end{cases}$$



$\mathbf{q} \to 0$ limit:

$\sim q^2$

Long-range excluded,
so RPA is ineffective

Needs $1/q^2$
component to
correct χ_{KS}

But ALDA is **constant**
for $\mathbf{q} \to 0$:

$$f_{xc}^{ALDA} = \lim_{q\to 0} f_{xc}^{\hom}(q, \omega = 0)$$

Long-range xc kernels for solids

- **LRC** (long-range correlation) kernel (with fitting parameter *α*):

$$f_{xc}^{LRC}(\mathbf{q}) = -\frac{\alpha}{q^2}$$

- **TDOEP** kernel (X-only):

$$f_x^{PGG}(\mathbf{r},\mathbf{r}') = -\frac{2\left|\sum_k f_k \phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|\, n(\mathbf{r})\, n(\mathbf{r}')}$$

Petersilka, Gossmann, Gross, PRL **76**, 1212 (1996)
EXX: Kim and Görling, PRL **89**, 096402 (2002)

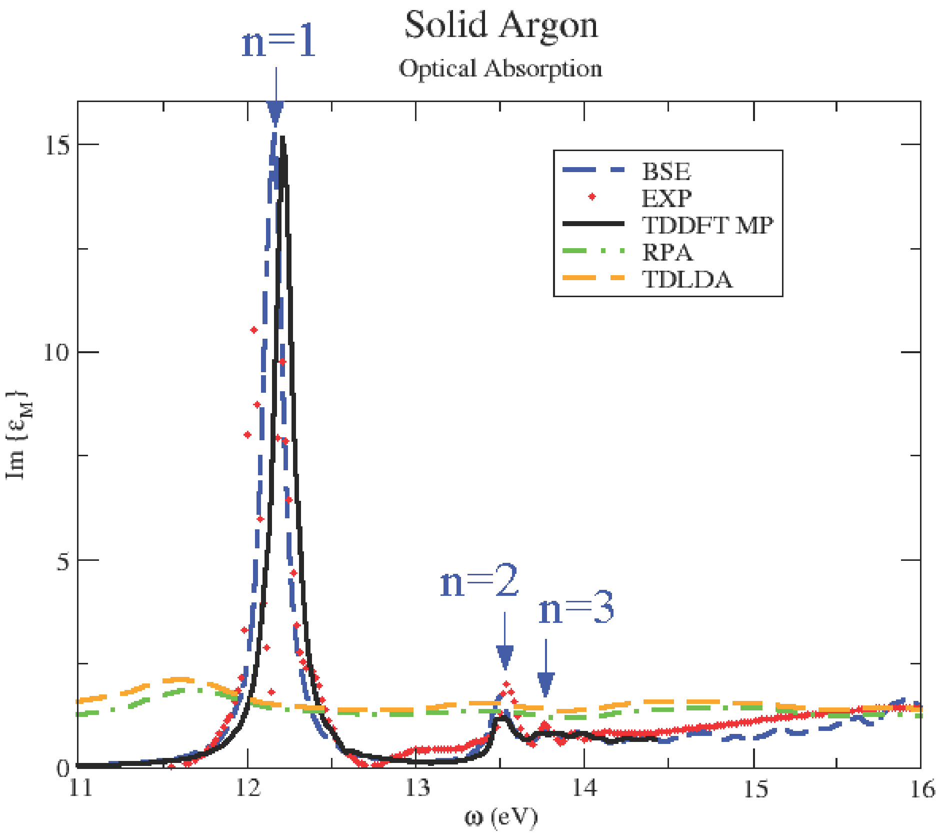
- **"Nanoquanta"** kernel (L. Reining et al, PRL **88**, 066404 (2002))

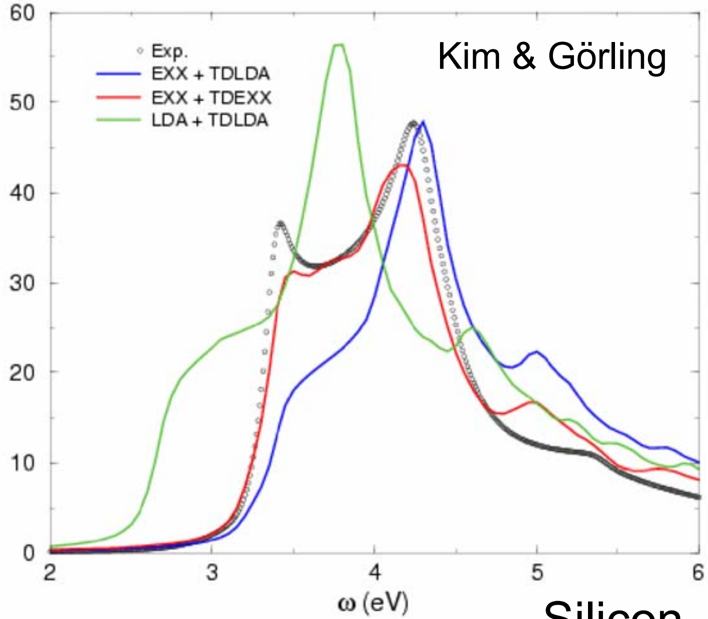
$$f_{xc}^{BSE}(\mathbf{q}\to 0,\mathbf{G},\mathbf{G}') = \sum_{vck,v'c'k'} \Phi_{\mathbf{G}}^{-1}(v\mathbf{k}c\mathbf{k};\mathbf{q}\to 0)\, F^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} \left(\Phi^*\right)^{-1}_{\mathbf{G}'}(v'\mathbf{k}'c'\mathbf{k}';\mathbf{q}\to 0)$$

pairs of quasiparticle wave functions

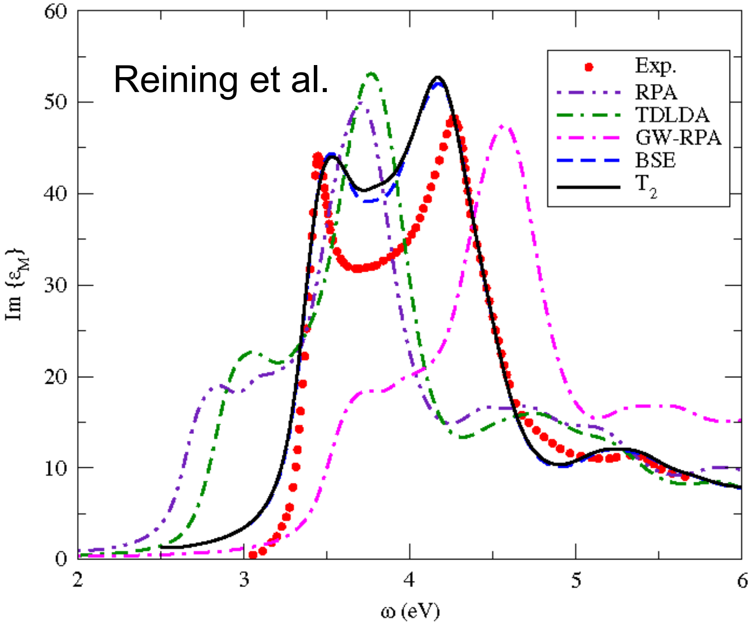
matrix element of screened Coulomb interaction (from Bethe-Salpeter equation)

Optical absorption of insulators, again





Silicon



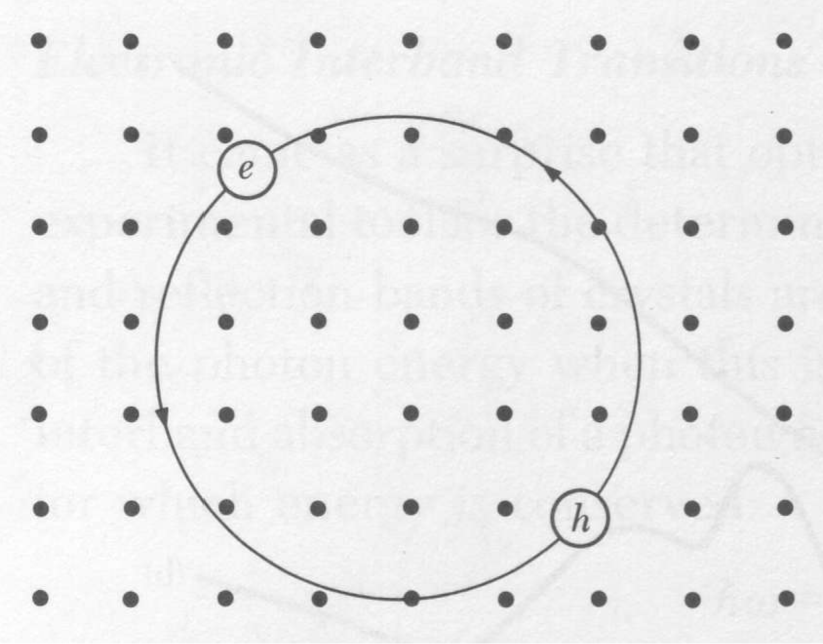
TDDFT/Bethe-Salpeter

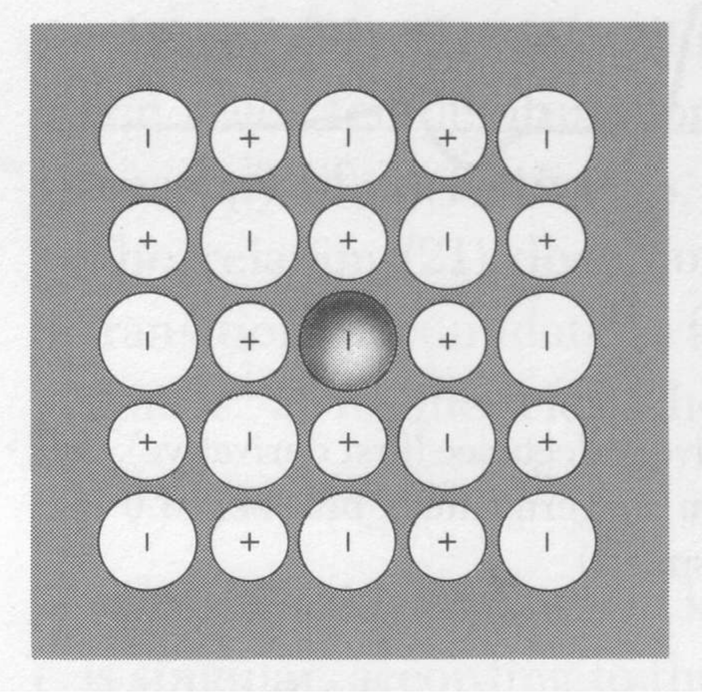
Reining, Olevano, Rubio, Onida,
PRL **88**, 066404 (2002)

F. Sottile et al., PRB **76**, 161103 (2007)

Elementary view of Excitons

Excitons are bound electron-hole pairs created in optical excitations of insulators.





Mott-Wannier exciton:
weakly bound, delocalized
over many lattice constants

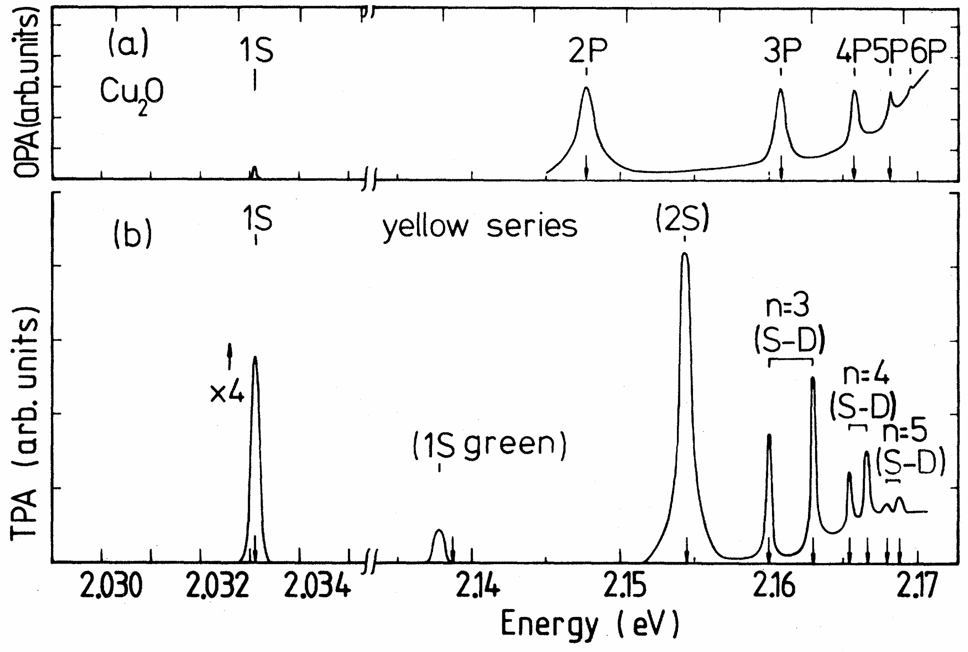
Frenkel exciton:
tightly bound, localized on
a single (or a few) atoms

Wannier equation and excitonic Rydberg Series

$$\left(-\frac{\hbar^2\nabla_r^2}{2m_r}-\frac{e^2}{\varepsilon r}\right)\phi(\mathbf{r})=E\phi(\mathbf{r})$$

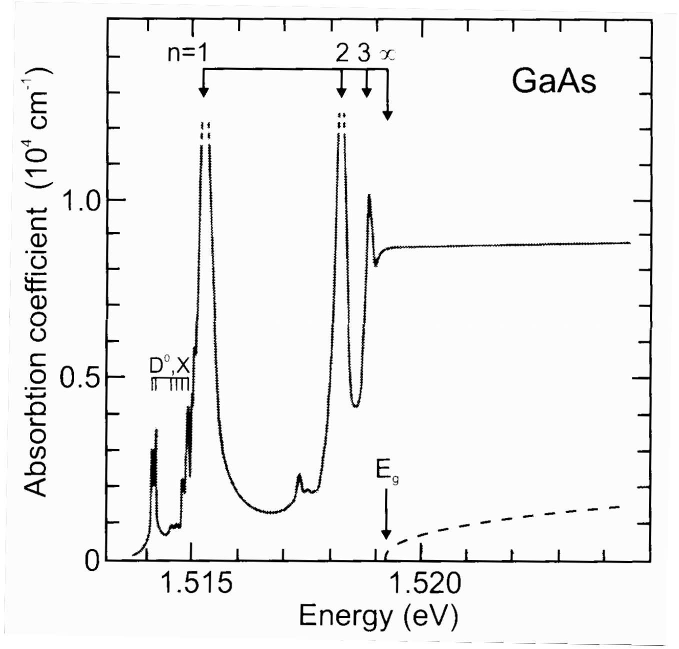
- $\phi(\mathbf{r})$ is exciton wave function
- derived from TDHF linearized Semiconductor Bloch equation
- includes dielectric screening

Cu_2O



R.J. Uihlein, D. Frohlich, and R. Kenklies, PRB **23**, 2731 (1981)

GaAs



R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

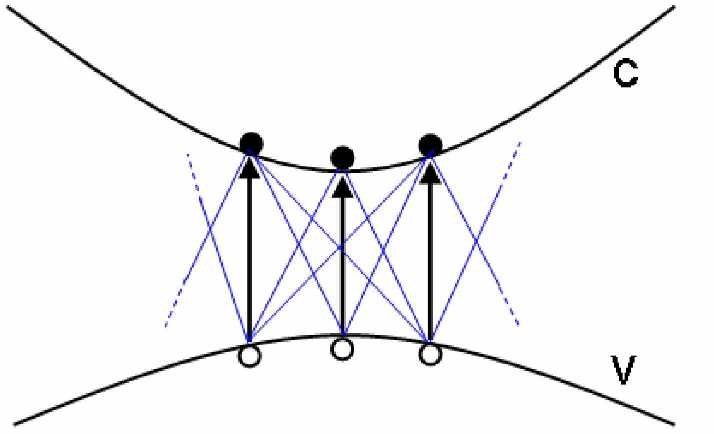
Exciton binding energies relative to KS band gap

from linearized TDDFT semiconductor Bloch equations (Tamm-Dancoff approx.):

$$\sum_{\mathbf{q}} \left[\omega_{\mathbf{q}}^{cv}\delta_{\mathbf{kq}} + F_{\mathbf{kq}}(\omega)\right]\rho_{\mathbf{q}}^{cv}(\omega) = \omega\rho_{\mathbf{k}}^{cv}(\omega)$$

$$F_{\mathbf{kq}}(\omega) = \frac{2}{\Omega^2}\int_{\Omega} d^3r\int_{\Omega} d^3r'\,\varphi_{c\mathbf{k}}^{*}(\mathbf{r})\varphi_{v\mathbf{k}}(\mathbf{r})\, f_{xc}(\mathbf{r},\mathbf{r}',\omega)\,\varphi_{v\mathbf{q}}^{*}(\mathbf{r}')\varphi_{c\mathbf{q}}(\mathbf{r}')$$

- Finite atomic/molecular system: single-pole approximation involves two discrete levels
- “Single-pole approximation” for excitons involves two entire bands
- Excitons are a collective phenomenon!



V. Turkowski, A. Leonardo, C.A.U., PRB **79**, 233201 (2009)

TDDFT Wannier Equation

Nonlocal effective electron-hole interaction:

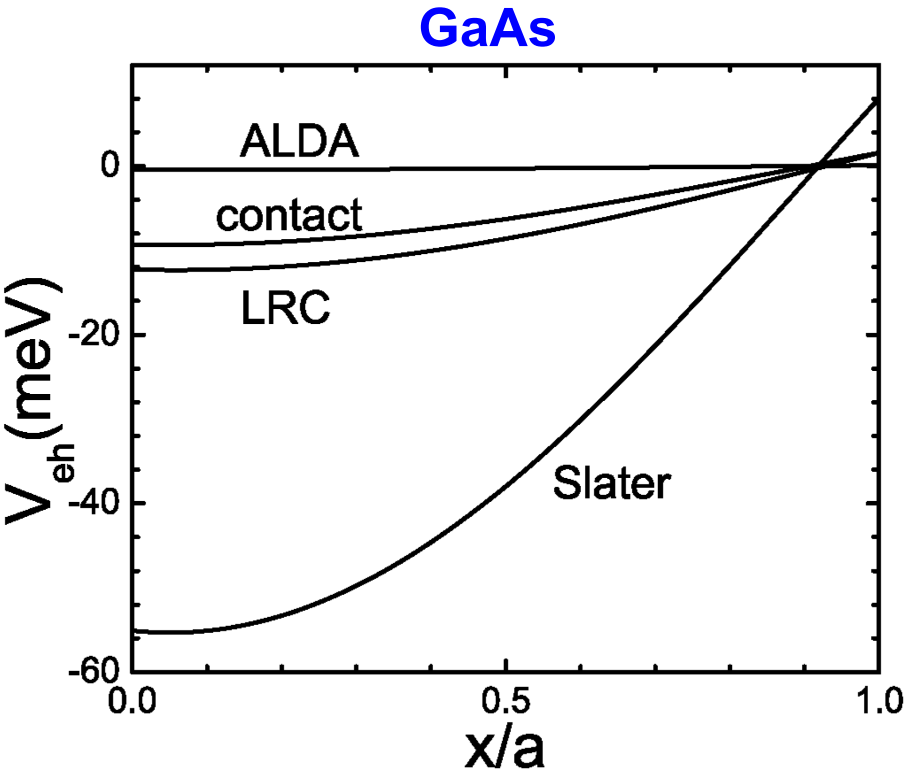
$$\boxed{V_{eh}(\mathbf{R},\mathbf{R}',\omega)=\sum_{\mathbf{k},\mathbf{q}} e^{-i\mathbf{kR}}F_{\mathbf{kq}}(\omega)e^{i\mathbf{qR}'}}$$

- assume exciton extends over many lattice constants, replace **R** by **r** (continuous variable)

- assume parabolic bands, effective masses

$$-\frac{\hbar^2\nabla_r^2}{2m_r}\phi_i(\mathbf{r})+\underbrace{\int d^3r' V_{eh}(\mathbf{r},\mathbf{r}',\omega)\phi_i(\mathbf{r}')}_{-\frac{e^2}{\varepsilon r}\phi(\mathbf{r}) \text{ in usual Wannier eq.}}=E_i\phi_i(\mathbf{r})$$

TDDFT effective nonlocal e-h interaction



$$f_x^{ALDA} = -\frac{\delta(\mathbf{r}-\mathbf{r}')}{\left(9\pi n_0^2(\mathbf{r})\right)^{1/3}}$$

$$f_x^{Slater} = -\frac{2\left|\sum_{\mathbf{k}} \varphi_k^v(\mathbf{r})\varphi_k^{v*}(\mathbf{r}')\right|^2}{|\mathbf{r}-\mathbf{r}'|\, n_0(\mathbf{r})\, n_0(\mathbf{r}')}$$

$$f_{xc}^{LRC} = -\frac{\alpha}{4\pi|\mathbf{r}-\mathbf{r}'|}$$

$$f_{xc}^{contact} = -A\delta(\mathbf{r}-\mathbf{r}')$$

- ALDA: no bound excitons
- LRC, contact: one bound exciton, can be fitted to experiment
- Slater (approximate EXX): one bound exciton

Exciton binding energies in meV

	Slater EXX	Experiment
GaAs	17.8	3.27
β-GaN	28.7	26.0
α-GaN	11.8	20.4
CdS	7.9	28.0
CdSe	8.3	15.0

- ► Overbinding could be expected due to lack of correlation/screening
- ► But: Slater EXX not ~$1/q^2$ (Lein 2000) which weakens e-h interaction

V. Turkowski, A. Leonardo, and C. A. Ullrich, PRB **79**, 233201 (2009)

Extended systems - Summary

► TDDFT works well for metallic and quasi-metallic systems already at the level of the ALDA. Successful applications for plasmon modes in bulk metals and low-dimensional semiconductor heterostructures.

► TDDFT for insulators is a much more complicated story:

- ALDA works well for EELS (electron energy loss spectra), but not for optical absorption spectra
- difficulties originate from long-range contribution to f_{xc}
- some excitonic XC kernels have become available, but the best ones are quite complicated.

$20 challenge!

Outline

- Introduction
- TDDFT in a nutshell
- TDDFT for excitation energies: how it works
- Extended systems
- **Multiple and charge-transfer excitations**

Double Excitations

$$\chi(\mathbf{r},\mathbf{r}',\omega)=\sum_m \frac{\langle 0|\hat{n}(\mathbf{r})|m\rangle\langle m|\hat{n}(\mathbf{r}')|0\rangle}{\omega-(E_m-E_0)+i\delta}+c.c.(-\omega)$$

$$\chi_0(\mathbf{r},\mathbf{r}',\omega)=\sum_{p,q}\left(f_p-f_q\right)\frac{\varphi_p^*(\mathbf{r})\varphi_q(\mathbf{r})\varphi_q^*(\mathbf{r}')\varphi_p(\mathbf{r}')}{\omega-(\varepsilon_p-\varepsilon_q)+i\delta}$$

χ has poles at **all** excitations (single, double, ...) of many-body system

χ_0 has only poles only at single KS excitations

►Shifting the KS poles just gives you single excitations

►new poles at multiple excitations have to be created

The Casida formalism again

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K}^{*} & \mathbf{A}^{*} \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$K_{ia\sigma,i'a'\sigma'} = \int d^{3}r \int d^{3}r' \varphi^{*}_{i\sigma}(\mathbf{r})\varphi_{a\sigma}(\mathbf{r})\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc,\sigma\sigma'}(\mathbf{r},\mathbf{r}',\Omega)\right]\varphi_{i'\sigma'}(\mathbf{r}')\varphi_{a'\sigma'}(\mathbf{r}')$$

►Frequency dependence of xc kernel makes the eigenvalue problem nonlinear, thus allowing additional solutions

►No (true) multiple excitations within adiabatic approximation (not even in higher-order response theory)

Double Excitations: a simple model kernel

Maitra, Zhang, Cave, and Burke, JCP **120**, 5932 (2004)

Consider a single and double excitation which lie close together and are well separated from all other excitations. Use SPA formula:

$$\omega = \omega_q + 2\langle q | f_{Hxc}(\omega) | q \rangle$$

where

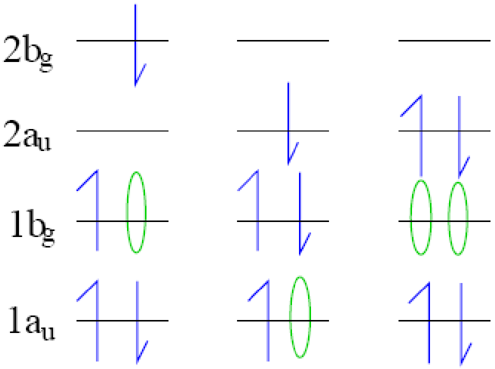
$$2\langle q | f_{Hxc}(\omega) | q \rangle = 2\langle q | f_{Hxc}(\omega_q) | q \rangle + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{qq})}$$

Example: short-chain polyenes

Lowest-lying excitations notoriously difficult to calculate due to significant double-excitation character.

Cave, Zhang, NTM, Burke, CPL (2004)

E.g. Butadiene, dark 2^1A_g state



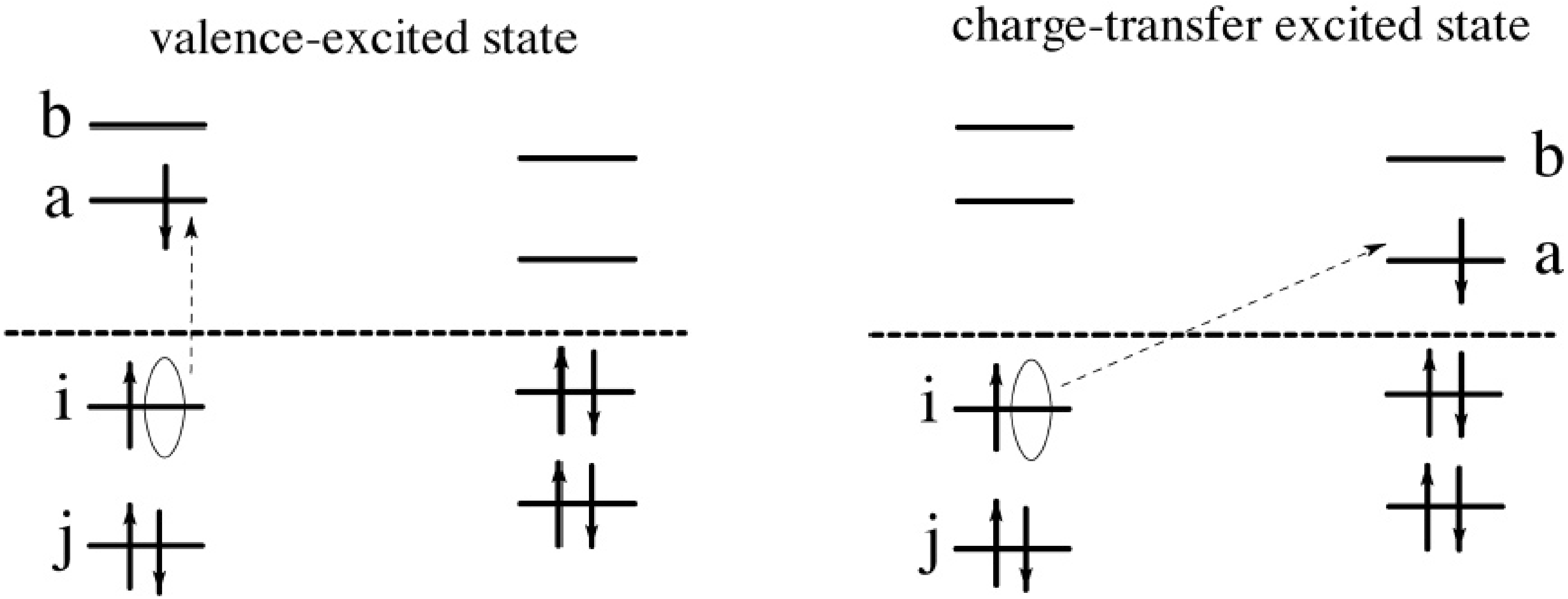
- 2^1A_g Vertical excitation energies (eV) for butadiene and hexatriene

System	CASPT2	ATDDFT	D-TD-TDDFT
C_4H_6	6.27	7.02	6.28
C_6H_8	5.20	5.83	5.16

- 2^1A_g Vertical and 0-0 excitations for butadiene at the estimated planar stationary point for 2^1A_g

ΔE	CASPT2	ATDDFT	D-TD-TDDFT
Vertical	4.3	5.8	4.16
0-0	5.2	6.8	5.28

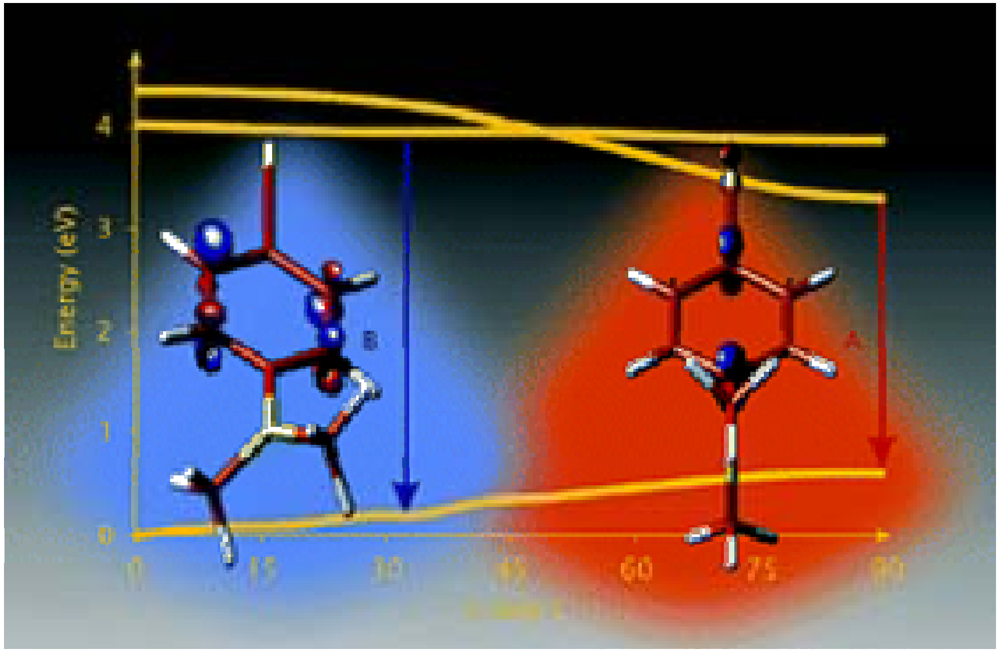
Long-Range Charge-Transfer Excitations



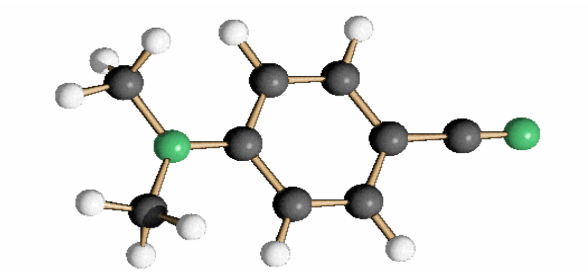
Dreuw and Head-Gordon, JACS (2004)

Long-Range Charge-Transfer Excitations

Example: Dual Fluorescence in DMABN in Polar Solvents



4-(dimethyl)amino
benzonitrile



Rappoport & Furche,
JACS 126, 1277 (2004).

“normal”

“Local” Excitation (LE)

“anomalous”

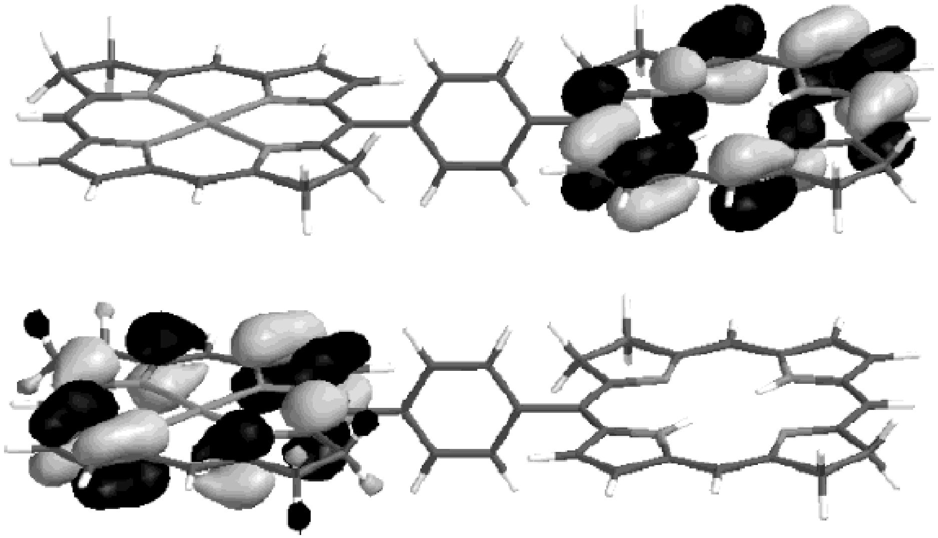
Intramolecular Charge Transfer (ICT)

TDDFT resolved the long debate on ICT structure (neither “PICT” nor “TICT”), and elucidated the mechanism of LE -- ICT reaction (in B3LYP)

Success in predicting ICT structure – How about CT energies ??

Long-Range Charge-Transfer Excitations

TDDFT typically **severely underestimates** long-range CT energies



Important process in biomolecules, large enough that TDDFT may be only feasible approach !

Eg. Zincbacteriochlorin-Bacteriochlorin complex
(light-harvesting in plants and purple bacteria)

Dreuw & Head-Gordon, JACS 126 4007, (2004).

TDDFT predicts CT states energetically well below local fluorescing states.
Predicts CT quenching of the fluorescence (BLYP)

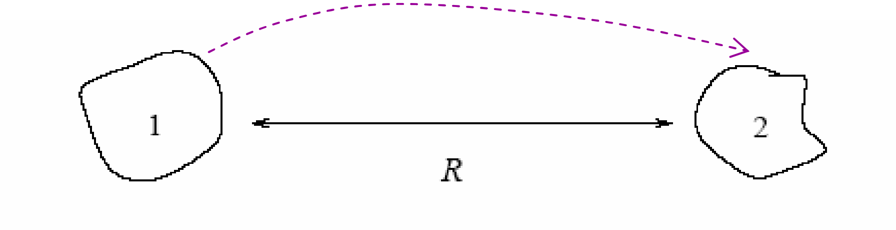
! Not observed !

TDDFT error ~ 1.4eV

Long-Range Charge-Transfer Excitations

Why do the usual approximations in TDDFT fail for these excitations?

We know what the *exact* energy for charge transfer at long range should be:



exact

$$\text{As } R \to \infty\,, \quad \boxed{\omega_{CT} = I_1 - A_2 - 1/R}$$

$$\omega = \omega_q + 2[q|f_{\rm HXC}(\omega_q)|q]$$

Why TDDFT typically severely underestimates this energy can be seen in SPA

$$\omega = \epsilon_2^L - \epsilon_1^H + \int\int d\mathbf{r}d\mathbf{r}'\, \underbrace{\phi_1^H(\mathbf{r})\phi_2^L(\mathbf{r})}\, f_{\rm HXC}(\mathbf{r},\mathbf{r}'\omega)\, \underbrace{\phi_1^H(\mathbf{r}')\phi_2^L(\mathbf{r}')}$$

$-A_{s,2}$ **$-I_1$**

~0 overlap

$$\approx I_1 - A_{s,2}$$

i.e. get just the bare KS orbital energy difference: missing xc contribution to acceptor's electron affinity, $A_{xc,2}$, and -1/R

(Also, usual g.s. approxs underestimate I)

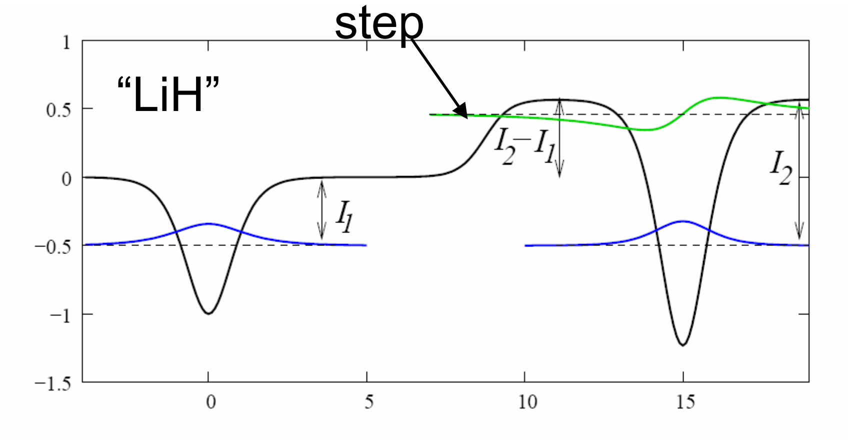
Long-Range Charge-Transfer Excitations

What are the properties of the unknown exact xc kernel that must be well-modelled to get long-range CT energies correct ?

- Exponential dependence on the fragment separation R,

$$f_{xc} \sim \exp(aR)$$

- For transfer between open-shell species, need strong frequency-dependence.



Step in V_{xc} re-aligns the 2 atomic HOMOs → near-degeneracy → static correlation, crucial double excitations → frequency-dependence!

(It's a rather ugly kernel…)

Gritsenko & Baerends (PRA, 2004), Maitra (JCP, 2005), Tozer (JCP, 2003)

Long-Range Charge-Transfer Excitations

$$E_{CT} \approx \varepsilon_a^A - \varepsilon_i^D \begin{cases} +\left\langle ai \middle| f_{xc} \middle| ia \right\rangle & \text{TDDFT} \\ -\left\langle ii \middle| r_{12}^{-1} \middle| aa \right\rangle & \text{TDHF} \end{cases}$$

► TDHF has correct qualitative -1/R behavior, but misses correlation

► Popular hybrid functionals which mix in a fraction c_{HF} will get $-c_{HF}/R$ behavior (which might be OK for not too large separation)

► Range-separated functionals promising (Tawada 2004)

Summary of hot topics for TDDFT

- Polarizabilities of long-chain molecules
- Rydberg states
- Quantum defects, scattering phase shifts

Local/semilocal approx inadequate.

Can improve with orbital functionals (EXX/sic), or **TD current-DFT**

- Double excitations
- Long-range charge transfer
- Conical Intersections

Adiabatic approx for fxc fails.

Need frequency-dependent kernel derived for *some* cases

Many more $$$ callenges!