TDDFT for extended systems II: Excitons

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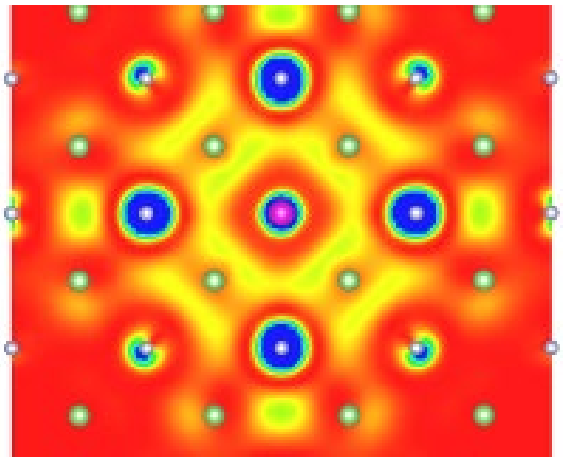
Rutgers University, August 9, 2019

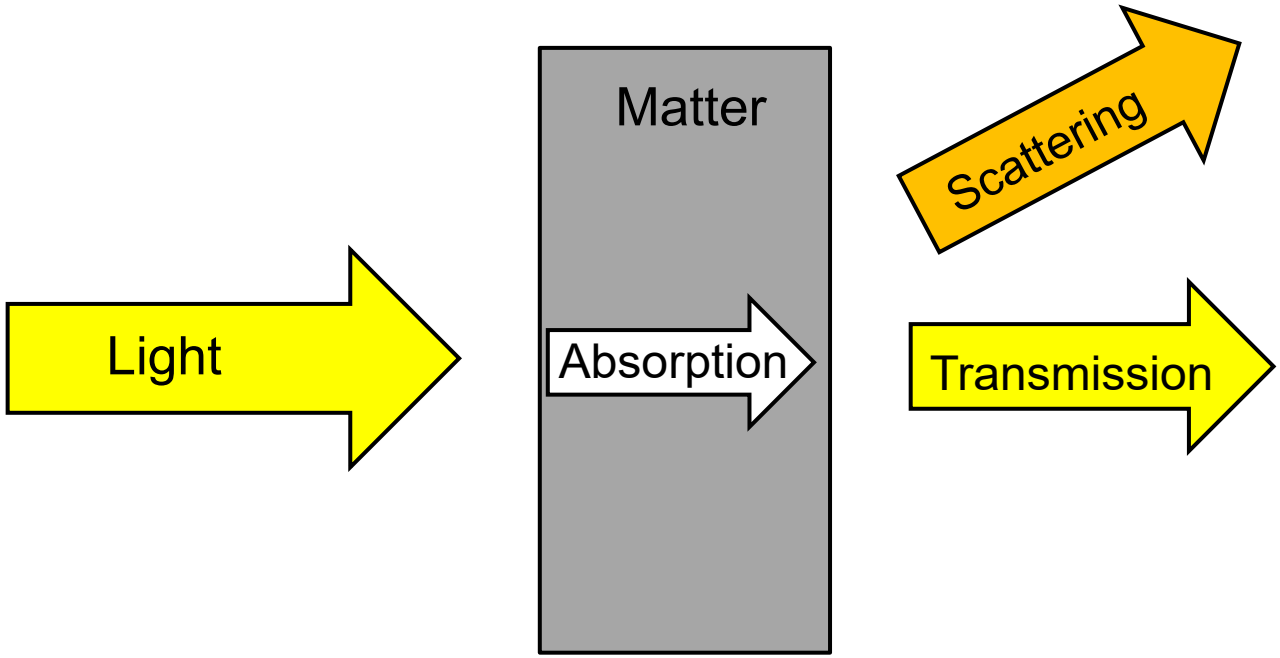
Outline

- Introduction to excitons
- TDDFT for periodic systems
- Optical spectra and exciton binding energies
- xc functionals for excitons
- TDDFT vs. BSE: derivation of Wannier equation



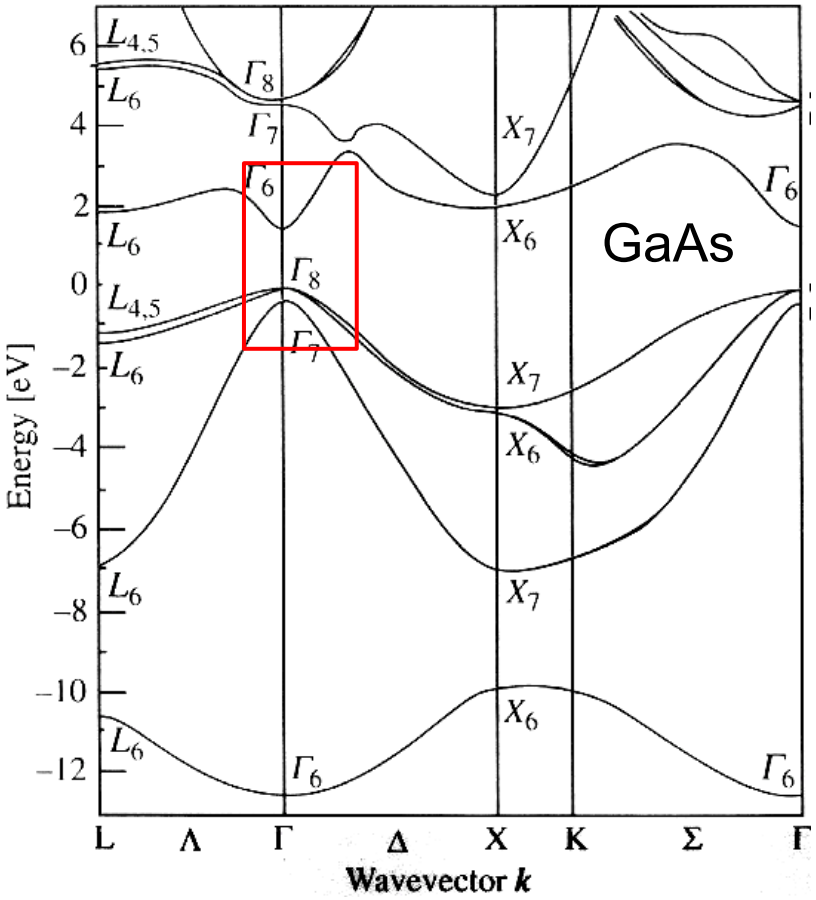
https://etsf.polytechnique.fr/Research/Excitons

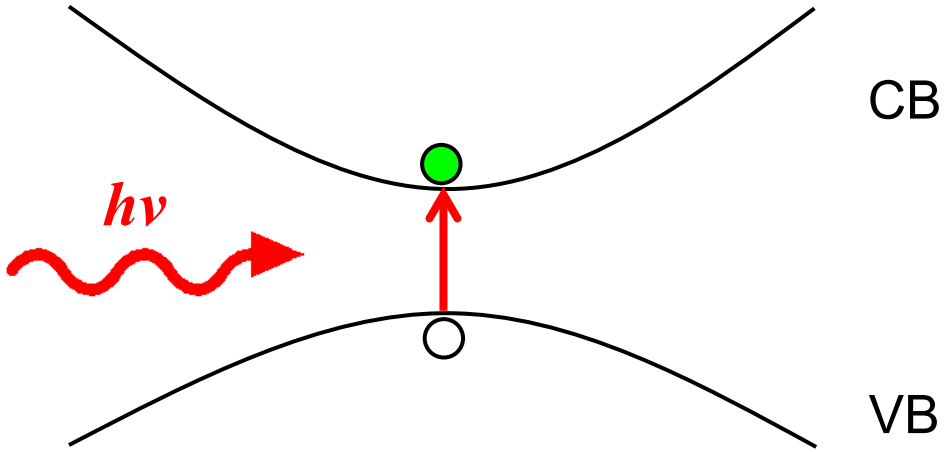
Absorption of light in a solid



Let us consider the absorption of light in a solid with a gap.

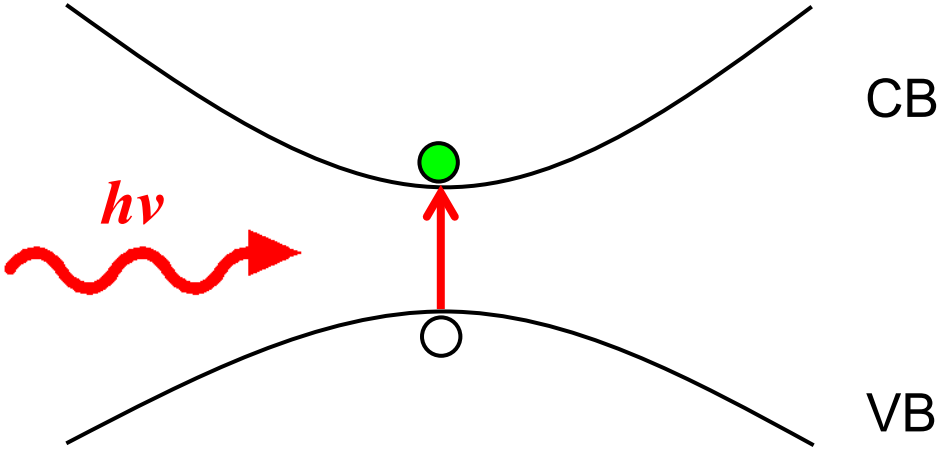
Absorption of light across the band gap



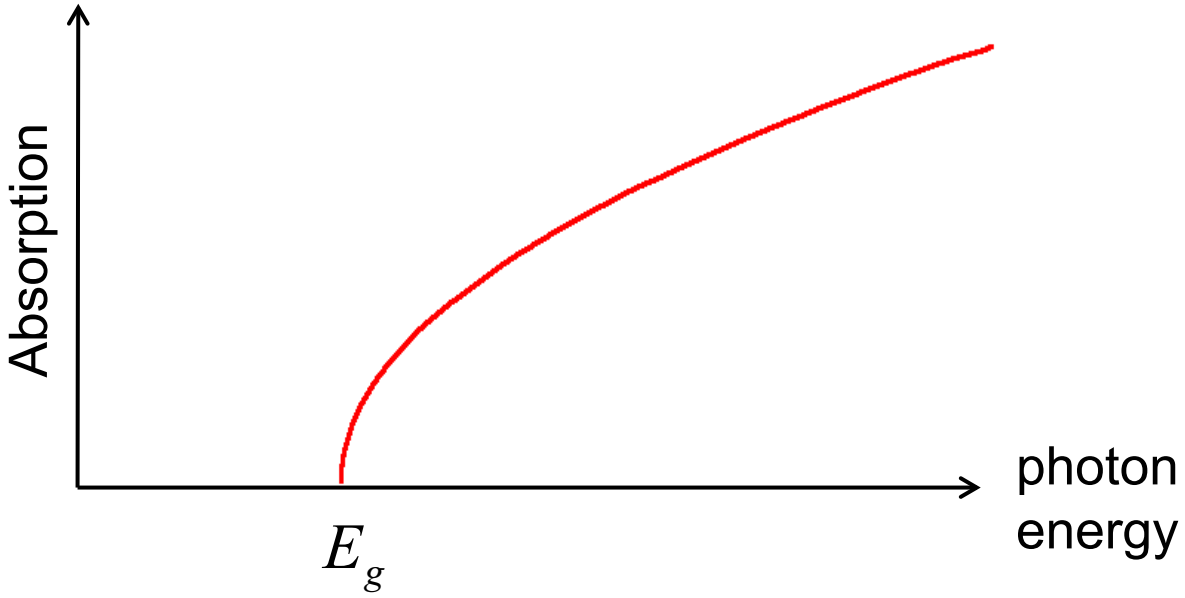


- Light comes in with photon energy at least as large as the band gap
- Photon gets absorbed, promotes electron across the gap, leaving a hole behind

Absorption spectra of insulators/semiconductors

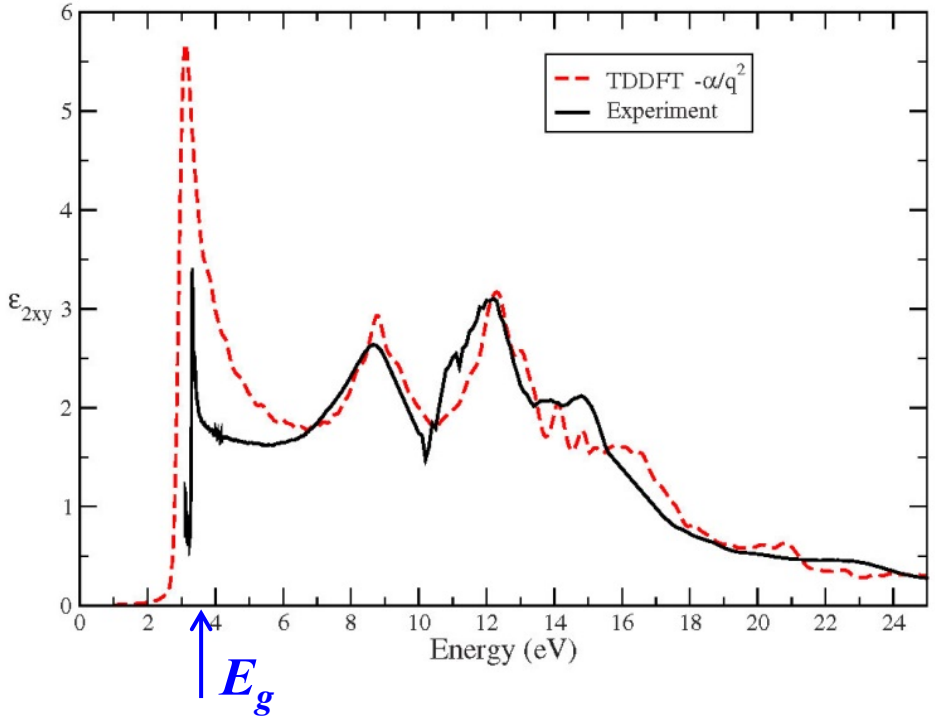


will produce an absorption spectrum like this:



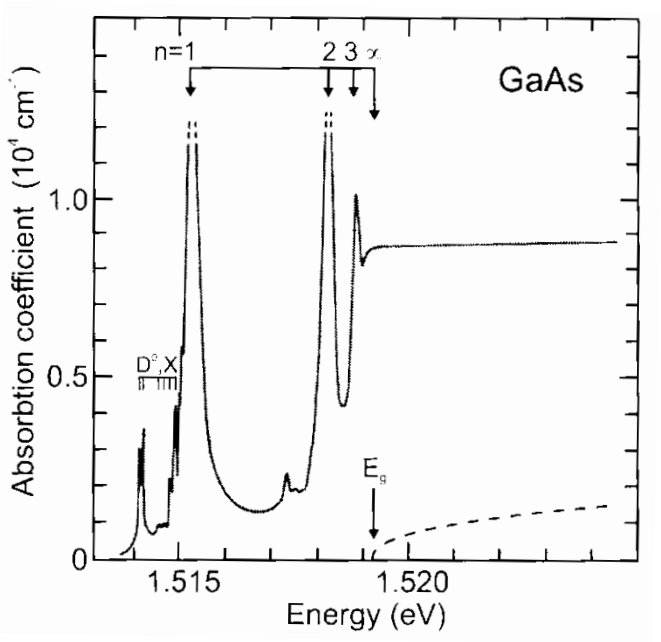
Absorption spectra of insulators/semiconductors

ZnO



P. Gori et al., Phys. Rev. B **81**, 125207 (2010)

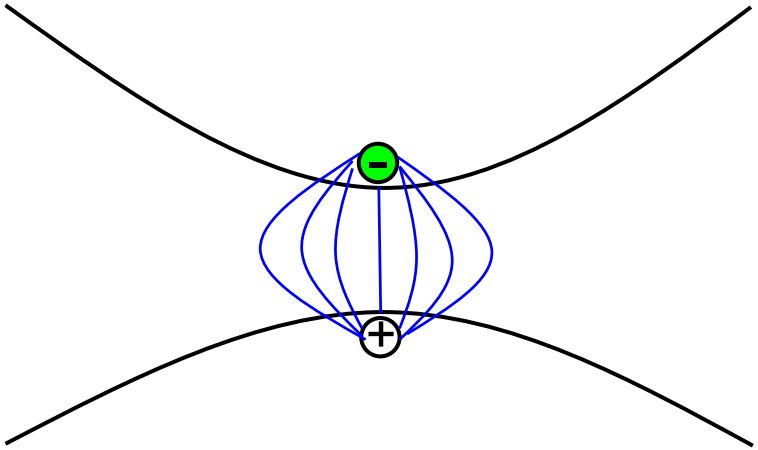
GaAs



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

In the experiment, one finds sharp peaks at the absorption threshold…
In fact, there are peaks below the band gap energy: Excitons.

What is an exciton?

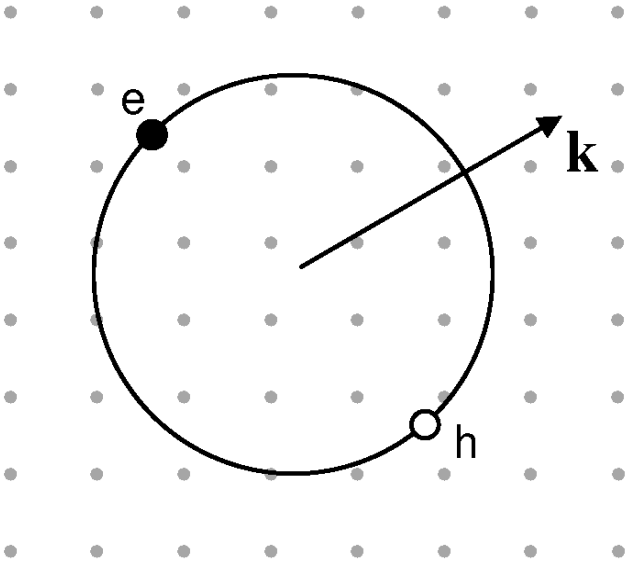


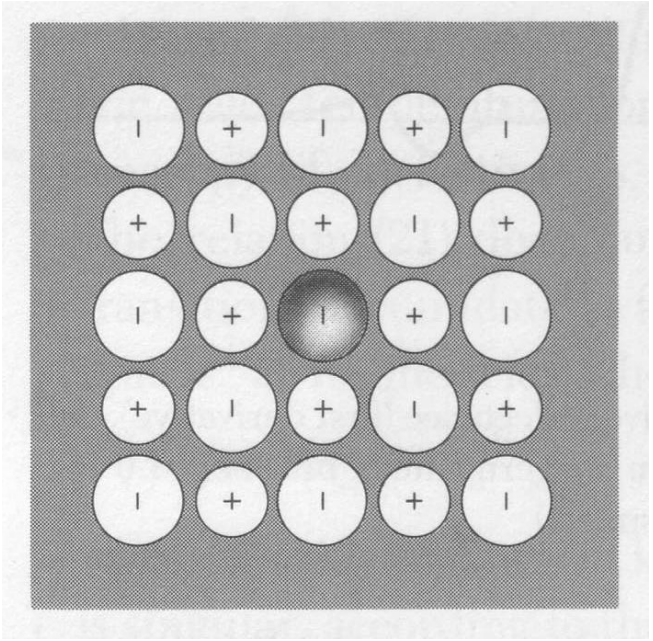
► After their creation, the electron and the hole are not completely free, but experience **Coulomb attraction.**

►This gain in electrostatic energy can lower the onset of absorption, and change the spectral strength.

Excitons are bound electron-hole pairs.

Elementary view of Excitons





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

►In semiconductors with small band gap and large ε

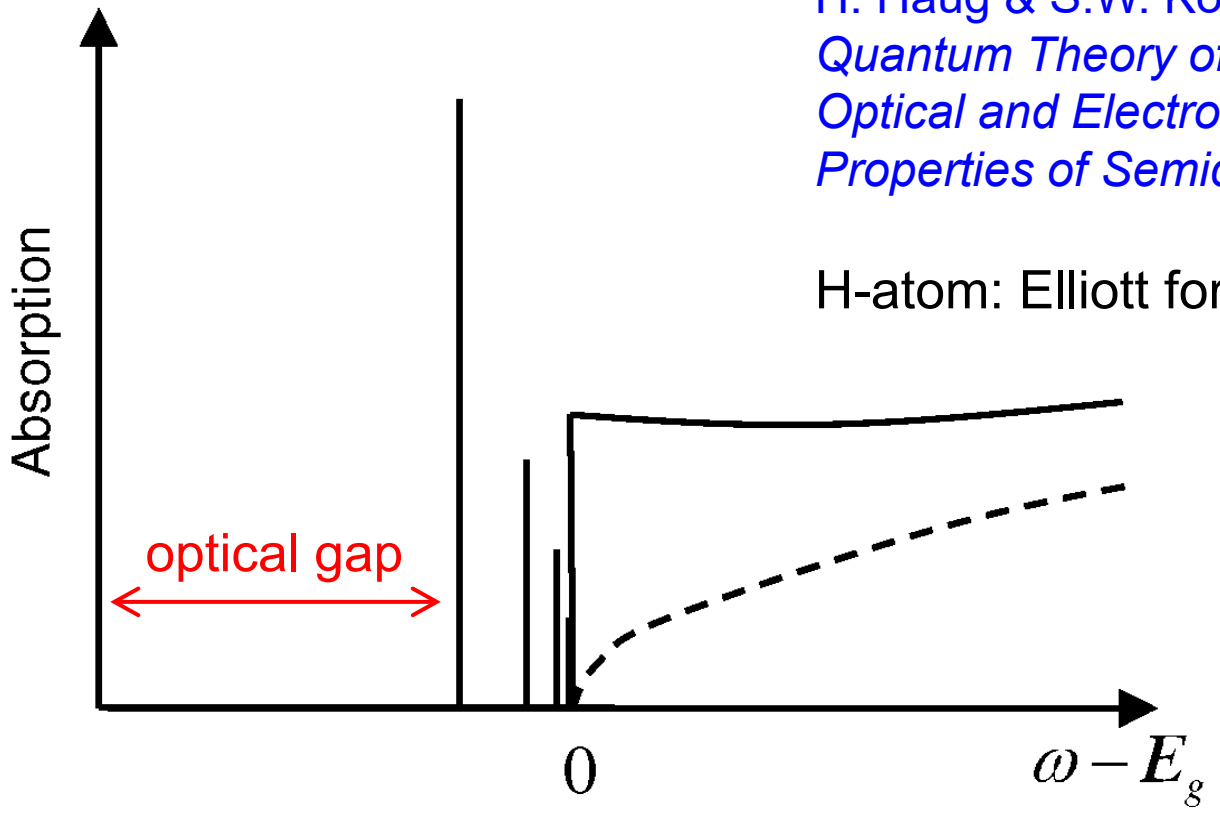
Frenkel exciton:
tightly bound, localized on a single (or a few) atoms

►In large-gap insulators, or in low-ε organic materials

Excitonic features in the absorption spectrum

H. Haug & S.W. Koch
Quantum Theory of the Optical and Electronic Properties of Semiconductors

H-atom: Elliott formula



- Sharp peaks below the onset of the single-particle gap
- Redistribution of oscillator strength: enhanced absorption close to the onset of the continuum

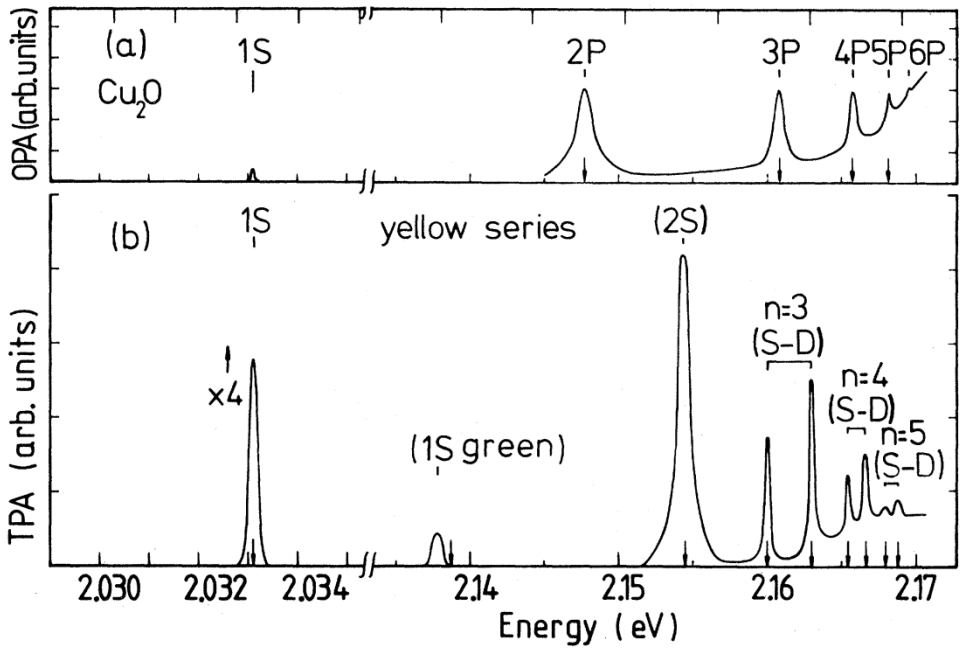
Wannier equation and excitonic Rydberg Series

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

- $\varphi(\mathbf{r})$ is exciton wave function
- includes dielectric screening
- derived from Bethe-Salpeter eq.

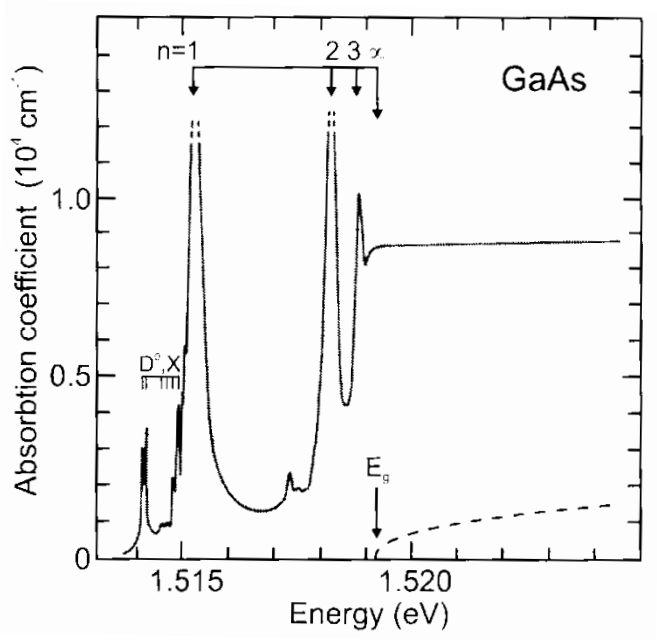
Sham and Rice, Phys. Rev. **144**, 708 (1966)

Cu_2O



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

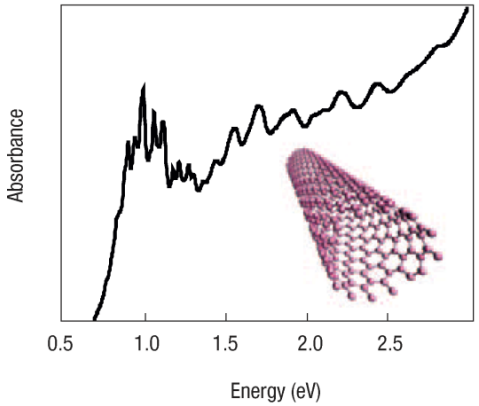
GaAs

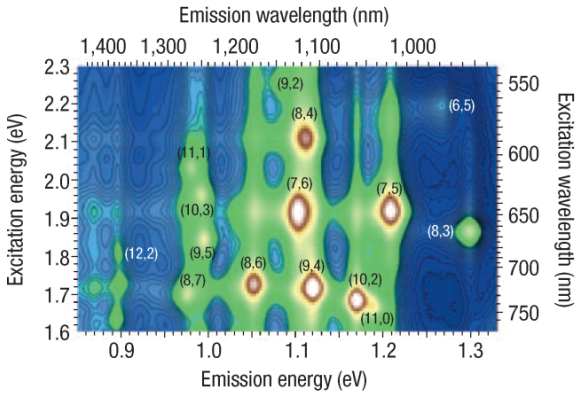


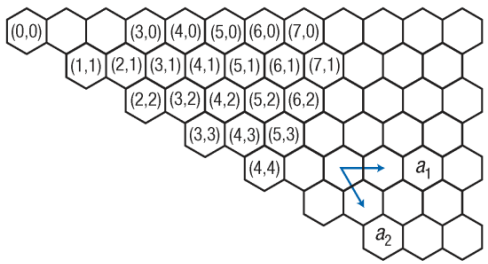
R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

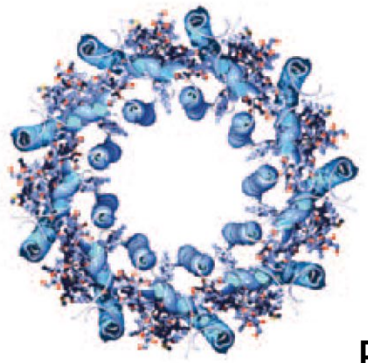
Excitons in nanoscale systems

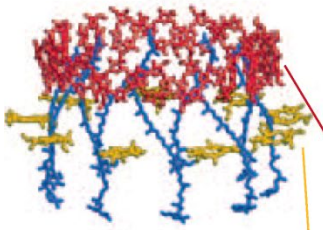
G. D. Scholes and G. Rumbles, Nature Mater. **5**, 683 (2006)
Jang & Mennucci, Rev. Mod. Phys. **90**, 035003 (2018)

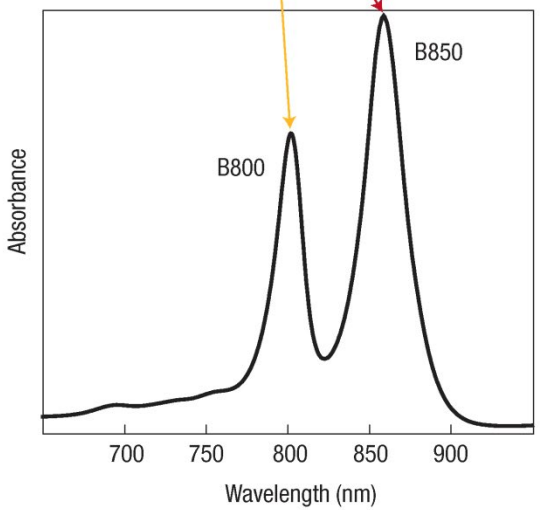






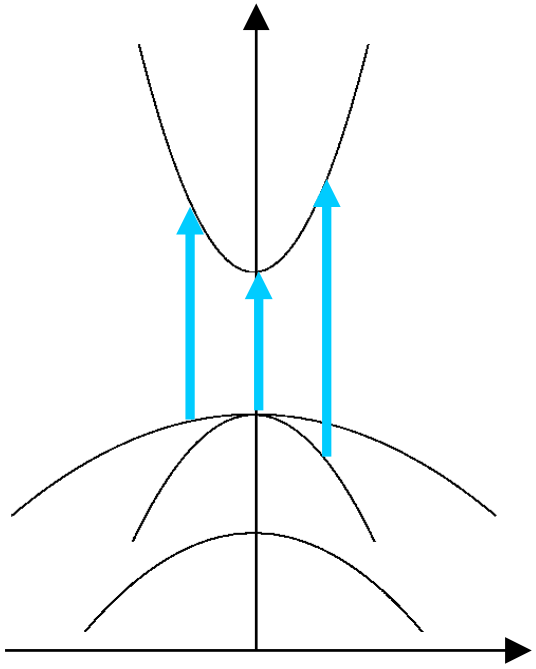






Frenkel excitons in light-harvesting systems: purple bacteria

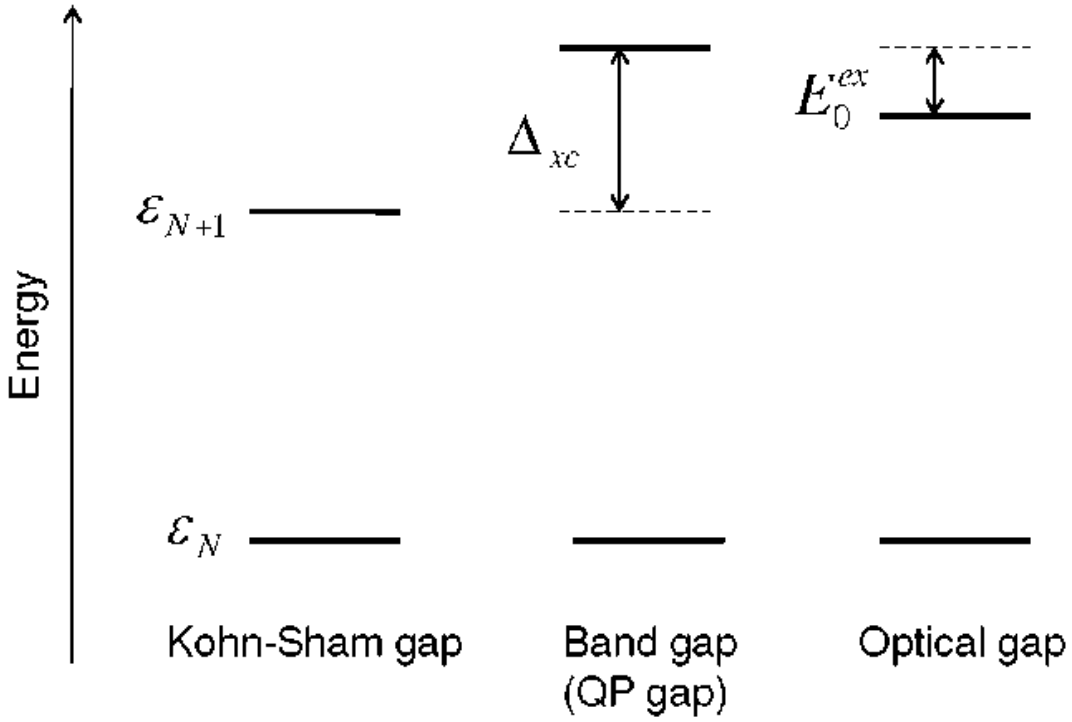
Optical excitations in bulk Insulators



Optical transitions in insulators are challenging for TDDFT:

- **band gap opening**
- **excitons**

Insulators: three different gaps

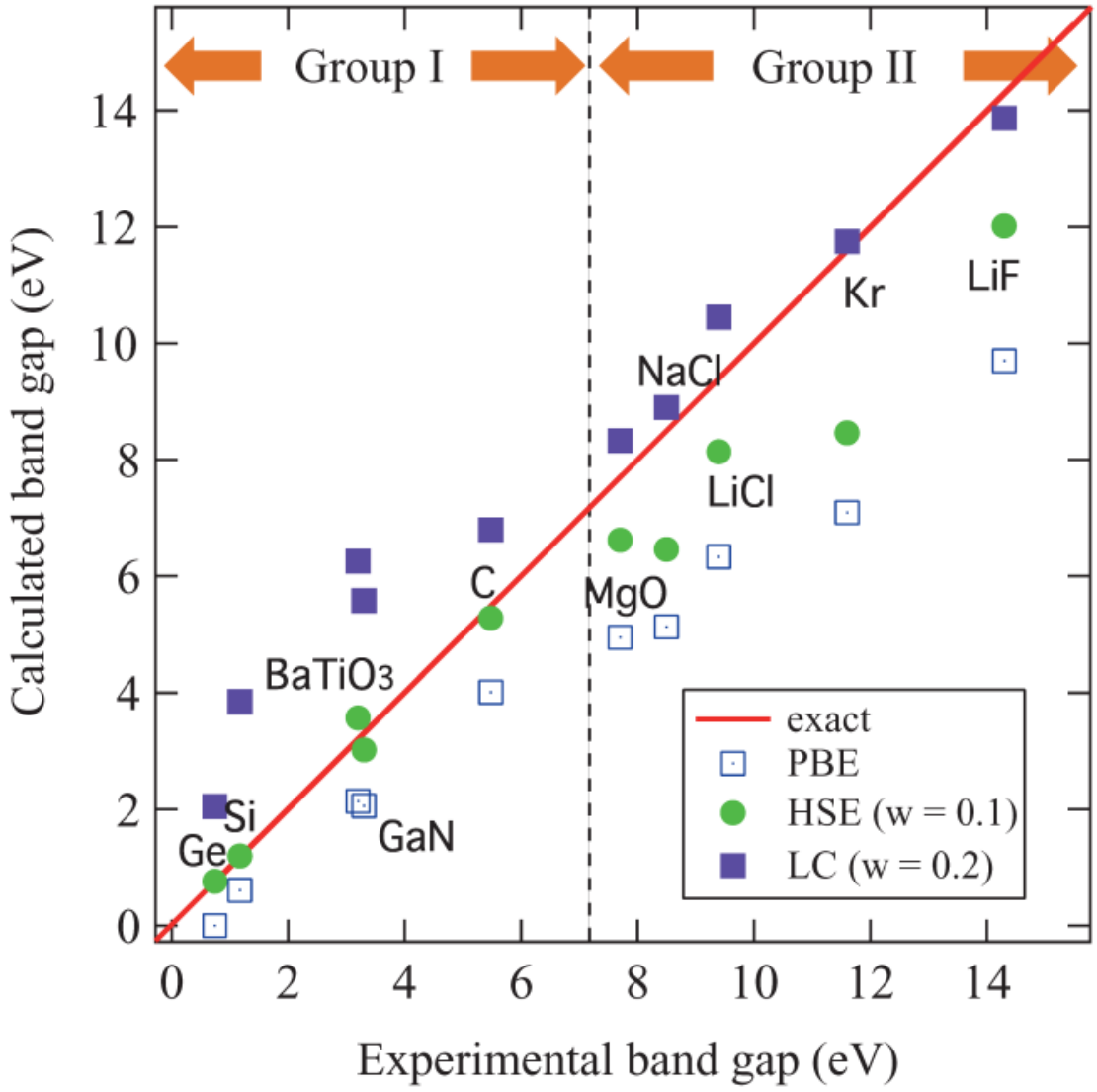


The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

Band gap: $E_g = E_{g,KS} + \Delta_{xc}$

Optical gap: $E_g^{optical} = E_g - E_0^{exciton}$

Hybrid functionals for the band gap



Matsushita, Nakamura and Oshiyama, PRB **84**, 075205 (2011)

see also Skone, Govoni and Galli, PRB **93**, 235106 (2016)

Excitons: comparison of first-principles methods*

L. J. Sham and T. M. Rice, Phys. Rev. **144**, 708 (1966)
M. Rohlfing and S. Louie, PRB **62**, 4927 (2000)
G. Onida, L. Reining, R. Rubio, RMP **74**, 601 (2002)
S. Sharifzadeh, J. Phys.: Cond. Mat. **30**, 153002 (2018)

Many-body perturbation theory: Based on Green's functions

- moves (quasi)particles around
- one-particle G: electron addition and removal – GW ground state
- two-particle L: electron-hole excitation – Bethe-Salpeter equation
- intuitive: contains the right physics (screened e-h interaction) by direct construction

Time-dependent DFT: Based on the electron density

- moves the density around
- Ground state: Kohn-Sham DFT
- response function χ: neutral excitations of the KS system
- efficient (all interactions are local), but less intuitive how the right physics is built in

* Matteo Gatti, TDDFT School 2010, Benasque

Excitons with TDDFT: equivalent approaches

1. Calculate the dielectric function via Dyson equation
(computationally more efficient, gives optical spectrum)

2. Solve Casida equation
(more expensive, gives precise exciton binding energies)

3. Real-time TDDFT
(potentially even more efficient)

C.A. Ullrich and Z.-H. Yang, Topics in Current Chem. **368** (2015)
Y.-M. Byun and C.A. Ullrich, Phys. Rev. B **95**, 205136 (2017)
T. Sander and G. Kresse, JCP **146**, 064110 (2017)

TDDFT Linear response in periodic systems

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi_s(\mathbf{r},\mathbf{r}',\omega) + \int d^3x \int d^3x' \chi_s(\mathbf{r},\mathbf{x},\omega) \times \left\{ \frac{1}{|\mathbf{x}-\mathbf{x}'|} + f_{xc}(\mathbf{x},\mathbf{x}',\omega) \right\} \chi(\mathbf{x}',\mathbf{r}',\omega)$$

Periodic systems: $\chi(\mathbf{r},\mathbf{r}',\omega) = \chi(\mathbf{r}+\mathbf{R},\mathbf{r}'+\mathbf{R},\omega)$

Fourier transform:

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{q}\in BZ} \sum_{\mathbf{G},\mathbf{G}'} e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} \chi(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)$$

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \chi_{s\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1\mathbf{G}_2} \chi_{s\mathbf{G}\mathbf{G}_1}(\mathbf{q},\omega) \times \left\{ V_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1\mathbf{G}_2} + f_{xc\mathbf{G}_1\mathbf{G}_2}(\mathbf{q},\omega) \right\} \chi_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)$$

The dielectric tensor

$$\nabla \cdot \mathbf{D} = n_{free} \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{H} = \mathbf{j}_{free} + \frac{\partial \mathbf{D}}{\partial t}$$

Maxwell equations

Def. of dielectric tensor: $$\mathbf{D}(\mathbf{r},\omega) = \int d^3 r' \underline{\underline{\varepsilon}}(\mathbf{r},\mathbf{r}',\omega)\mathbf{E}(\mathbf{r}',\omega)$$

In periodic solids: $$\mathbf{D}_{\mathbf{G}}(\mathbf{q},\omega) = \sum_{\mathbf{G}'} \underline{\underline{\varepsilon}}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\mathbf{E}_{\mathbf{G}'}(\mathbf{q},\omega)$$

This is the **microscopic** dielectric tensor. But for comparison with spectroscopy, we would like the **macroscopic** dielectric function:

$$\mathbf{D}_{mac}(\omega) = \underline{\underline{\varepsilon}}_{mac}(\omega)\mathbf{E}_{mac}(\omega)$$

Problem: we cannot calculate the macroscopic dielectric function directly! This would ignore the **local-field effects** (microscopic fluctuations).

Homogeneous systems

In a homogeneous, isotropic system, things would be easy:

$$\underline{\underline{\varepsilon}}^{\,\mathrm{hom}}_{mac}(\omega) = \lim_{q\to 0} \underline{\underline{\varepsilon}}^{\,\mathrm{hom}}(\mathbf{q},\omega)$$

and $$\underline{\underline{\varepsilon}}^{\,\mathrm{hom}}(\mathbf{q},\omega) = \varepsilon_L^{\mathrm{hom}}(\mathbf{q},\omega)\hat{q}\hat{q}^T + \varepsilon_T^{\mathrm{hom}}(\underline{\underline{1}} - \hat{q}\hat{q}^T)$$

and $$\varepsilon_L^{\mathrm{hom}}(0,\omega) = \varepsilon_T^{\mathrm{hom}}(0,\omega)$$

The connection to optics is via the refractive index:

$$\varepsilon_{mac}(\omega) = \tilde{n}^2$$

$$\mathrm{Re}\,\varepsilon_{mac} = n^2 + \kappa^2$$

$$\mathrm{Im}\,\varepsilon_{mac} = 2n\kappa$$

The macroscopic dielectric function

For cubic symmetry, one can prove that

$$\varepsilon_{mac}(\omega) = \lim_{q\to 0}\left[\left|\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\right|_{\substack{\mathbf{G}=0\\ \mathbf{G}'=0}}\right]^{-1}$$

$\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$: longitudinal component of dielectric tensor (a.k.a. dielectric matrix)

To make progress, we need a connection with response theory:

scalar dielectric function:

$$V_1(\mathbf{r},\omega) = \int d^3r'\varepsilon(\mathbf{r},\mathbf{r}',\omega)\left[V_1(\mathbf{r},\omega) + \int d^3r''\frac{n_1(\mathbf{r}'',\omega)}{|\mathbf{r}'-\mathbf{r}''|}\right]$$

so that $$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') + \int d^3r''\frac{\chi(\mathbf{r}'',\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}''|}$$

and for a periodic system,

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

The macroscopic dielectric function

From this, one obtains

$$\varepsilon_{mac}(\omega) = 1 - \lim_{q\to 0} V_0(\mathbf{q})\,\bar{\chi}_{00}(\mathbf{q},\omega)$$

There is a subtle, but very important point to be noted. Here we use a modified response function $\bar{\chi}_{\mathbf{GG}'}(\mathbf{q},\omega)$:

$$\bar{\chi}_{\mathbf{GG}'}(\mathbf{q},\omega) = \chi_{s\mathbf{GG}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1\mathbf{G}_2} \chi_{s\mathbf{GG}_1}(\mathbf{q},\omega) \times \left\{ \bar{V}_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1\mathbf{G}_2} + f_{xc\mathbf{G}_1\mathbf{G}_2}(\mathbf{q},\omega) \right\} \bar{\chi}_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)$$

where the long-range part of the Coulomb interaction has been removed:

$$\bar{V}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{for} \quad \mathbf{G} = 0 \\ \dfrac{4\pi}{|\mathbf{q}+\mathbf{G}|^2} & \text{for} \quad \mathbf{G} \neq 0 \end{cases}$$

G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)

Density response of periodic systems

$$\delta n_{\mathbf{G}}(\mathbf{q},\omega) = \sum_{\mathbf{G}'} \chi_{s\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\left\{ \delta V^{ext}_{\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}''} f^{Hxc}_{\mathbf{G}'\mathbf{G}''}(\mathbf{q},\omega)\delta n_{\mathbf{G}''}(\mathbf{q},\omega) \right\}$$

Loss function:
response to a
microscopic
external scalar potential.
Loss spectrum
includes **plasmons**.

Optical absorption:
response to total
macroscopic
classical perturbation.
Optical spectrum
includes **excitons**.

Density eigenmode:
set

$$\delta V^{ext}_{\mathbf{G}'}(\mathbf{q},\omega) = 0$$

Density eigenmode:
set

$$\delta V^{ext}_{\mathbf{G}'}(\mathbf{q},\omega) + f^{H}_{\mathbf{00}}\delta n_{\mathbf{0}}(\mathbf{q},\omega) = 0$$

Excitation energies from TDDFT

Excitation energies follow from eigenvalue problem (Casida 1995):

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

$$A_{vc\mathbf{k},v'c'\mathbf{k}'} = (E_{c\mathbf{k}} - E_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'} + F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}$$

$$B_{vc\mathbf{k},v'c'\mathbf{k}'} = F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}$$

$$F^{H}_{vc\mathbf{k},v'c'\mathbf{k}'} = \frac{2}{\mathrm{V}} \sum_{\mathbf{G}\neq\mathbf{0}} \frac{4\pi}{G^2} \langle c\mathbf{k}| e^{i\mathbf{G}\cdot\mathbf{r}} |v\mathbf{k}\rangle \langle v'\mathbf{k}'| e^{-i\mathbf{G}\cdot\mathbf{r}} |c'\mathbf{k}'\rangle$$

$$F^{xc}_{vc\mathbf{k},v'c'\mathbf{k}'} = \frac{2}{\mathrm{V}} \lim_{\mathbf{q}\to\mathbf{0}} \sum_{\mathbf{G}\mathbf{G}'} f_{xc,\mathbf{G}\mathbf{G}'}(\mathbf{q}) \langle c\mathbf{k}| e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |v\mathbf{k}\rangle \langle v'\mathbf{k}'| e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} |c'\mathbf{k}'\rangle$$

Direct calculation of exciton binding energies

$$\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{cv\mathbf{k}}+F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]X_{v'c'\mathbf{k}'}+\sum_{v'c'\mathbf{k}'}F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}Y_{v'c'\mathbf{k}'}=-\Omega_n X_{vc\mathbf{k}}$$

$$\sum_{v'c'\mathbf{k}'}F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}}X_{v'c'\mathbf{k}'}+\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{cv\mathbf{k}}+F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]Y_{v'c'\mathbf{k}'}=\Omega_n Y_{vc\mathbf{k}}$$

Tamm-Dancoff Approximation (TDA)

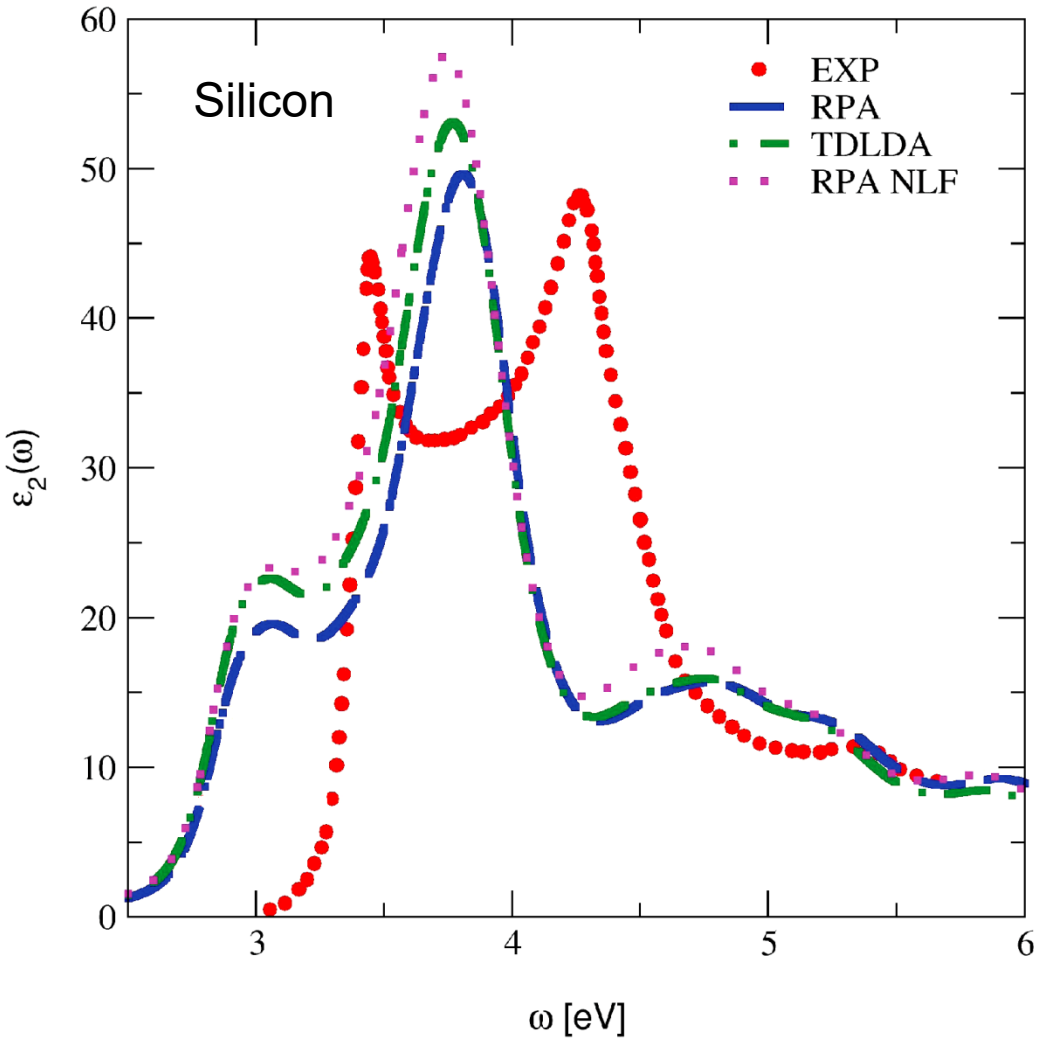
Using time-reversal symmetry, Full Casida eq. can be transformed into

$$\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega^2_{vc\mathbf{k}}+2\sqrt{\omega_{cv\mathbf{k}}\omega_{c'v'\mathbf{k}'}}\,F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]Z_{v'c'\mathbf{k}'}=\Omega^2_n Z_{vc\mathbf{k}}$$

T. Sander, E. Maggio, and G. Kresse, PRB **92**, 045209 (2015)

More expensive than calculating Im ε(ω), but more precise (no artificial line broadening)

Optical absorption in Insulators: TDDFT



RPA and ALDA both bad!

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

Why does the LDA fail??

- **►lacks long spatial range**
- **►need new classes of xc functionals**

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)

The xc kernel for periodic systems

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega)=\sum_{\mathbf{q}\in FBZ}\sum_{\mathbf{G},\mathbf{G}'}e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}f_{xc,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}}$$

TDDFT requires the following matrix elements as input:

$$F^{xc}_{vc\mathbf{k},v'c'\mathbf{k}'}=\lim_{\mathbf{q}\to\mathbf{0}}\sum_{\mathbf{G}\mathbf{G}'}f_{xc,\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\left\langle c\mathbf{k}\left|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\right|v\mathbf{k}\right\rangle\left\langle v'\mathbf{k}'\left|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\right|c'\mathbf{k}'\right\rangle$$

Most important: long-range $(\mathbf{q}\to 0)$ limit of "head" $(\mathbf{G}=\mathbf{G}'=0)$:

$$\left\langle c\mathbf{k}\left|e^{i\mathbf{q}\mathbf{r}}\right|v\mathbf{k}\right\rangle\xrightarrow[\mathbf{q}\to\mathbf{0}]{}\mathbf{q}\qquad f^{exact}_{xc,\mathbf{00}}(\mathbf{q},\omega)\xrightarrow[\mathbf{q}\to 0]{}\frac{1}{q^2}$$

but $f^{ALDA}_{xc,\mathbf{00}}(\mathbf{q})\xrightarrow[\mathbf{q}\to 0]{}\text{const}.$ **Therefore, no excitons in ALDA!**

The xc kernel for periodic systems

The **exact** xc kernel can be written as

Stubner, Tokatly & Pankratov, PRB **70**, 245119 (2004)
Bruneval et al., PRL **94**, 186402 (2005)

$$f_{xc} = f_{xc}^{qp} + f_{xc}^{ex}$$

"quasiparticle", opens the gap $\chi_{KS} \rightarrow \chi_{qp}$

"excitonic", accounts for electron-hole interaction

- Usually, f_{xc}^{qp} is neglected. Instead, one uses hybrids, GW, or DFT+ scissors, which directly approximates χ_{qp}
- Only f_{xc}^{ex} is then approximated

Long-range xc kernels for solids

- **LRC** (long-range corrected) kernel (with fitting parameter α):
  (L. Reining et al., 2002)

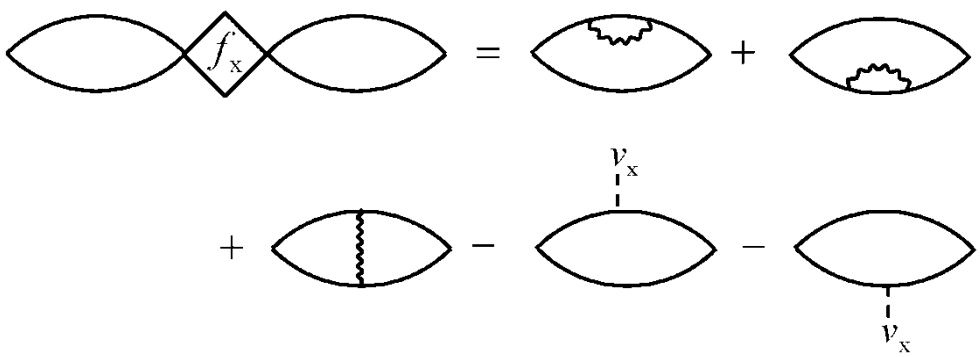
$$f_{xc,\mathbf{GG'}}^{LRC}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q}+\mathbf{G}|^2}\delta_{\mathbf{GG'}}$$

- **"bootstrap"** kernel (S. Sharma et al., PRL **107**, 186401 (2011)

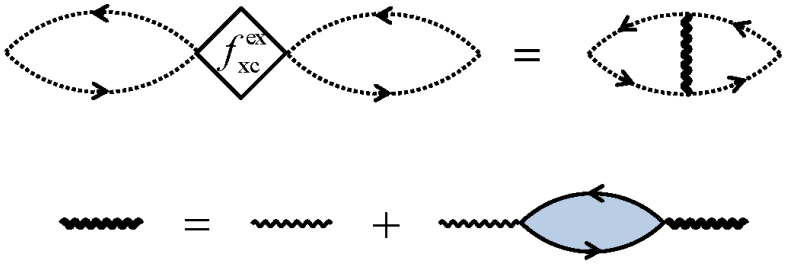
$$f_{xc,\mathbf{GG'}}^{boot}(\mathbf{q},\omega) = \frac{\varepsilon_{\mathbf{GG'}}^{-1}(\mathbf{q},0)}{\chi_{s00}(\mathbf{q},0)}$$

(depends on unoccupied bands, may need large number of bands)

- **Functionals from many-body theory:** (requires matrix inversion)



exact exchange

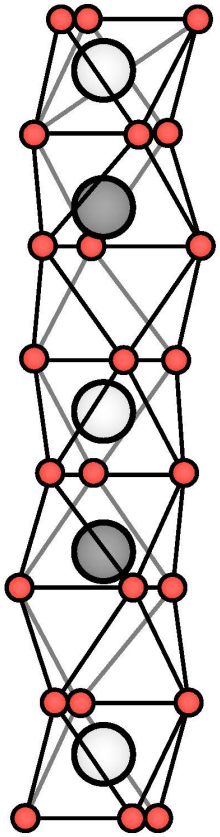


"nanoquanta" kernel, reverse-engineered from BSE
(L. Reining et al., 2002)

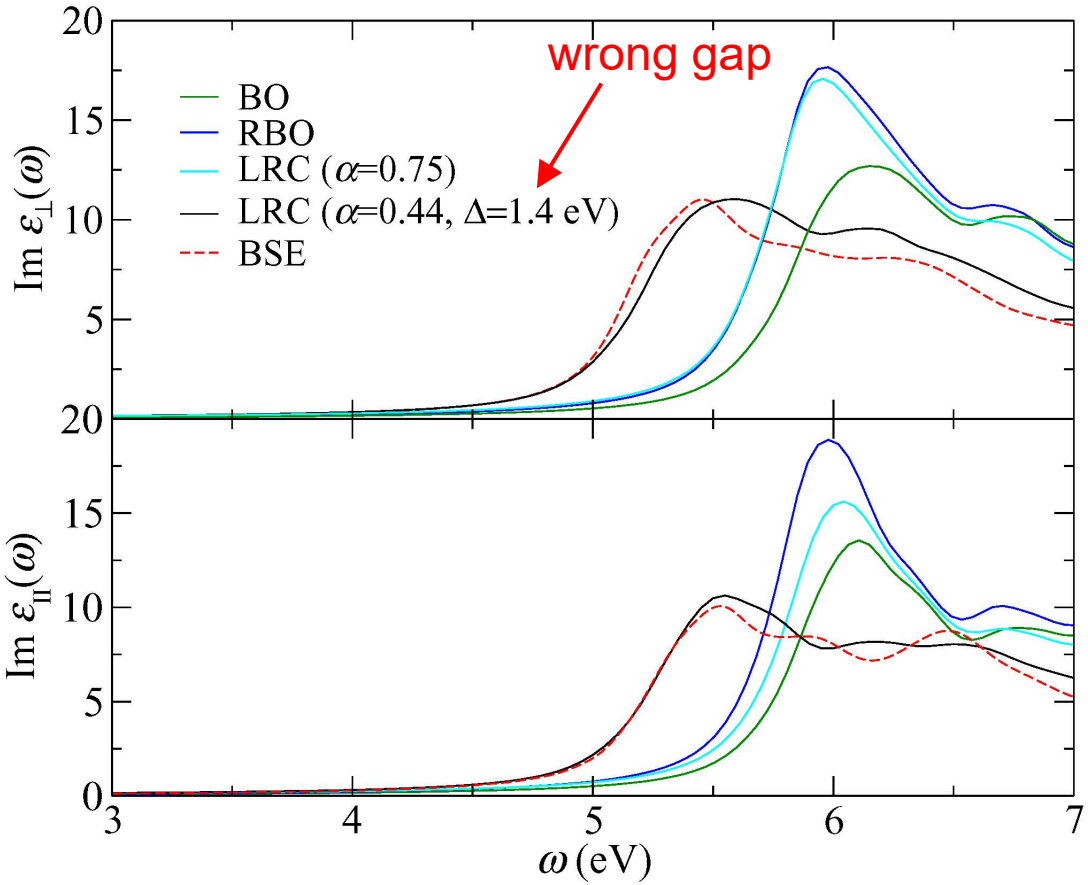
Excitons: which xc kernels to use?

- Local functionals (ALDA/GGA) don't work
- **Nanoquanta kernel**: accurate but expensive
  Reining, Olevano, Rubio, Onida, PRL **88**, 066404 (2002)
- **Long-range corrected (LRC) kernel:** simple but ad-hoc
  Botti *et al.,* PRB **69**, 155112 (2004)
- **Bootstrap kernel:** several versions
  Sharma, Dewhurst, Sanna and Gross, PRL **107**, 186401 (2011)
  Rigamonti, Botti, Veniard, Draxl, Reining & Sottile, PRL **114**, 146402 (2015)
- **Jellium with a gap:**
  Trevisanutto *et al.,* PRB **87**, 205143 (2013)
- **Current-TDDFT:**
  A.J. Berger, PRL 115, 137402 (2015)
- **Hybrid functionals, meta-GGAs:**
  B3LYP: Bernasconi *et al.* PRB **83**, 195325 (2011)
  HSE: Paier, Marsman and Kresse, PRB **78**, 121201 (2008)
  VS98/TPSS: Nazarov and Vignale, PRL **107**, 216401 (2011)
  Range separated: Refaely-Abramson *et al.*, PRB **92**, 081204 (2015)

The family of LRC/Bootstrap xc kernels



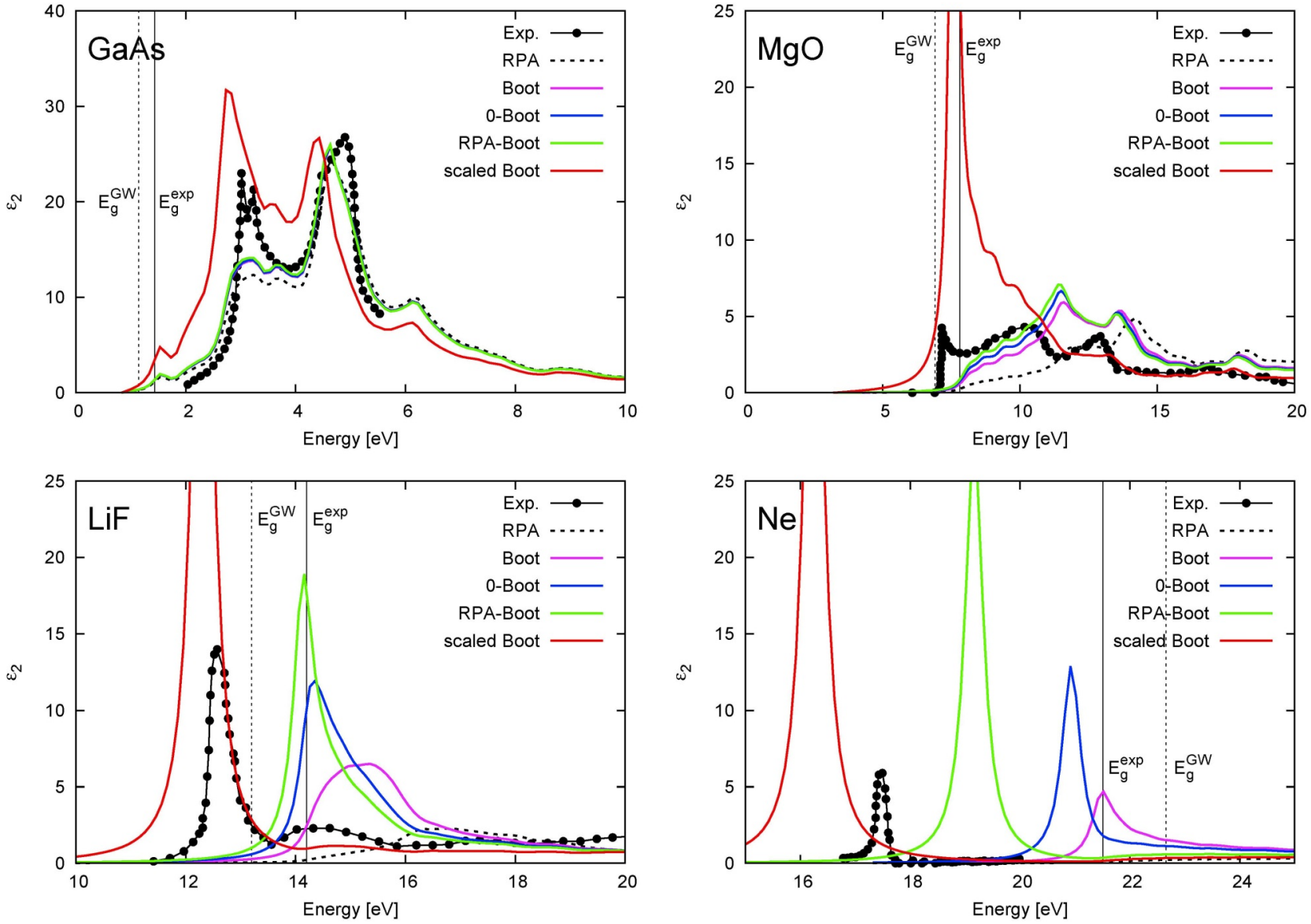
$LiNbO_3$



With some tricks, LRC kernel can produce quite accurate optical spectra!
Systematic assessment: workshop talk on Monday.

Friedrich, Schmidt, Schindlmayr & Sanna, Phys. Rev. Mater. **1**, 034401 (2017)

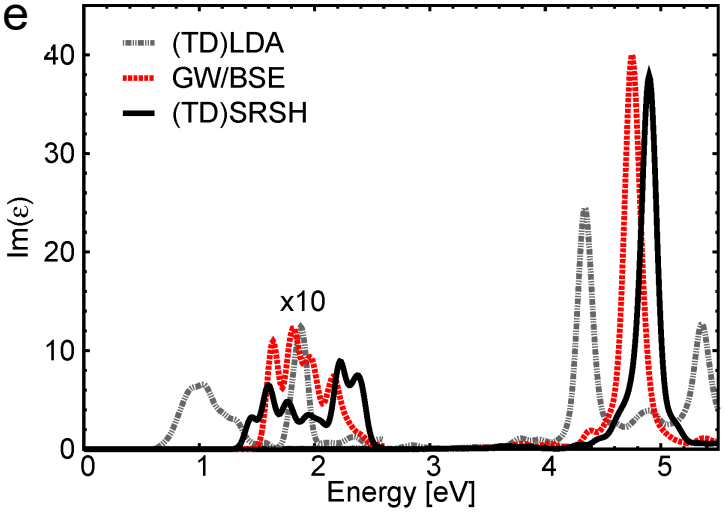
Optical spectra

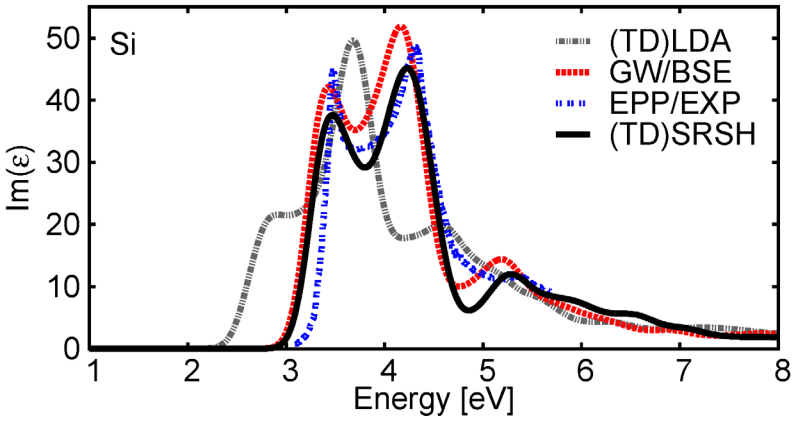


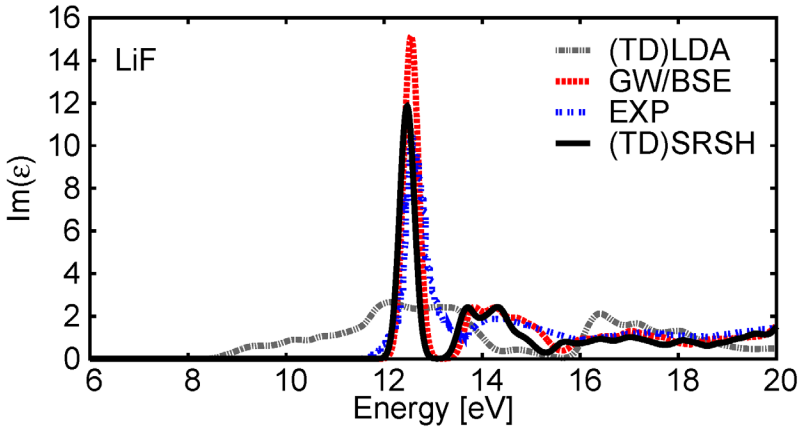
Young-Moo Byun and C. A. Ullrich, PRB **95**, 205136 (2017)

Optical spectra with range-separated hybrid

pentacene



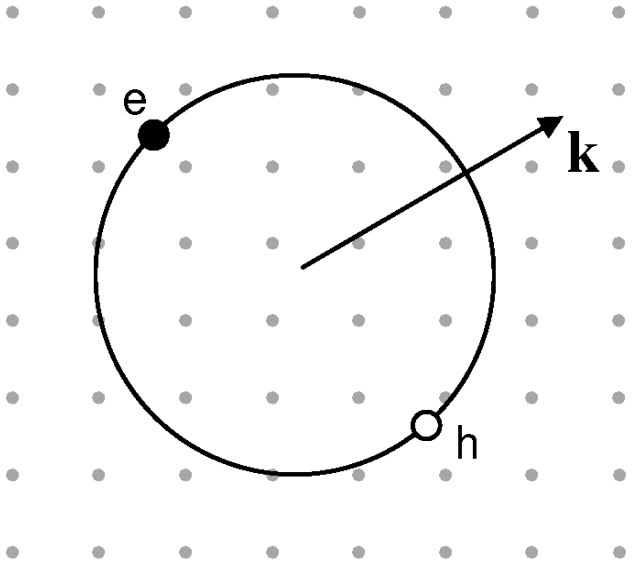




S. Refaely-Abramson, M. Jain,
S. Sharifzadeh, J.B. Neaton,
L. Kronik, PRB **92**, 081204 (2015)

Contains adjustable
range separation parameter

Back to the basics



►How does the simple picture of excitons as bound e-h pairs come out of the general formalism?

►How are TDDFT and MBPT different?

Back to the basics

$$\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{cv\mathbf{k}}+F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]X_{v'c'\mathbf{k}'}+\sum_{v'c'\mathbf{k}'}F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}Y_{v'c'\mathbf{k}'}=-\Omega_n X_{vc\mathbf{k}}$$

$$\sum_{v'c'\mathbf{k}'}F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}}X_{v'c'\mathbf{k}'}+\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{cv\mathbf{k}}+F^{Hxc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]Y_{v'c'\mathbf{k}'}=\Omega_n Y_{vc\mathbf{k}}$$

Tamm-Dancoff Approximation (TDA)

Ignore the Hartree term (only gives local-field corrections):

$$\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{cv\mathbf{k}}+F^{xc}_{vc\mathbf{k},v'c'\mathbf{k}'}\right]Y_{v'c'\mathbf{k}'}=\Omega_n Y_{vc\mathbf{k}}$$

Derivation of Wannier equation

1. Two-band model: only one valence and conduction band

2. Effective-mass approximation with parabolic bands:

$$\begin{aligned}\omega_{cv\mathbf{k}} &= \varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}} \\ &= \frac{\hbar^2 k^2}{2m_c} + \frac{\hbar^2 k^2}{2m_v} + E_g \\ &= \frac{\hbar^2 k^2}{2m_r} + E_g\end{aligned}$$

reduced electron-hole effective mass:

$$m_r^{-1} = m_c^{-1} + m_v^{-1}$$

$$\frac{\hbar^2 k^2}{2m_r} Y_{vc\mathbf{k}} + \sum_{\mathbf{k}'} F^{xc}_{vc\mathbf{k},vc\mathbf{k}'} Y_{vc\mathbf{k}'} = (\Omega_n - E_g) Y_{vc\mathbf{k}}$$

Now look at the coupling matrix elements!

TDDFT vs BSE coupling matrix elements

$$F^{TDDFT}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int d\mathbf{r}\int d\mathbf{r}'\varphi^{*}_{c\mathbf{k}}(\mathbf{r})\varphi_{v\mathbf{k}}(\mathbf{r})f_{xc}(\mathbf{r},\mathbf{r}')\varphi^{*}_{v'\mathbf{k}'}(\mathbf{r}')\varphi_{c'\mathbf{k}'}(\mathbf{r}')$$

$$F^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int d\mathbf{r}\int d\mathbf{r}'\varphi^{*}_{v'\mathbf{k}'}(\mathbf{r})\varphi_{v\mathbf{k}}(\mathbf{r})W(\mathbf{r},\mathbf{r}')\varphi^{*}_{c\mathbf{k}}(\mathbf{r}')\varphi_{c'\mathbf{k}'}(\mathbf{r}')$$

Fourier transformation:

$$W(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{G}\mathbf{G}'}\sum_{\mathbf{q}\in \mathrm{BZ}} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}W_{\mathbf{G}\mathbf{G}'}(\mathbf{q})e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}$$

TDDFT vs BSE coupling matrix elements

$$F^{TDDFT}_{vc\mathbf{k},v'c'\mathbf{k}'} = \sum_{\mathbf{GG}'\mathbf{q}} f^{xc}_{\mathbf{GG}'}(\mathbf{q}) \langle c\mathbf{k}| e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} |v\mathbf{k}\rangle \langle v'\mathbf{k}'| e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |c'\mathbf{k}'\rangle$$

$$F^{BSE}_{vc\mathbf{k},v'c'\mathbf{k}'} = \sum_{\mathbf{GG}'\mathbf{q}} W_{\mathbf{GG}'}(\mathbf{q}) \langle v'\mathbf{k}'| e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} |v\mathbf{k}\rangle \langle c\mathbf{k}| e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} |c'\mathbf{k}'\rangle$$

$$W_{\mathbf{GG}'}(\mathbf{q}) = -4\pi \frac{\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega=0)}{|\mathbf{q}+\mathbf{G}'|^2}$$

← replace with ε^{-1}

TDDFT vs BSE coupling matrix elements

Optical transitions $(\mathbf{q} \to 0)$: very different behavior of the matrix elements!

$$\left\langle v\mathbf{k}' \left| e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \right| v\mathbf{k} \right\rangle \to \delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'}\delta_{\mathbf{G},0}$$

$$\left\langle c\mathbf{k} \left| e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \right| v\mathbf{k} \right\rangle \to \frac{\mathbf{G}\,\mathbf{p}_{cv}(\mathbf{k})}{\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k})}$$

$$\Rightarrow \quad F^{TDDFT}_{vc\mathbf{k},vc\mathbf{k}} = \sum_{\mathbf{GG}'} f^{xc}_{\mathbf{GG}'}(\mathbf{q}\to\mathbf{0}) \frac{\mathbf{GG}'\, p_{cv}(\mathbf{k})\, p_{vc}(\mathbf{k}')}{(\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k}))(\varepsilon_c(\mathbf{k}') - \varepsilon_v(\mathbf{k}'))}$$

$$\Rightarrow \quad F^{BSE}_{vc\mathbf{k},vc\mathbf{k}} = W_{00}(\mathbf{k}-\mathbf{k}')$$

F. Bechstedt, *Many-Body Approach to Electronic Excitations* (Springer, 2015)

Derivation of Wannier equation

$$\frac{\hbar^2 k^2}{2m_r} Y_{vc\mathbf{k}} + \sum_{\mathbf{k}'} F^{xc}_{vc\mathbf{k},vc\mathbf{k}'} Y_{vc\mathbf{k}'} = (\Omega_n - E_g) Y_{vc\mathbf{k}}$$

Fourier transformation leads to the following equations:

$$-\frac{\hbar^2 \nabla^2}{2m_r} Y(\mathbf{r}) + \int d\mathbf{r}' F^{TDDFT}(\mathbf{r},\mathbf{r}') Y(\mathbf{r}') = (\Omega_n - E_g) Y(\mathbf{r})$$

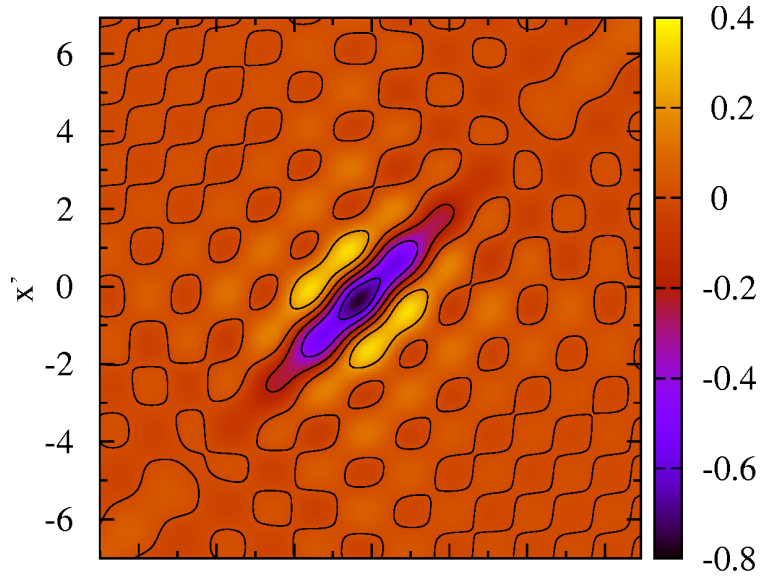
The TDDFT excitonic equation has a nonlocal potential.

$$\left[-\frac{\hbar^2 \nabla^2}{2m_r} - \frac{1}{\varepsilon r}\right] Y(\mathbf{r}) = (\Omega_n - E_g) Y(\mathbf{r})$$

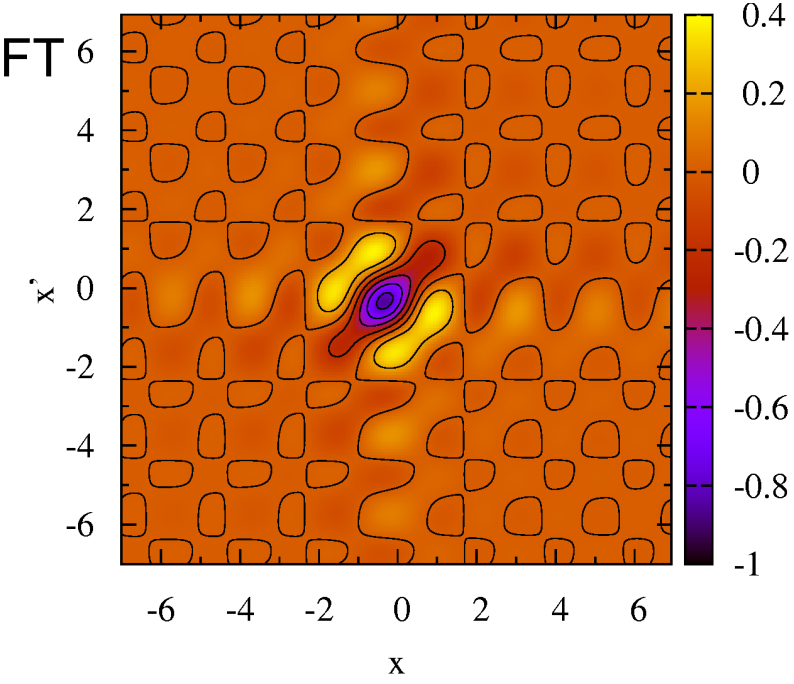
BSE reduces to the original Wannier equation.

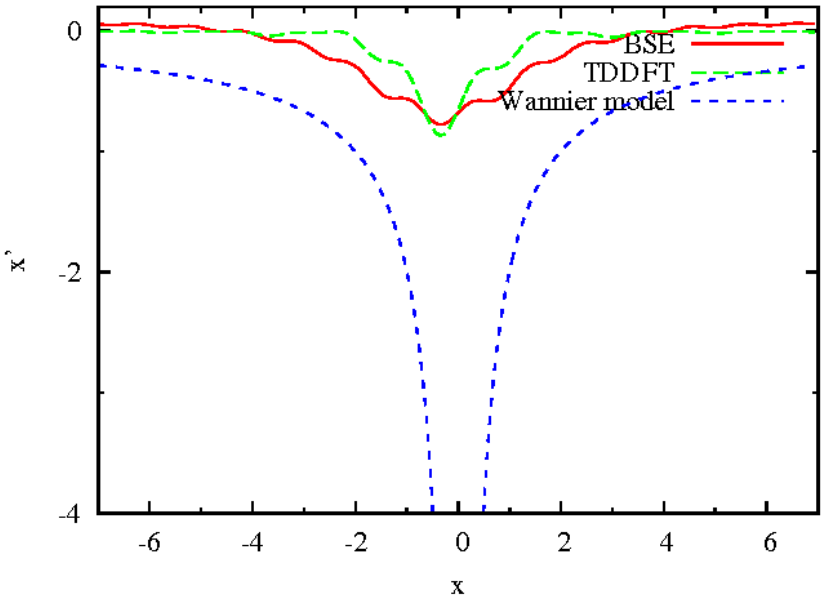
Nonlocal e-h potential (1D model solid)

BSE



TDDFT

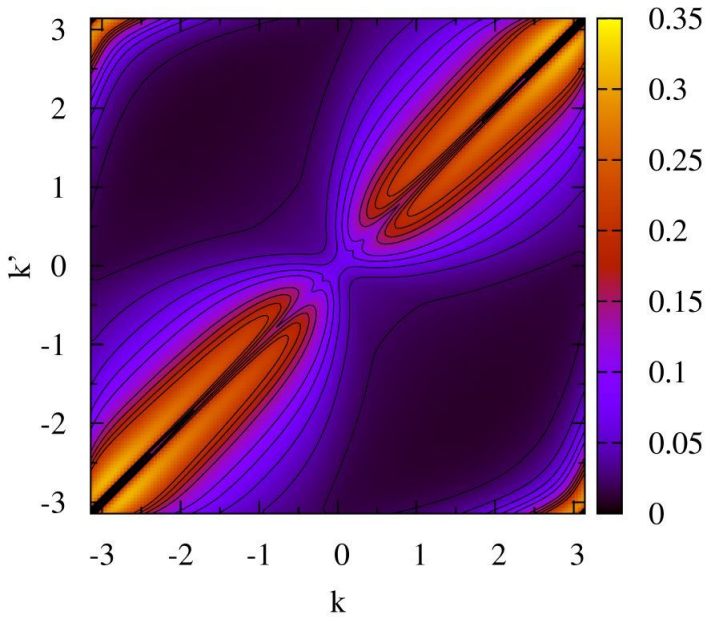




- V_{eh} is dominant along the diagonal.
- BSE and TDDFT look similar, but TDDFT too shallow (no multiple bound excitons)

Z.-H. Yang, Y. Li, and C. A. Ullrich, JCP **137**, 014513 (2012)

BSE vs. TDDFT coupling matrix (1D model)



$$F^{ij,mn}_{BSE,\mathbf{kk}'} = 2\langle ij|f_H|mn\rangle - \langle im|W|jn\rangle$$

$$F^{ij,mn}_{TDDFT,\mathbf{kk}'} = 2\langle ij|f_H|mn\rangle + 2\langle ij|f_{xc}|mn\rangle$$

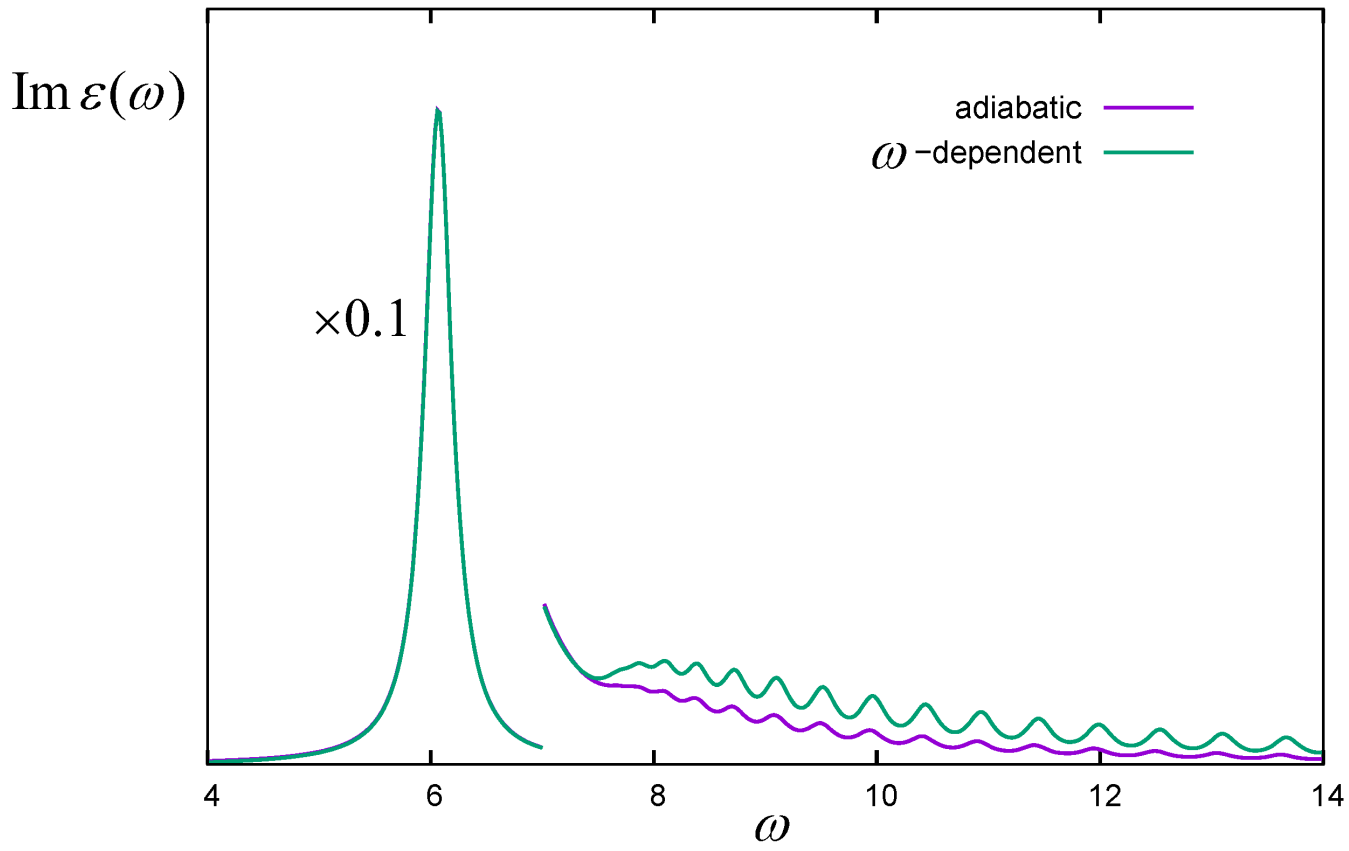
Depends on $W_{\mathbf{GG}'}(\mathbf{q})$

Depends on $f_{xc,\mathbf{GG}'}(\mathbf{q}\to 0,\omega)$

- ►Impossible to reproduce BSE coupling matrix with adiabatic xc
- ►xc needs complex **ω-dependence** for excitonic Rydberg series, and for better spectral shape

Z.-H. Yang, Y. Li, and C. A. Ullrich, J. Chem. Phys. **137**, 014513 (2012)

Beyond the adiabatic approximation (1D model)



$$f_{xc}(x,x',\omega) = \frac{A + B\omega}{\sqrt{(x-x')^2 + \alpha^2}}$$

Botti et al., PRB (2005): LRC with $\alpha + \beta\omega^2$

Summary

► TDDFT is capable of describing excitons in solids with a gap. The main formalism is similar to the BSE, but there are some important differences in the details.

► We now have a number of approximate xc kernels which can produce bound excitons, but none of them is sufficiently accurate (without empirical fitting). More work is needed.

► Generalized TDDFT (i.e., hybrid functionals) may be the best way to go: can be viewed as simplified BSE plus local xc.

► There are many challenges:

- excitons in more complex materials,
- Excitonic Rydberg series
- Biexcitons, trions etc.
- real-time exciton dynamics, including lattice relaxation

Literature on Excitons and TDDFT/MBPT

Textbooks:

H. Haug and S.W. Koch, *Quantum Theory of the Electronic and Optical Properties of Semiconductors* (World Scientific, 2009)
P. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, 2010)
F. Bechstedt, *Many-Body Approach to Electronic Excitations* (Springer, 2015)
R.M. Martin, L. Reining, D.M. Ceperley, *Interacting Electrons: Theory and Computational Approaches* (Cambridge, 2016)

Review Articles:

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C.A. Ullrich and Z.-H. Yang, Topics in Current Chem. **368** (2015)
V. Turkowski, N.U. Din, T.S. Rahman, Computation **5**, 39 (2017)
S. Sharifzadeh, J. Phys.: Cond. Mat. **30**, 153002 (2018)