TDDFT for extended systems II: Excitons

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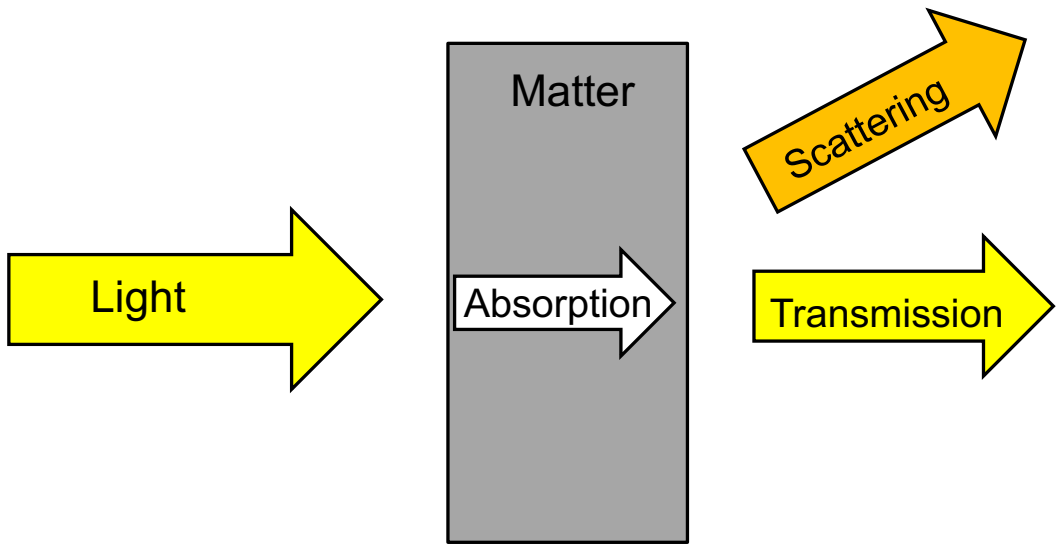
2023 TDDFT School and Workshop
Rutgers University-Newark
July 2, 2023

Outline

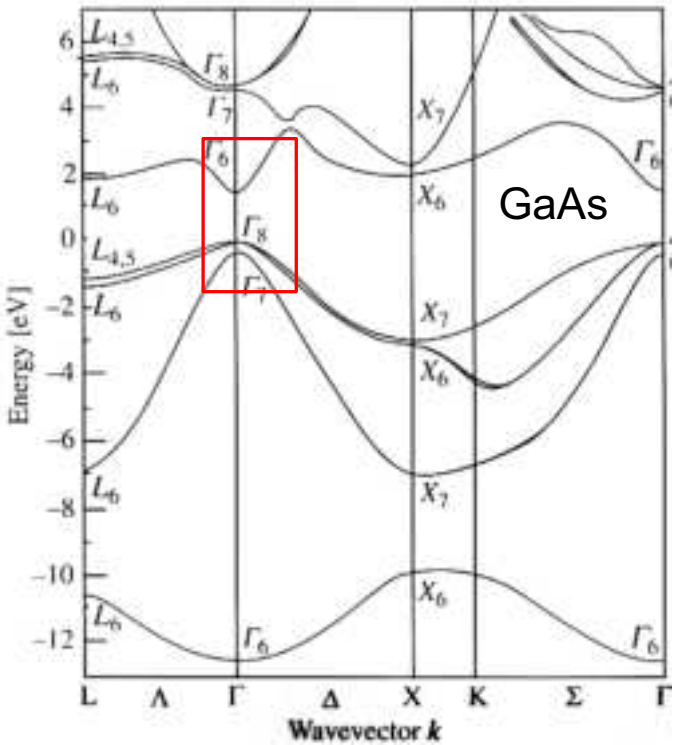
- Introduction to excitons
- TDDFT for periodic systems
- Optical spectra and exciton binding energies
- xc functionals for excitons
- Real-time TDDFT for solids
- Summary

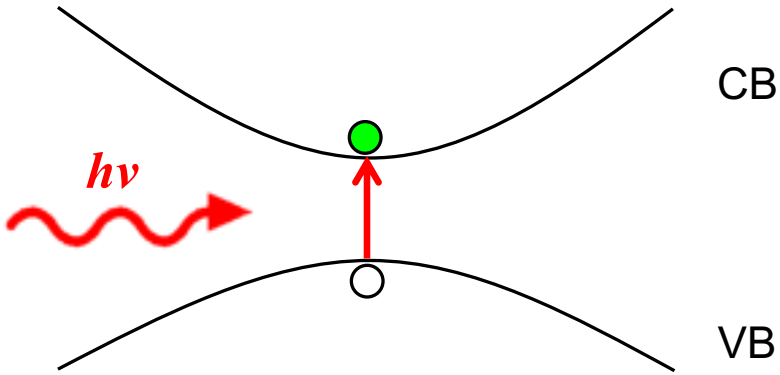
Absorption of light in a solid



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

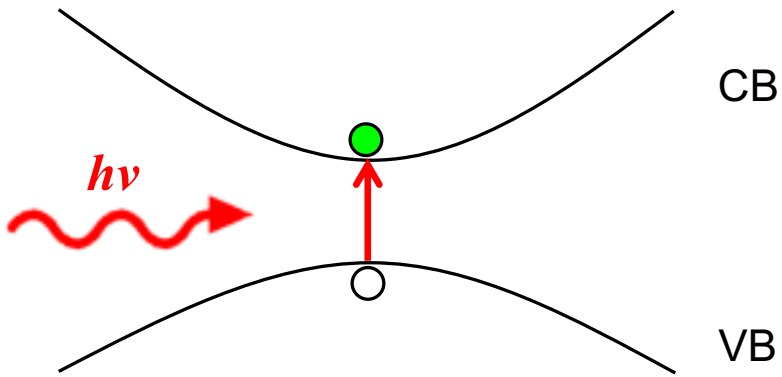
Absorption of light across the band gap





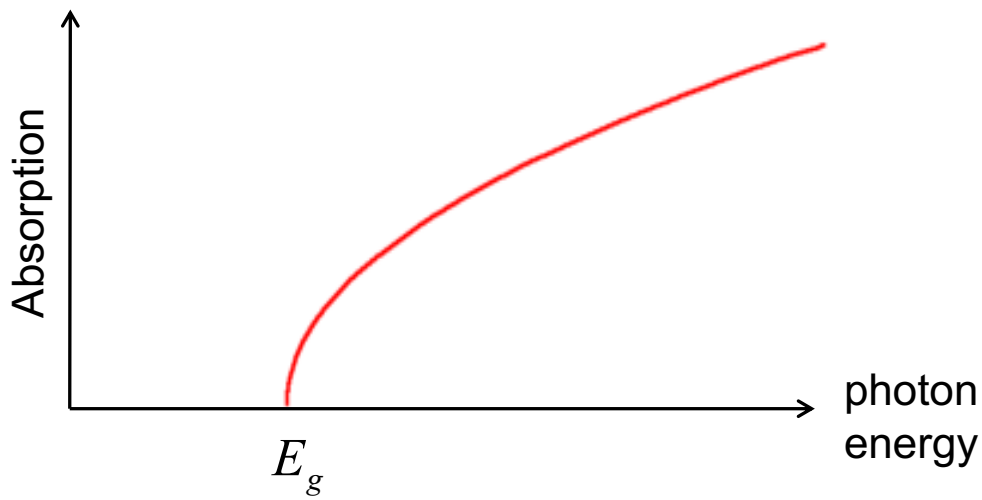
- Light comes in with photon energy at least as large as the band gap
- Photon gets absorbed, promotes electron across the gap, leaving a hole behind

Absorption spectra of insulators/semiconductors



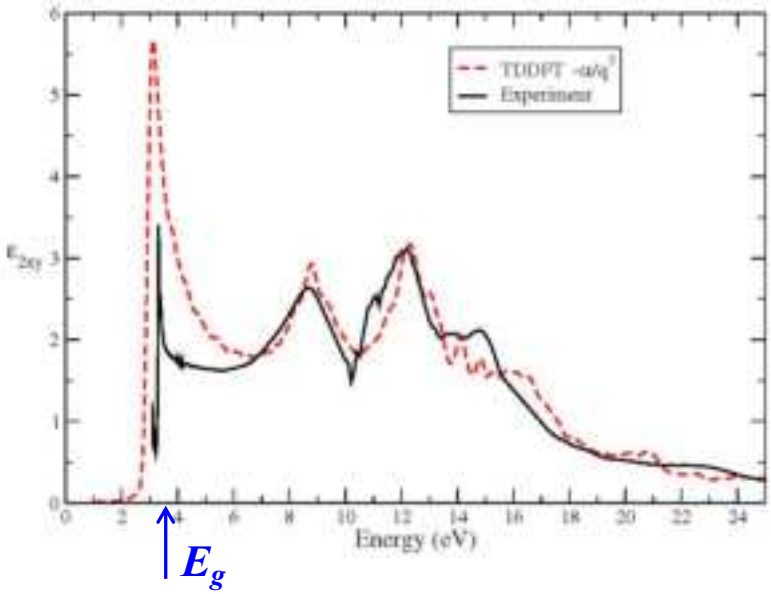
see John H. Davies *"The Physics of low-dimensional semiconductors"* Chapter 8

will produce an absorption spectrum like this (in 3D):



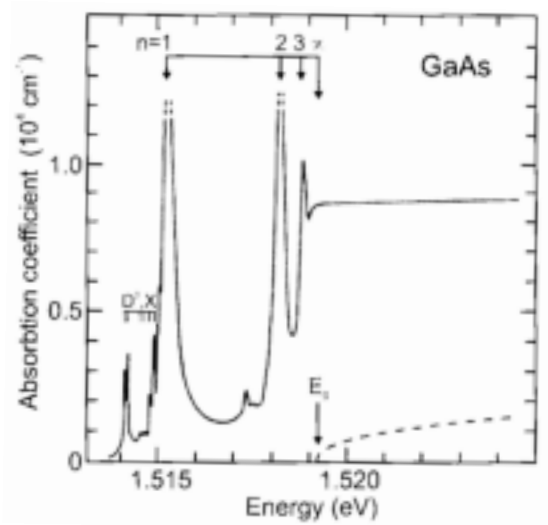
Absorption spectra of insulators/semiconductors

ZnO



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

GaAs

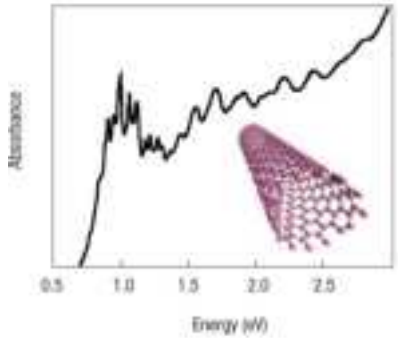


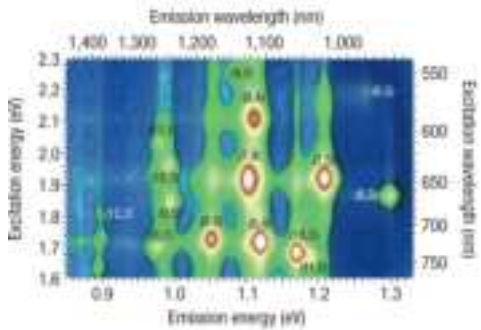
R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

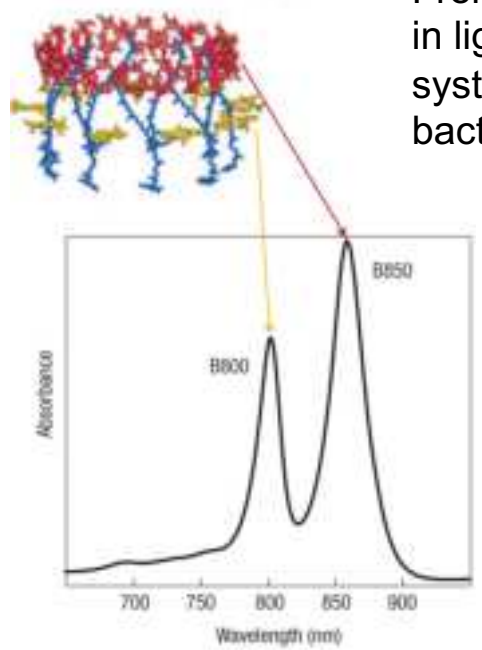
In the experiment, one finds sharp peaks at the absorption threshold…
In fact, there are peaks below the band gap energy: Excitons.

Excitons in nanoscale systems

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

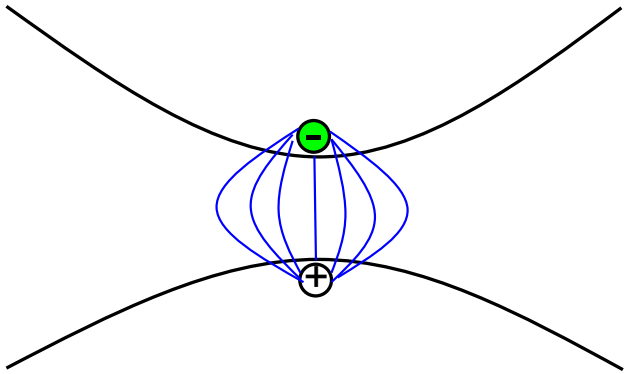






Frenkel excitons in light-harvesting systems: purple bacteria

What is an exciton?



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

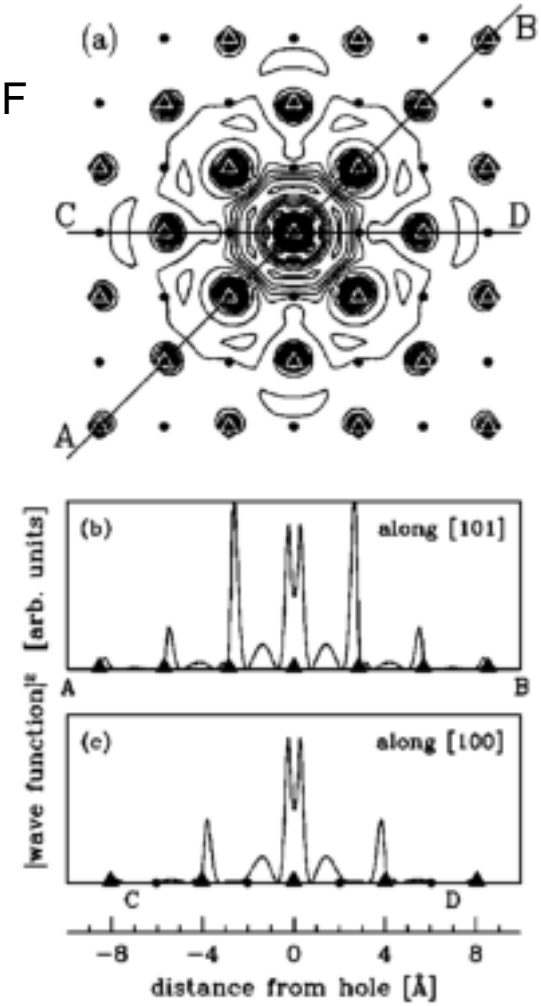
►This gain in (mostly electrostatic) energy can lower the onset of absorption and change the spectral strength.

Excitons are bound electron-hole pairs.

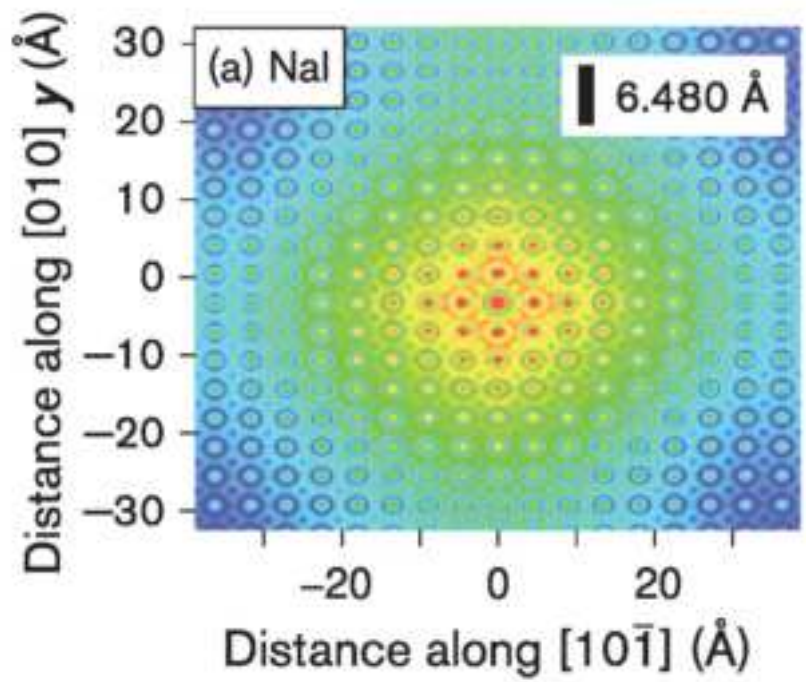
C. A. Ullrich and Zeng-hui Yang, Topics in Current Chemistry **368**, 185 (2015)

Exciton wave functions in 3D solids

LiF

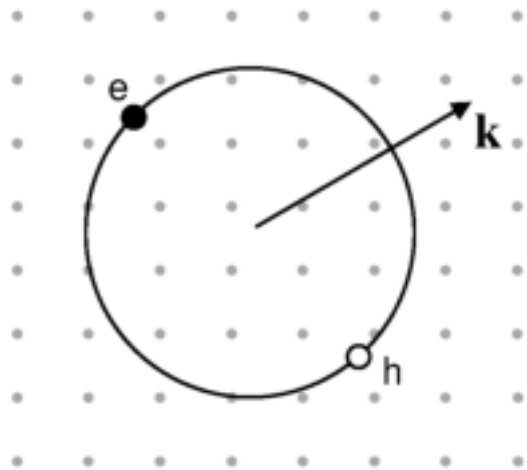


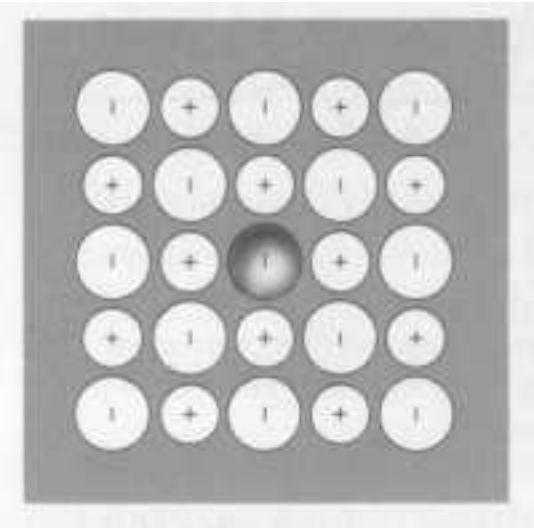
Rohlfing and Louie,
PRB **62**, 4927 (2000)



Erhart, Schleife, Sadigh and
Aberg, PRB **89**, 075132 (2014)

Elementary view of Excitons





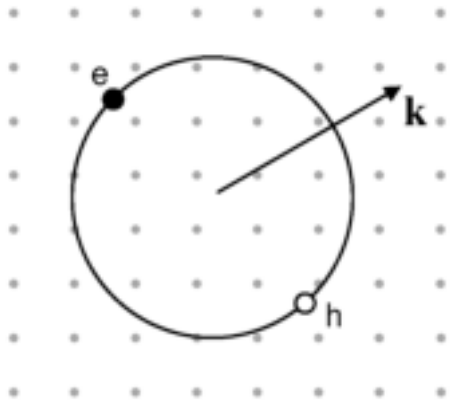
Mott-Wannier exciton:
weakly bound, delocalized over many lattice constants

►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

Excitons: the Wannier equation

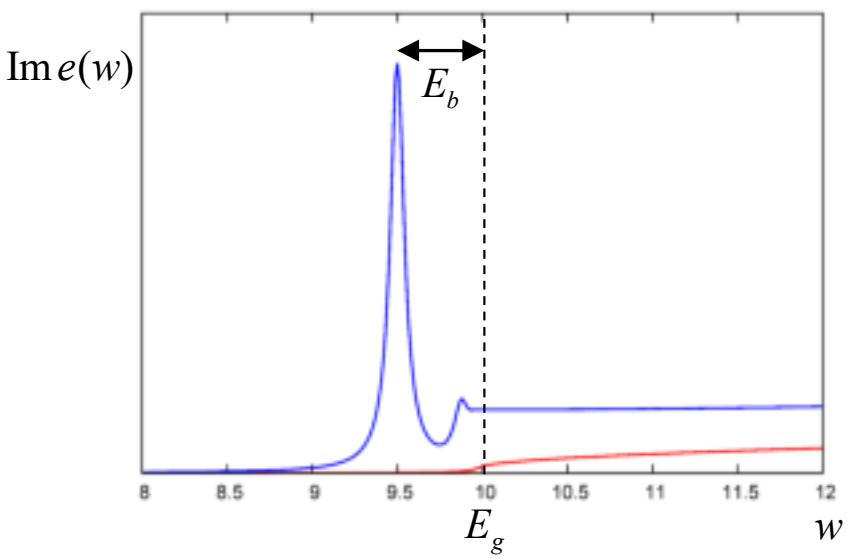


Derivation of Wannier eq. from many-body theory:
Sham and Rice, Phys. Rev. **144**, 708 (1966)

$$\left[-\frac{\hbar^2\nabla^2}{2m_{eh}}-\frac{e^{*2}}{4\pi\varepsilon_0 r}\right]\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$$\frac{1}{m_{eh}}=\frac{1}{m_e^*}+\frac{1}{m_h^*}$$

$$E_n^*=-\frac{m_{eh}}{2\hbar^2 n^2}\left(\frac{e^{*2}}{4\pi\varepsilon_0}\right)^2$$



Exciton binding energy for GaAs:

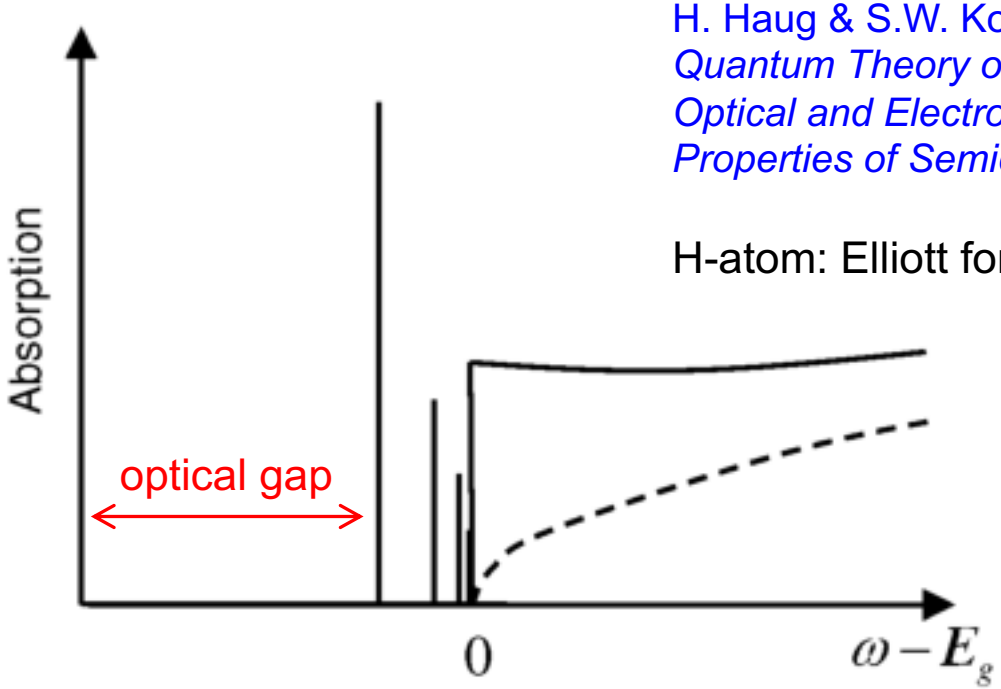
$$E_0^*=4.75\ meV$$

Experiment: $E_0^*=3.3\ meV$

Excitonic features in the absorption spectrum

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

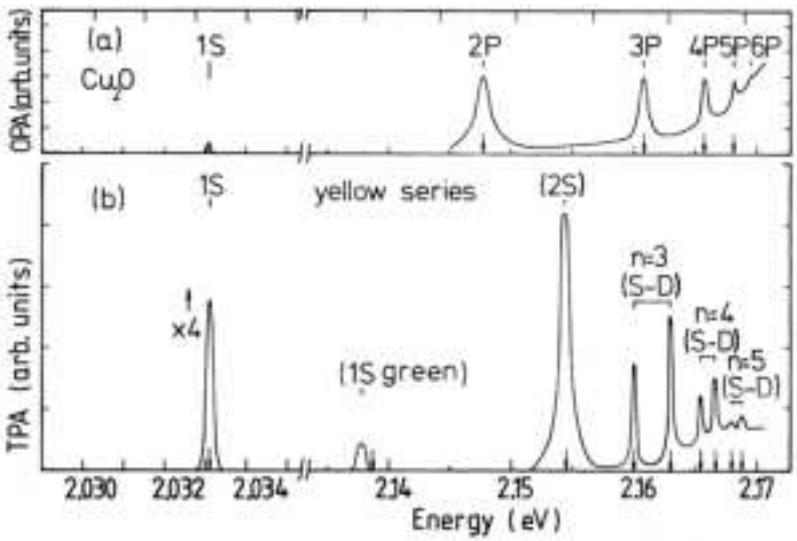
H-atom: Elliott formula



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

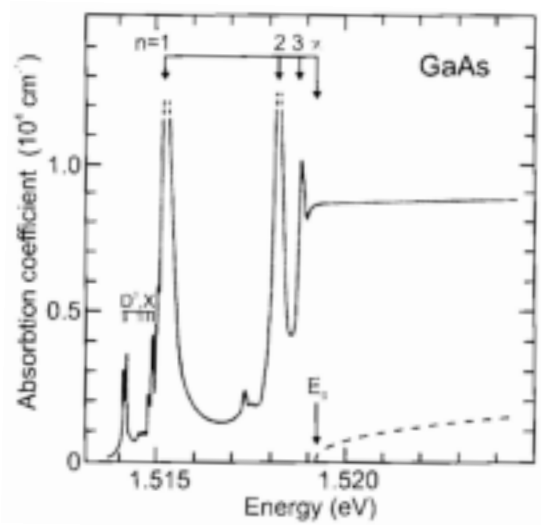
Wannier equation and excitonic Rydberg Series

Cu_2O



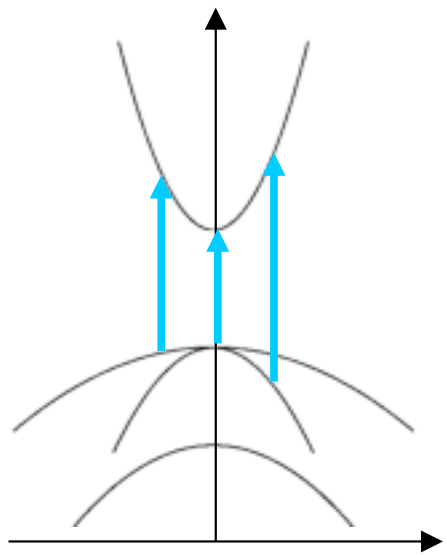
R.J. Uihlein, D. Frohlich, and R. Kenklies, PRB **23**, 2731 (1981)

GaAs



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

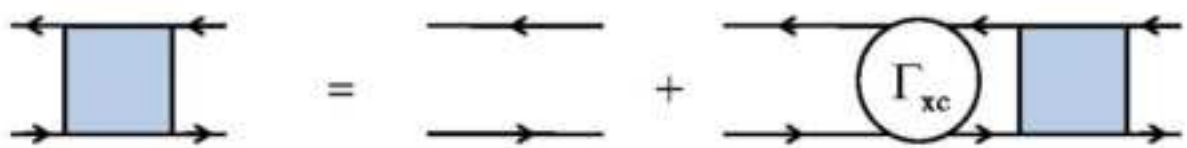
Optical excitations in bulk Insulators: theory



Optical transitions in insulators are challenging for TDDFT:

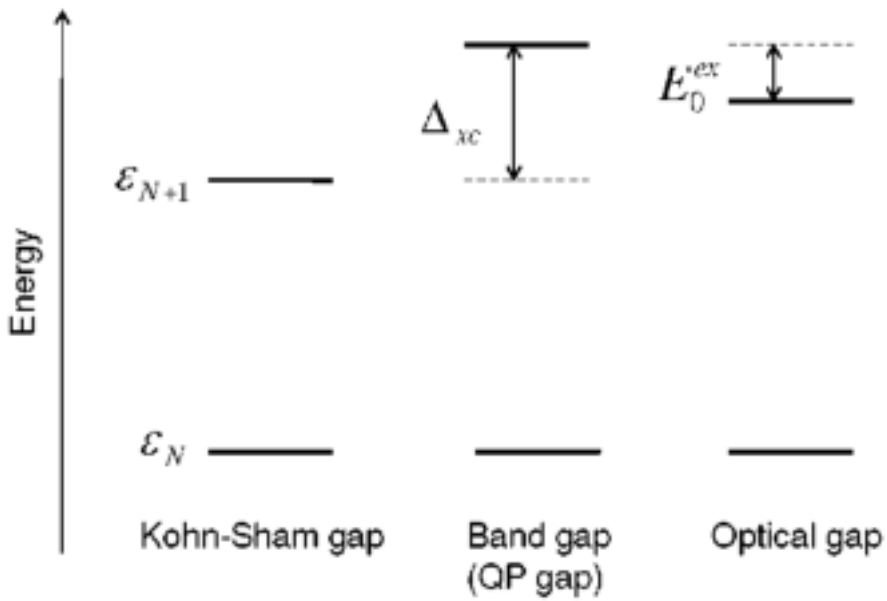
- **band gap opening**
- **excitons**

Standard approach:
Bethe-Salpeter equation (combined with GW)



►Gives good results, but computationally expensive
►Want to use TDDFT instead!

Insulators: three different gaps

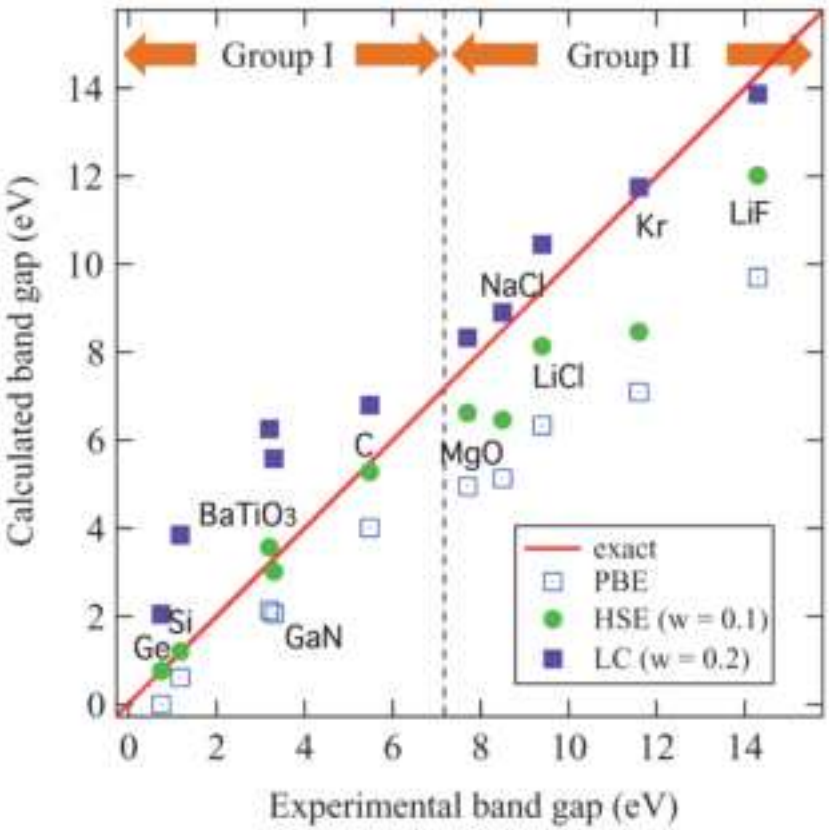


The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

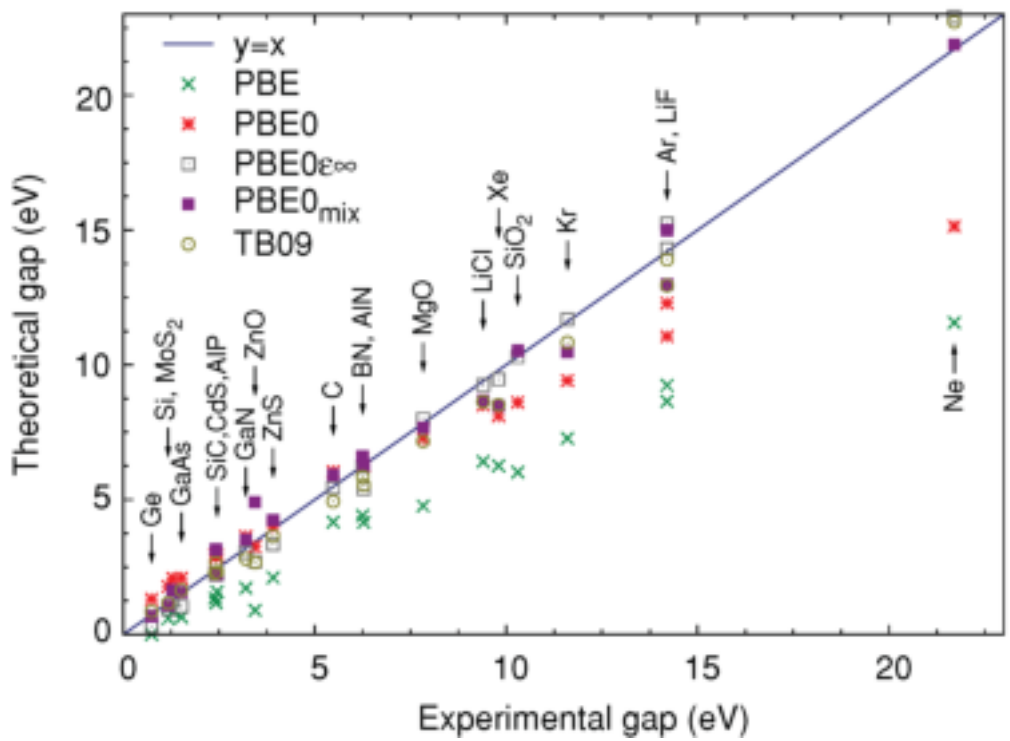
Band gap: $$E_g = E_{g,KS} + \Delta_{xc}$$

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

Hybrid functionals for the band gap



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



Marques, Vidal, Oliveira, Reining & Botti, PRB **83**, 035119 (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

* thanks to Matteo Gatti

Excitons with TDDFT: three equivalent approaches

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

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

3. Via real-time propagation
(can consider ultrafast or nonlinear regime)

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

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

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

Fourier transform:

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

$$\boxed{\begin{aligned}\chi_{\mathbf{GG}'}(\mathbf{q},\omega)&=\chi_{s\mathbf{GG}'}(\mathbf{q},\omega)+\sum_{\mathbf{G}_1\mathbf{G}_2}\chi_{s\mathbf{GG}_1}(\mathbf{q},\omega)\\&\quad\times\left\{V_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1\mathbf{G}_2}+f_{xc\mathbf{G}_1\mathbf{G}_2}(\mathbf{q},\omega)\right\}\chi_{\mathbf{G}_2\mathbf{G}'}(\mathbf{q},\omega)\end{aligned}}$$

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

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:

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

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

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

The connection to optics is via the refractive index:

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

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

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

see
Yu and Cardona
The Physics of Semiconductors

The macroscopic dielectric function

For cubic symmetry, one can prove that

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

Adler 1962
Wiser 1963

$\varepsilon_{\mathbf{GG}'}(\mathbf{q},\omega)$: 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,

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

The macroscopic dielectric function

From this, one obtains

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

Notice a subtle, but very important point:
we use a modified response function $\bar{\chi}_{\mathbf{GG}'}(\mathbf{q},\omega)$:

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

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**.

Density eigenmode:
set

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

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

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):

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

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

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

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

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

Direct calculation of exciton binding energies

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

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

Tamm-Dancoff Approximation (TDA)

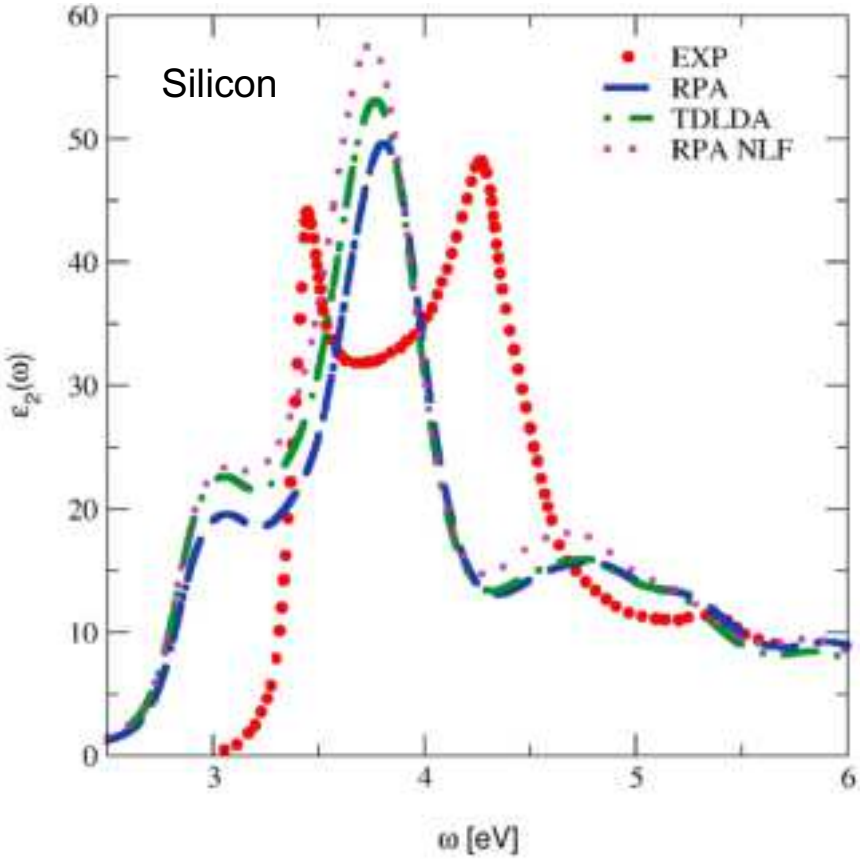
Using time-reversal symmetry, Full Casida eq. can be transformed into

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

Sander, Maggio & Kresse, PRB 92, 045209 (2015)

More expensive than calculating Im ε(ω) via Dyson eqn, but can resolve very small exciton binding energies

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

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

TDDFT requires the following matrix elements as input:

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

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

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

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 ε_{KS} Æ ε_{qp}

"excitonic", accounts for electron-hole interaction

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

See also: Cavo, Berger & Romaniello, PRB **101**, 115109 (2020)
Di Sabatino, Berger & Romaiello, Faraday Discuss. **224**, 467 (2020)

Long-range xc kernels for solids

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

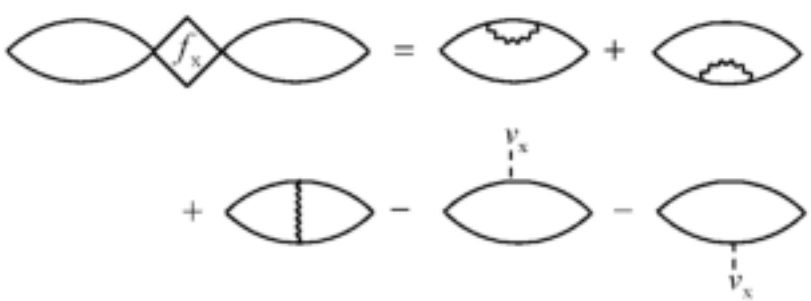
$$f^{LRC}_{xc,\mathbf{GG'}}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q}+\mathbf{G}|^2}\delta_{\mathbf{GG'}}$$

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

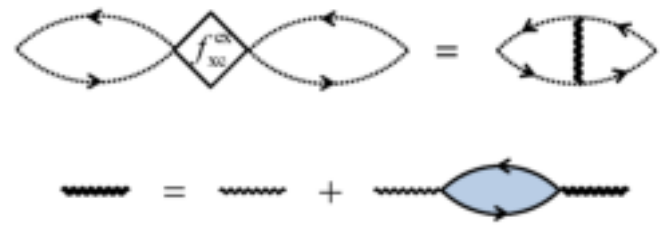
$$f^{boot}_{xc,\mathbf{GG'}}(\mathbf{q},\omega) = \frac{\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)}{\chi_{s00}(\mathbf{q},0)}$$

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

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



exact exchange

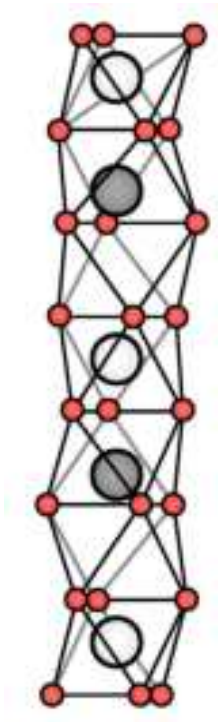


"nanoquanta" kernel, reverse-engineered from BSE
(L. Reining et al., 2002)

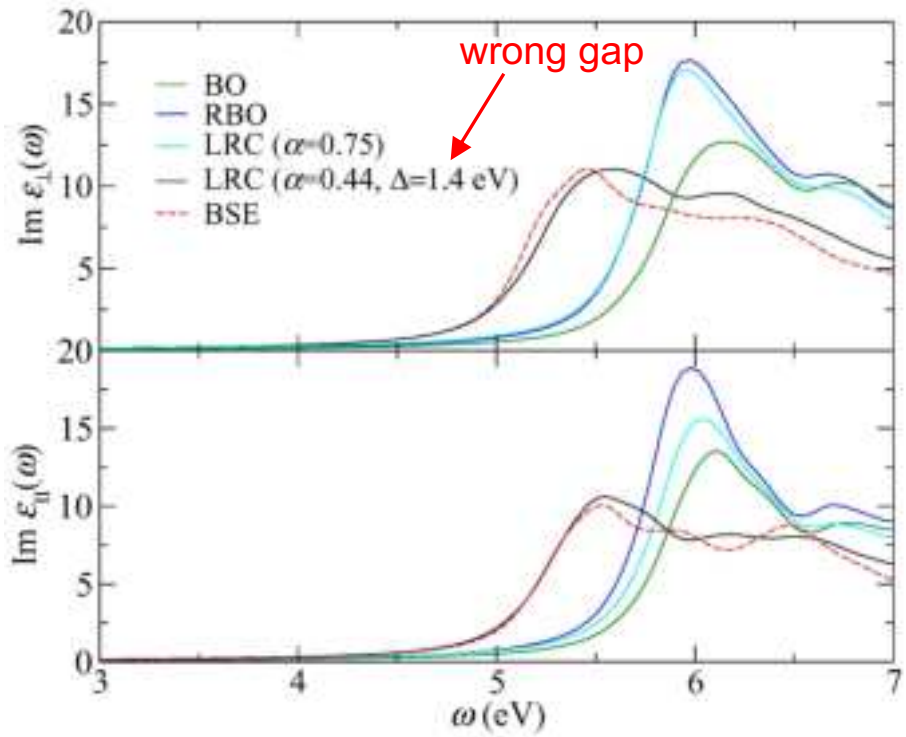
Excitons: which xc kernels to use?

- **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)
  Byun, Sun & Ullrich, Electron. Struct. **2**, 023002 (2020)
- **Jellium with a gap:**
  Trevisanutto *et al.,* PRB **87**, 205143 (2013)
- **Current-TDDFT:**
  Berger, PRL **115**, 137402 (2015)
  Cavo, Berger & Romaniello, PRB **101**, 115109 (2020)
- **Hybrid functionals:**
  Refaely-Abramson *et al.*, PRB **92**, 081204 (2015)
  Wing *et al.*, PRMat **3**, 064603 (2019)
  Tal, Liu, Kresse & Pasquarello, PRREs **2**, 032019 (2020)
  Zivkovic, de Leeuw, Searle & Bernasconi, JPC C **124**, 24995 (2020)
  Sun, Li & Liang, PCCP **21**, 16296 (2021)

The family of LRC/Bootstrap xc kernels



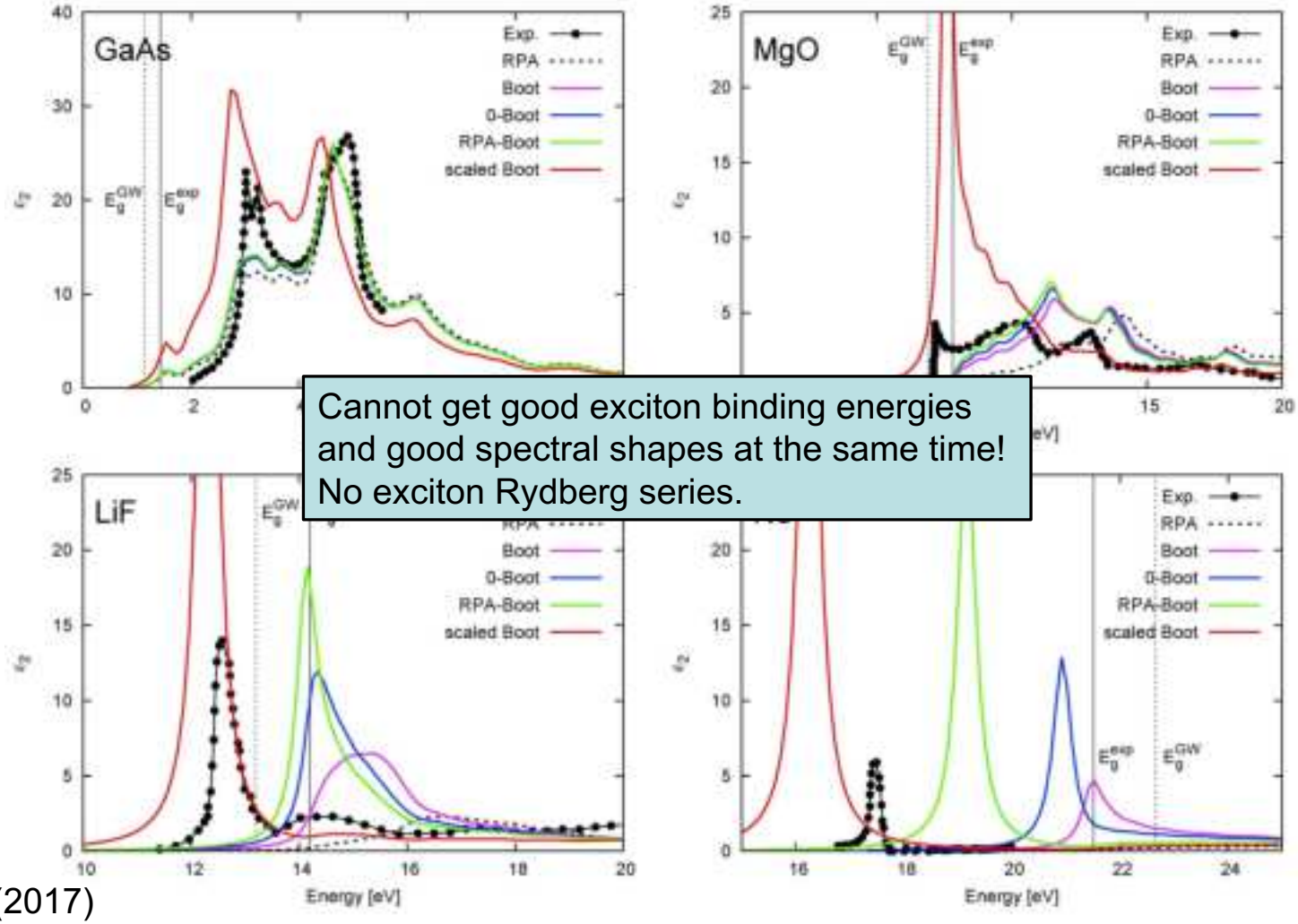
$LiNbO_3$



With some tricks, LRC kernel can produce quite accurate optical spectra!

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

Optical spectra with LRC-type kernels



Cannot get good exciton binding energies and good spectral shapes at the same time! No exciton Rydberg series.

Byun and Ullrich, PRB **95**, 205136 (2017)

TDDFT vs MBPT

$$\sum_{v'c'\mathbf{k}'}\left[\delta_{v\mathbf{k},v'\mathbf{k}'}\delta_{c\mathbf{k},c'\mathbf{k}'}\omega_{vc\mathbf{k}}^2+2\sqrt{\omega_{cv\mathbf{k}}\omega_{c'v'\mathbf{k}'}}\;F_{vc\mathbf{k},v'c'\mathbf{k}'}^{Hxc}\right]Z_{v'c'\mathbf{k}'}=\Omega_n^2 Z_{vc\mathbf{k}}$$

TDDFT coupling matrix:

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

Bethe-Salpeter equation (BSE) coupling matrix:

$$F_{vc\mathbf{k},v'c'\mathbf{k}'}^{xc}=\sum_{\mathbf{GG}'}g_{\mathbf{GG}'}(\mathbf{q})\left\langle c\mathbf{k}\left|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\right|c'\mathbf{k}'\right\rangle\left\langle v'\mathbf{k}'\left|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}\right|v\mathbf{k}\right\rangle\delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'}$$

screened Coulomb interaction

Screened exact exchange (SXX)

BSE: $$g_{\mathbf{GG'}}(\mathbf{q}) = -4\pi \frac{\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q}, \omega = 0)}{|\mathbf{q} + \mathbf{G'}|^2}$$ ← **full dielectric matrix**

TDHF: $$g_{\mathbf{GG'}}(\mathbf{q}) = -4\pi \frac{1}{|\mathbf{q} + \mathbf{G'}|^2} \delta_{\mathbf{GG'}}$$ **unscreened**

SXX: $$g_{\mathbf{GG'}}(\mathbf{q}) = -4\pi \frac{\gamma}{|\mathbf{q} + \mathbf{G'}|^2} \delta_{\mathbf{GG'}}$$ **simple screening parameter**

$$\gamma = \varepsilon^{-1}_{00}(0,0)$$ **Calculated with RPA**

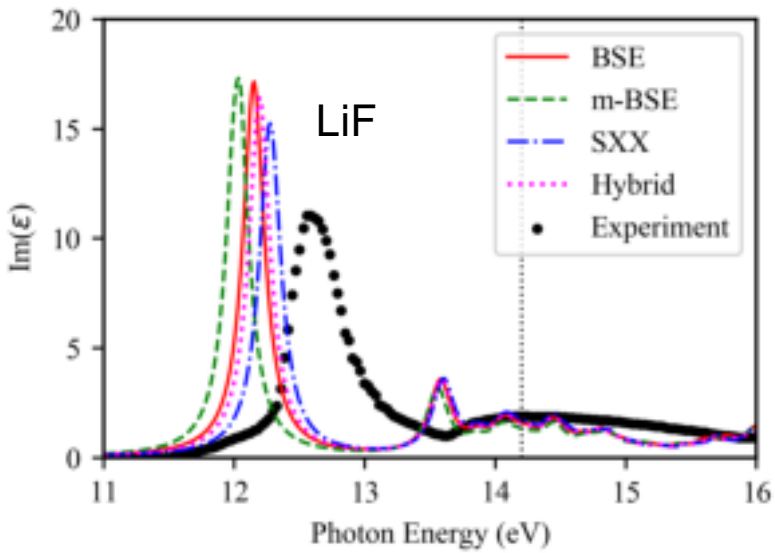
Z.-h. Yang, F. Sottile, and C.A. Ullrich, PRB **92**, 035202 (2015)

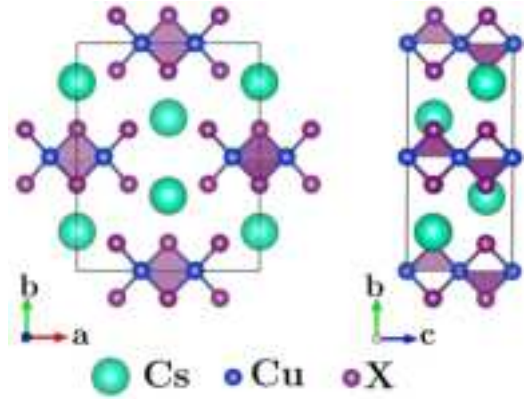
Dielectrically screened hybrid functionals

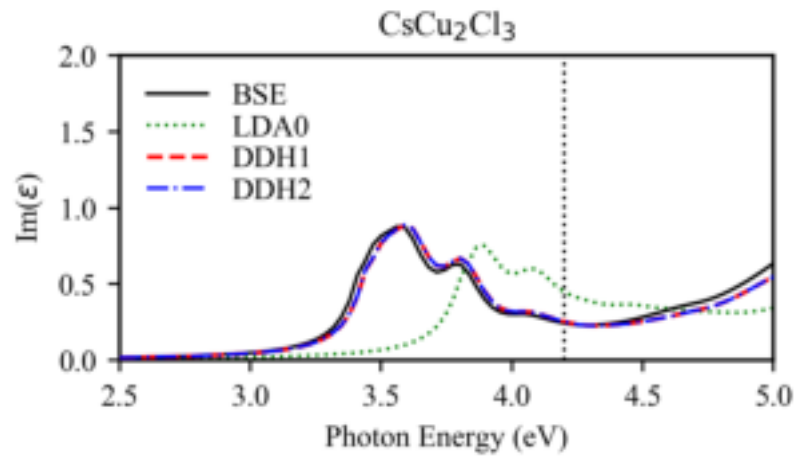
Sun, Yang, and Ullrich, Phys. Rev. Research **2**, 013091 (2020)
Sun and Ullrich, Phys. Rev. Materials **4**, 095402 (2020)

$$K_{xc}^{hybrid} = \gamma K_x^{XX} + (1-\gamma) K_{xc}^{ALDA}$$

$$\gamma = \varepsilon_{00}^{-1}(0,0)$$



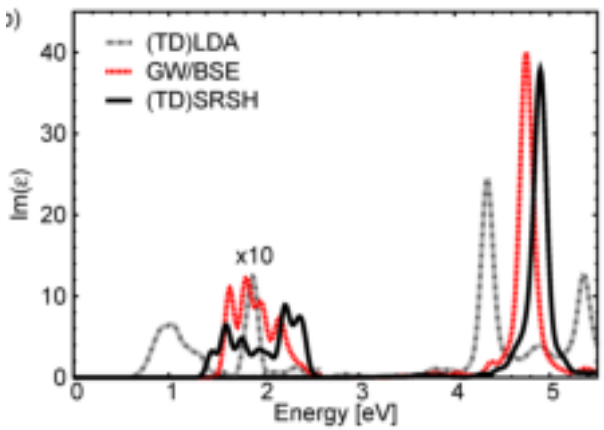




Very close to BSE, but 1-2 orders of magnitude faster.

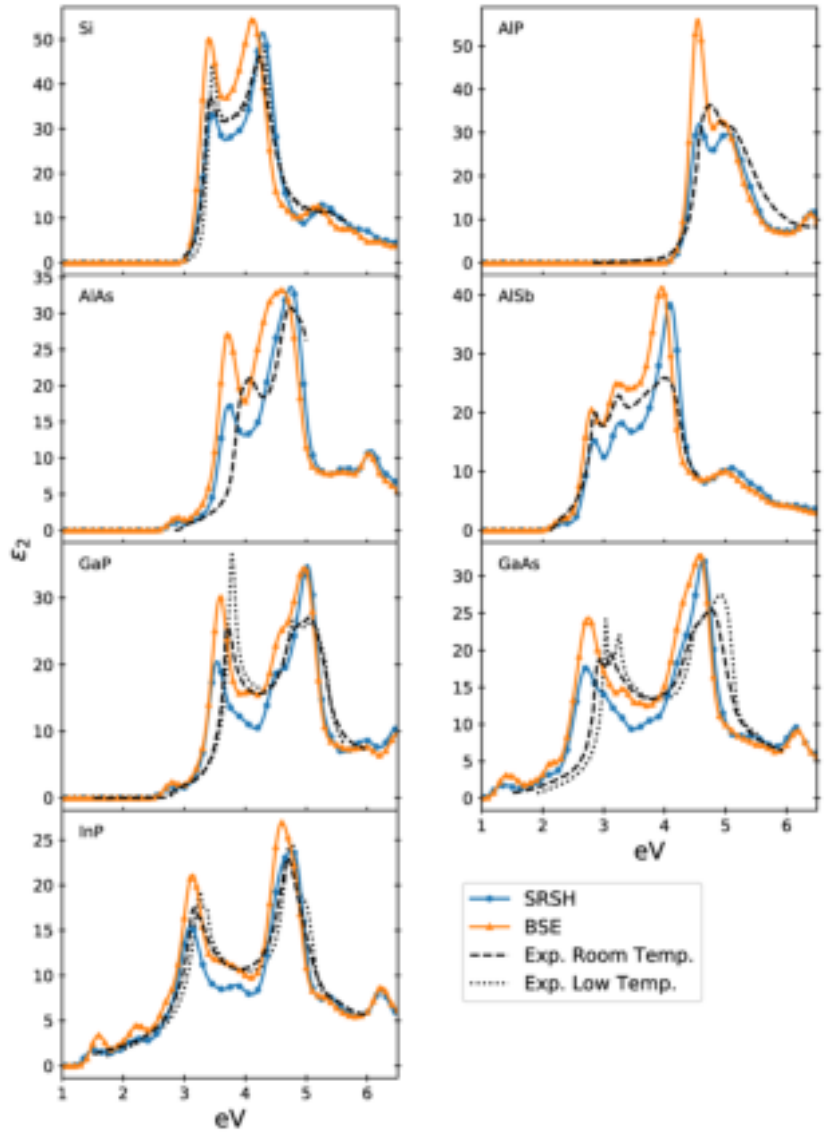
Optical spectra with screened range-separated hybrid

pentacene

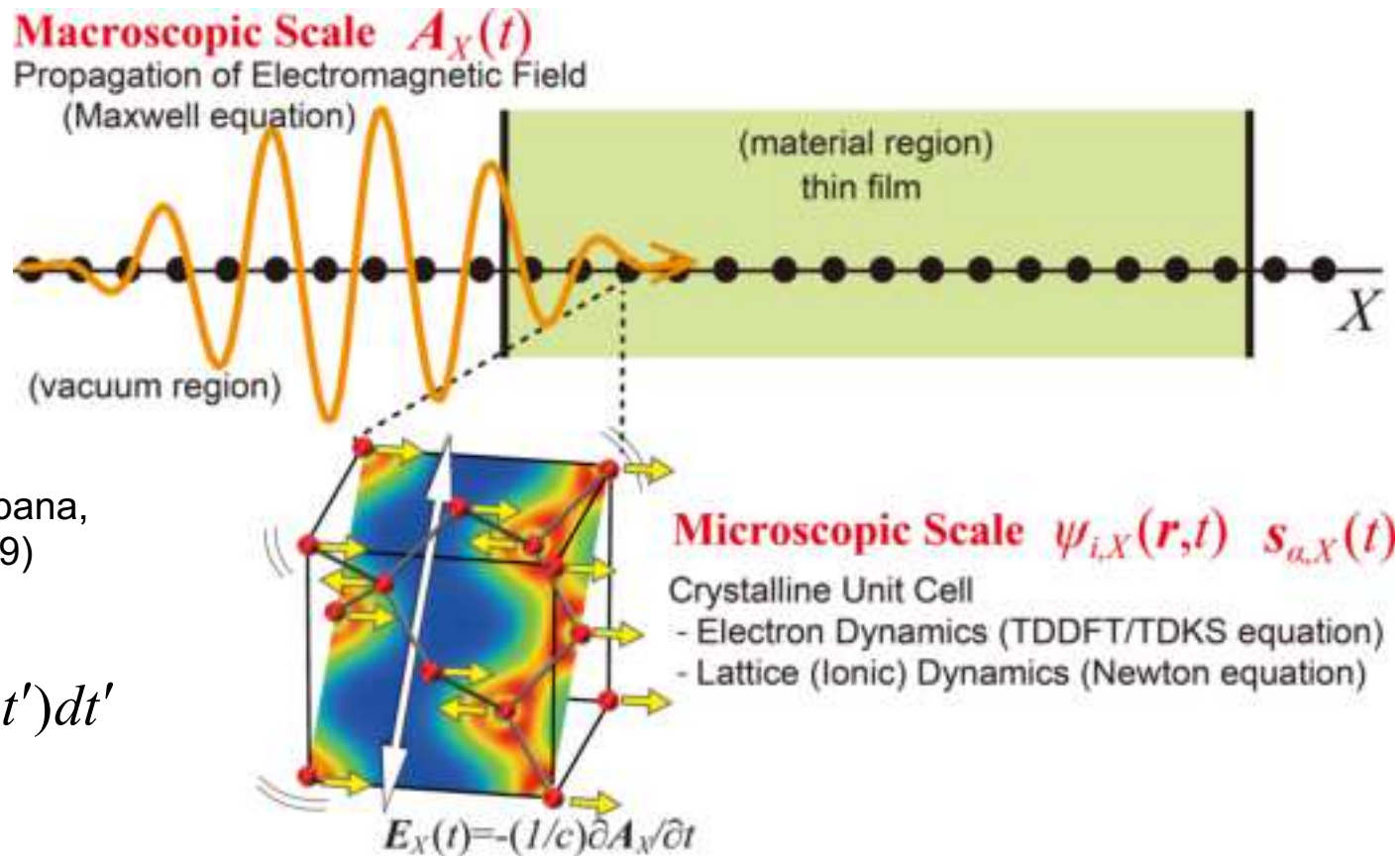


Refaely-Abramson, Jain, Sharifzadeh, Neaton & Kronik, PRB **92**, 081204 (2015)

Wing, Haber, Noff, Barker, Egger, Ramasubramaniam, Louie, Neaton & Kronik, PRMat **3**, 064603 (2019)



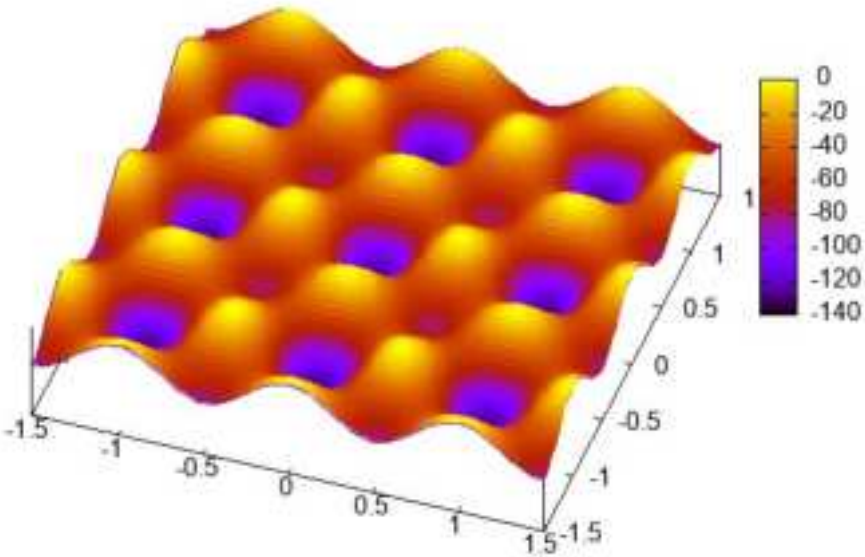
Real-time electron dynamics in solids

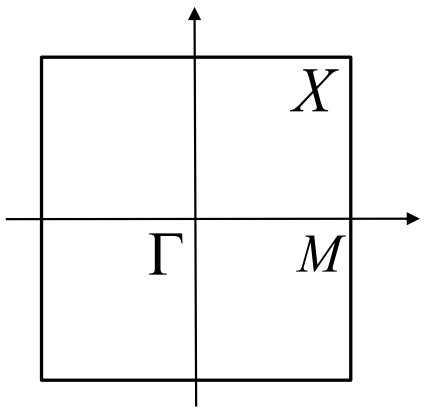


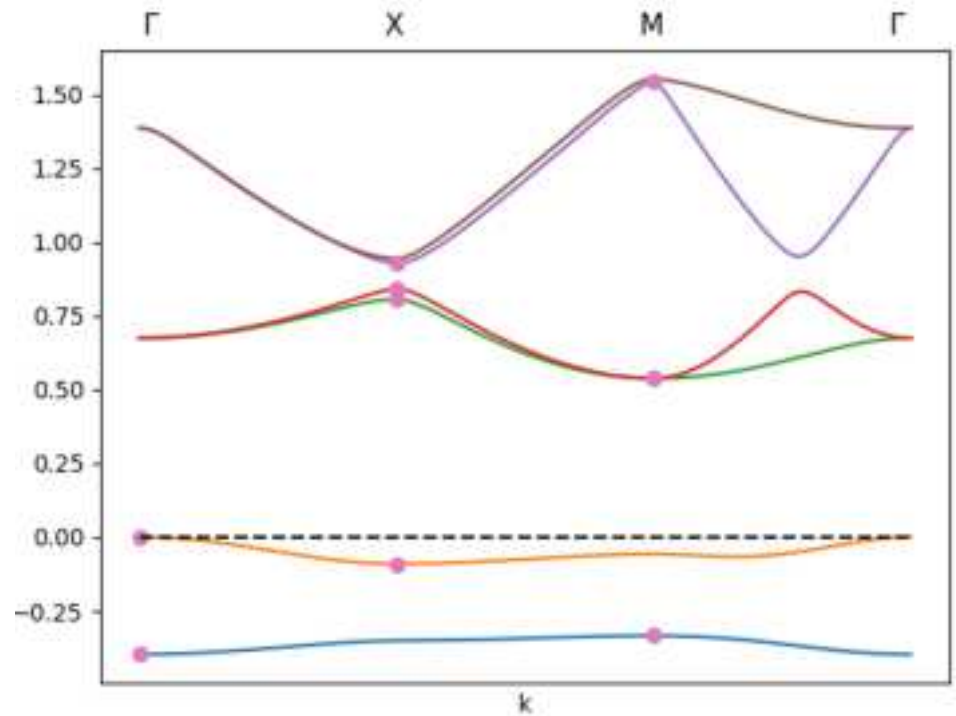
A. Yamada and K. Yabana,
PRB **99**, 245103 (2019)

$$\mathbf{A}_{laser}(t) = -c\int_0^t \mathbf{E}(t')dt'$$

Equivalence of LR- and RT-TDDFT for optical spectra







- 4 electrons per unit cell
- two lowest valence bands are occupied
- use simple plane-wave basis

Equivalence of LR- and RT-TDDFT for optical spectra

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t)=\left[\frac{1}{2}\left(\frac{\nabla}{i}+\mathbf{A}(t)\right)^2+V_{eff}(\mathbf{r},t)\right]\varphi_j(\mathbf{r},t)$$

"delta-kick": $V(\mathbf{r},t)=\mathbf{E}_0\mathbf{r}\delta(t-t_0) \Longrightarrow \mathbf{A}(t)=\mathbf{E}_0\theta(t-t_0)$

Calculate the time-dependent dipole moment:

$$\mathbf{d}(t)=\int_{cell}\mathbf{r}n(\mathbf{r},t)d\mathbf{r}$$

$$=\int_{cell}d\mathbf{r}\sum_{\mathbf{k}}\sum_{i}u^*_{i\mathbf{k}}(\mathbf{r},t)\mathbf{r}u_{i\mathbf{k}}(\mathbf{r},t)$$

expand time-dependent Bloch fcts:

$$u(\mathbf{r},t)=\sum_n\xi(t)u^{(0)}_{n\mathbf{k}}(\mathbf{r})$$

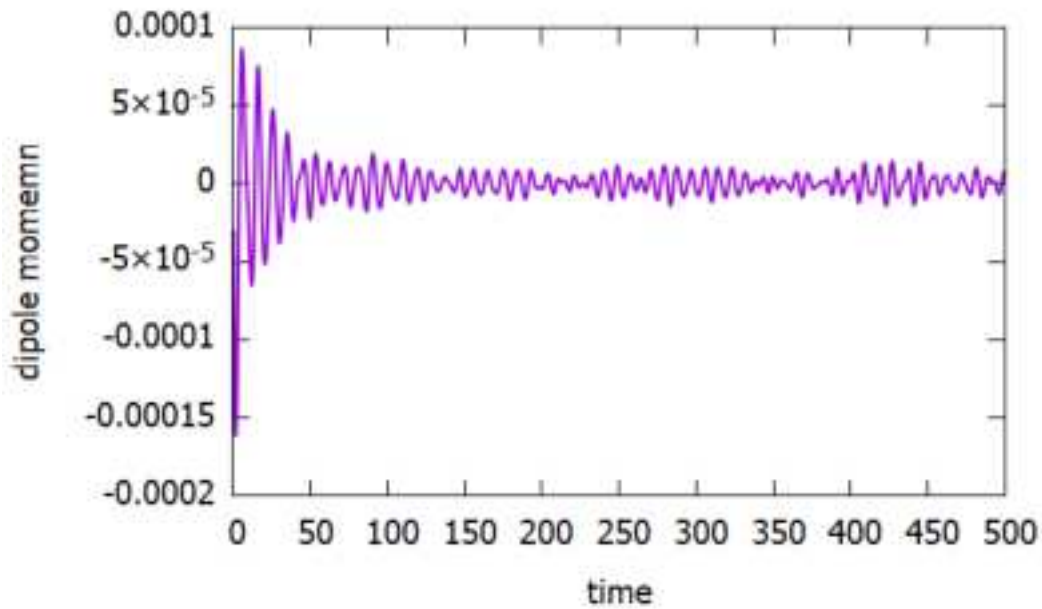
ill defined for periodic solids!

Equivalence of LR- and RT-TDDFT for optical spectra

dipole matrix elements:

$$\mu_{nn'\mathbf{k}} = \int_{cell} d\mathbf{r} u_{n\mathbf{k}}^{(0)*}(\mathbf{r})\mathbf{r}u_{n\mathbf{k}}^{(0)}(\mathbf{r}) = \frac{\int d\mathbf{r}\, u_{n\mathbf{k}}^{(0)*}(\mathbf{r})\left(i\nabla - \mathbf{k}\right)u_{n\mathbf{k}}^{(0)}(\mathbf{r})}{E_{n\mathbf{k}} - E_{n'\mathbf{k}}}$$

well behaved!



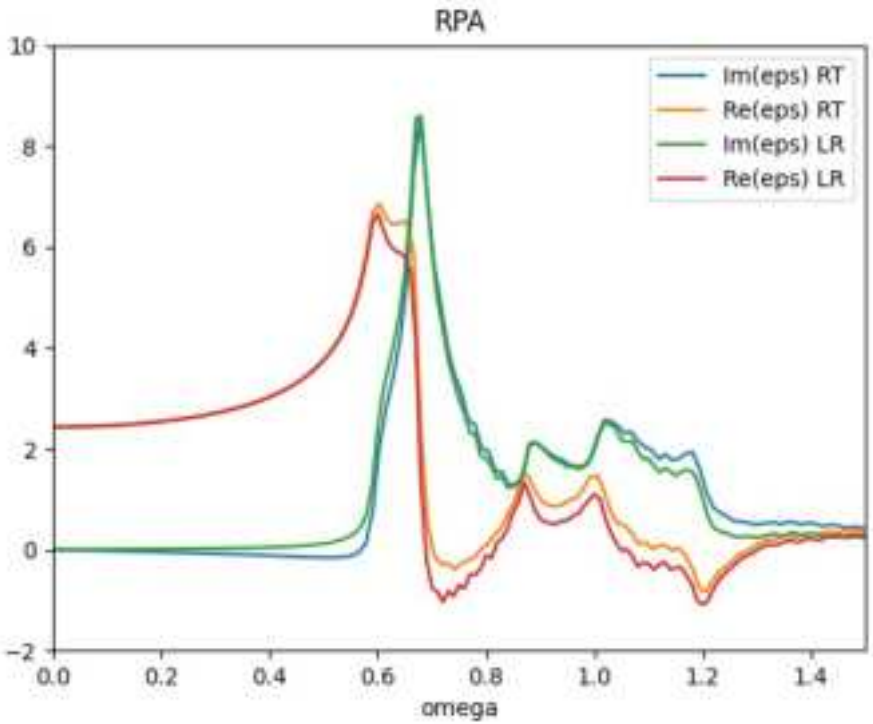
Fourier transform:

$$\mathbf{d}(\omega) = \int dt\, \mathbf{d}(t)e^{-i\eta t}e^{i\omega t}$$

Dynamic polarizability: $\alpha(\omega) = \dfrac{d(\omega)}{E_0}$

T. Sander and G. Kresse, JCP **146**, 064110 (2017)

Equivalence of LR- and RT-TDDFT for optical spectra



LR TDDFT:

$$\varepsilon_{mac}^{RPA}(\omega) = 1 - \lim_{q \to 0} v_{\mathbf{q}} \chi_{00}(\mathbf{q}, \omega)$$

RT TDDFT:

$$\varepsilon_{mac}^{RPA}(\omega) = 1 - 4\pi\alpha(\omega)$$

How to get excitons with this?
See my talk on Wednesday morning!

Real-time electron dynamics in solids: codes

- Ultrafast magnetization dynamics, femtomagnetism
  ELK (Full-potential LAPW)

  Krieger, Dewhurst, Elliott, Sharma & Gross, JCTC. **11**, 4870 (2015)

- High-harmonic generation, magnons
  Octopus (real-space grid)

  N. Tancogne-Dejean, O.D. Mücke, F.X. Kärtner, & A. Rubio, PRL **118**, 087403 (2017)

- Core-level spectroscopy.
  SIESTA (LCAO)

  Pemmaraju, Vila, Kas, Sato, Rehr, Yabana & Prendergast, Comput. Phys. Comm. **226**, 30 (2018)

- Ultrafast nonlinear spectroscopy, coherent phonons.
  Salmon (real-space grid, norm-conserving PP)

  Noda, Ishimura, Nobusada, Yabana & Boku, J. Comput. Phys. **265,** 145 (2014)

- Stopping power of materials under ion impact.
  Qb@ll, INQ (plane waves)

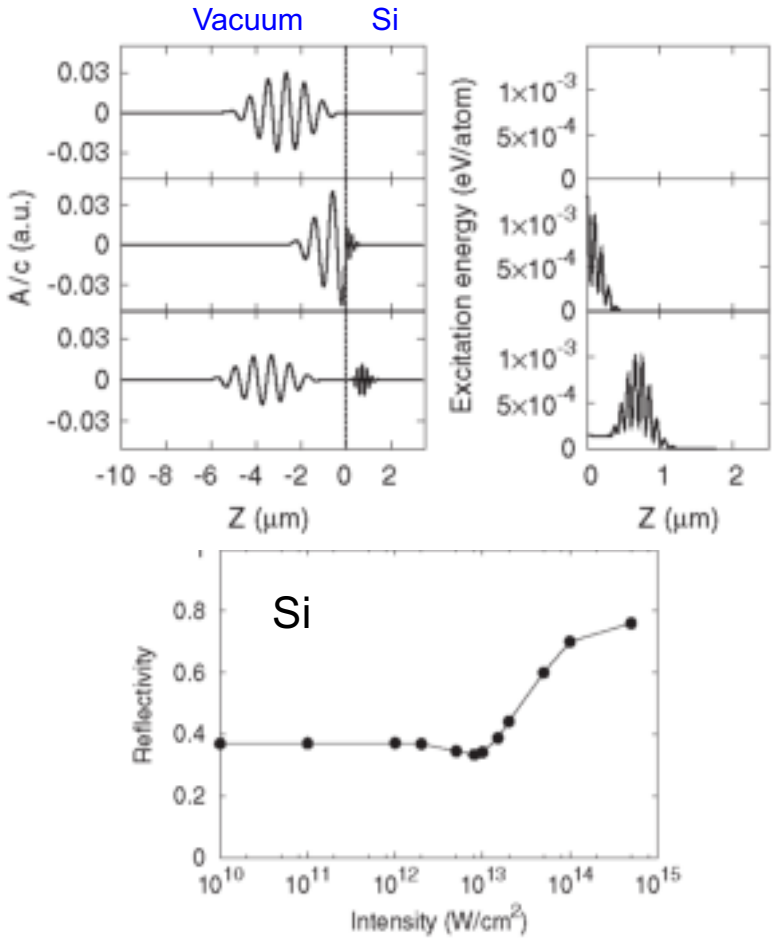
  Schleife, Kanai & Correa, Phys. Rev. B **91**, 014306 (2015)
  Andrade et al. JCTC 17, 7447 (2021)

C. Draxl (2021)

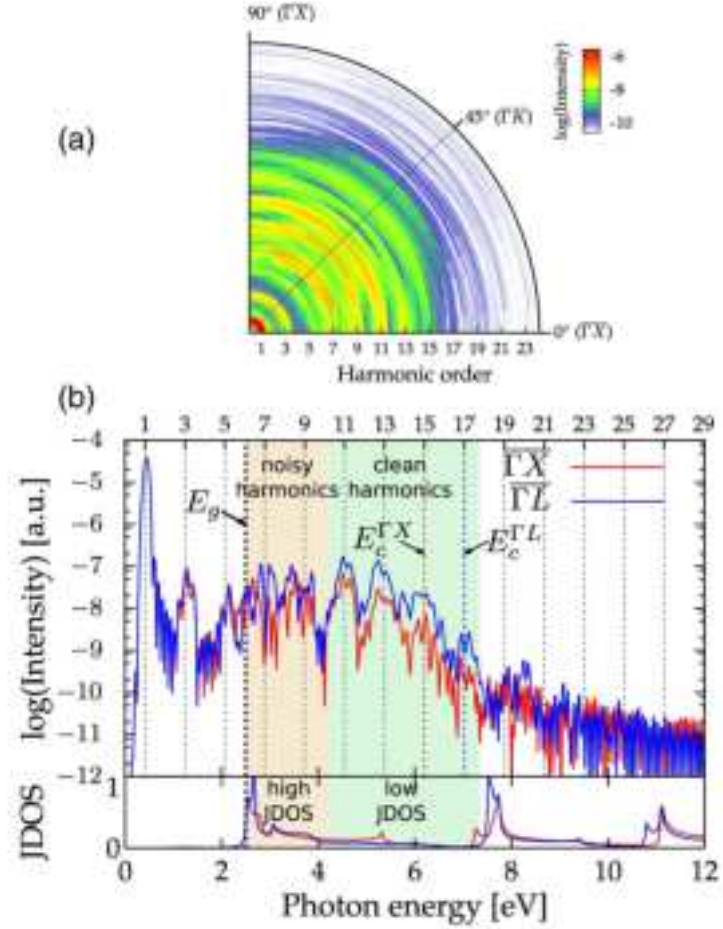
B. Wong (2023)

...and there are more.....

RT-TDDFT for periodic solids: nonlinear effects

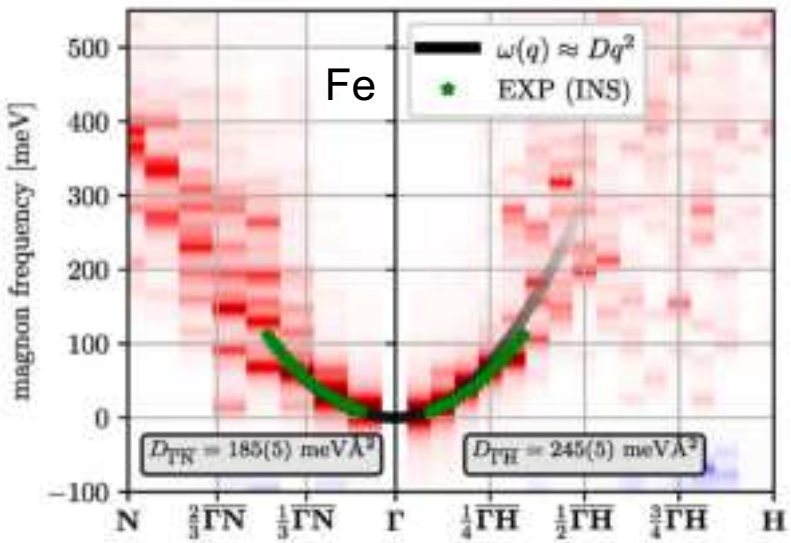


Dielectric breakdown
Yabana et al., PRB **85**, 045134 (2012)



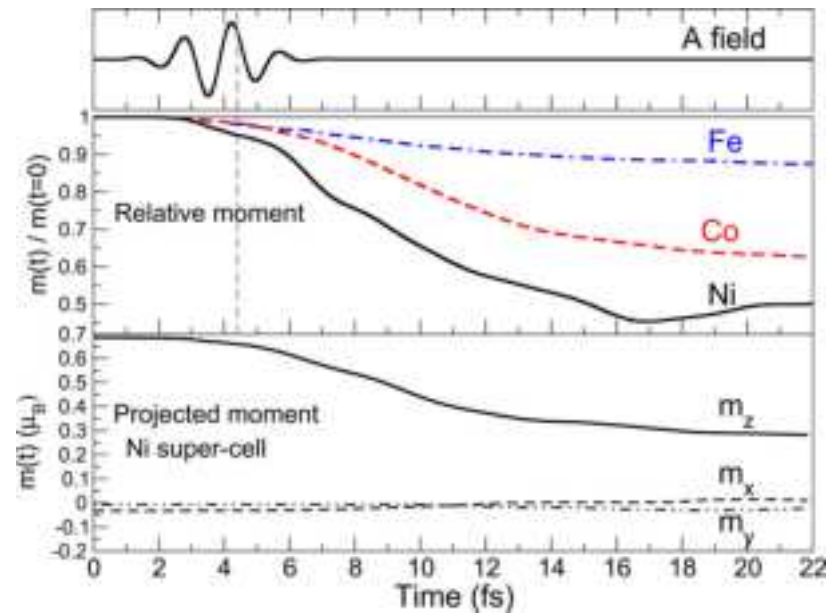
High harmonic generation (HHG) in Si
Tancogne-Dejean et al. (2017)

RT-TDDFT for periodic solids: magnetic materials



N. Tancogne-Dejean, F.G. Eich & A. Rubio, JCTC **16**, 1007 (2020)

RT-TDDFT to calculate magnon dispersions



Krieger, Dewhurst, Elliott, Sharma & Gross JCTC **11**, 4870 (2015)

Nonlinear regime: ultrafast demagnetization

see also: Singh, Elliott, Dewhurst, Gross & Sharma, pss-b **257**, 1900654 (2020)

Summary

- TDDFT methods can describe excitons, but difficult to get good exciton BE and good oscillator strengths. No exciton Rydberg series with LRC-type adiabatic xc kernels.

- Challenges: xc kernel that works for small-gap semiconductors and for large-gap insulators; numerically very sensitive.

- Alternative to BSE: hybrid functionals – similar accuracy but cheaper. Very promising! But more expensive than pure TDDFT.

- Real-time TDDFT for solids now more and more common. Allows description of ultrafast/nonlinear effects.

G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)
S. Botti, A. Schindlmayr, R. Del Sole, L. Reining, Rep. Prog. Phys. **70**, 357 (2007)
C.A. Ullrich and Z.-H. Yang, Topics in Current Chem. **368** (2015)

Suggested exercises

- Test the **Wannier model** for different materials, and compare with experimental data. For what materials does it give reasonable exciton binding energies, when does it fail?

- Go over the derivation of the **Elliott formula** in the textbook of Haug and Koch, Chapter 10. This is a highly instructive exercise, and a beautiful analytic derivation. Then write a short Python code to implement the formula to produce optial absorption spectra like the one on slide 7. You can do it for 3D, 2D and 1D.

- An excellent introduction to light-matter interaction, dielectric properties, and excitons is given in the textbook of Yu and Cardona, "Fundamental of Semiconductors." It is highly recommended to read Chapter 6.

- To learn more about the many-body formalism in solids, consult:
  Martin, Reining & Ceperley, "Interacting Electrons"
  Bechstedt, " Many-Body Approach to Electronic Excitations"

Acknowledgments

Thanks to all collaborators, students and postdocs over the years.

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