TDDFT for extended systems: Excitons

Carsten A. Ullrich
University of Missouri

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Benasque
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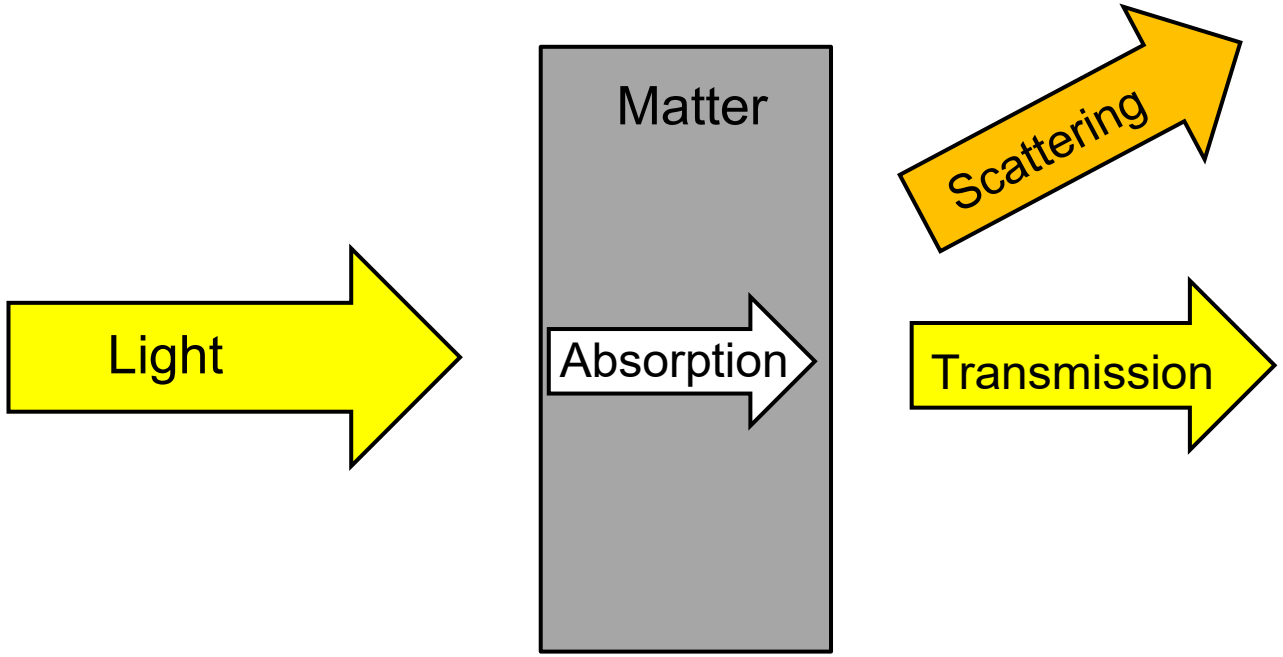
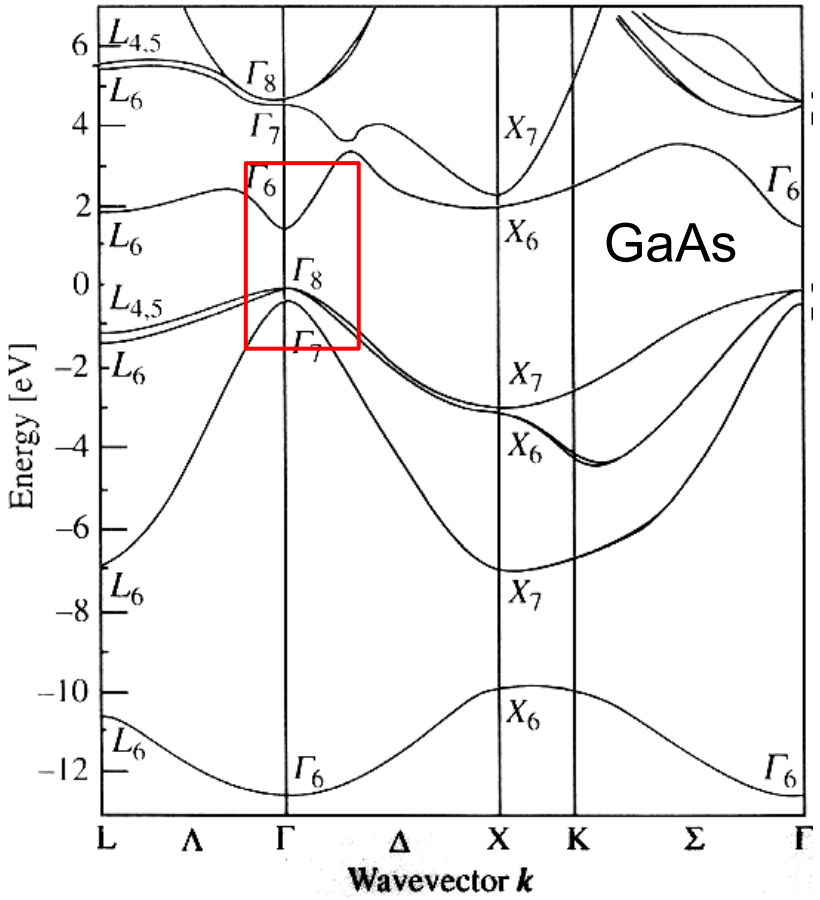
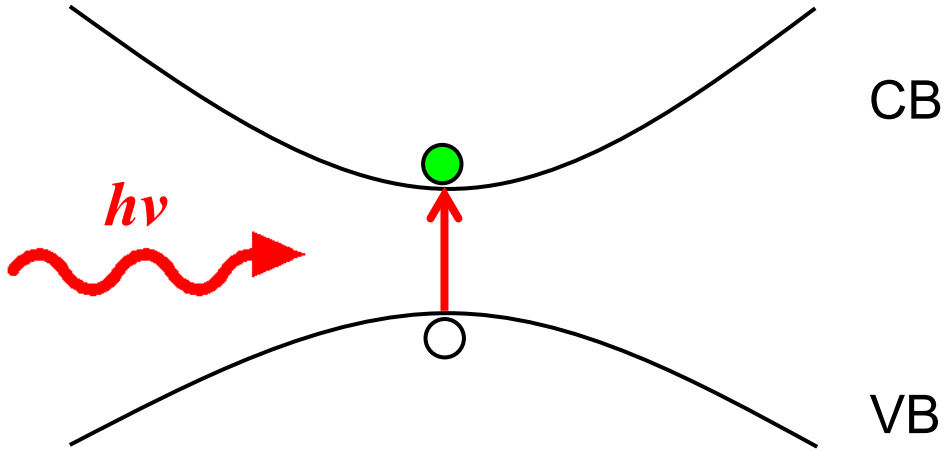
Absorption of light in a solid



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

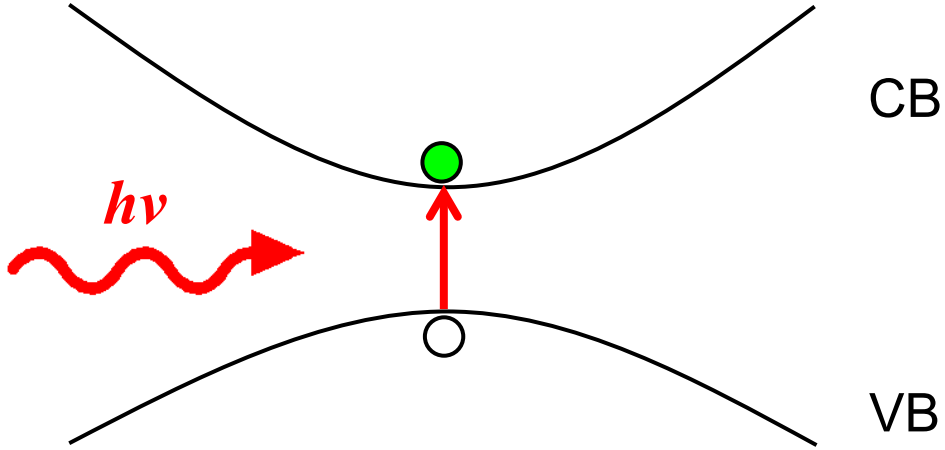
Absorption of light across the band gap





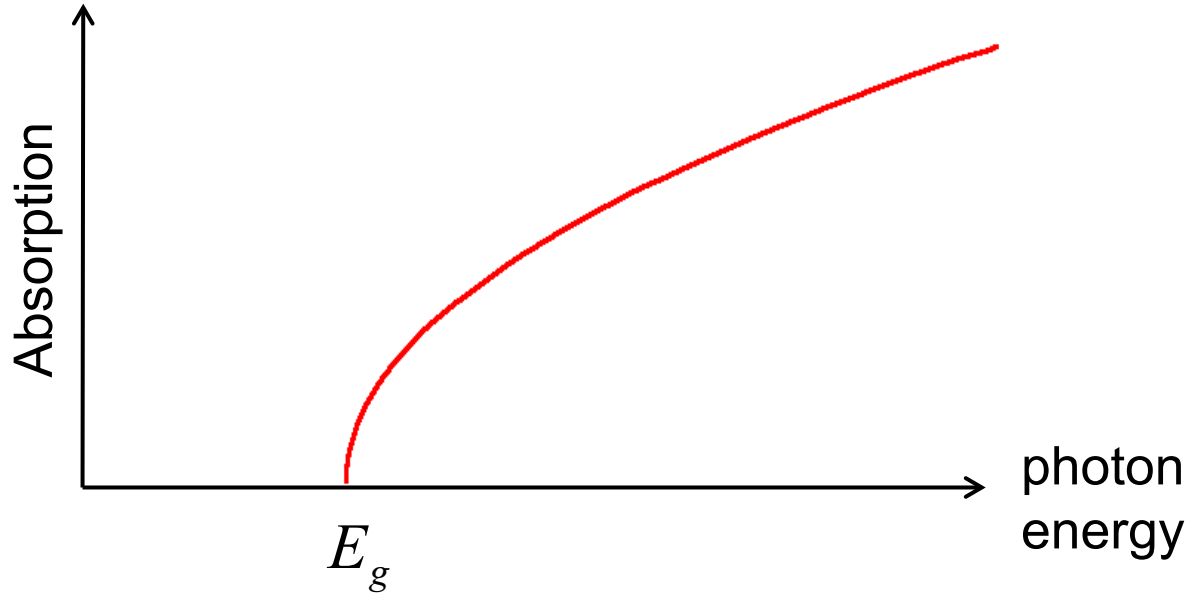
- Light comes in with photon energy at least as large as the band gap
- Photon gets absorbed, promotes electron across the gap, leaving a hole behind

Absorption spectra of insulators/semiconductors



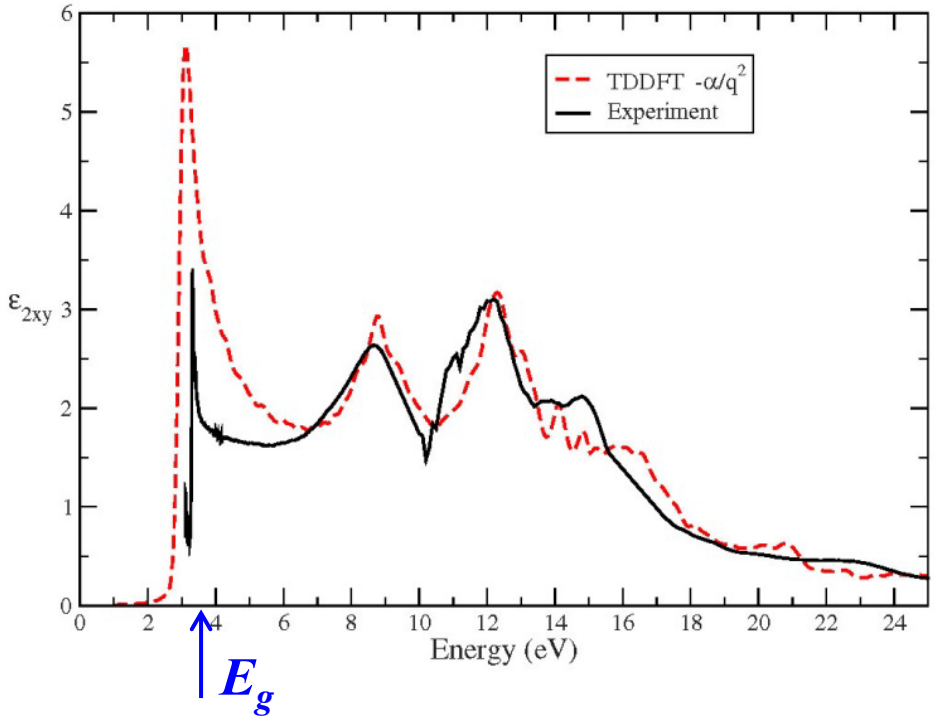
see John H. Davies *"The Physics of low-dimensional semiconductors"* Chapter 8

Fermi's Golden Rule produces an absorption spectrum like this (in 3D):



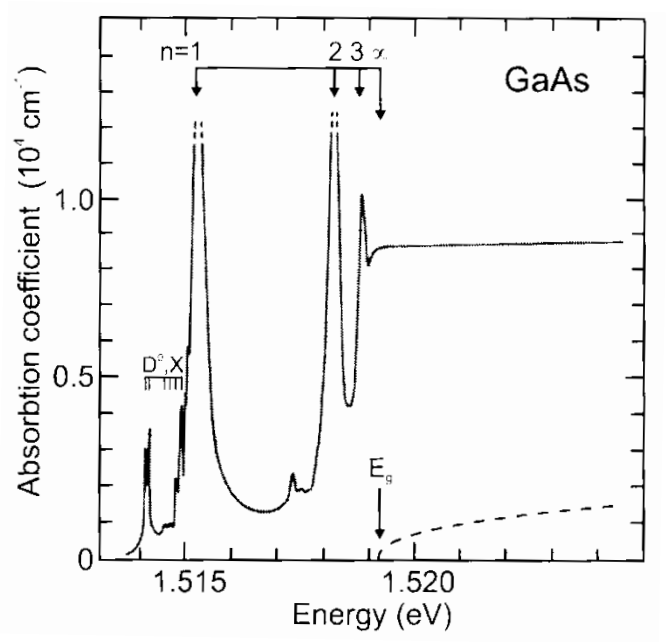
Absorption spectra of insulators/semiconductors

ZnO



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

GaAs

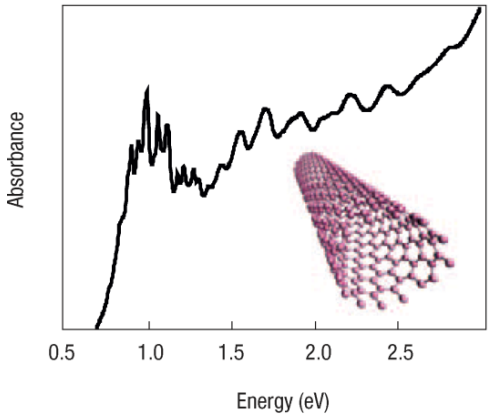


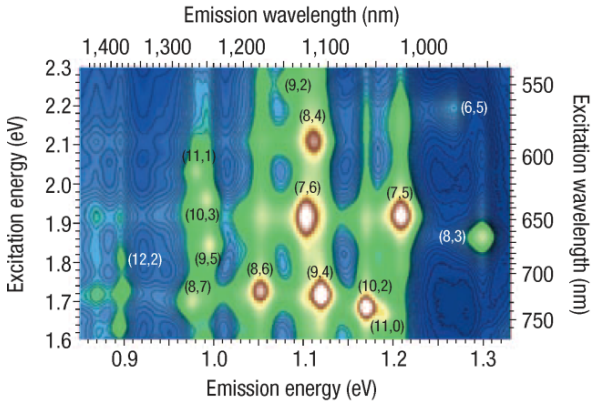
R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

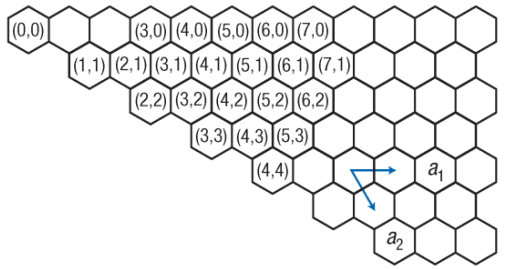
In the experiment, one finds sharp peaks at the absorption threshold…
In fact, there can be peaks below the band gap energy: Excitons.

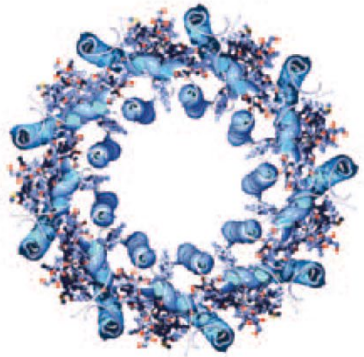
Excitons in nanoscale and 2D systems

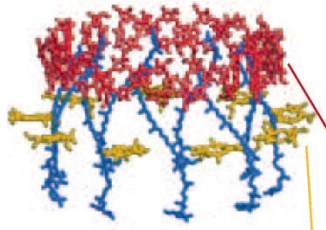
G. D. Scholes and G. Rumbles, Nature Mater. **5**, 683 (2006)
Jang & Mennucci, Rev. Mod. Phys. **90**, 035003 (2018)



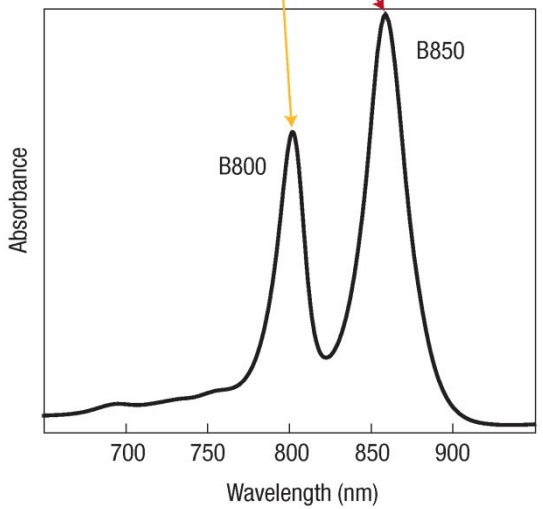


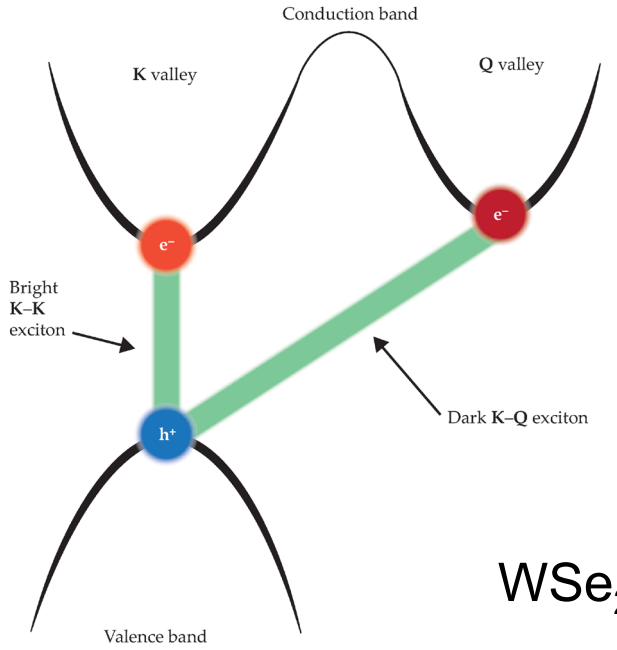




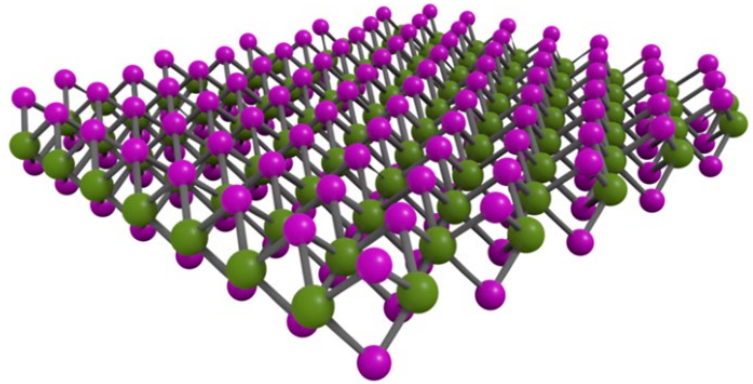


Frenkel excitons in light-harvesting systems: purple bacteria



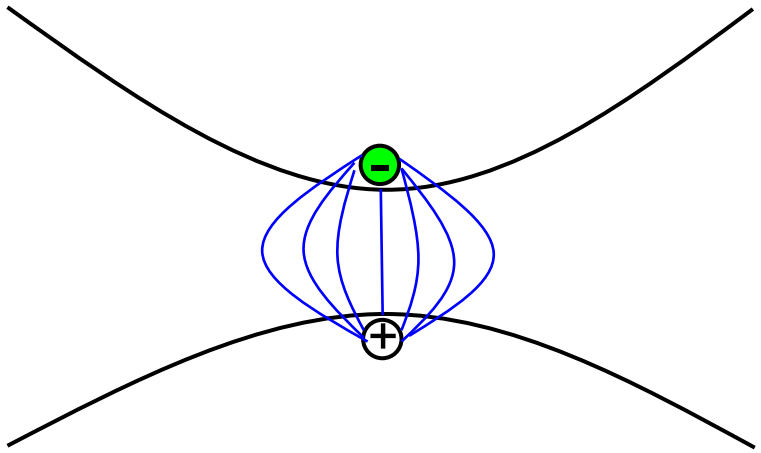


WSe_2



Dark excitons in TMD (Physics Today 2/2021)

What is an exciton?



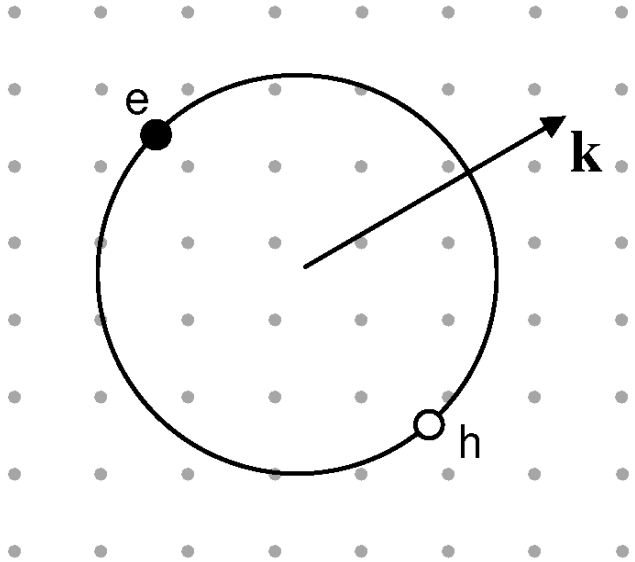
► After their creation, electron and hole are not completely free, but experience **screened Coulomb attraction.**

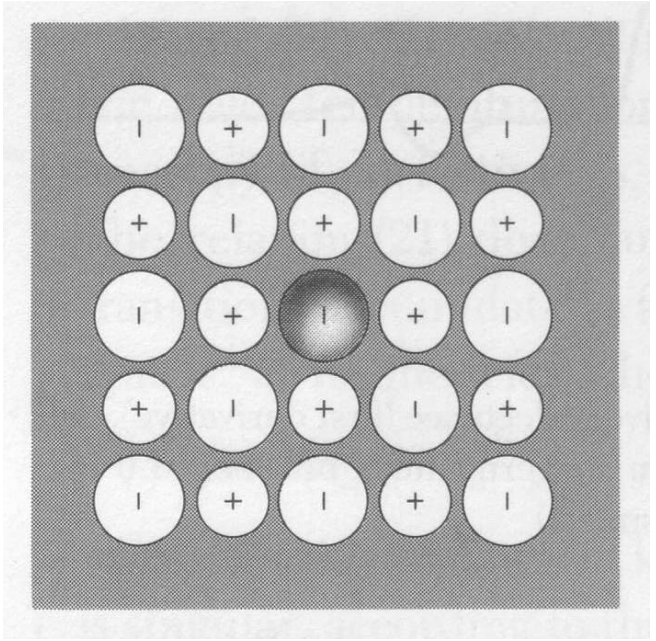
►This gain in (mostly electrostatic) energy can lower the onset of absorption and change the spectral strength.

Excitons are bound electron-hole pairs.

More precisely: excitons are collective excitations of the electronic many-body system.

Elementary view of Excitons





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

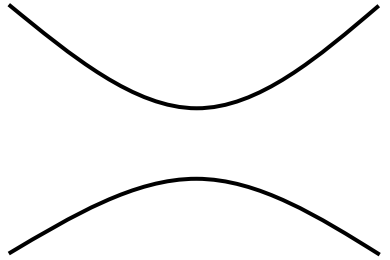
►In semiconductors with small band gap and large ε

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

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

The effective-mass approximation

(1) Electrons move in the crystal as if they had an effective mass m^*



$m^* \sim (\text{curvature})^{-1}$

(2) Charges are screened by the dielectric constant:

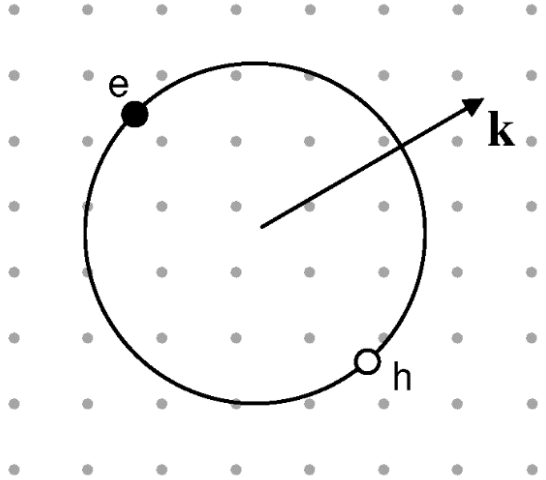
$$e^* = e/\sqrt{\varepsilon}$$

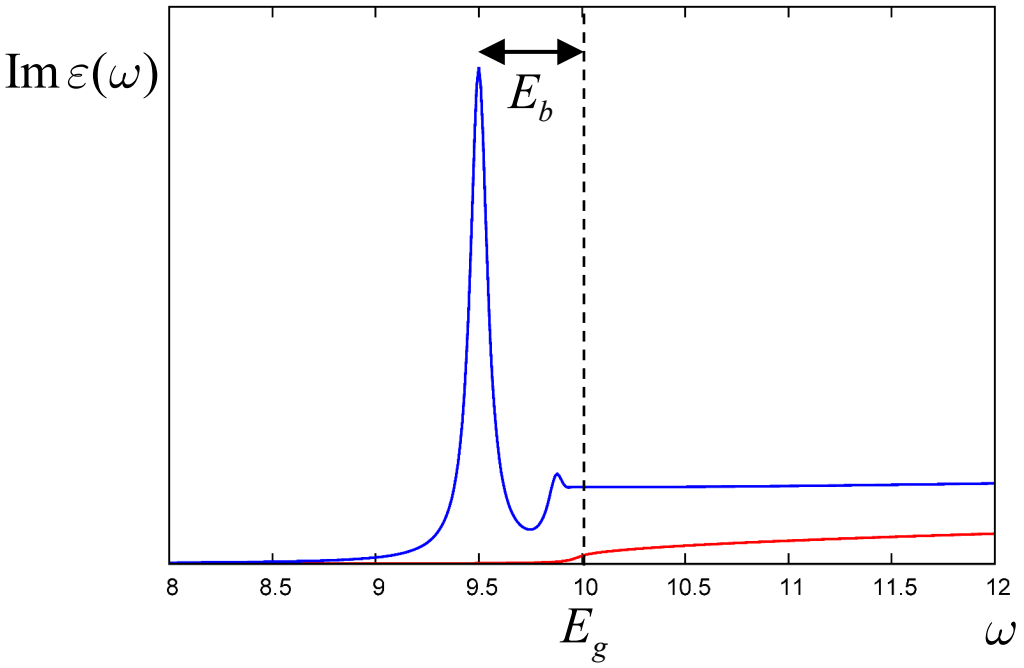
For GaAs:

$$m_e^* = 0.067m$$

$$e^* = e/\sqrt{13}$$

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:

$$E_0^*=4.75\ meV$$

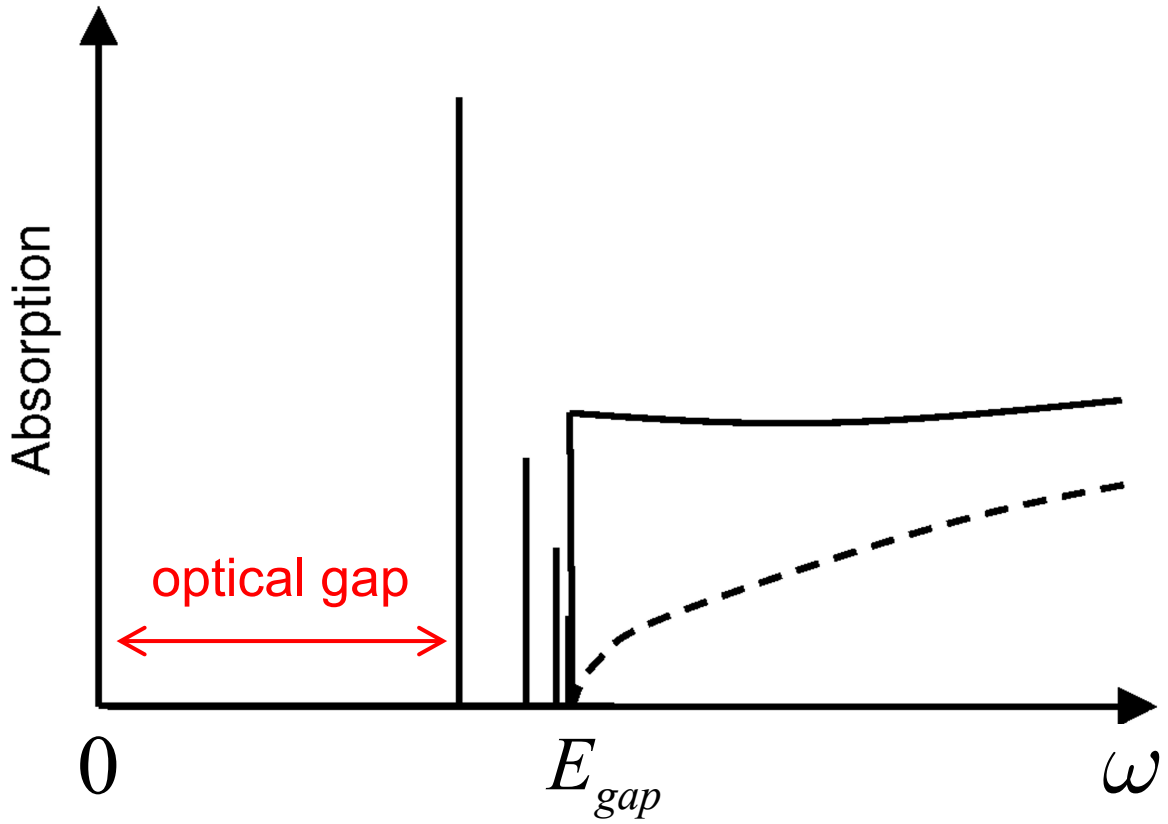
Experiment: $E_0^*=3.3\ meV$

The Elliott formula (3D)

Optical absorption: $$\alpha(\omega) = \alpha_0^{3D} \frac{\hbar\omega}{E_0}\left[\sum_{n=1}^{\infty}\frac{4\pi}{n^3}\delta(\Delta+\frac{1}{n^2}) + \Theta(\Delta)\frac{\pi e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})}\right]$$

Excitonic Rydberg series

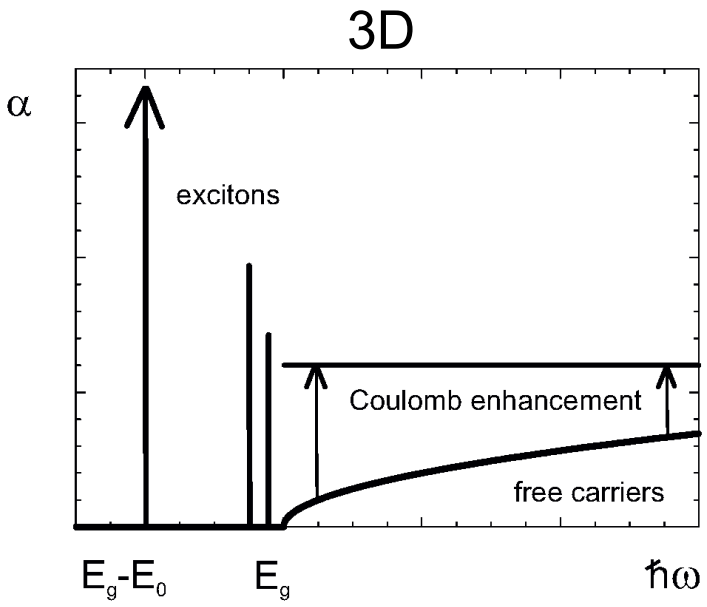
Renormalized Continuum

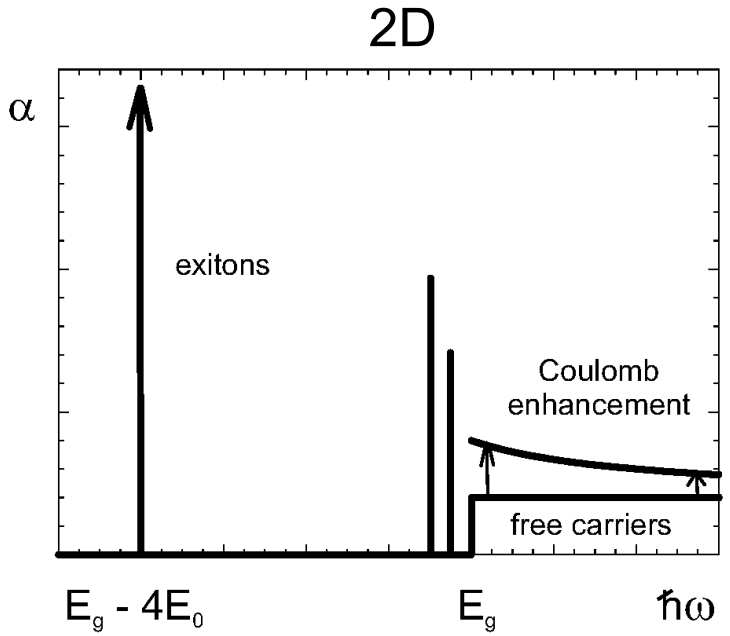


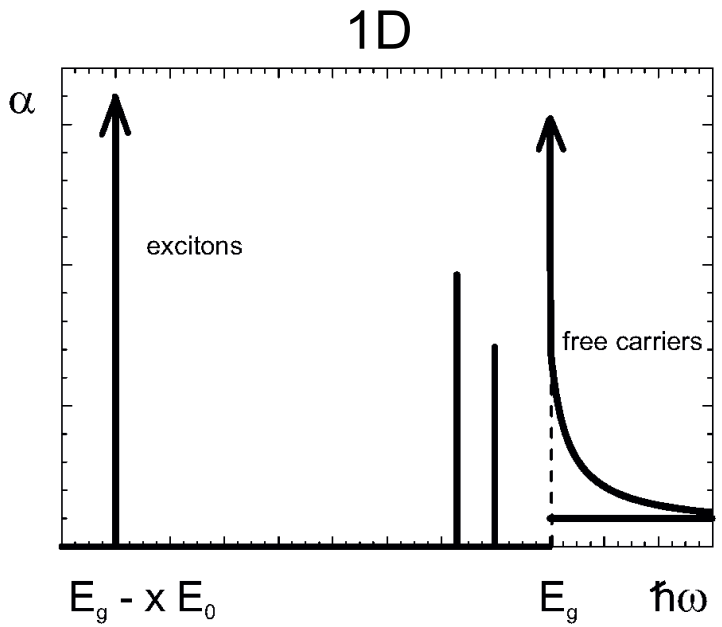
where $$\Delta = \frac{\hbar\omega - E_{gap}}{E_0}$$

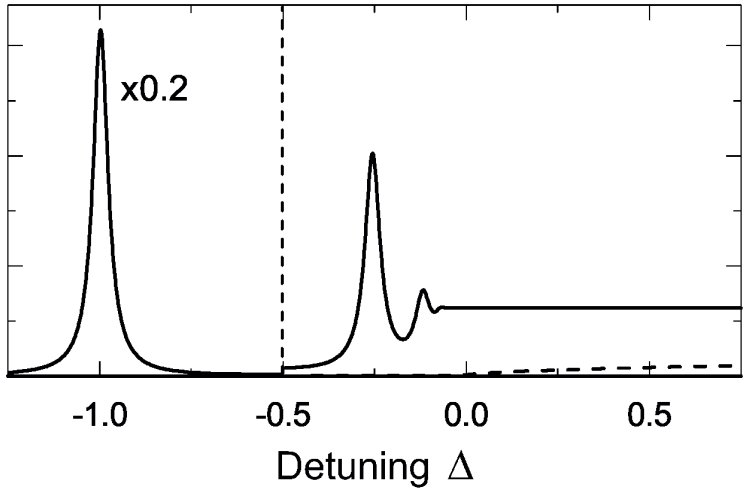
H. Haug & S.W. Koch
Quantum Theory of the Optical and Electronic Properties of Semiconductors

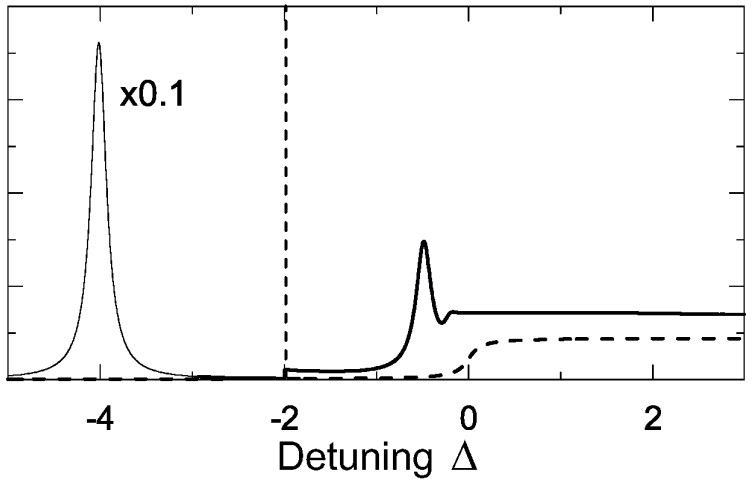
The Elliott formula in 3D, 2D, 1D

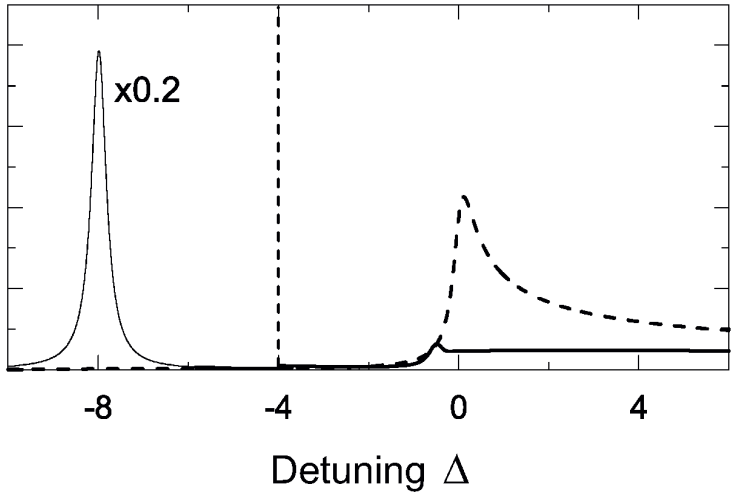






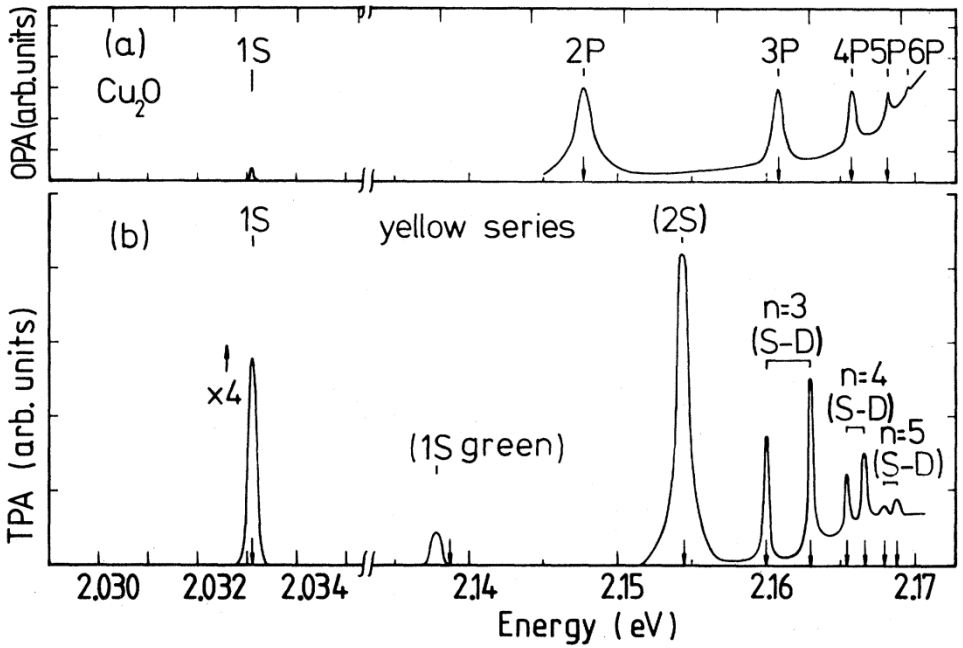






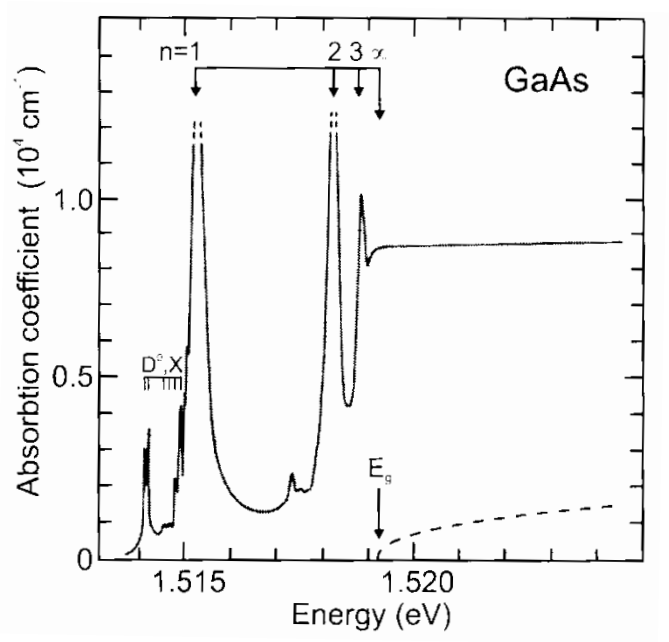
Wannier equation and excitonic Rydberg Series

Cu_2O



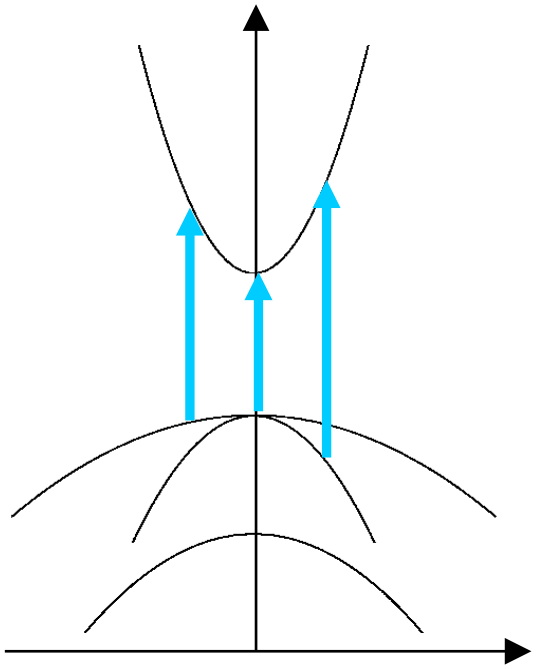
R.J. Uihlein, D. Frohlich, and R. Kenklies, PRB **23**, 2731 (1981)

GaAs



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

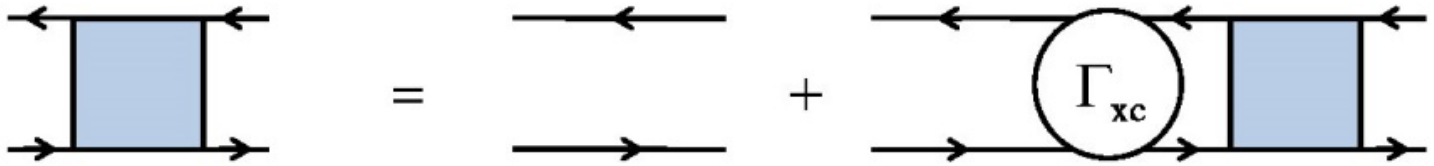
Optical excitations in bulk Insulators: theory



Optical transitions in insulators are challenging for TDDFT:

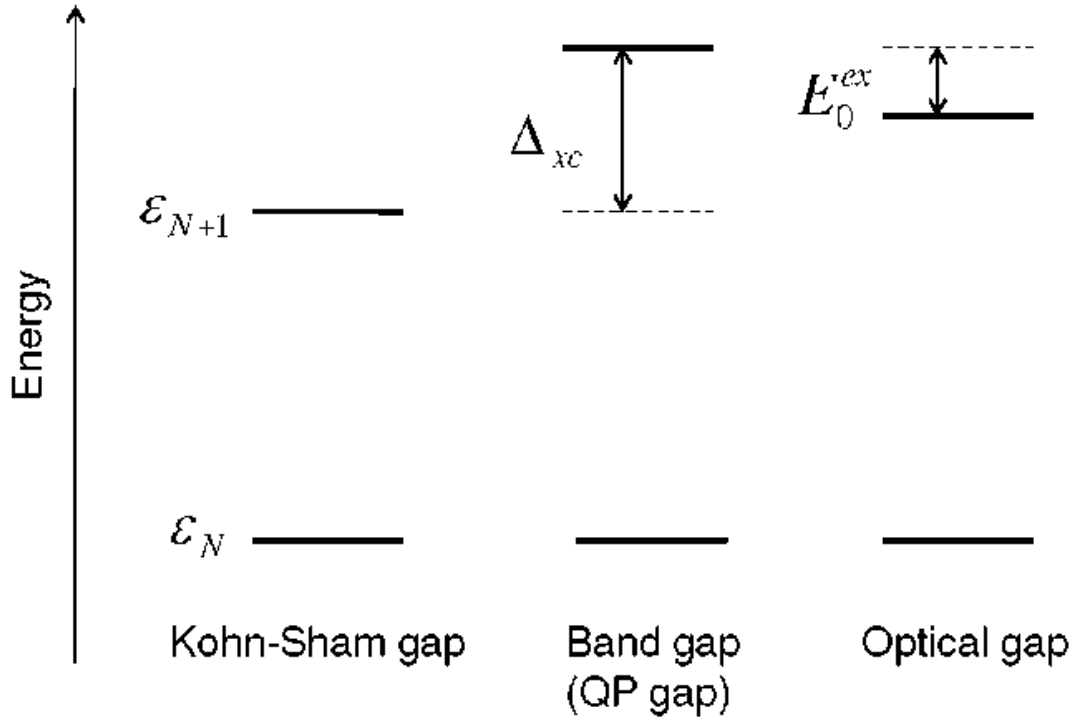
- **band gap opening**
- **excitons**

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



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

Insulators: three different gaps



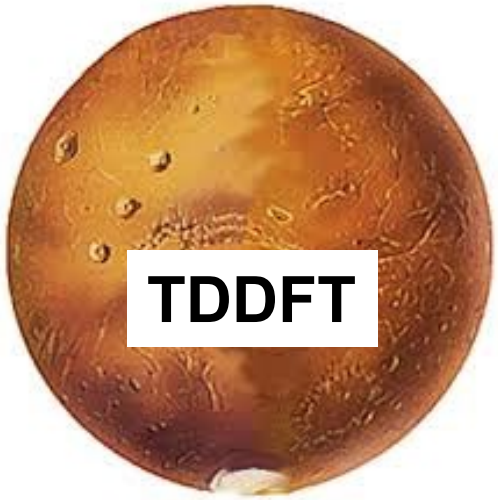
The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

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

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

Many-body perturbation theory vs TDDFT

Hybrid functionals



Quasiparticle-based:

electron addition+removal (GW)

e-h interaction+screening (BSE)

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

Density-based:

ground state KS: $V_{xc}(\mathbf{r})$

linear response:

$$f_{xc}(\mathbf{r},\mathbf{r}',\omega)$$

C. A. Ullrich and Z.-H. Yang, Topics in Current Chem. **368** (2015)
Turkowski, Din & Rahman, Computation **5**, 39 (2017)

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)

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

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

Fourier transform:

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

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

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).

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:

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

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

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

see
Yu and Cardona
The Physics of Semiconductors

The macroscopic dielectric function

For cubic symmetry, one can prove that

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

Adler 1962
Wiser 1963

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

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

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

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)

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

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:

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

Density eigenmode:

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

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)

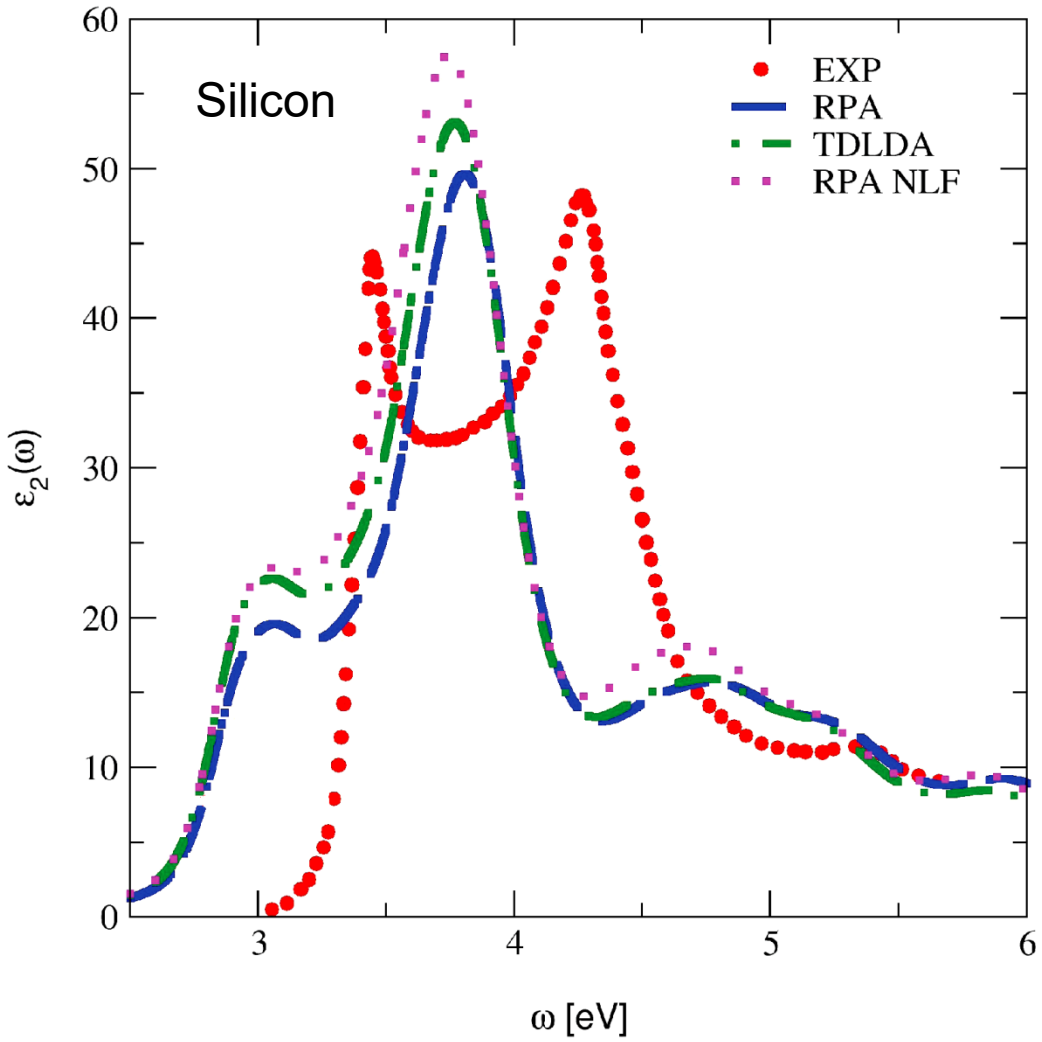
Using time-reversal symmetry, Full Casida eq. can be transformed into

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

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)

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

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

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

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

"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

See also: Cavo, Berger & Romaniello, PRB **101**, 115109 (2020)
Di Sabatino, Berger & Romaniello, 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)

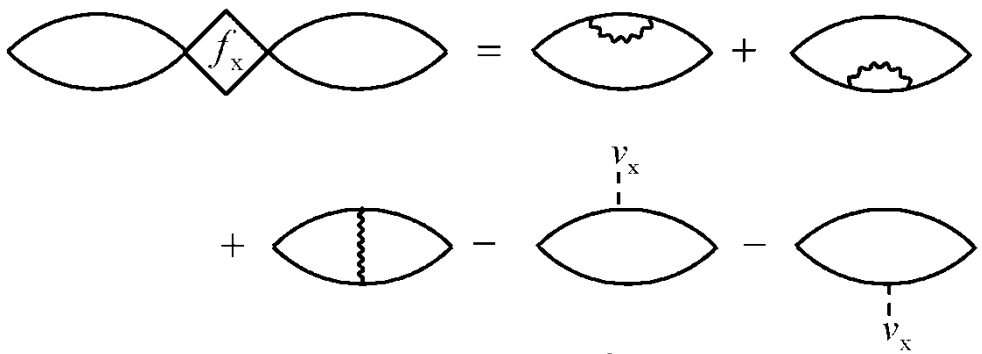
$$f_{xc,\mathbf{GG'}}^{LRC}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q}+\mathbf{G}|^2}\delta_{\mathbf{GG'}}$$

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

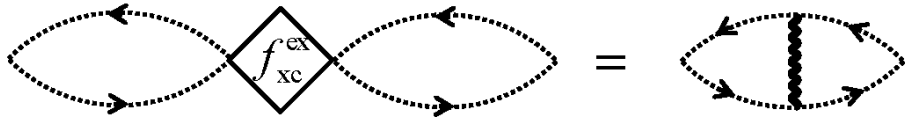
$$f_{xc,\mathbf{GG'}}^{boot}(\mathbf{q},\omega) = \frac{\varepsilon_{\mathbf{GG'}}^{-1}(\mathbf{q},0)}{\chi_{s00}(\mathbf{q},0)}$$

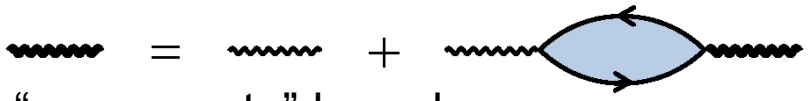
(depends on unoccupied bands, may need large number of bands)

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



exact exchange



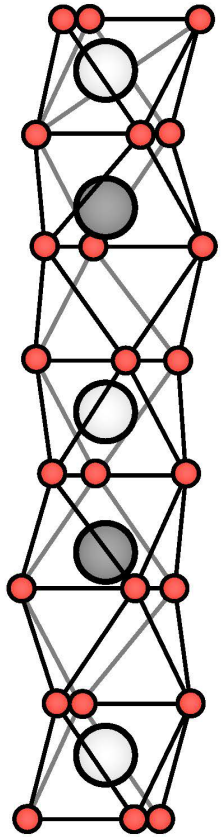


"nanoquanta" kernel,
reverse-engineered from BSE
(L. Reining et al., 2002)

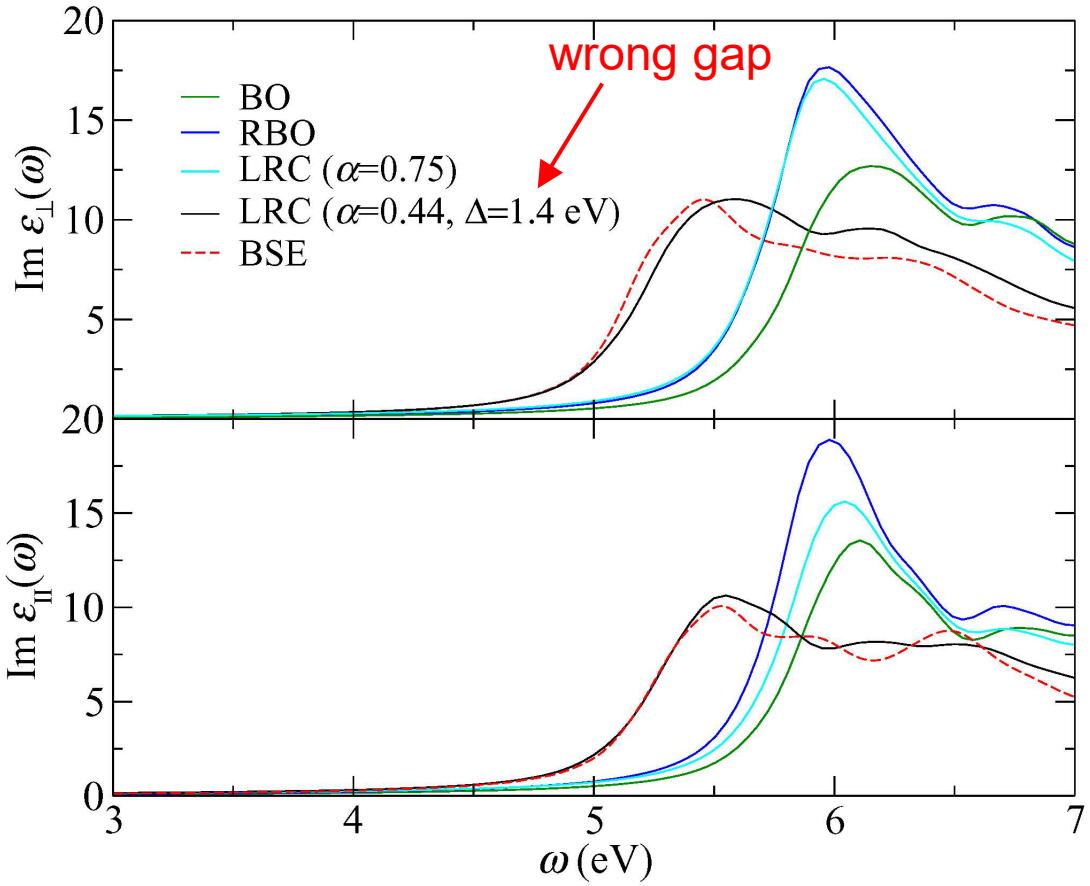
Excitons: which xc kernels to use?

- **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, Yang, and Ullrich, PRRes **2**, 013091 (2020)

The family of LRC/Bootstrap xc kernels



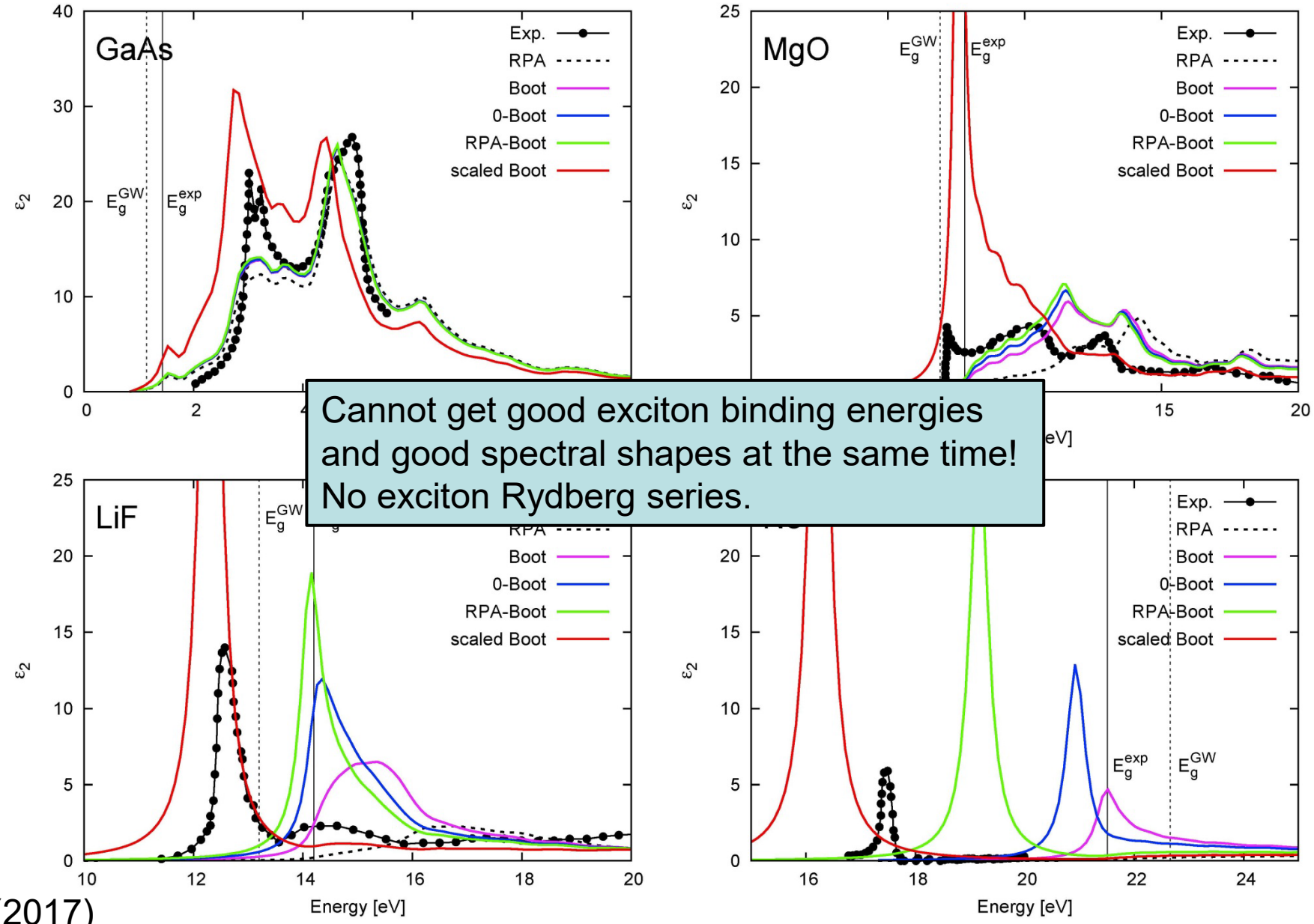
$LiNbO_3$



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)

$$E_{xc}^{hybrid} = \alpha E_x^{exact} + (1-\alpha) E_x^{sl} + E_c^{sl}$$

$\alpha \times$ **nonlocal (Hartree-Fock) exchange**

$+ (1-\alpha) \times$ **semilocal exchange**

$+$ **semilocal correlation**

- **Very widely used in computational chemistry**
- **Needs to be appropriately modified for solids!**

Excitation spectra from TDDFT vs BSE

$$\left[(E_{c\mathbf{k}} - E_{v\mathbf{k}'})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'} + K_{cv\mathbf{k}',c'v'\mathbf{k}'}\right]\mathbf{Y}_n = \Omega_n \mathbf{Y}_n$$

TDDFT coupling matrix contains xc kernel: $f_{xc,\mathbf{G}\mathbf{G}'}$

BSE coupling matrix contains screened Coulomb interaction:

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

Hybrid functionals: $W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = -4\pi \frac{\gamma}{|\mathbf{q}+\mathbf{G}'|^2}\delta_{\mathbf{G}\mathbf{G}'}$

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

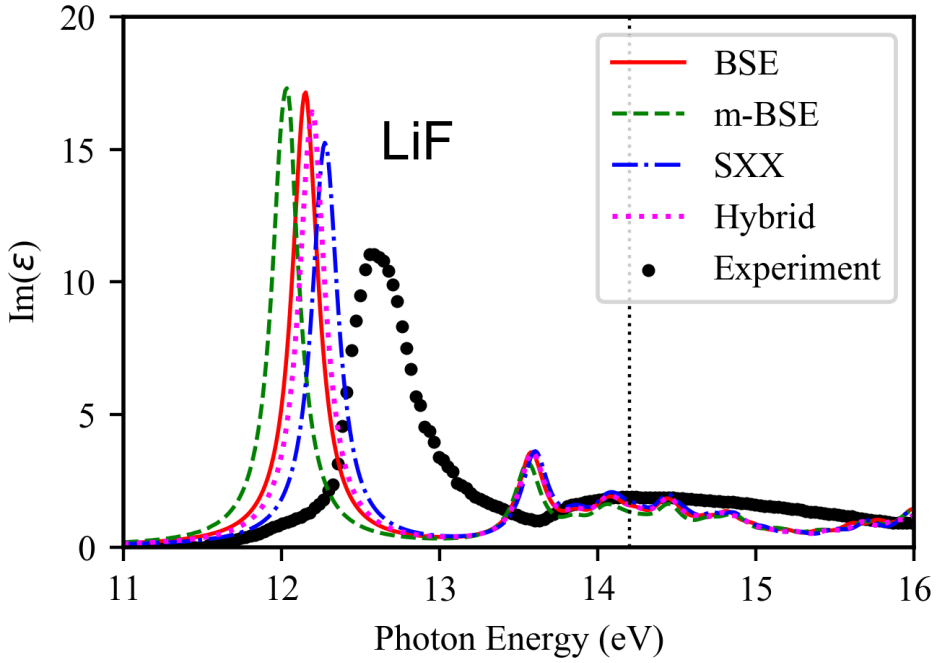
Calculated with RPA

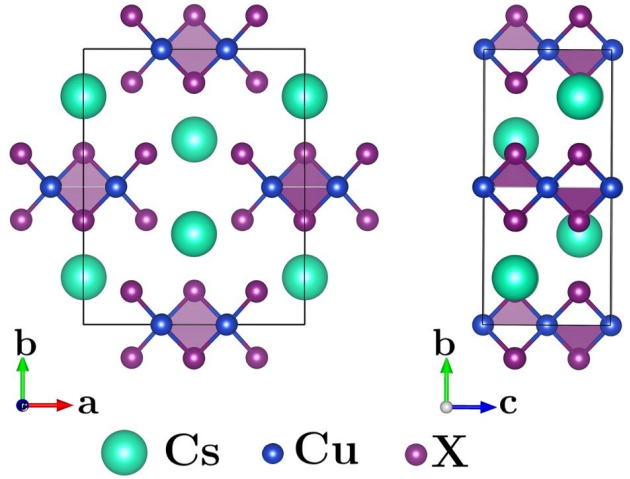
Dielectrically screened hybrid functionals

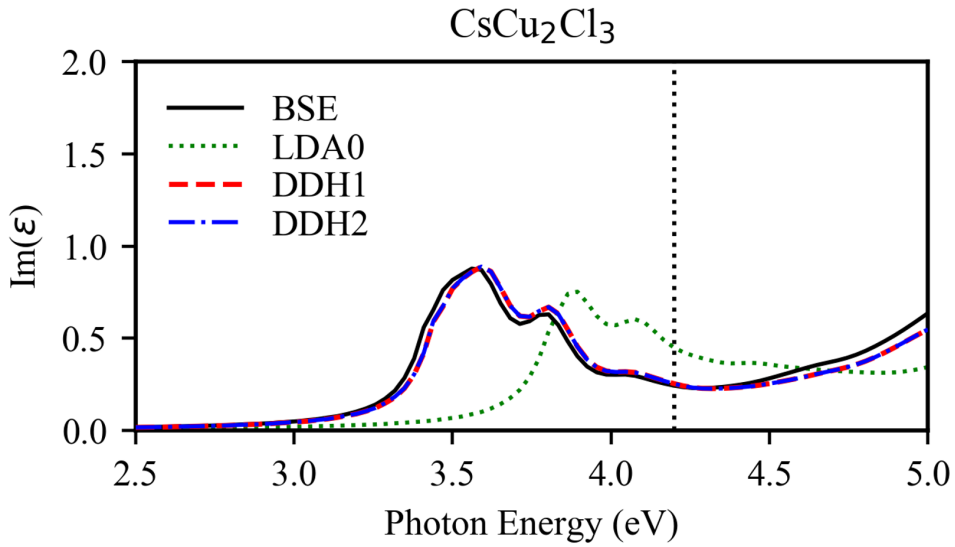
Sun, Yang, and Ullrich, Phys. Rev. Research **2**, 013091 (2020)
Sun and Ullrich, Phys. Rev. Materials **4**, 095402 (2020)

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

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

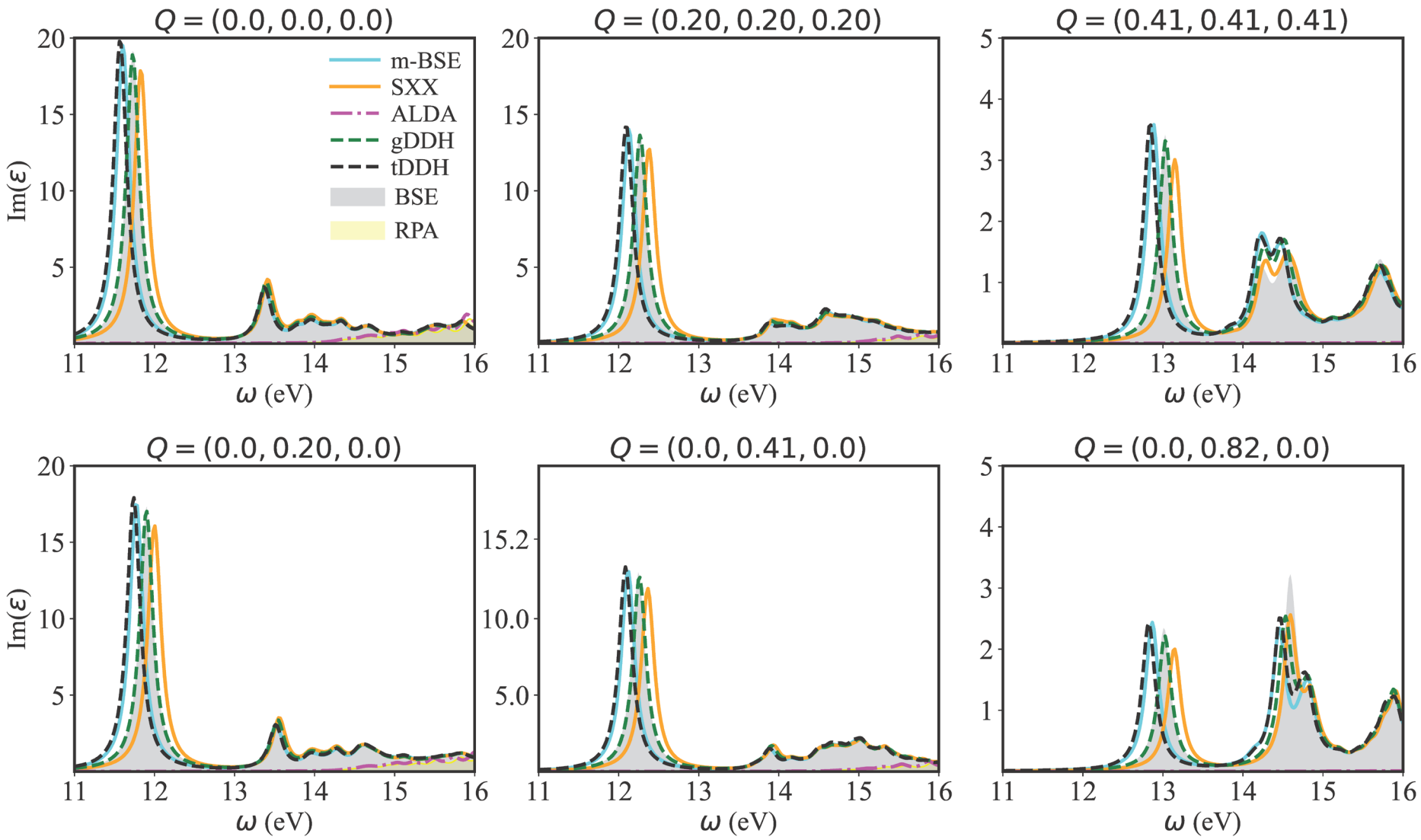






Very close to BSE, but 1-2 orders of magnitude faster.

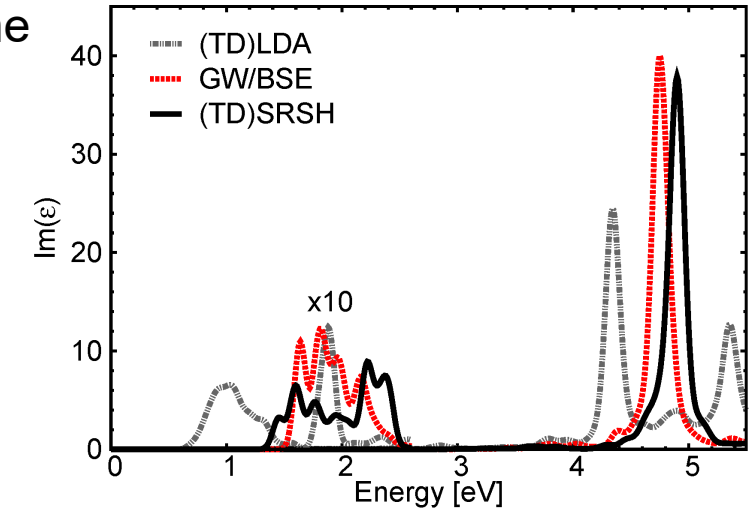
Excitons at finite momentum: LiF



D. Alam, J. Sun, and C.A. Ullrich, arXiv:2502.20683 (to appear in PRB)

Optical spectra with screened range-separated hybrid

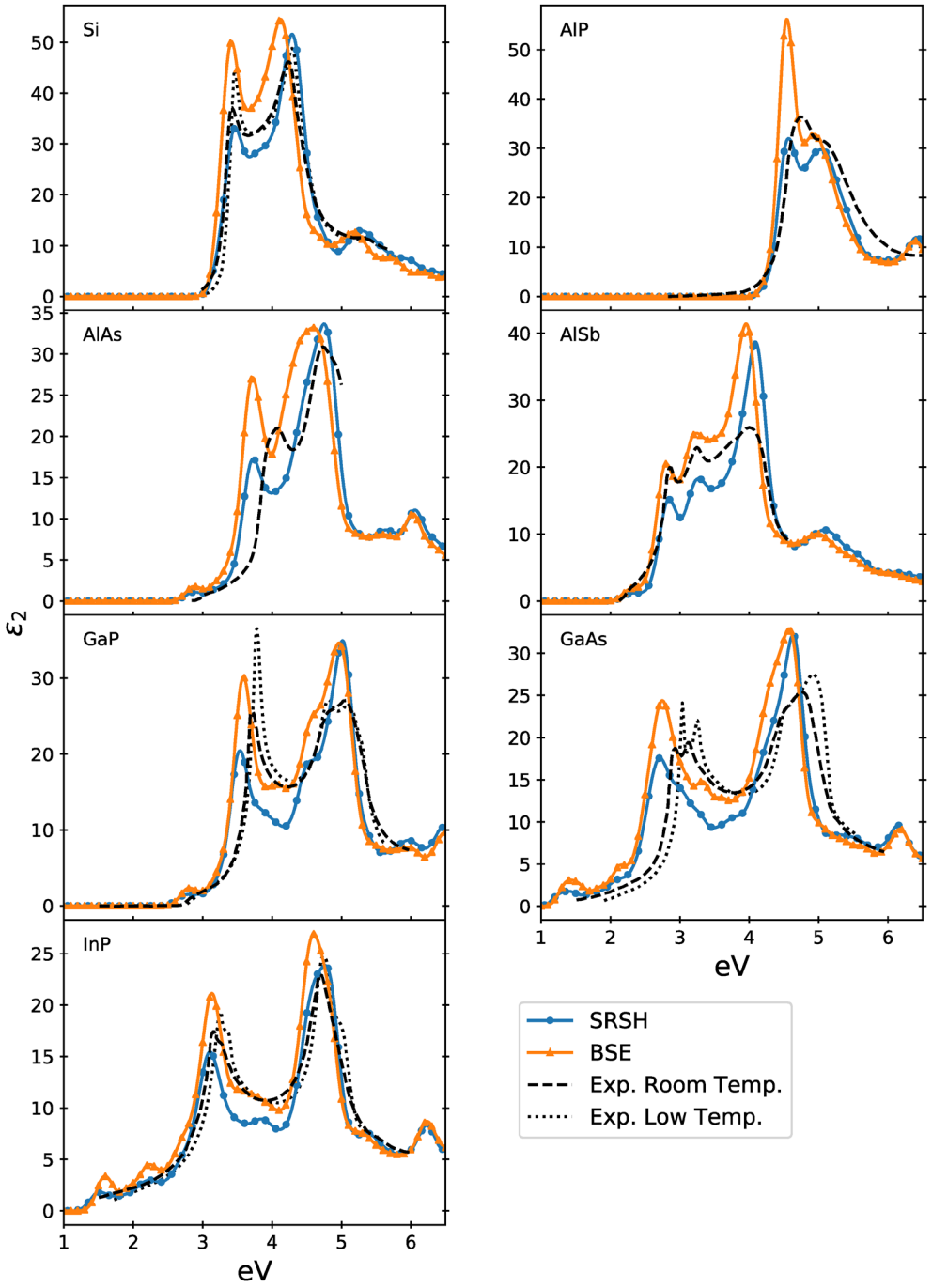
pentacene



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

Wing, Haber, Noff, Barker, Egger, Ramasubramaniam,
Louie, Neaton & Kronik, PRMat **3**, 064603 (2019)
Camarasa-Gómez, Gant, Ohad, Neaton,
Ramasubramaniam & Kronik, npj Comput. Mater. (2024)

Useses Wannier localized orbitals.



Summary

- Pure 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 excitonic effects.
  See my talk on Monday!

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)
Y.-M. Byun, J. Sun, and C. A. Ullrich, Electron. Struct. **2**, 023002 (2020)