TDDFT for extended systems II: Excitons

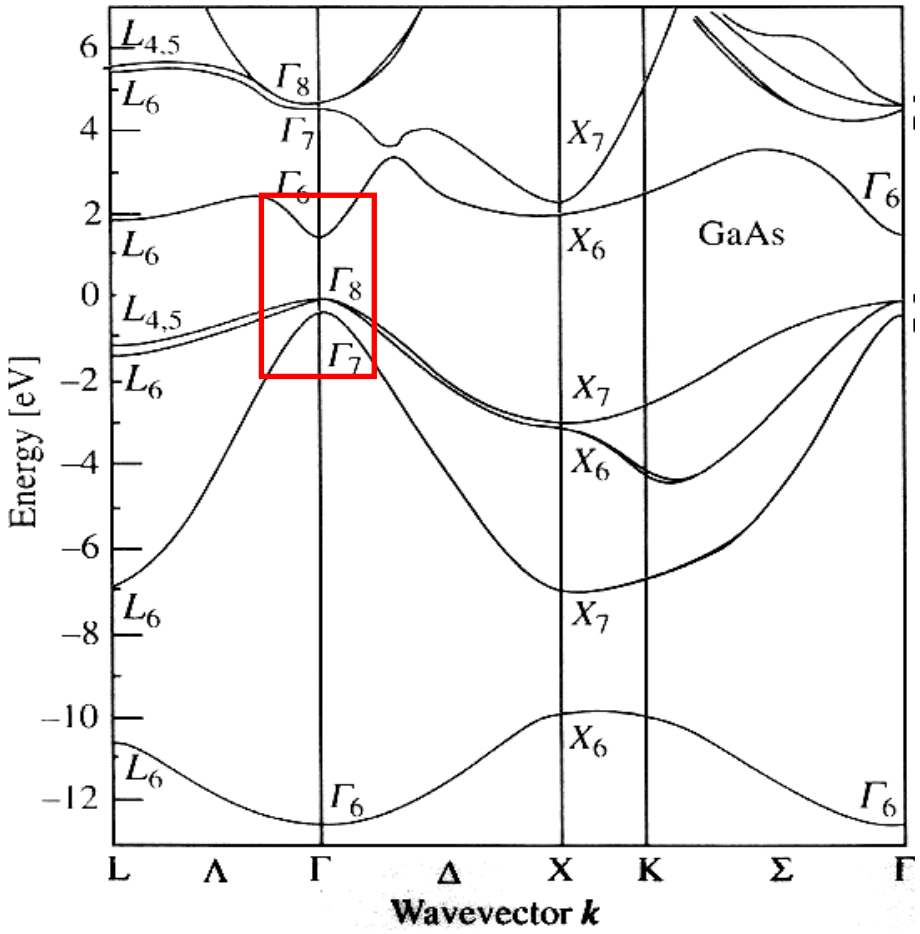
Carsten A. Ullrich
University of Missouri

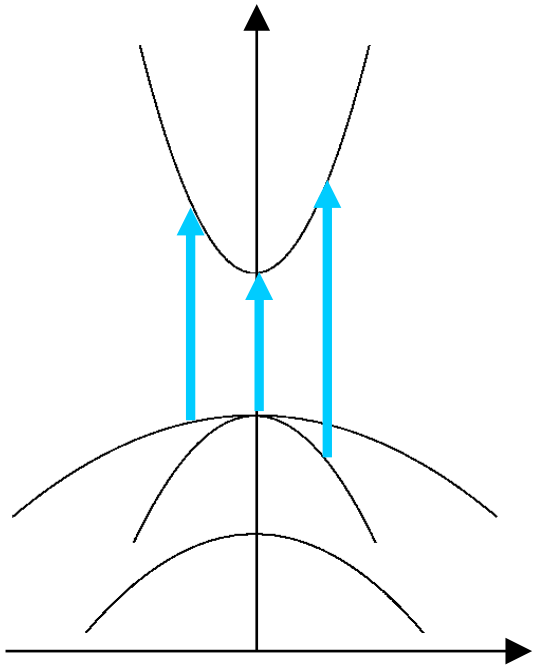
Benasque, September 2016

Outline

- A brief introduction to excitons
- TDDFT for periodic systems
- Exciton binding energies for solids
- The bootstrap kernel and other functionals
- Simplified BSE: the SXX approach
- Summary

Optical excitations in bulk Insulators

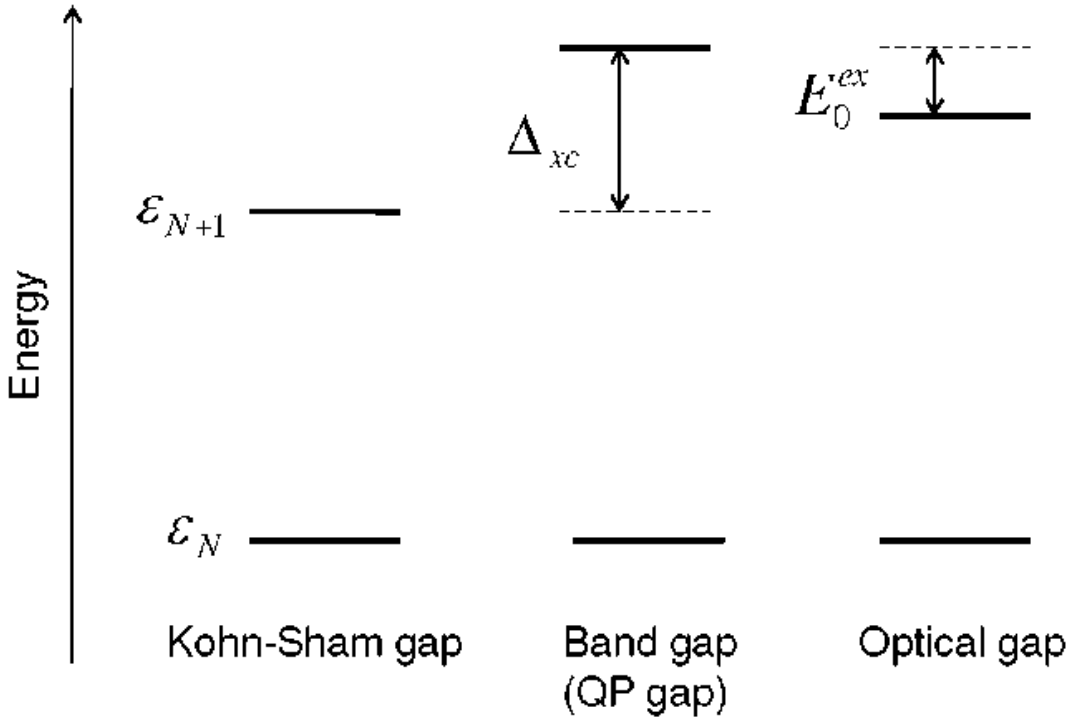




Interband optical transitions are challenging for ab initio methods:

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

Insulators: three different gaps

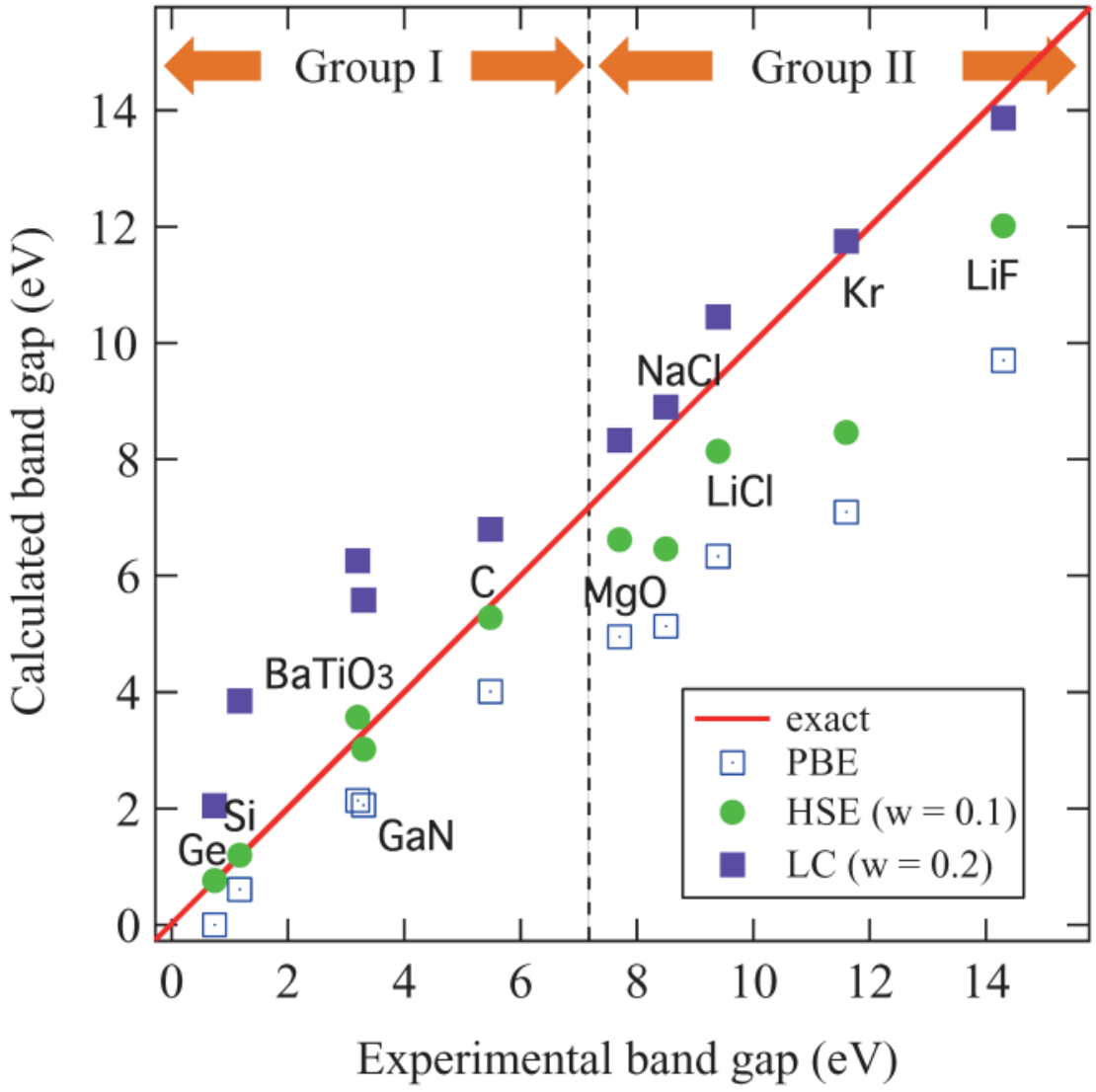


The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

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

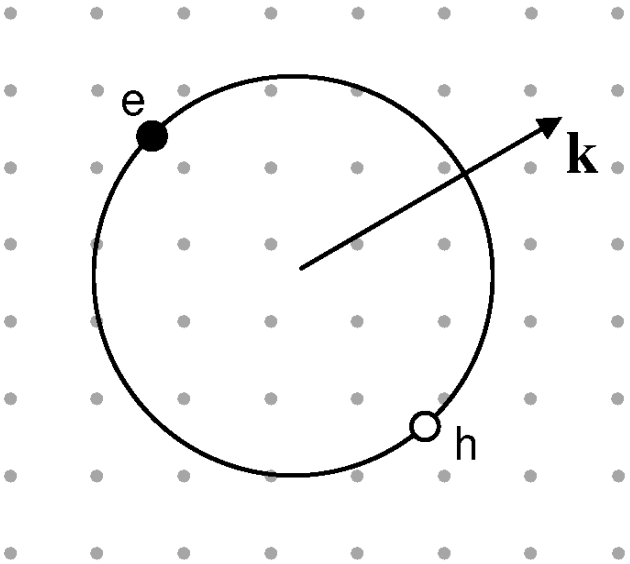


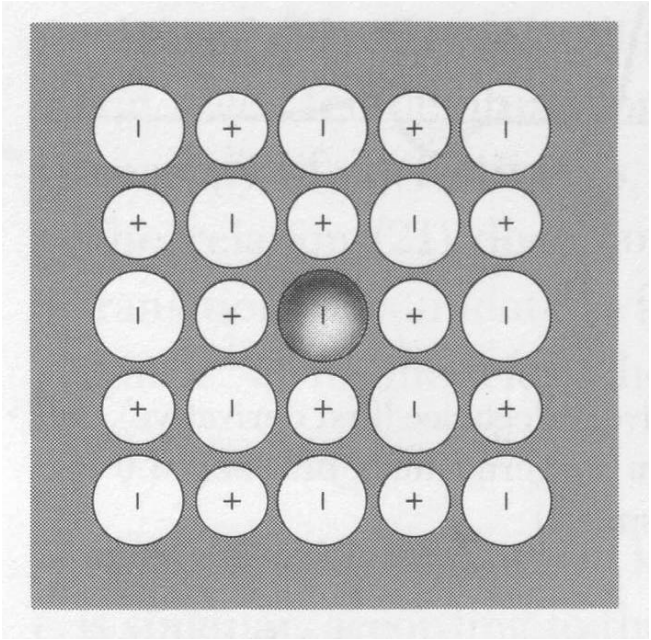
Matsushita, Nakamura and Oshiyama, PRB **84**, 075205 (2011)

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

Elementary view of Excitons

Bound electron-hole pairs created in optical excitations of insulators.





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

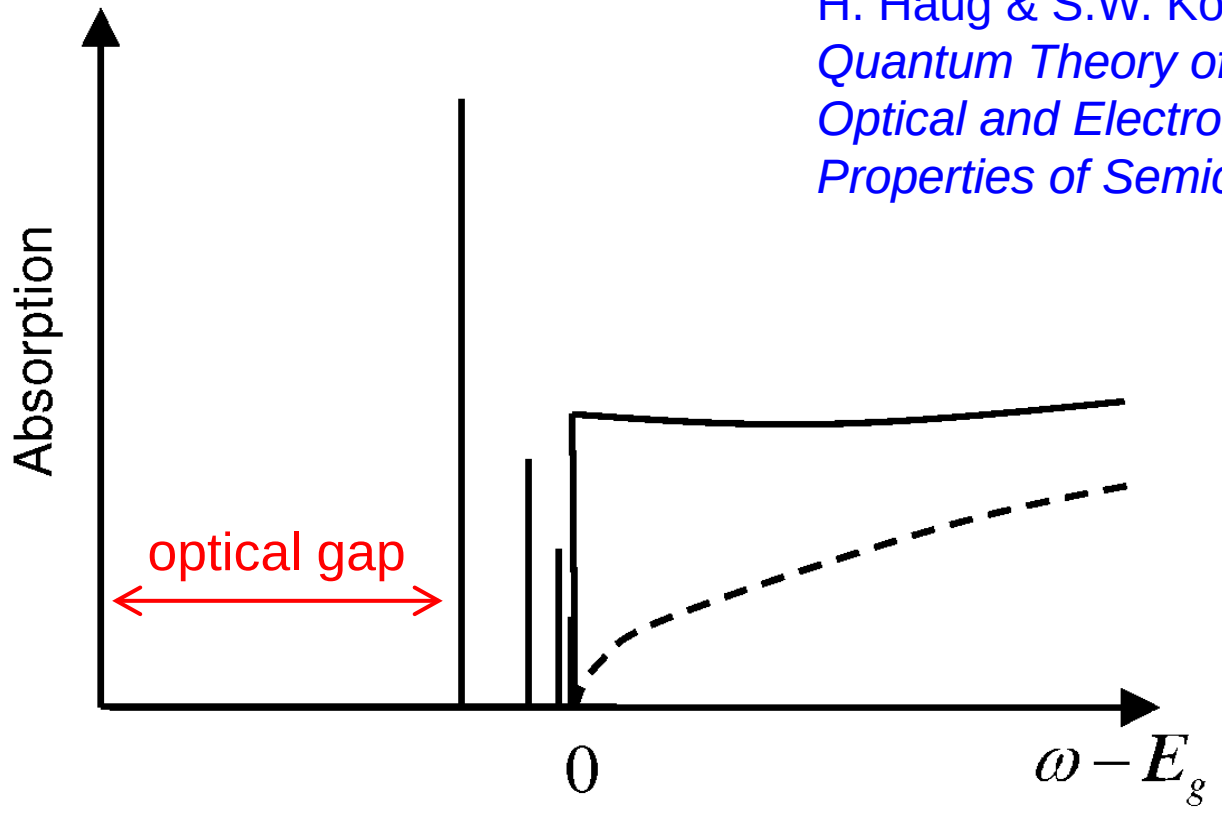
►In semiconductors with small band gap and large ε

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



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

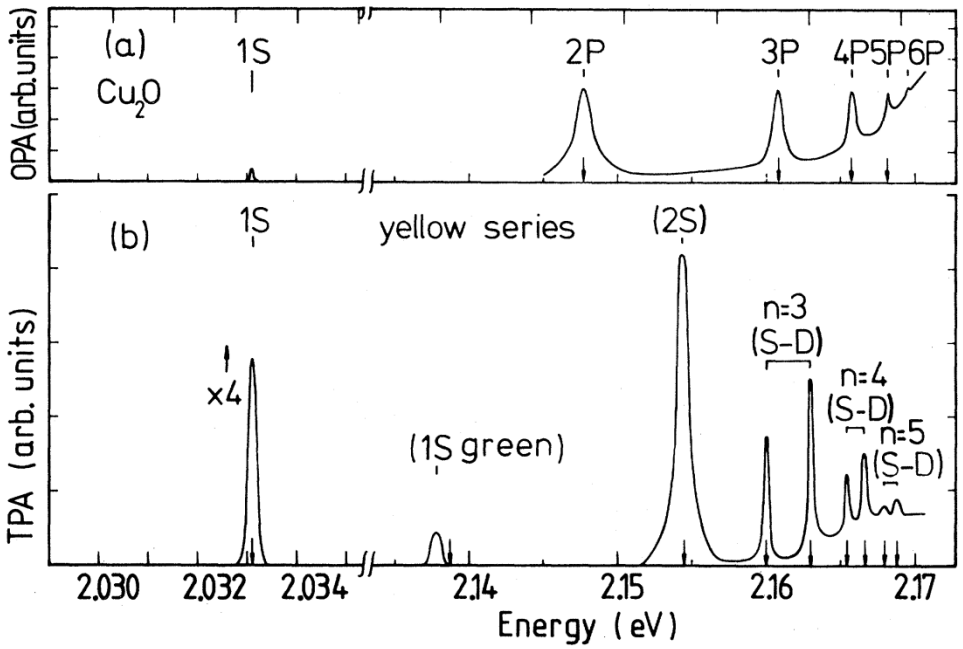
Wannier equation and excitonic Rydberg Series

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

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

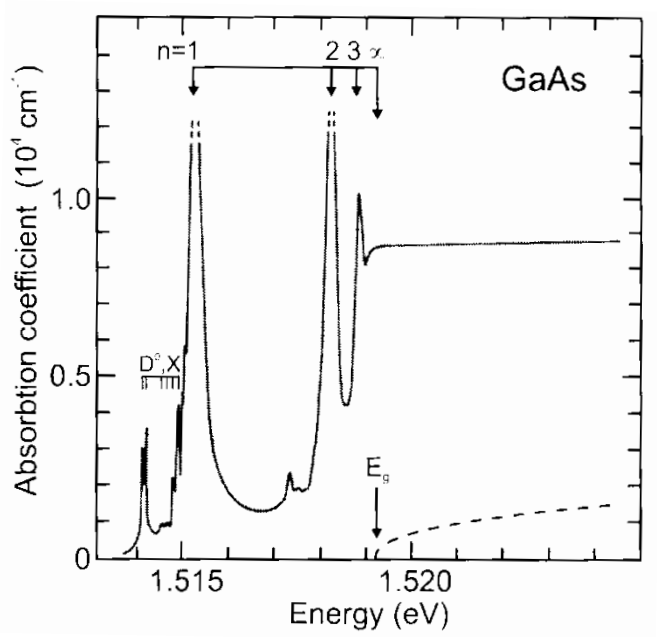
Sham and Rice, Phys. Rev. **144**, 708 (1966)

Cu_2O



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

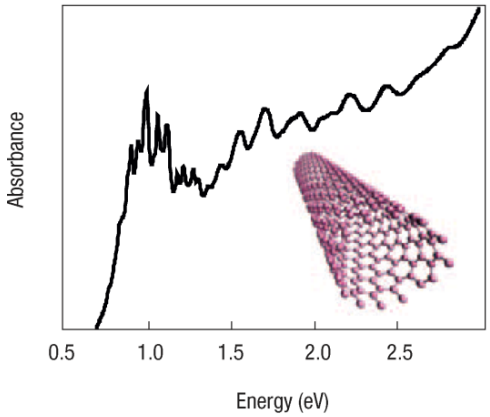
GaAs

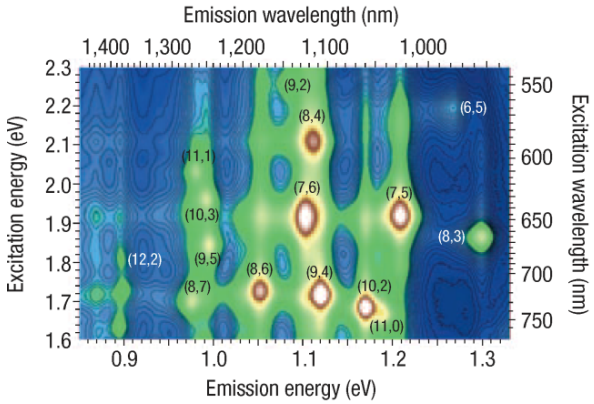


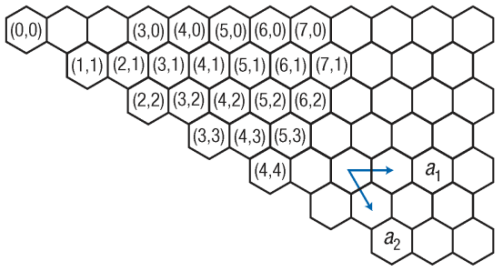
R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

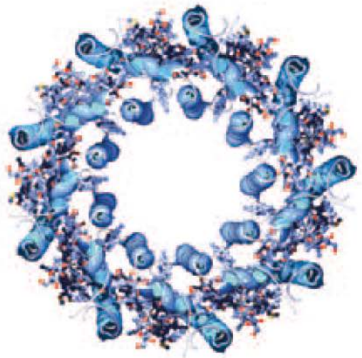
Excitons in nanoscale systems

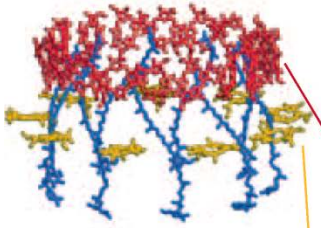
G. D. Scholes and G. Rumbles, Nature Mater. **5**, 683 (2006)



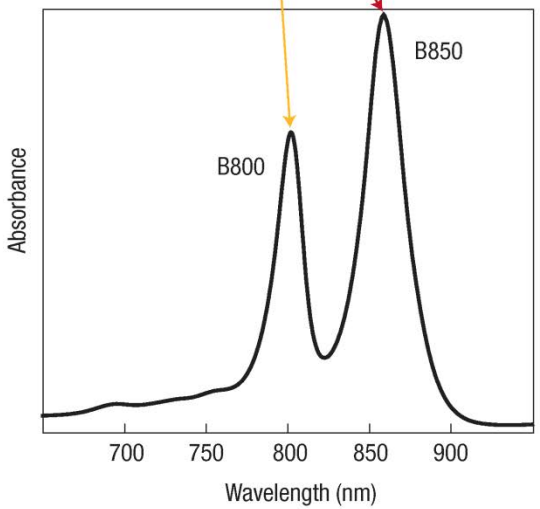








Frenkel excitons in light-harvesting systems: purple bacteria



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)

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

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

Therefore, we can Fourier transform the response function:

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

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

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: $$\mathbf{D}_{\mathbf{G}}(\mathbf{k},\omega) = \sum_{\mathbf{G}'} \underline{\underline{\varepsilon}}_{\mathbf{G}\mathbf{G}'}(\mathbf{k},\omega)\mathbf{E}_{\mathbf{G}'}(\mathbf{k},\omega)$$

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:

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

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

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

The macroscopic dielectric function

For cubic symmetry, one can prove that

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

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

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

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

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,

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

The macroscopic dielectric function

From this, one obtains

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

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

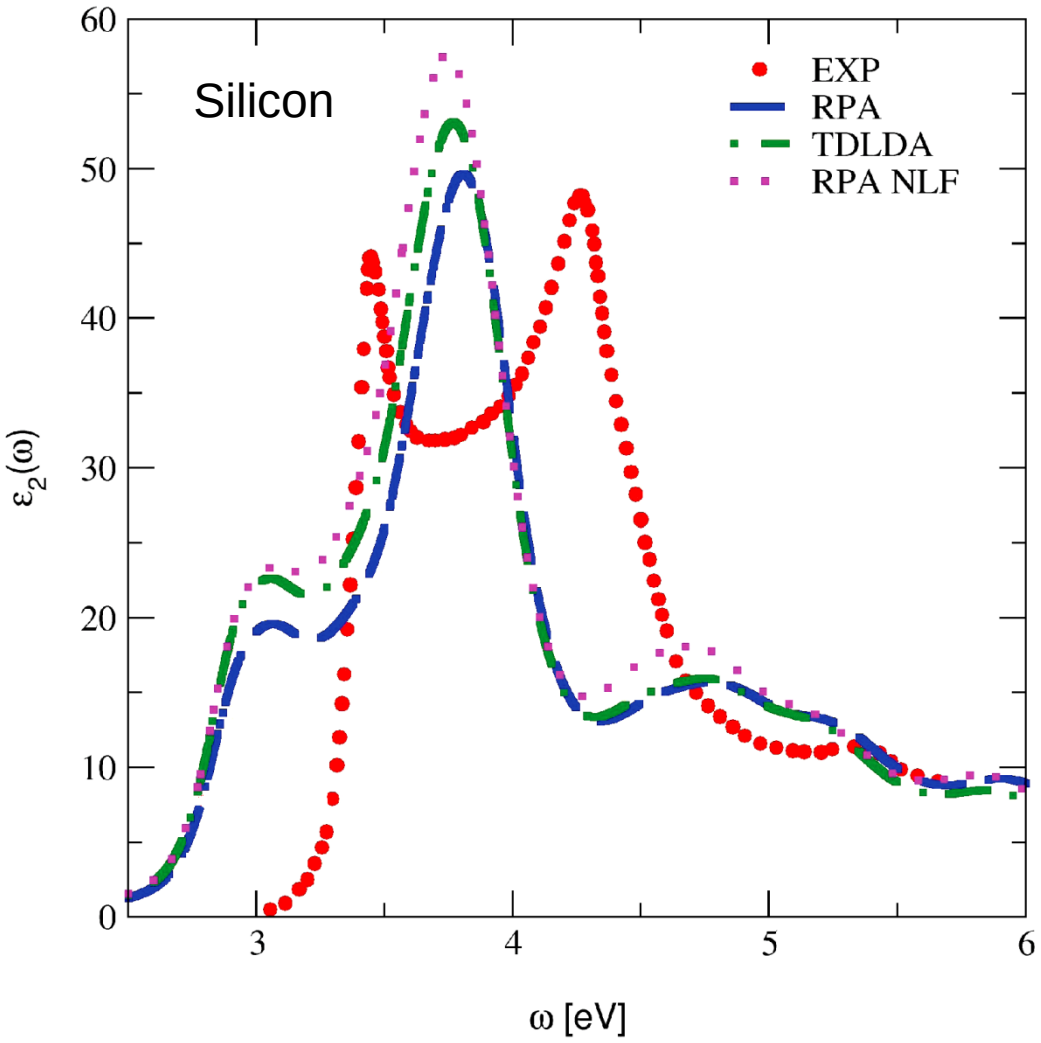
$$\overline{\chi}_{\mathbf{GG}'}(\mathbf{k},\omega) = \chi_{s\mathbf{GG}'}(\mathbf{k},\omega) + \sum_{\mathbf{G}_1\mathbf{G}_2} \chi_{s\mathbf{GG}_1}(\mathbf{k},\omega) \times \left\{ \overline{V}_{\mathbf{G}_1}(\mathbf{k})\delta_{\mathbf{G}_1\mathbf{G}_2} + f_{xc\mathbf{G}_1\mathbf{G}_2}(k,\omega) \right\}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

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

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

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

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:

$$K_{ia,i'a'}^{\mathbf{G}_0\mathbf{G}'_0}=\sum_{\mathbf{q}\in FBZ}\sum_{\mathbf{GG}'}\left\langle i\mathbf{k}_i\left|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}\right|a\mathbf{k}_a\right\rangle f_{xc,\mathbf{GG}'}(\mathbf{q},\omega)\left\langle a'\mathbf{k}_{a'}\left|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}\right|i'\mathbf{k}_{i'}\right\rangle$$
$$\times\delta_{\mathbf{k}_a-\mathbf{k}_i+\mathbf{q},\mathbf{G}_0}\;\delta_{\mathbf{k}_{a'}-\mathbf{k}_{i'}+\mathbf{q},\mathbf{G}'_0}$$

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

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

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

Long-range xc kernels for solids

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

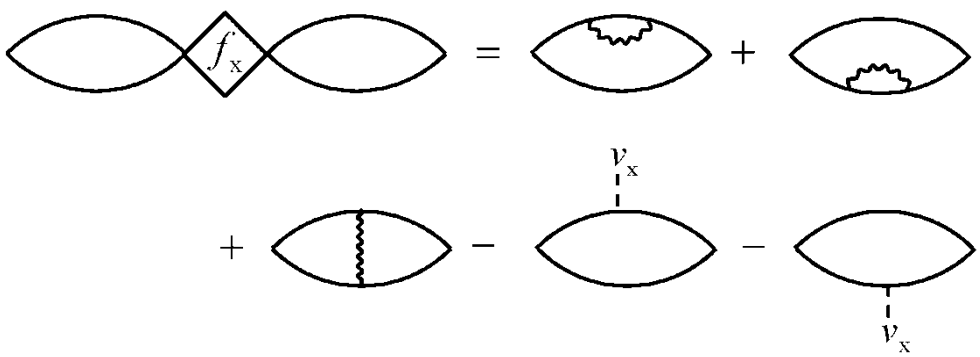
$$f_{xc,\mathbf{GG'}}^{LRC}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q}+\mathbf{G}|^2}\delta_{\mathbf{GG'}}$$

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

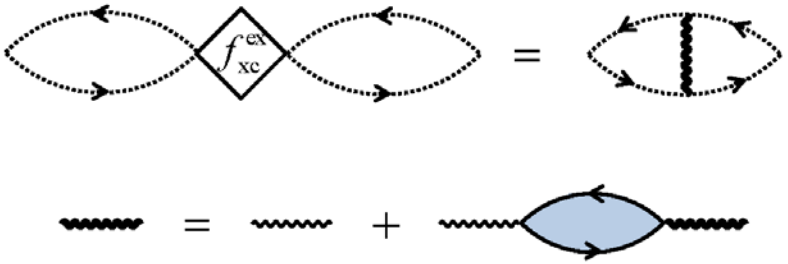
$$f_{xc,\mathbf{GG'}}^{boot}(\mathbf{q},\omega) = \frac{\varepsilon_{\mathbf{GG'}}^{-1}(\mathbf{q},0)}{\chi_{s00}(\mathbf{q},0)}$$

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

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



exact exchange



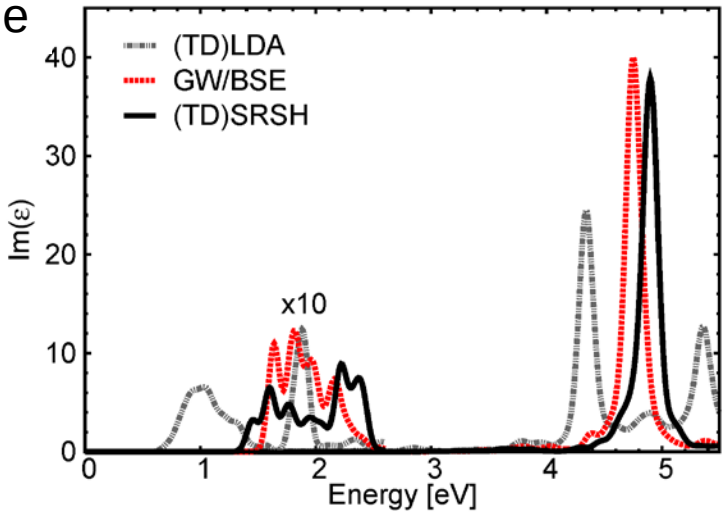
excitonic xc kernel from Bethe-Salpeter equation
(L. Reining et al., 2002)

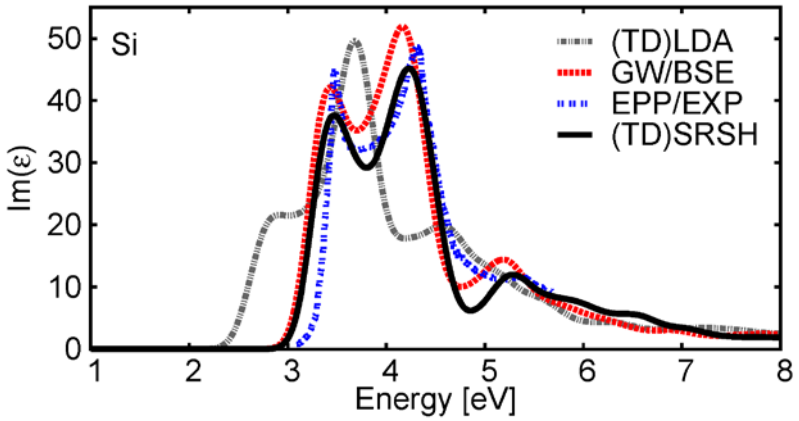
Excitons: which xc kernels to use?

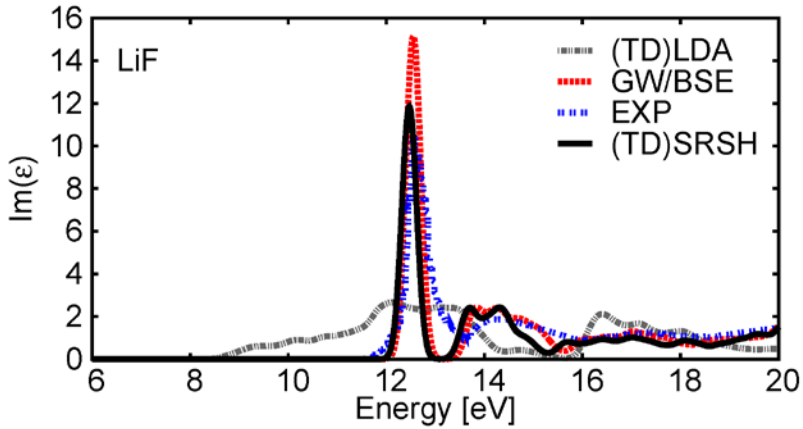
- Local functionals (ALDA/GGA) don't work
- **Nanoquanta kernel**: accurate but expensive
  Reining, Olevano, Rubio, Onida, PRL **88**, 066404 (2002)
- **Long-range corrected (LRC) kernel:** simple but ad-hoc
  Botti *et al.,* PRB **69**, 155112 (2004)
- **Bootstrap kernel:** several versions
  Sharma, Dewhurst, Sanna and Gross, PRL **107**, 186401 (2011)
- **Jellium with a gap:**
  Trevisanutto *et al.,* PRB **87**, 205143 (2013)
- **Hybrid functionals, meta-GGAs:** much activity lately
  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)

Optical spectra with range-separated hybrid

pentacene



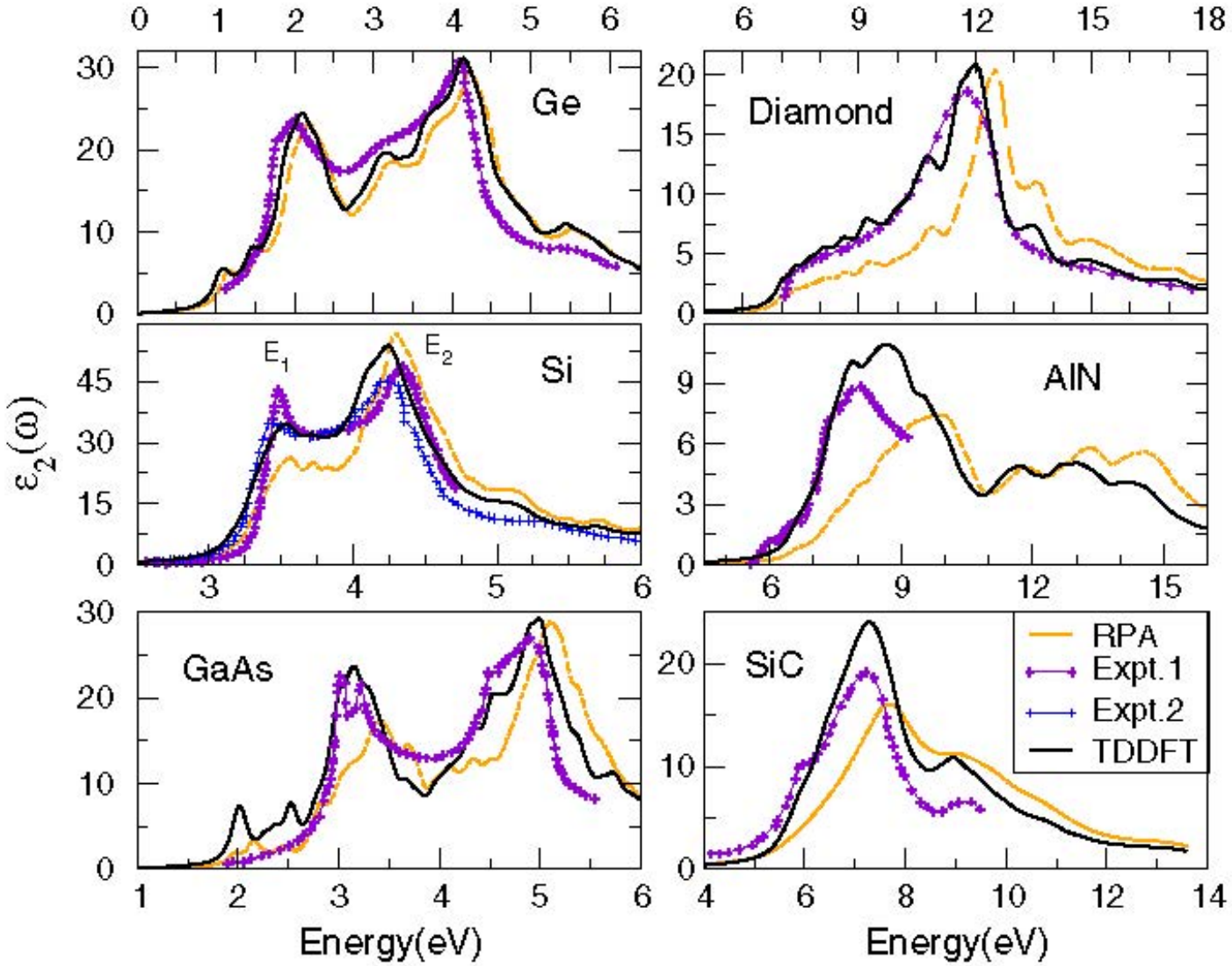




S. Refaely-Abramson, M. Jain, S. Sharifzadeh, J.B. Neaton, and L. Kronik, PRB **92**, 081204 (2015)

Contains adjustable range separation parameter

Optical spectra with TDDFT: “bootstrap” xc kernel



S. Sharma et al., PRL **107**, 186401 (2011)

Excitons with TDDFT: “bootstrap” xc kernel

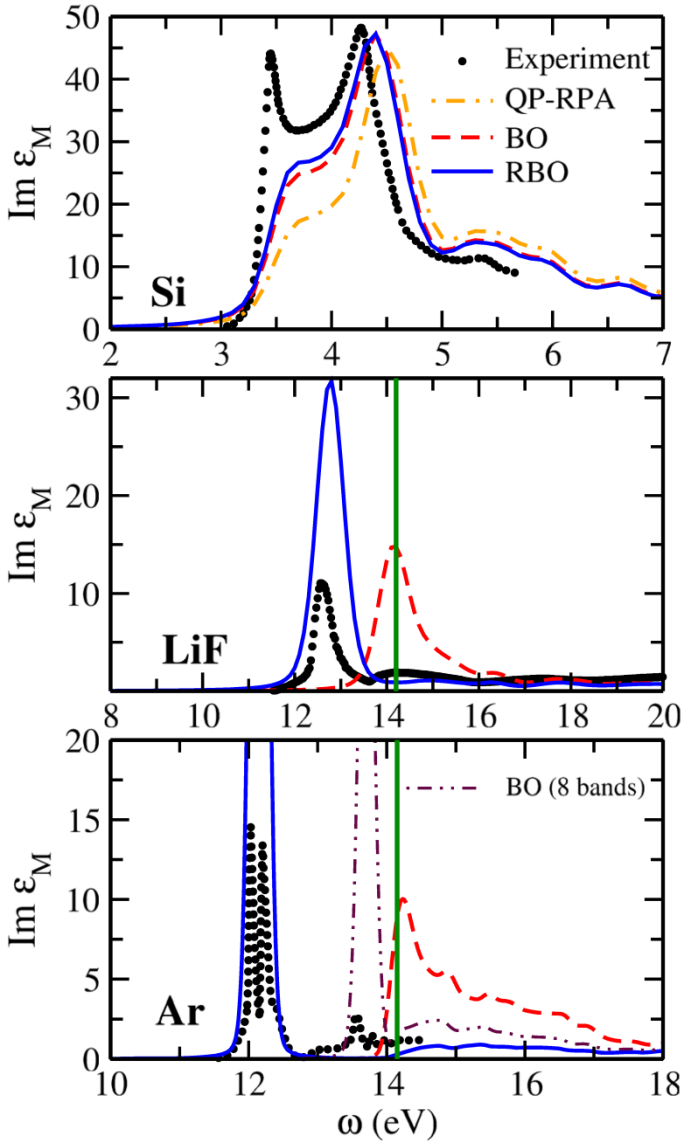
S. Sharma, J.K. Dewhurst, A. Sanna & E.K.U. Gross, PRL **107**, 186401 (2011)

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

$$\varepsilon^{-1} = 1 + v\chi_s[1-(v+f_{xc})\chi_s]^{-1}$$

Original bootstrap kernel: self-consistent iteration

Modified bootstrap xc kernels



Rigamonti *et al.*, PRL **114**, 146402 (2015)

$$f_{xc}^{RPA-boot} = \frac{[\varepsilon^{RPA}]^{-1}}{\chi^{RPA}}$$

S. Sharma, unpublished (2015)

$$f_{xc}^{0-boot} = \frac{[\varepsilon^{RPA}]^{-1}}{\chi_s}$$

See also TDCDFT:
J.A. Berger, PRL **115**, 137402 (2015)

Excitation energies from TDDFT

Excitation energies follow from eigenvalue problem (Casida 1995):

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

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

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

For real orbitals we can rewrite this as

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

Direct calculation of exciton binding energies

Casida equation of TDDFT (1995):

$$\sum_{jb\mathbf{k}'}\left[\delta_{i\mathbf{k},j\mathbf{k}'}\delta_{a\mathbf{k},b\mathbf{k}'}\omega_{ai\mathbf{k}}+K^{Hxc}_{ia\mathbf{k},jb\mathbf{k}'}\right]X_{jb\mathbf{k}'}+\sum_{jb\mathbf{k}'}K^{Hxc}_{ia\mathbf{k},jb\mathbf{k}'}Y_{jb\mathbf{k}'}=-\Omega X_{ia\mathbf{k}}$$

$$\sum_{jb\mathbf{k}'}K^{Hxc}_{ia\mathbf{k},jb\mathbf{k}'}X_{jb\mathbf{k}'}+\sum_{jb\mathbf{k}'}\left[\delta_{i\mathbf{k},j\mathbf{k}'}\delta_{a\mathbf{k},b\mathbf{k}'}\omega_{ai\mathbf{k}}+K^{Hxc}_{ia\mathbf{k},jb\mathbf{k}'}\right]Y_{jb\mathbf{k}'}=\Omega Y_{ia\mathbf{k}}$$

TDA

Full Casida equation can be transformed (using time-reversal symmetry)

$$\sum_{jb\mathbf{k}'}\left[\delta_{i\mathbf{k},j\mathbf{k}'}\delta_{a\mathbf{k},b\mathbf{k}'}\omega^2_{ai\mathbf{k}}+2\sqrt{\omega_{ai\mathbf{k}}\omega_{jb\mathbf{k}'}}\;K^{Hxc}_{ia\mathbf{k},jb\mathbf{k}'}\right]Z_{jb\mathbf{k}'}=\Omega^2 Z_{jb\mathbf{k}'}$$

Same computational cost as TDA!.

T. Sander, E. Maggio & G. Kresse, PRB **92**, 045209 (2015):
TDA in Bethe-Salpeter equation makes only tiny difference,
but in TDDFT it makes a difference for large-gap insulators

Direct calculation of exciton binding energies

$$\sum_{(mn\mathbf{k}')} \left[\delta_{i\mathbf{k},m\mathbf{k}'} \delta_{j\mathbf{k},n\mathbf{k}'} (\varepsilon_{j\mathbf{k}} - \varepsilon_{i\mathbf{k}}) + F_{Hxc}^{(ij\mathbf{k})(mn\mathbf{k}')} \right] \rho_{\lambda}^{(mn\mathbf{k}')} = \omega_{\lambda} \rho_{\lambda}^{(ij\mathbf{k})}$$

TDDFT coupling matrix:

$$F_{xc}^{(ij\mathbf{k})(mn\mathbf{k}')} = \frac{2}{V_{crys}} \sum_{\mathbf{GG}'} f_{xc,\mathbf{GG}'}(\mathbf{q}=0) \left\langle j\mathbf{k} \left| e^{i\mathbf{G}\cdot\mathbf{r}} \right| i\mathbf{k} \right\rangle \left\langle m\mathbf{k}' \left| e^{-i\mathbf{G}'\cdot\mathbf{r}} \right| n\mathbf{k}' \right\rangle$$

- **Exciton binding energy from diagonalizing the TDDFT excitonic Hamiltonian**
- **More expensive than calculating Im ε(ω), but more precise**

TDDFT vs MBPT

$$\sum_{(mn\mathbf{k}')}\left[\delta_{i\mathbf{k},m\mathbf{k}'}\delta_{j\mathbf{k},n\mathbf{k}'}(\varepsilon_{j\mathbf{k}}-\varepsilon_{i\mathbf{k}})+F_{Hxc}^{(ij\mathbf{k})(mn\mathbf{k}')}\right]\rho_{\lambda}^{(mn\mathbf{k}')}=\omega_{\lambda}\rho_{\lambda}^{(ij\mathbf{k})}$$

TDDFT coupling matrix:

xc kernel

$$F_{xc}^{(ij\mathbf{k})(mn\mathbf{k}')}=\frac{2}{V_{crys}}\sum_{\mathbf{GG}'}f_{xc,\mathbf{GG}'}(\mathbf{q}=0)\left\langle j\mathbf{k}\left|e^{i\mathbf{G}\cdot\mathbf{r}}\right|i\mathbf{k}\right\rangle\left\langle m\mathbf{k}'\left|e^{-i\mathbf{G}'\cdot\mathbf{r}}\right|n\mathbf{k}'\right\rangle$$

BSE coupling matrix:

$$F_{xc}^{(ij\mathbf{k})(mn\mathbf{k}')}=\frac{1}{V_{crys}}\sum_{\mathbf{GG}'}g_{\mathbf{GG}'}(\mathbf{q})\left\langle j\mathbf{k}\left|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\right|n\mathbf{k}'\right\rangle\left\langle m\mathbf{k}'\left|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}\right|n\mathbf{k}'\right\rangle\delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'}$$

screened Coulomb interaction

Screened exact exchange (SXX)

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

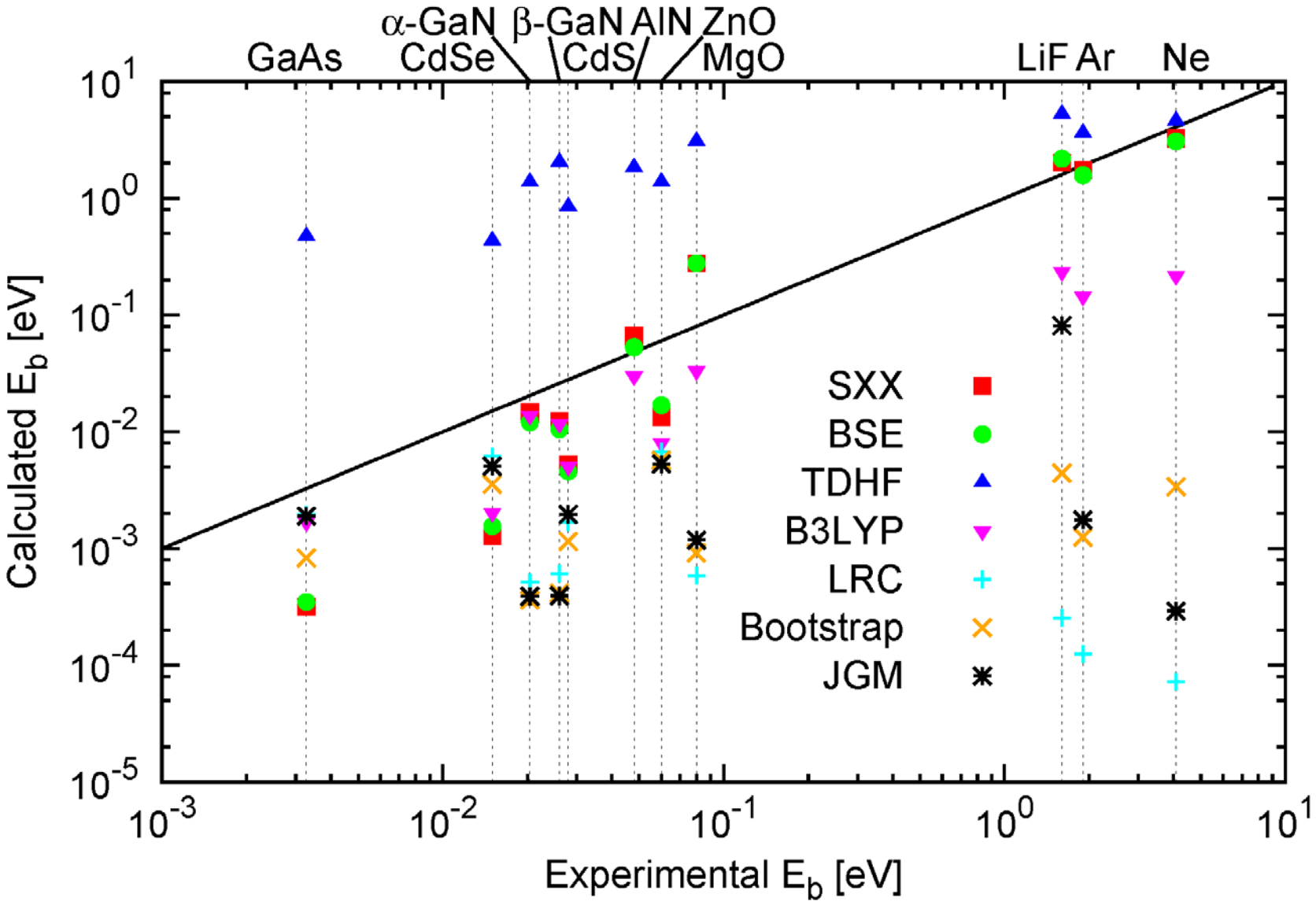
TDHF: $$g_{GG'}(\mathbf{q}) = -4\pi \frac{1}{|\mathbf{q} + \mathbf{G}'|^2} \delta_{GG'}$$ **unscreened**

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

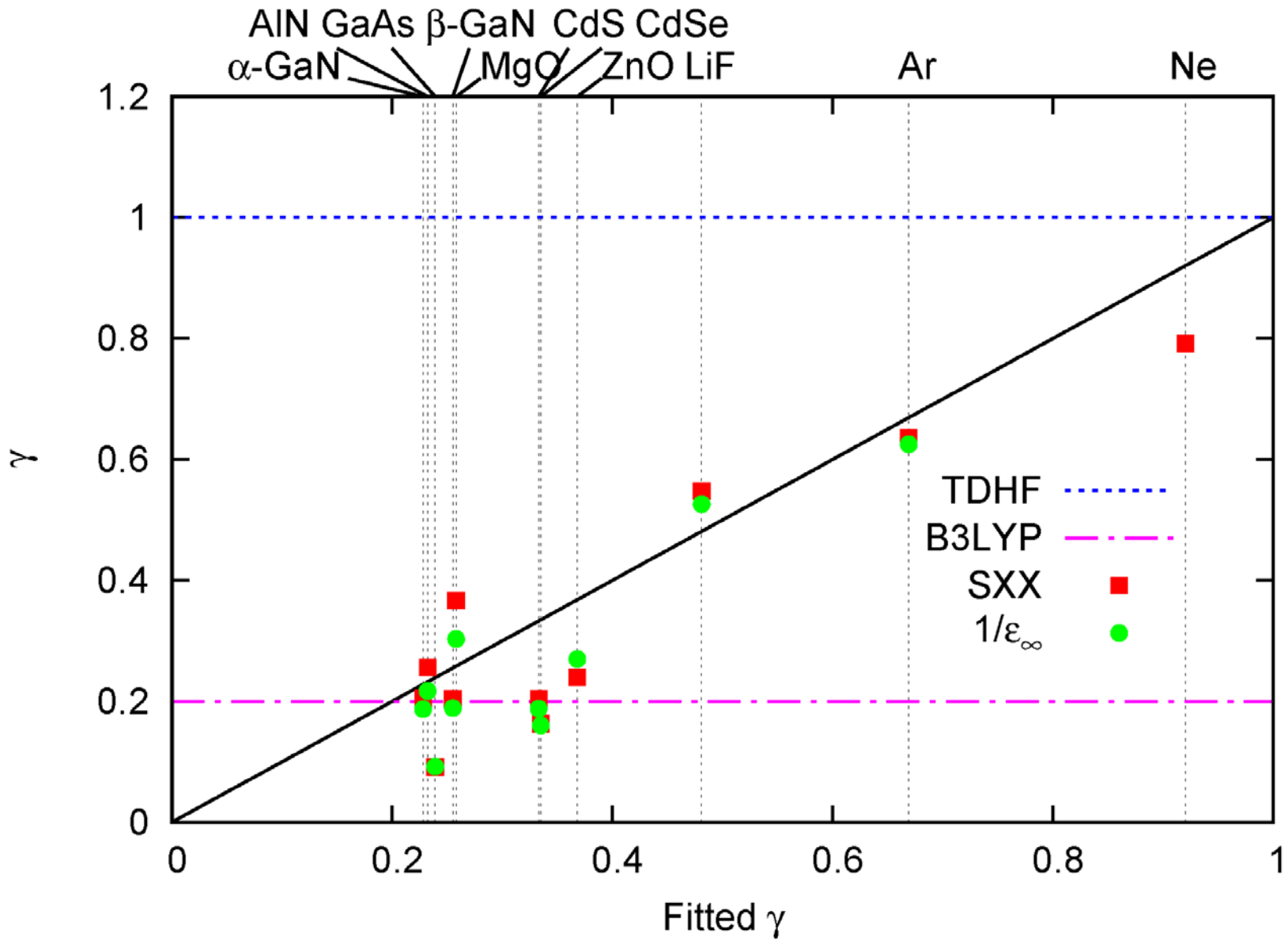
$$\gamma = \varepsilon^{-1}_{00}(0,0)$$ **Calculated with RPA**

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

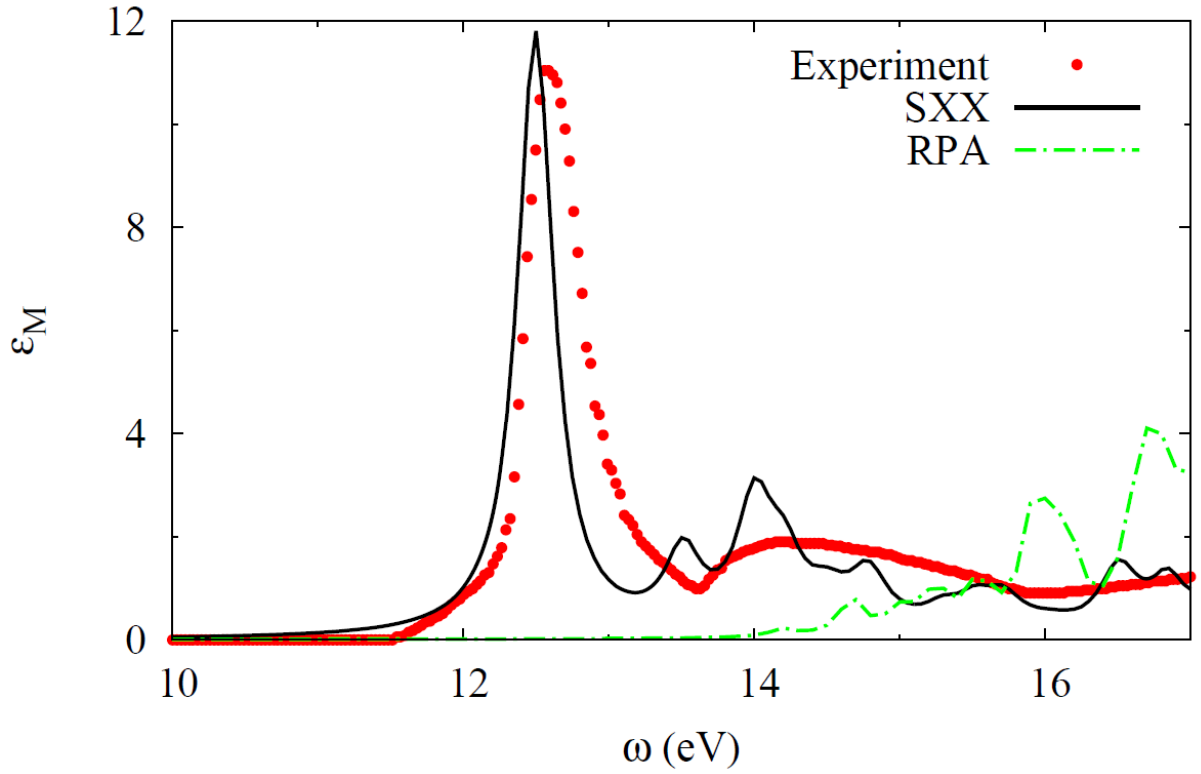
Exciton binding energies (4-band model)



Screening parameter

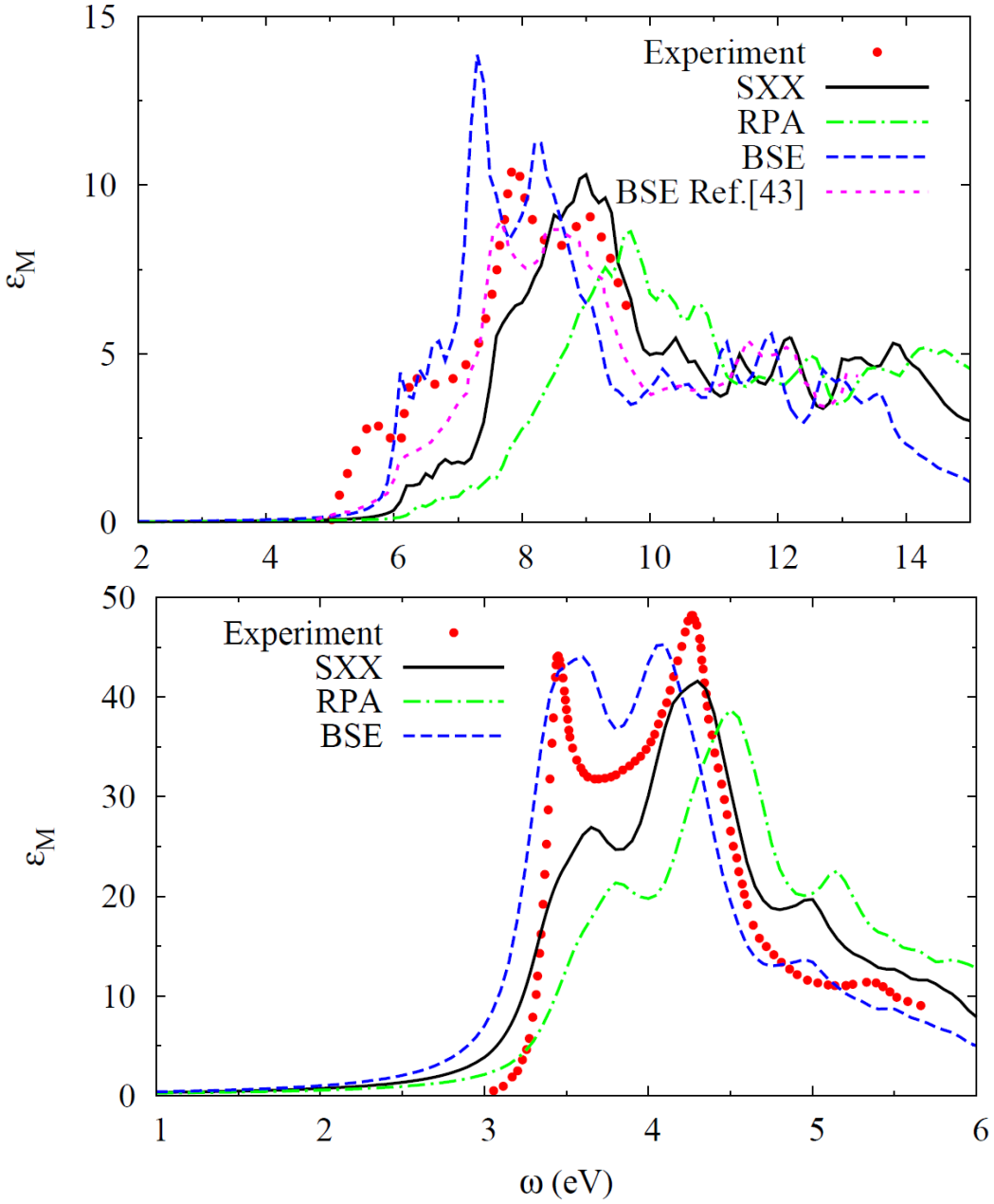


Absorption spectrum of LiF



- ►good oscillator strength
- ►second excitonic peak

Absorption spectra of AlN and Si



Summary

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

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

- Alternative to BSE: SXX kernel – same accuracy but cheaper

- SXX works very well for exciton binding energies for large- and small-gap materials (still room for improvement). Promising goal: excitonic hybrid kernel

- Challenge: real-time TDDFT description of excitonic effects

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