TDDFT for extended systems II: Excitons

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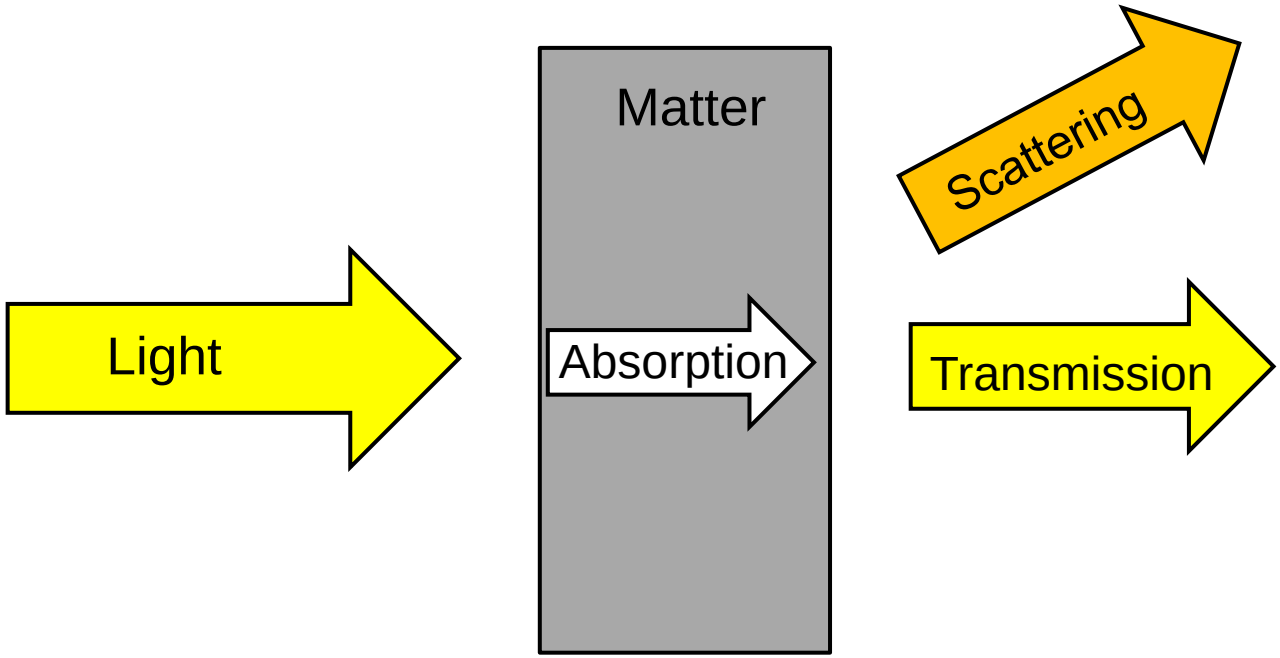
Benasque, August 27, 2018

Outline

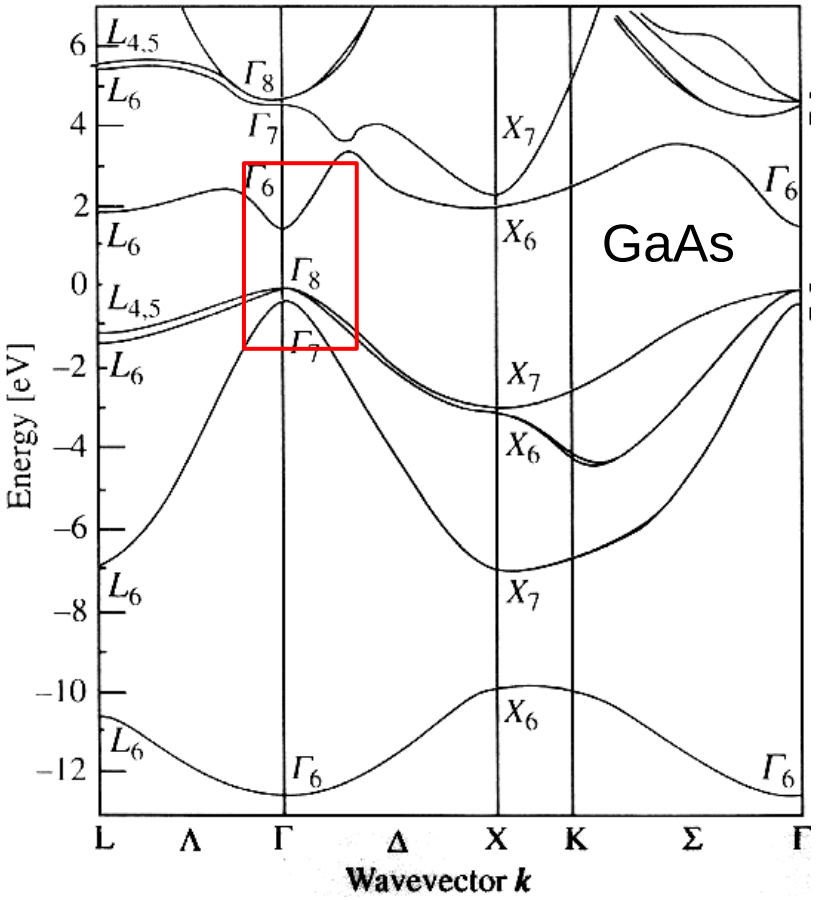
- Introduction to excitons
- TDDFT for periodic systems
- Optical spectra and exciton binding energies
- xc functionals for excitons
- Simplified BSE: the SXX approach
- Summary

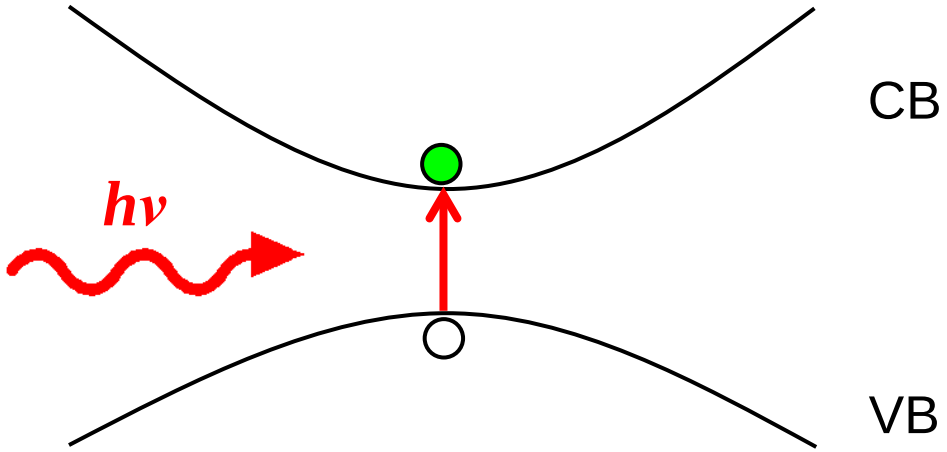
Absorption of light in a solid



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

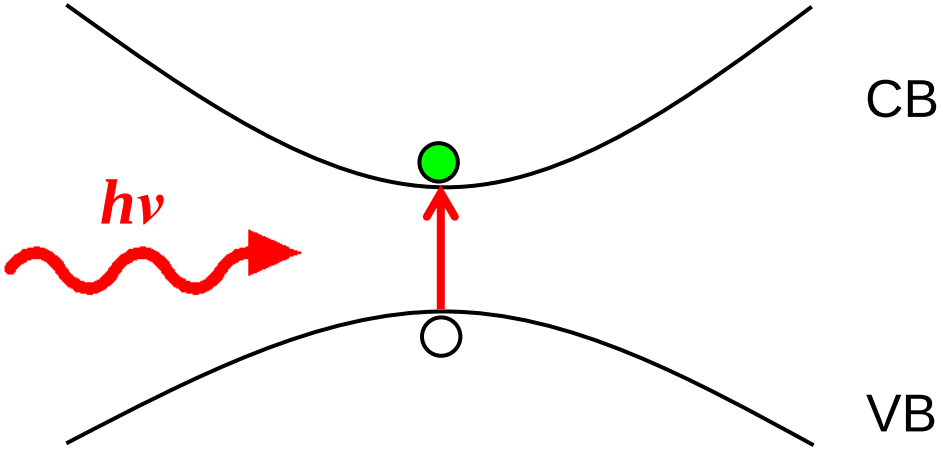
Absorption of light across the band gap



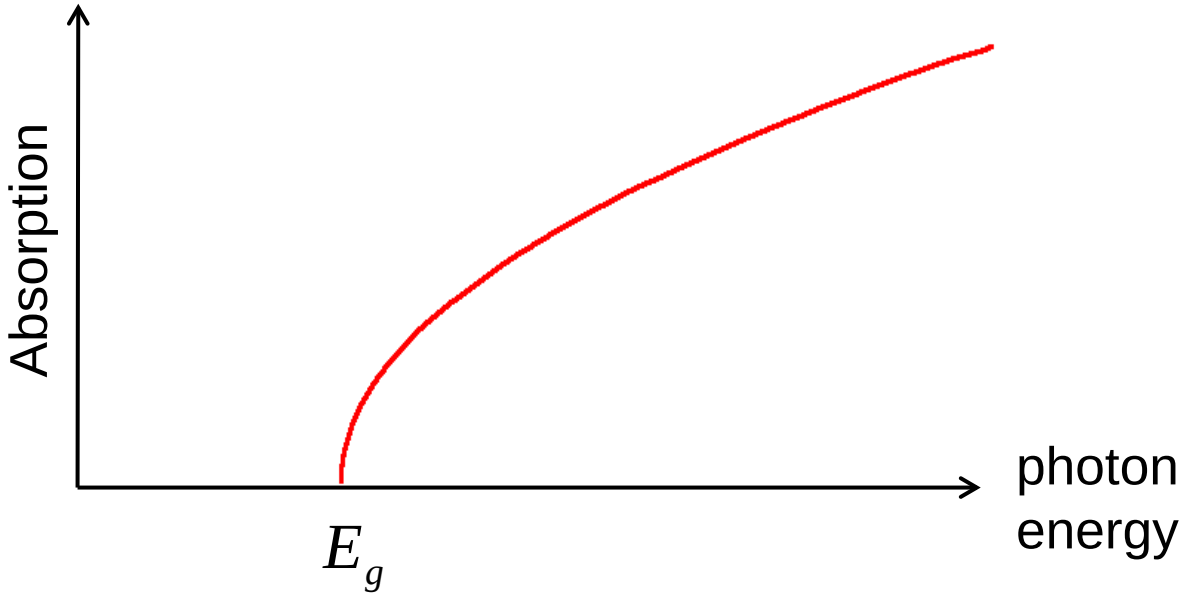


- Light comes in with photon energy at least as large as the band gap
- Photon gets absorbed, promotes electron across the gap, leaving a hole behind

Absorption spectra of insulators/semiconductors

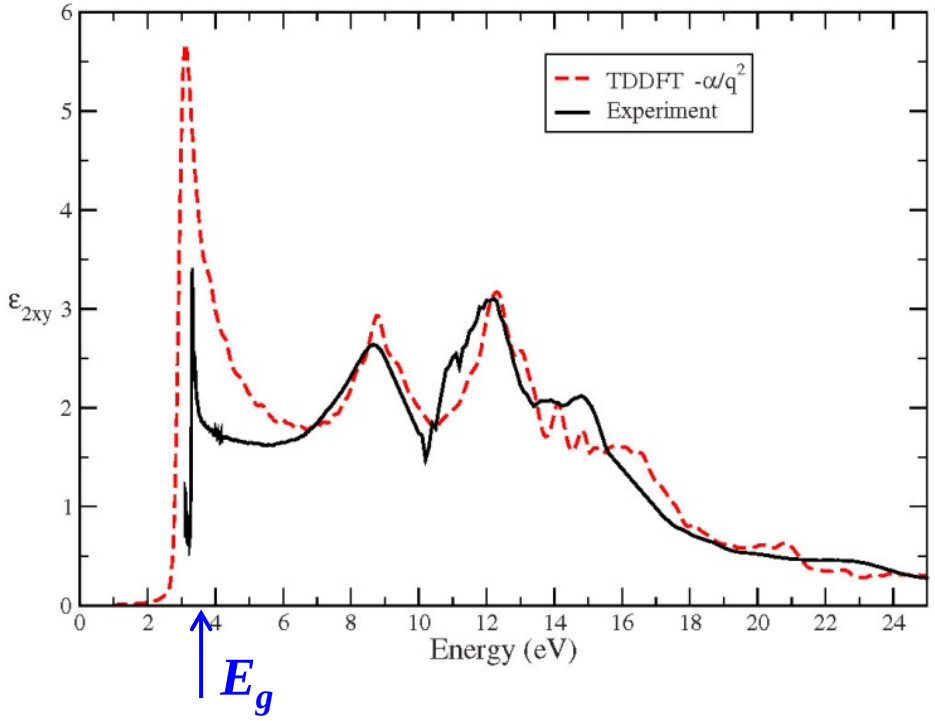


will produce an absorption spectrum like this:



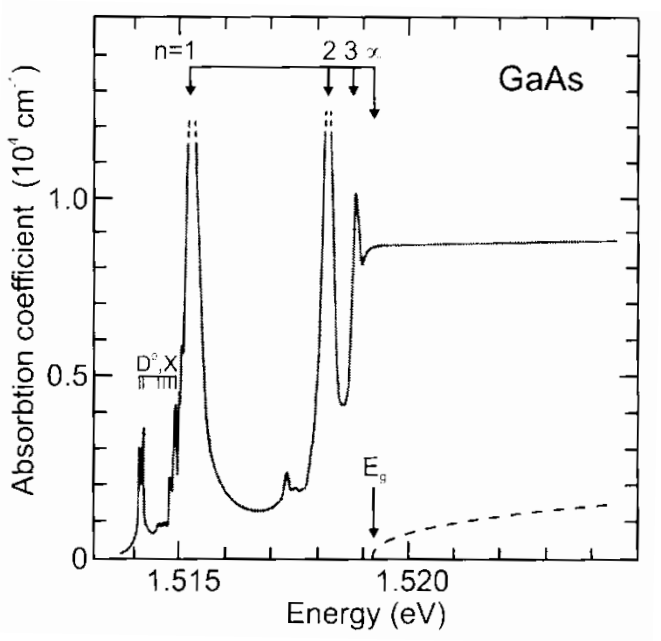
Absorption spectra of insulators/semiconductors

ZnO



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

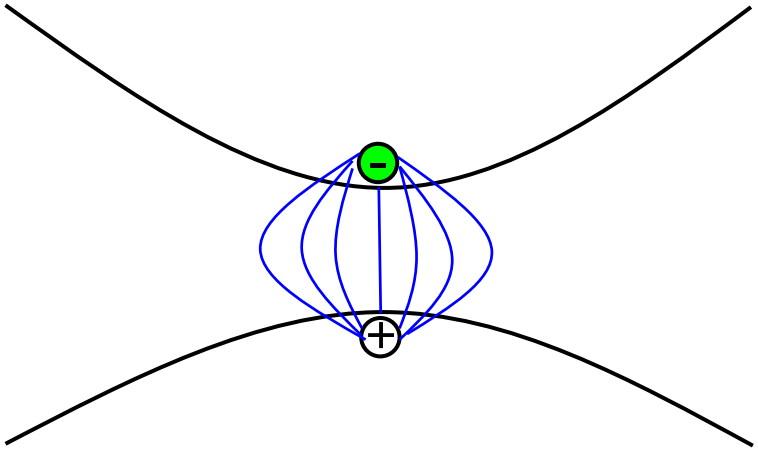
GaAs



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

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

What is an exciton?

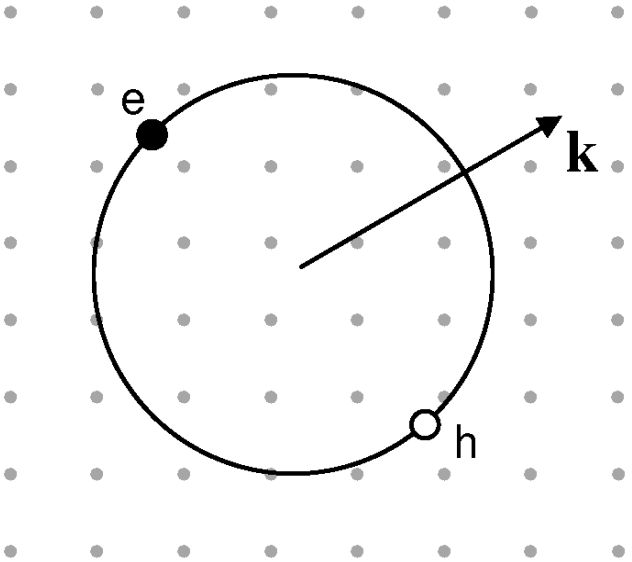


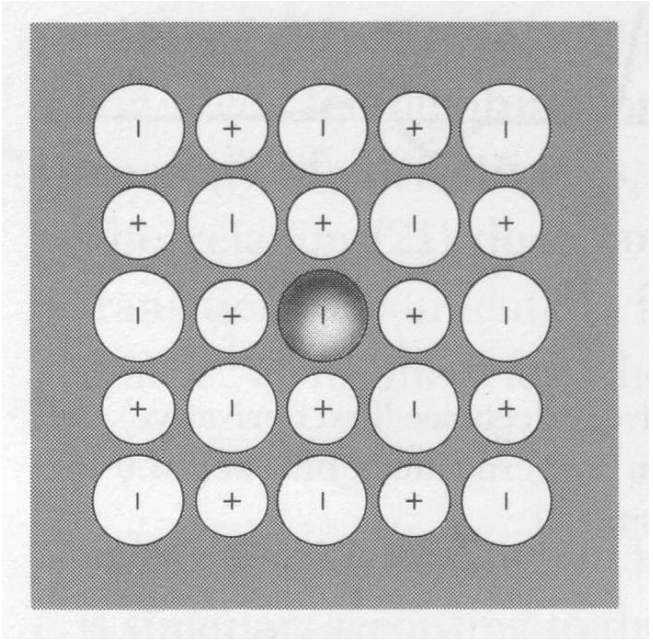
► After their creation, the electron and the hole are not completely free, but experience **Coulomb attraction.**

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

Excitons are bound electron-hole pairs.

Elementary view of Excitons





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

►In semiconductors with small band gap and large ε

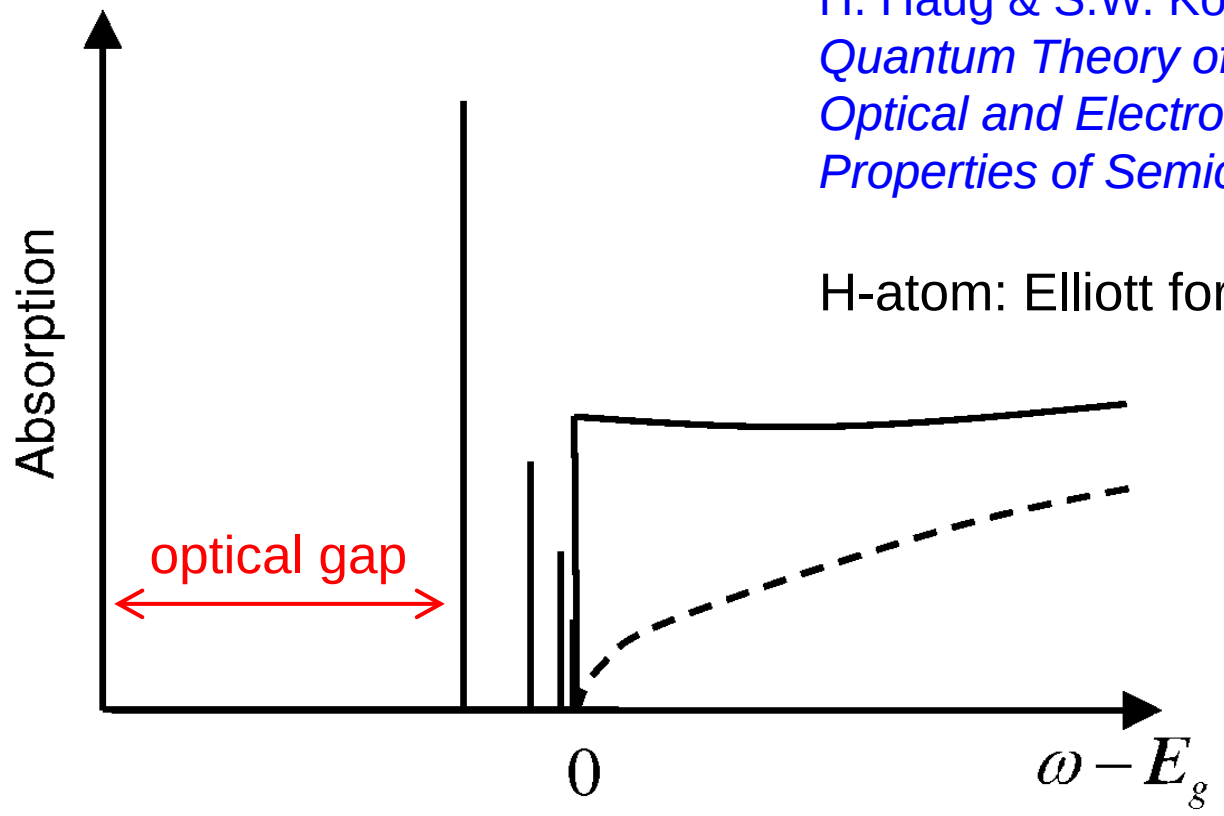
Frenkel exciton:
tightly bound, localized on a single (or a few) atoms

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

Excitonic features in the absorption spectrum

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

H-atom: Elliott formula



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

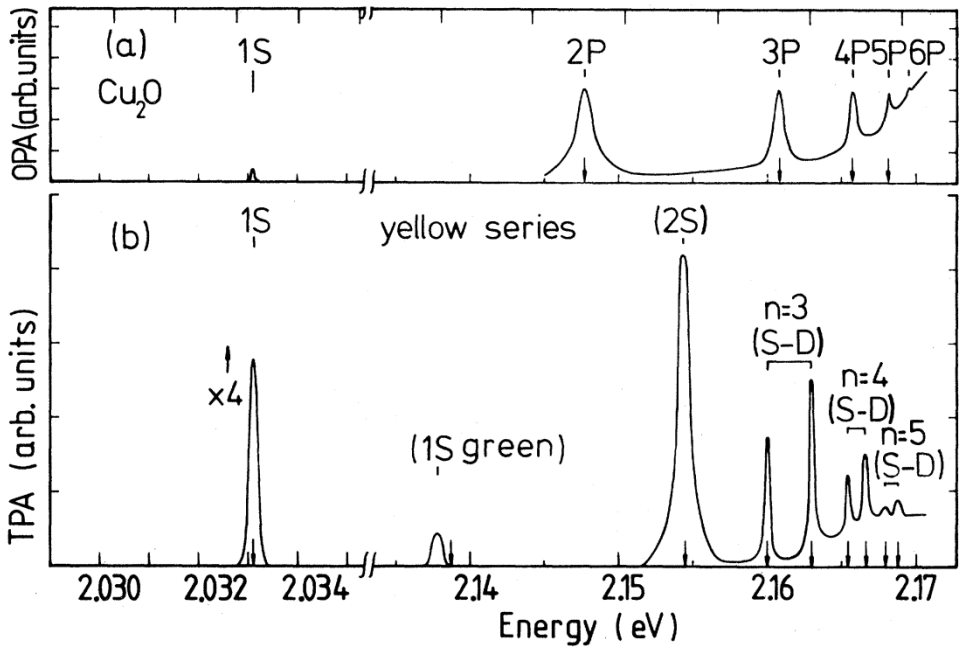
Wannier equation and excitonic Rydberg Series

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

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

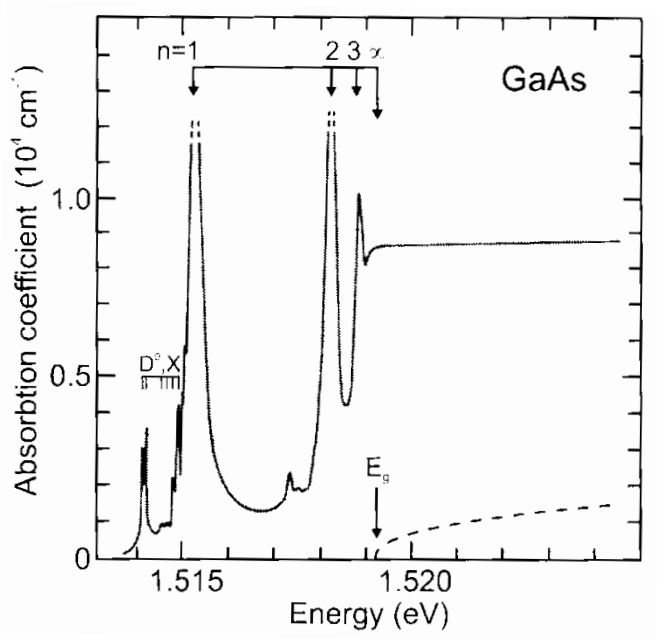
Sham and Rice, Phys. Rev. **144**, 708 (1966)

Cu_2O



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

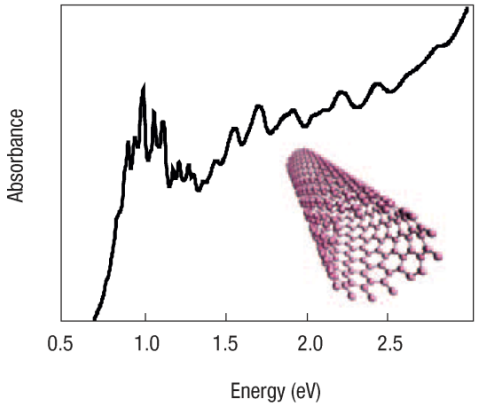
GaAs

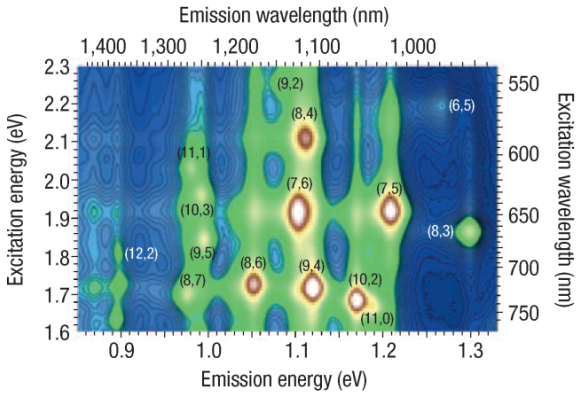


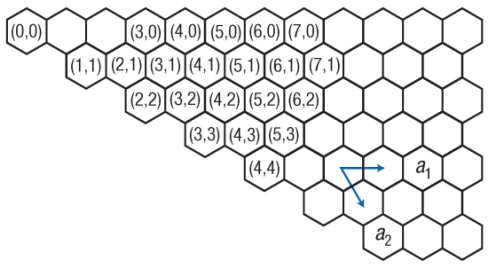
R.G. Ulbrich, Adv. Solid State Phys. **25**, 299 (1985)

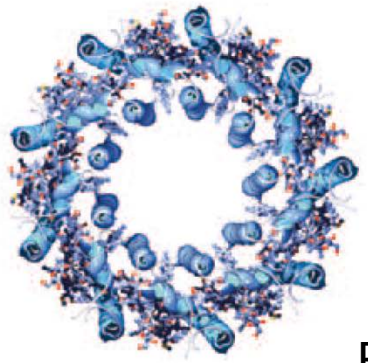
Excitons in nanoscale systems

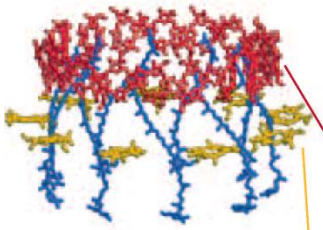
G. D. Scholes and G. Rumbles, Nature Mater. **5**, 683 (2006)
Jang & Mennucci, Rev. Mod. Phys. **90**, 035003 (2018)

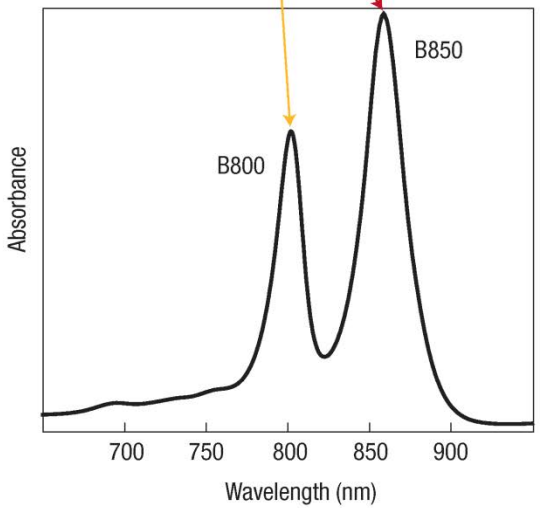






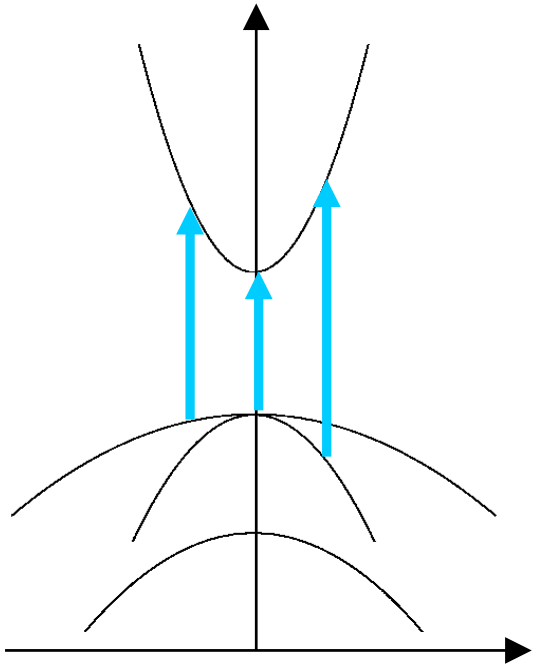






Frenkel excitons in light-harvesting systems: purple bacteria

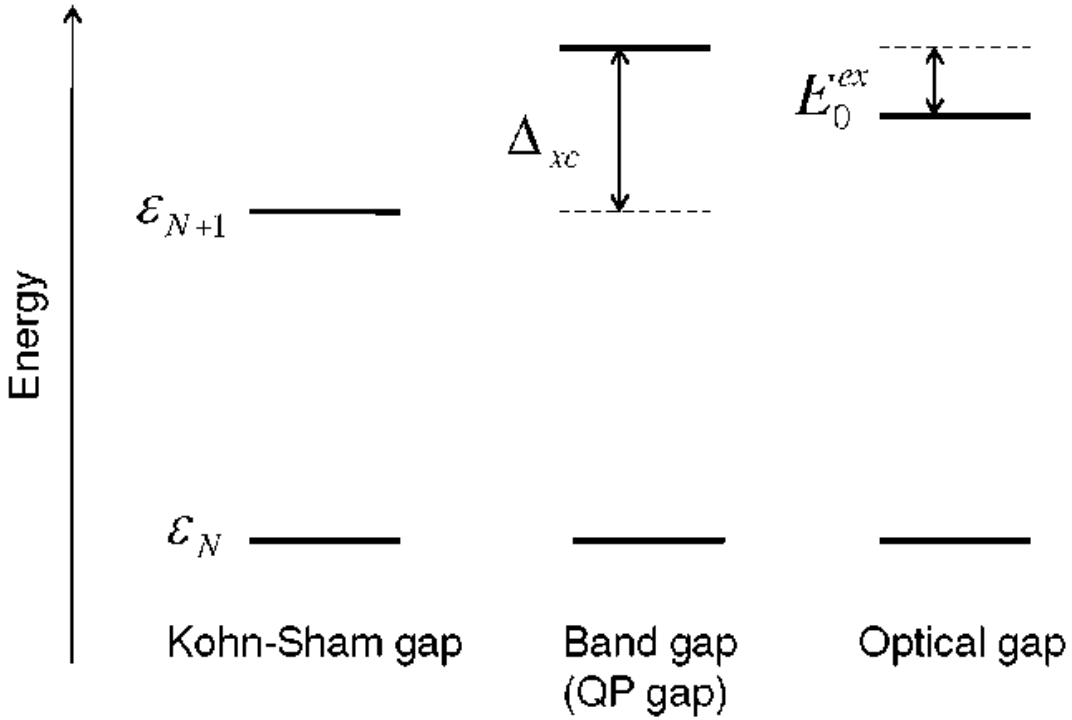
Optical excitations in bulk Insulators



Optical transitions in insulators are challenging for TDDFT:

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

Insulators: three different gaps

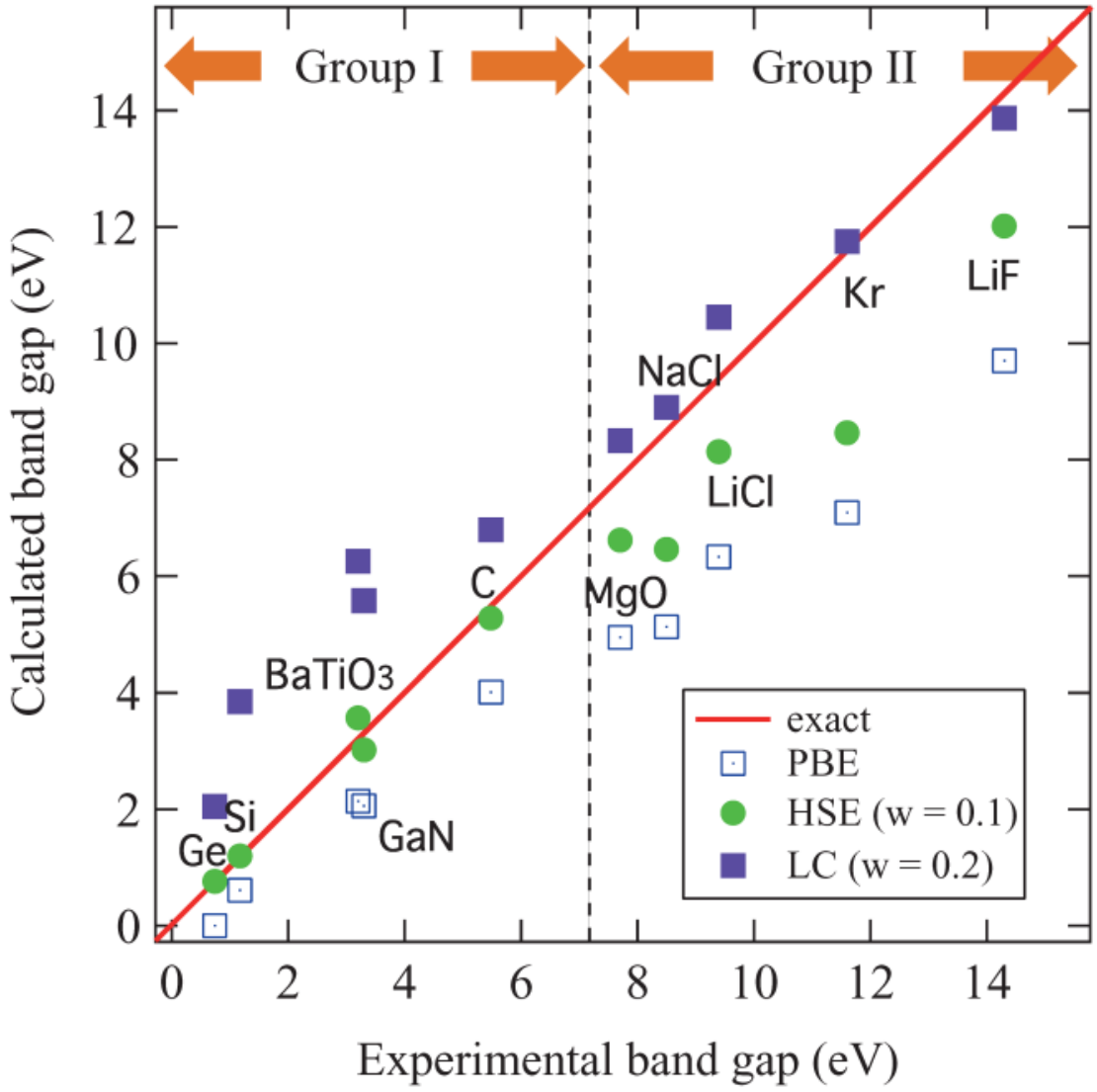


The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

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

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

Hybrid functionals for the band gap



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

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

Excitons: comparison of first-principles methods*

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

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

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

Time-dependent DFT: Based on the electron density

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

* Matteo Gatti, TDDFT School 2010, Benasque

Excitons with TDDFT: two equivalent methods

1. Calculate the dielectric function via Dyson equation

(computationally more efficient, gives optical spectrum)

2. Solve Casida equation

(more expensive, gives precise exciton binding energies)

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)

TDDFT Linear response in periodic systems

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

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

Fourier transform:

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

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

The dielectric tensor

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

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

Maxwell equations

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

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

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

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

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

Homogeneous systems

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

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

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

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

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

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

scalar dielectric function:

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

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

and for a periodic system,

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

The macroscopic dielectric function

From this, one obtains

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

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

$$\bar{\chi}_{\mathbf{GG}'}(\mathbf{q},\omega) = \chi_{s\mathbf{GG}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1\mathbf{G}_2} \chi_{s\mathbf{GG}_1}(\mathbf{q},\omega)$$

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

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

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

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

Density response of periodic systems

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

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

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

Density eigenmode:
set

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

Density eigenmode:
set

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

Excitation energies from TDDFT

Excitation energies follow from eigenvalue problem (Casida 1995):

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

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

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

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

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

Direct calculation of exciton binding energies

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

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

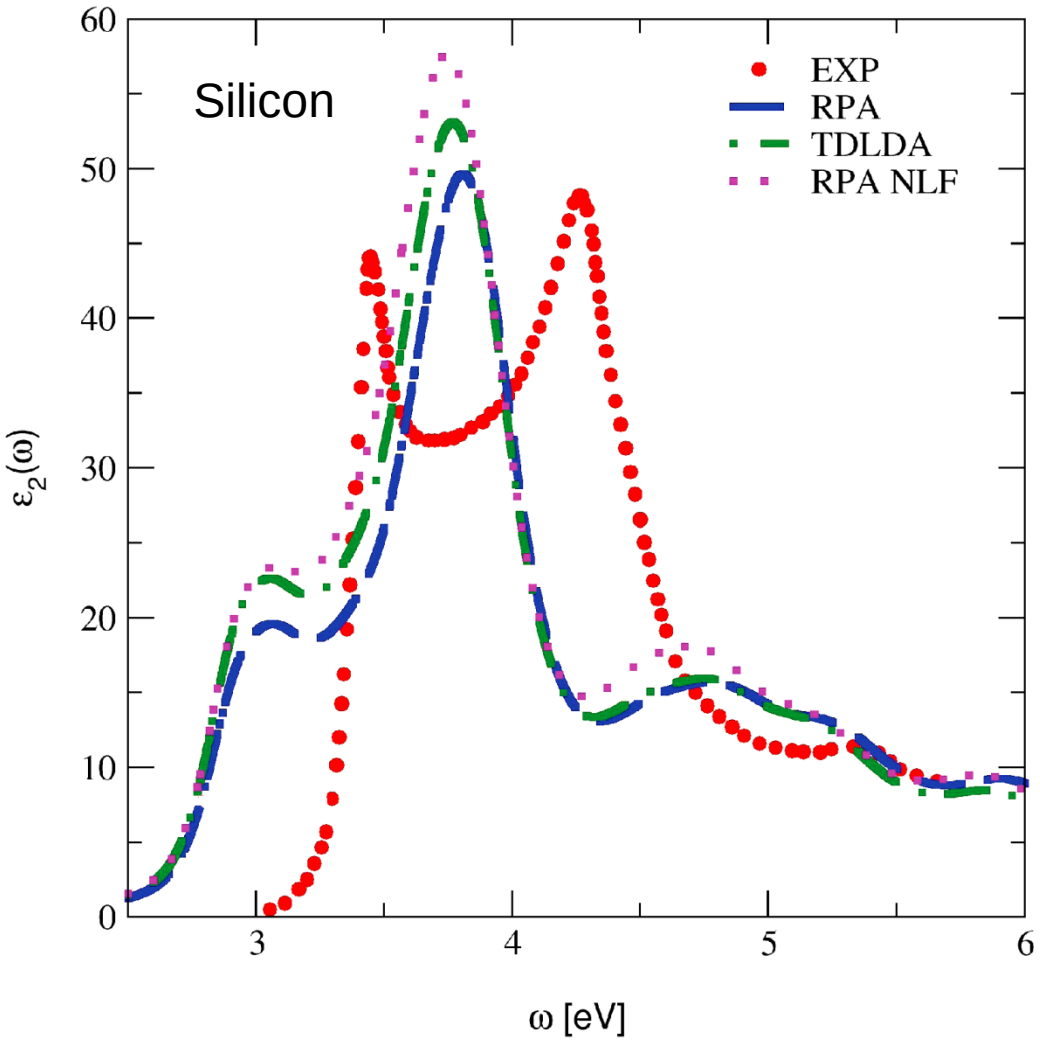
Tamm-Dancoff Approximation (TDA)

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

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

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

Optical absorption in Insulators: TDDFT



RPA and ALDA both bad!

►absorption edge red shifted (electron self-interaction)

►first excitonic peak missing (electron-hole interaction)

Why does the LDA fail??

►lacks long spatial range

►need new classes of xc functionals

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

The xc kernel for periodic systems

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

TDDFT requires the following matrix elements as input:

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

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

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

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

The xc kernel for periodic systems

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

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

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

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

"excitonic", accounts for electron-hole interaction

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

Long-range xc kernels for solids

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

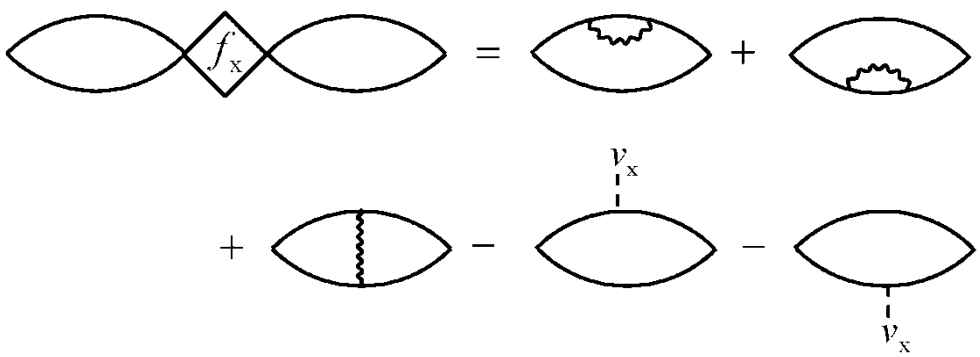
$$f^{LRC}_{xc,\mathbf{GG'}}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q}+\mathbf{G}|^2}\delta_{\mathbf{GG'}}$$

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

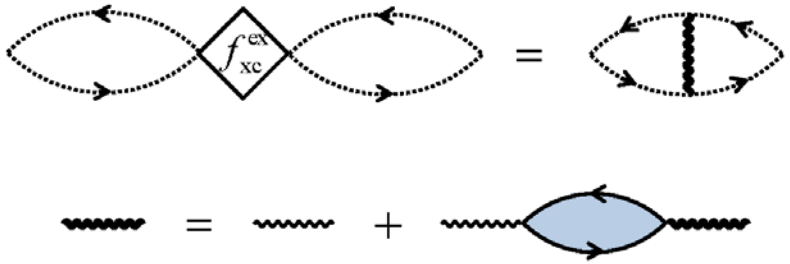
$$f^{boot}_{xc,\mathbf{GG'}}(\mathbf{q},\omega) = \frac{\varepsilon^{-1}_{\mathbf{GG'}}(\mathbf{q},0)}{\chi_{s00}(\mathbf{q},0)}$$

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

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



exact exchange



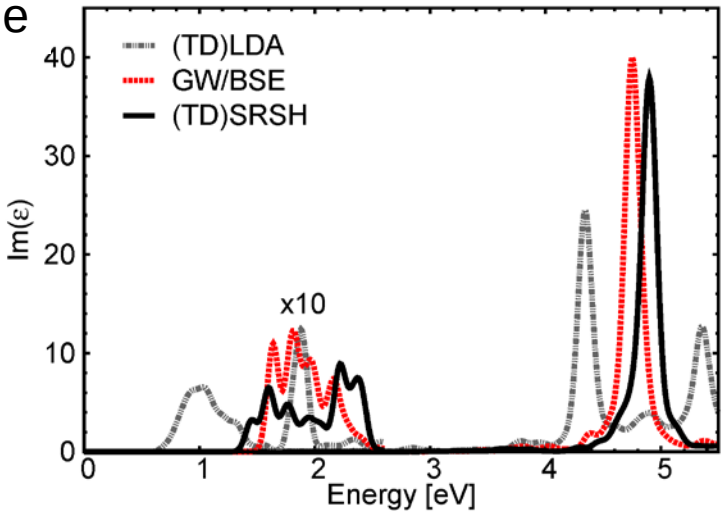
"nanoquanta" kernel, reverse-engineered from BSE
(L. Reining et al., 2002)

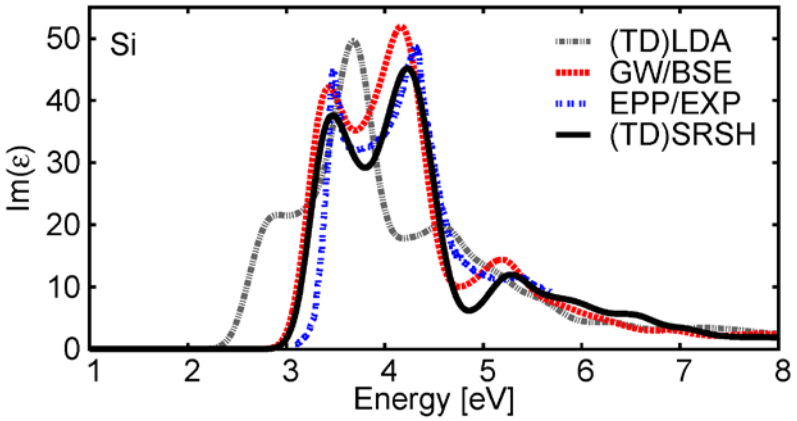
Excitons: which xc kernels to use?

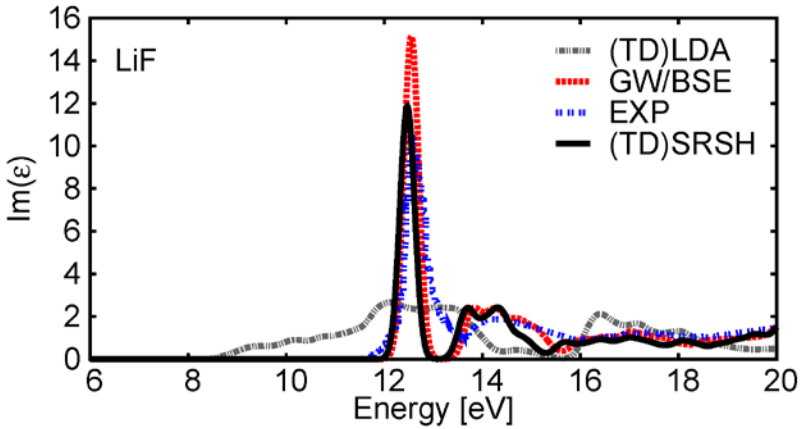
- Local functionals (ALDA/GGA) don't work
- **Nanoquanta kernel**: accurate but expensive
  Reining, Olevano, Rubio, Onida, PRL **88**, 066404 (2002)
- **Long-range corrected (LRC) kernel:** simple but ad-hoc
  Botti *et al.,* PRB **69**, 155112 (2004)
- **Bootstrap kernel:** several versions
  Sharma,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

Optical spectra with range-separated hybrid

pentacene







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

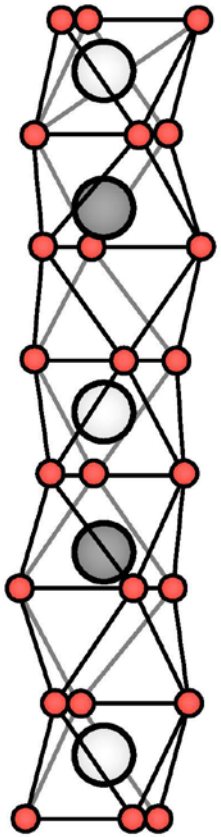
Contains adjustable
range separation parameter

The family of LRC/Bootstrap xc kernels

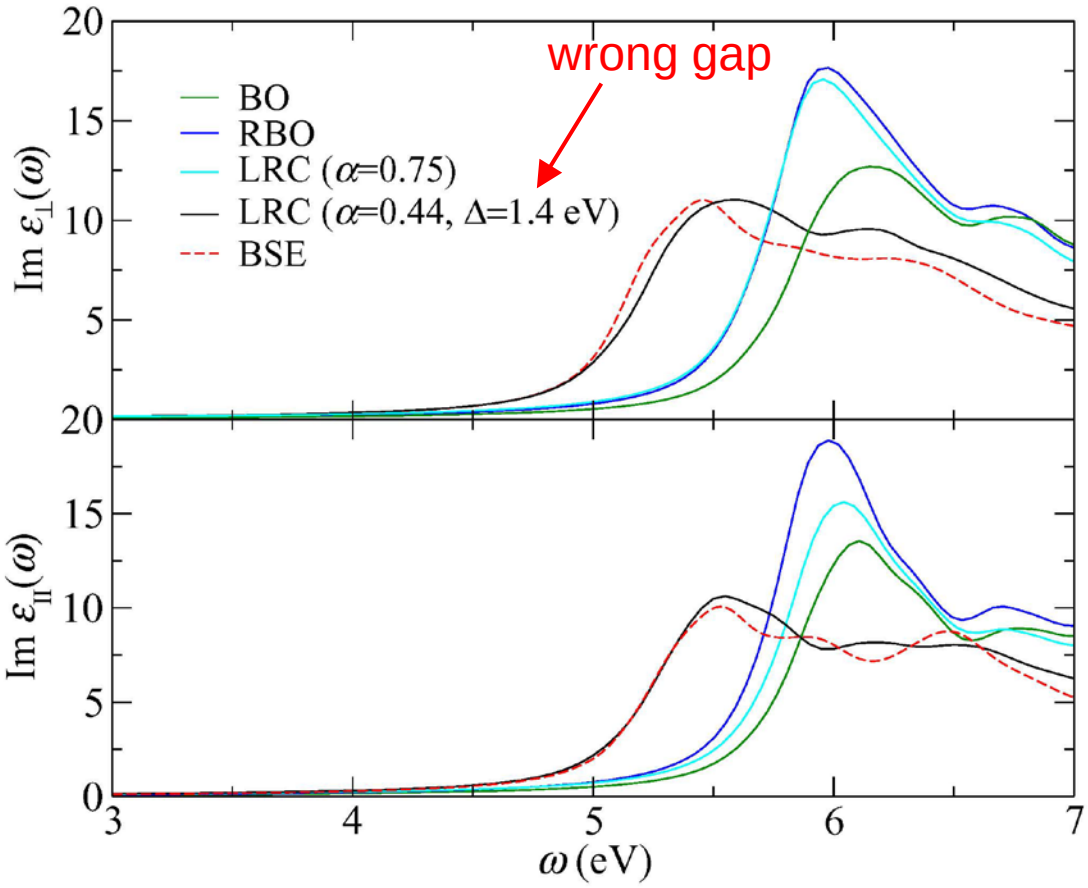
$$f_{xc}^{LRC} = -\frac{\alpha}{\mathbf{q}^2}$$

- Empirical LRC kernel: $\alpha = 4.615\varepsilon_{\infty}^{-1} - 0.213$ (Botti 2004)
- Bootstrap kernel: $f_{xc}^{Boot} = \varepsilon^{-1} / \chi_0$ (Sharma 2011)
- 0-Bootstrap kernel: $f_{xc}^{0-Boot} = \varepsilon_{RPA}^{-1} / \chi_0$ (Sharma 2015)
- RPA-Bootstrap kernel: $f_{xc}^{RPA-Boot} = \varepsilon_{RPA}^{-1} / \chi_{RPA}$ (Rigamonti 2015)
- Jellium with a gap: $\alpha \approx E_g^2 / n$ (Trevisanutto 2013)

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)

Assessing the Tamm-Dancoff approximation

T. Sander, E. Maggio & G. Kresse, PRB **92**, 045209 (2015)
M. Shao, F.H. da Jornada, C. Yang, J. Deslippe & S.G. Louie, Lin. Alg. Appl (2016)
TDA in Bethe-Salpeter equation makes only tiny difference.

Bootstrap kernel exciton binding energy:

	GaAs	β-GaN	α-GaN	MgO	LiF	Ar	Ne
exp	3.27	20.4	26.0	80.0	1600	1900	4080
Full	0.537	1.46	1.58	4.28	484	1210	2860
TDA	0.523	1.35	1.46	3.57	201	430	916

semiconductors:
small difference

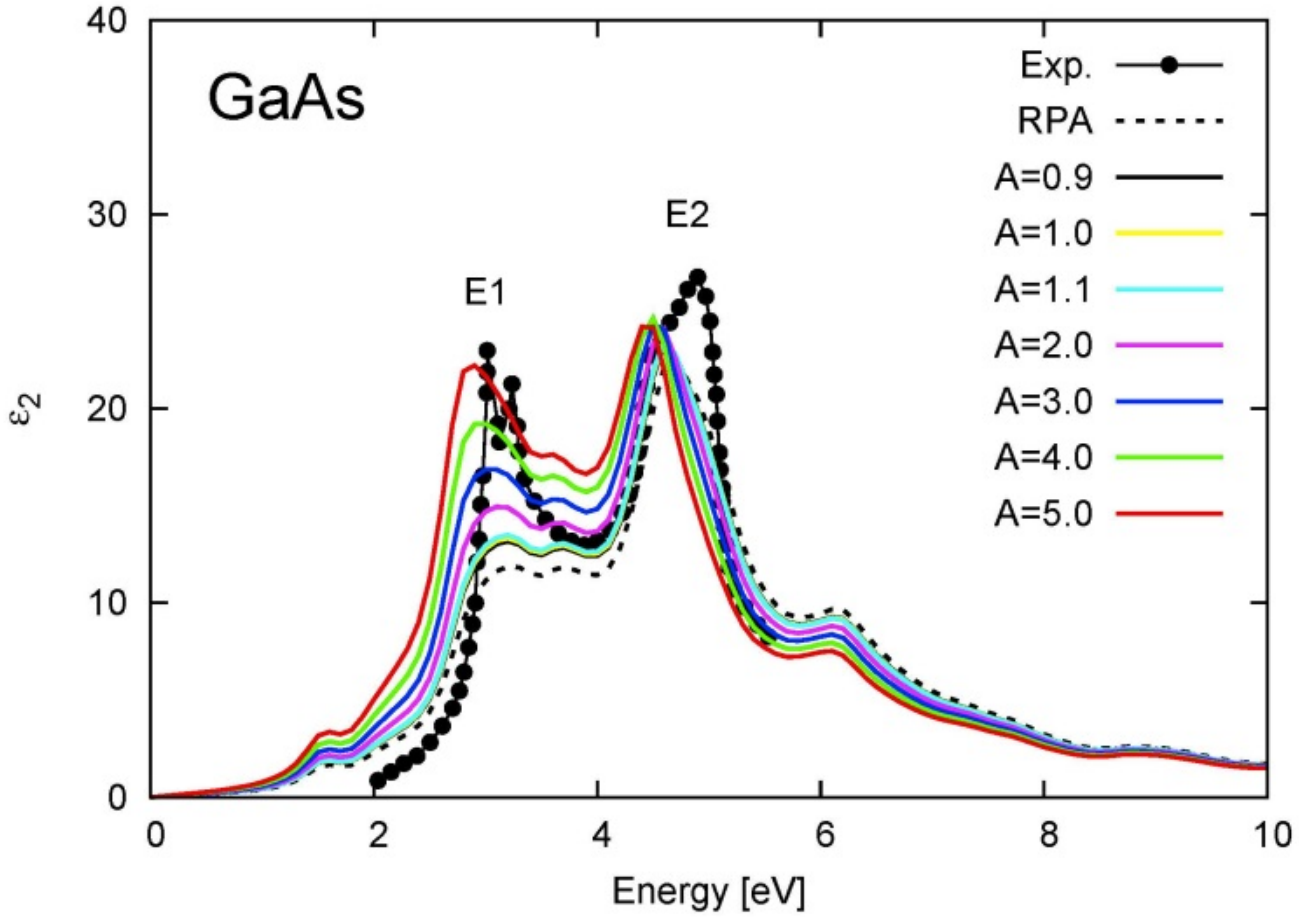
large-gap insulators:
huge difference

TDA always underestimates exciton binding energies, but the error is negligible if $E_b << E_{gap}$

Young-Moo Byun and C. A. Ullrich, Computation **5**, 9 (2017)

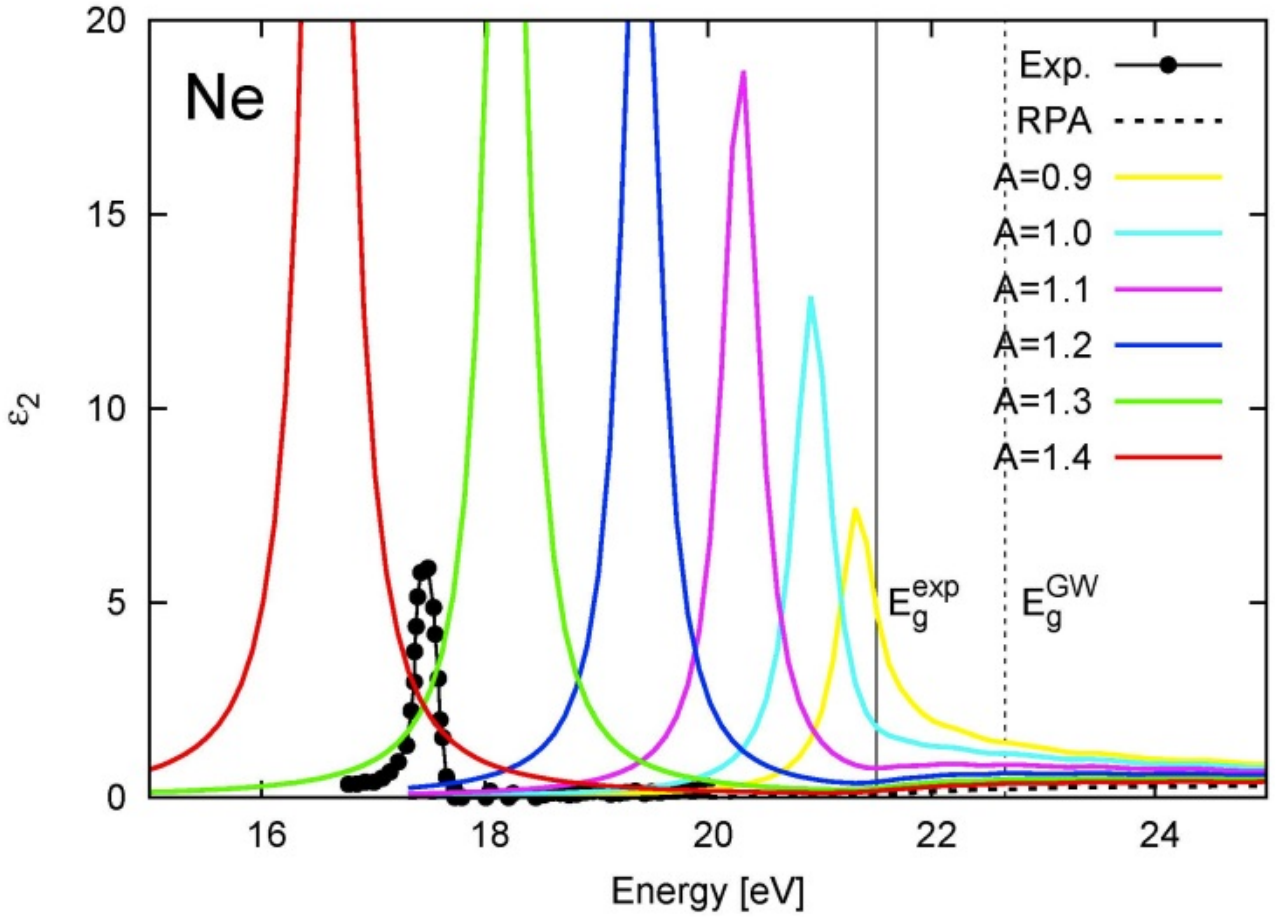
Scaled bootstrap kernel: GaAs

$$f_{xc} = A\, f_{xc}^{RPA-Boot}$$

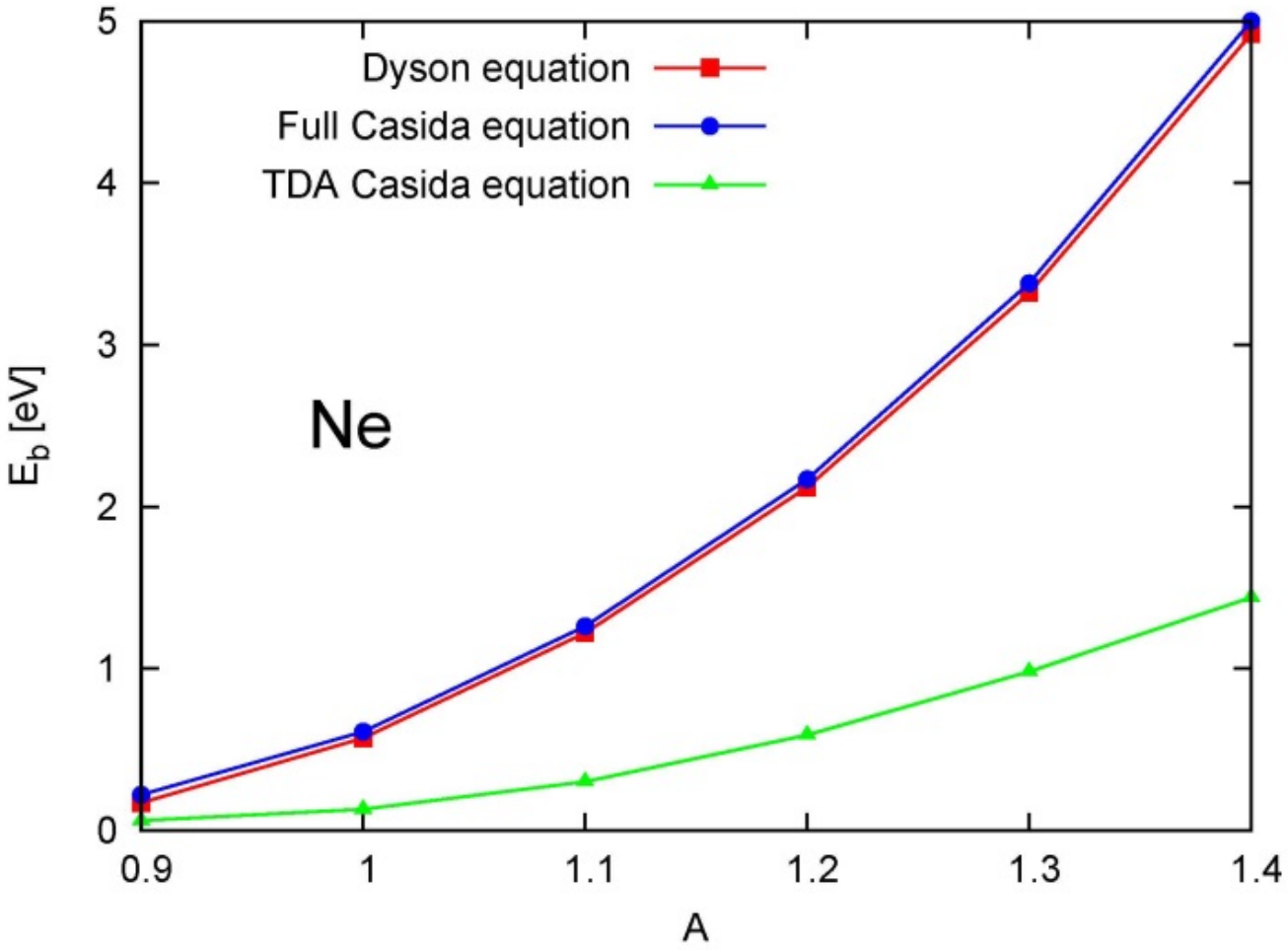


Scaled bootstrap kernel: solid Ne

$$f_{xc} = A\, f_{xc}^{RPA-Boot}$$

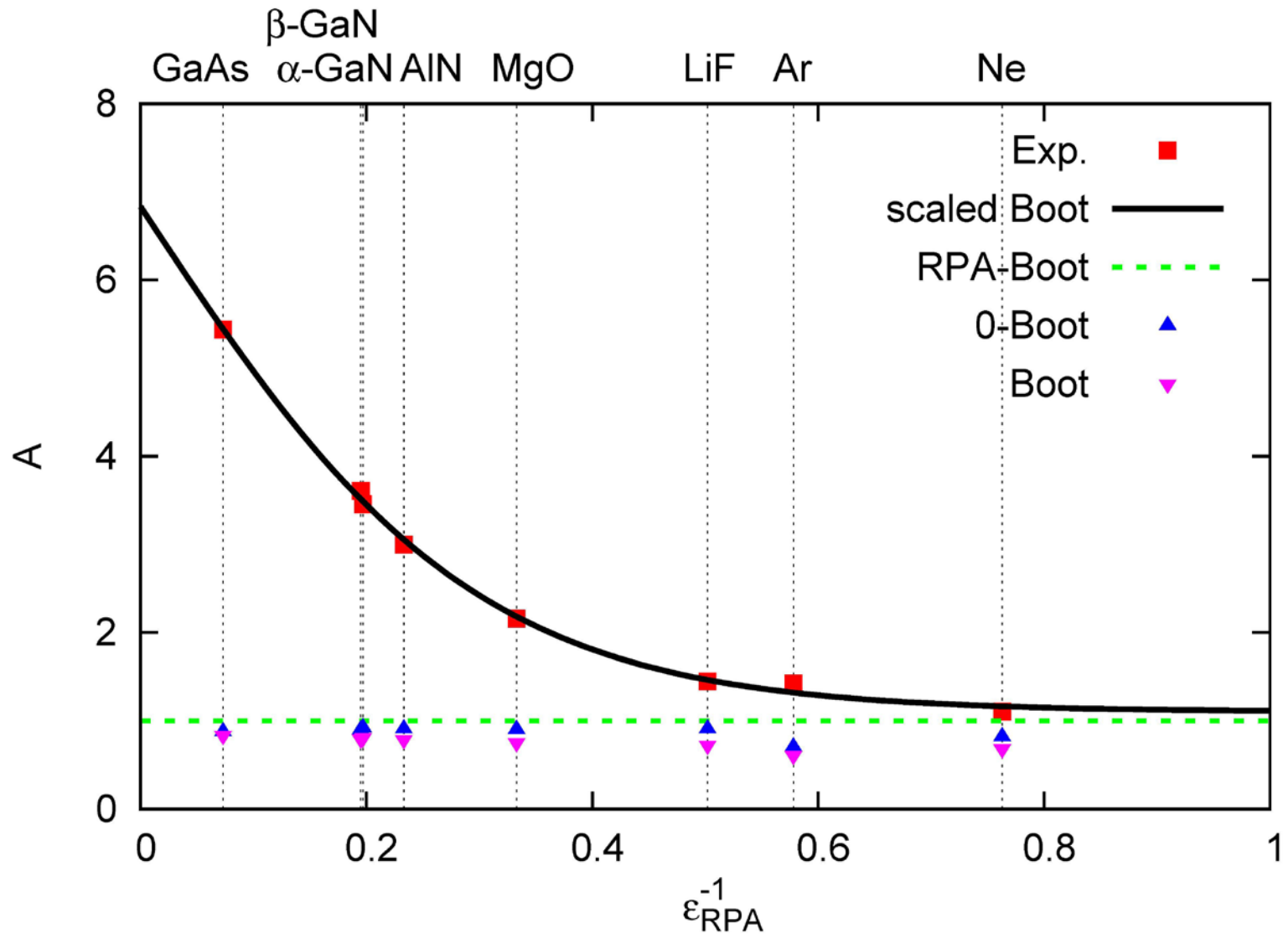


Scaled bootstrap kernel: solid Ne

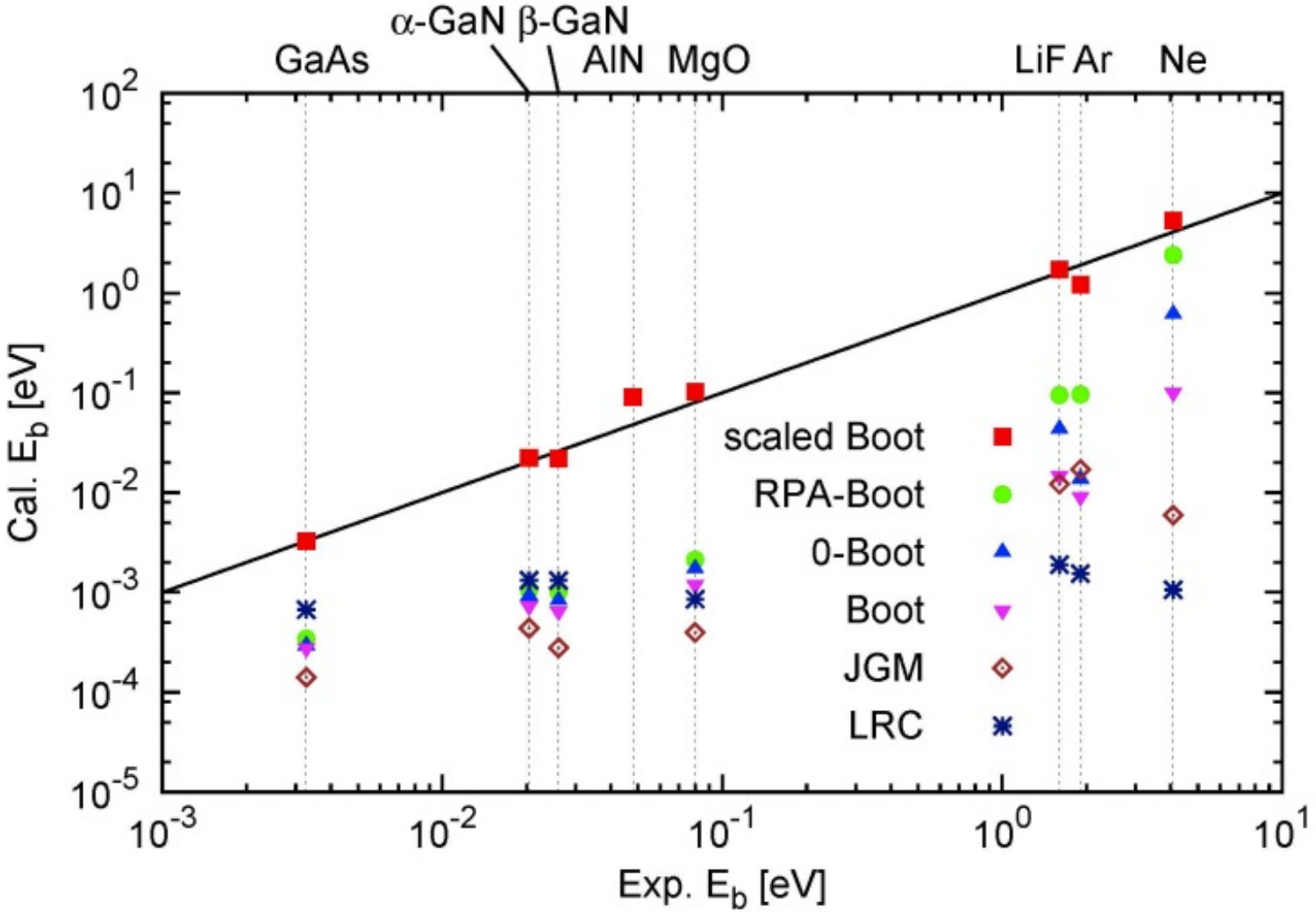


Demonstrates equivalence of Dyson equation and Casida equation approach for calculating excitons. Note: different codes were used.

Scaled bootstrap xc kernel: best fit

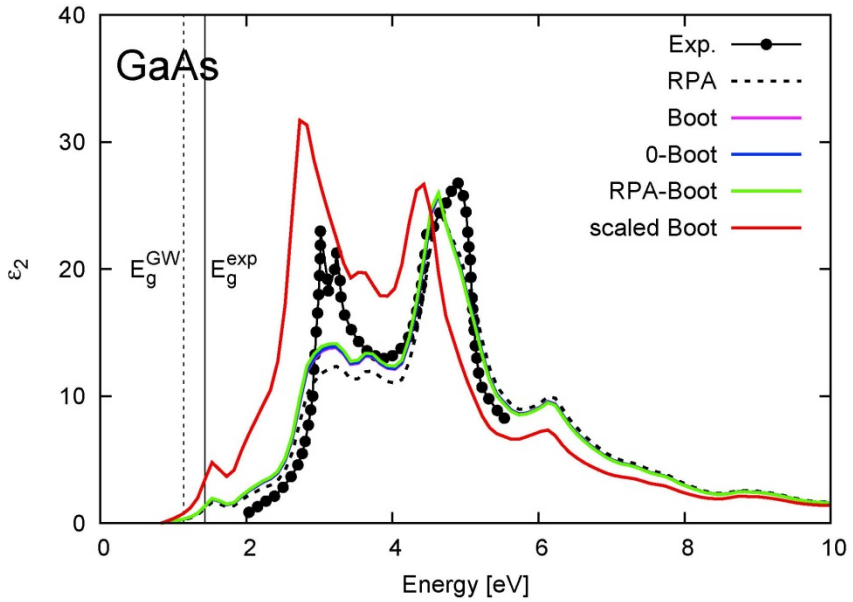


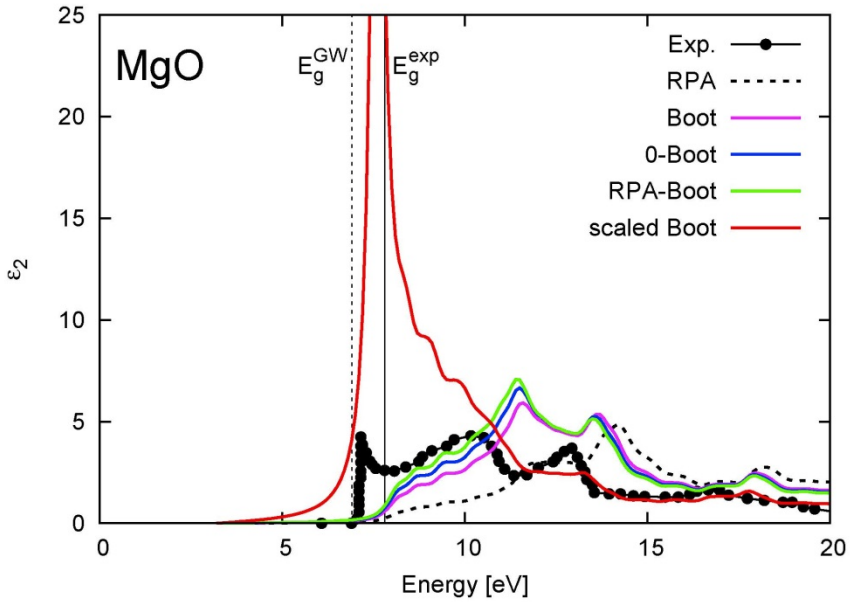
Exciton binding energies

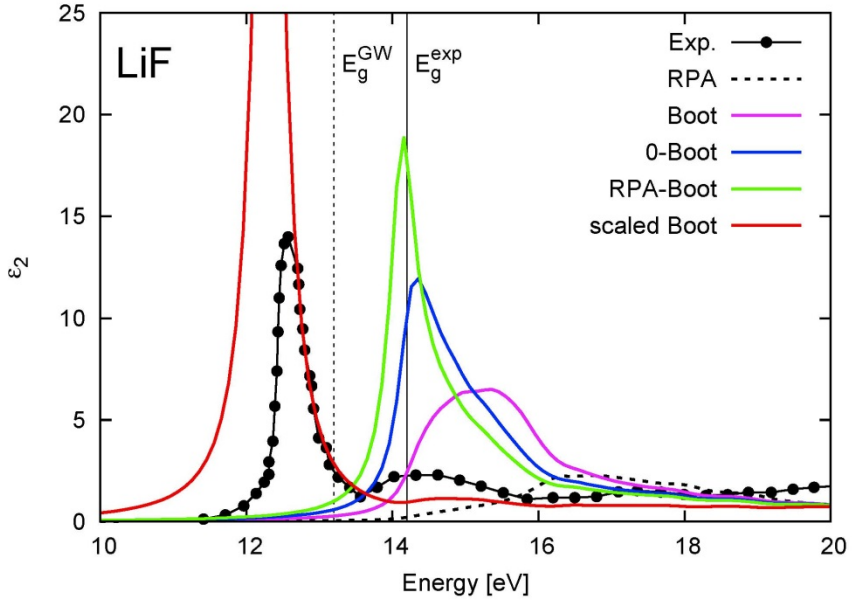


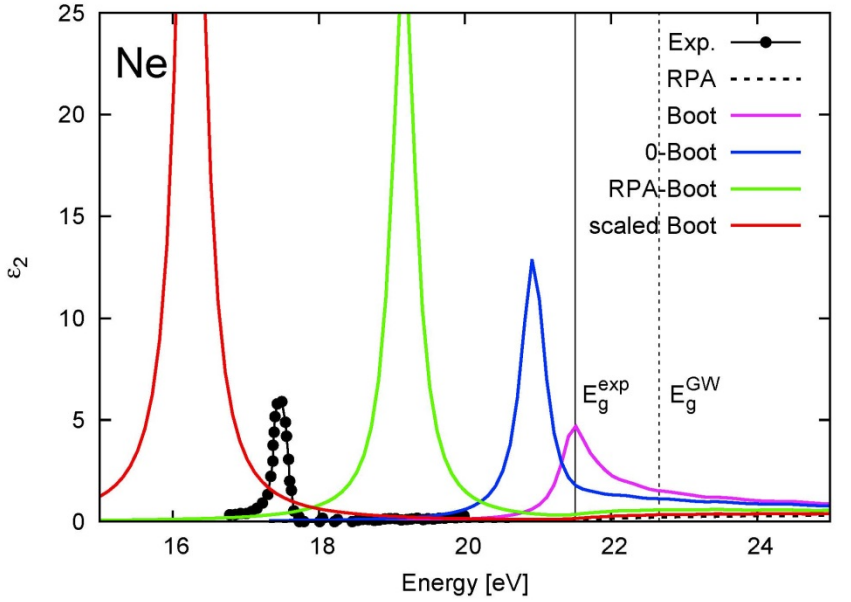
Young-Moo Byun and C. A. Ullrich, Phys. Rev. B **95**, 205136 (2017)

Optical spectra









Excitons with simple LRC-type xc kernels

►**Impossible to get good exciton binding energies and good spectral shapes at the same time!**

►**Here, we used LRC xc kernels ignoring their matrix form:**

$$f_{xc,\mathbf{GG'}}(\mathbf{q}\to\mathbf{0}) = \begin{pmatrix} \frac{k_{00}}{q^2} & \frac{k_{01}}{q} & \frac{k_{02}}{q} & \cdots \\ \frac{k_{10}}{q} & k_{11} & k_{12} & \cdots \\ \frac{k_{20}}{q} & k_{21} & k_{22} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \approx \begin{pmatrix} \frac{k_{00}}{q^2} & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

►**possible improvement: use full matrix form**

►**could also try to make kernel frequency-dependent**

TDDFT vs MBPT

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

TDDFT coupling matrix:

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

BSE coupling matrix:

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

screened Coulomb interaction

Screened exact exchange (SXX)

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

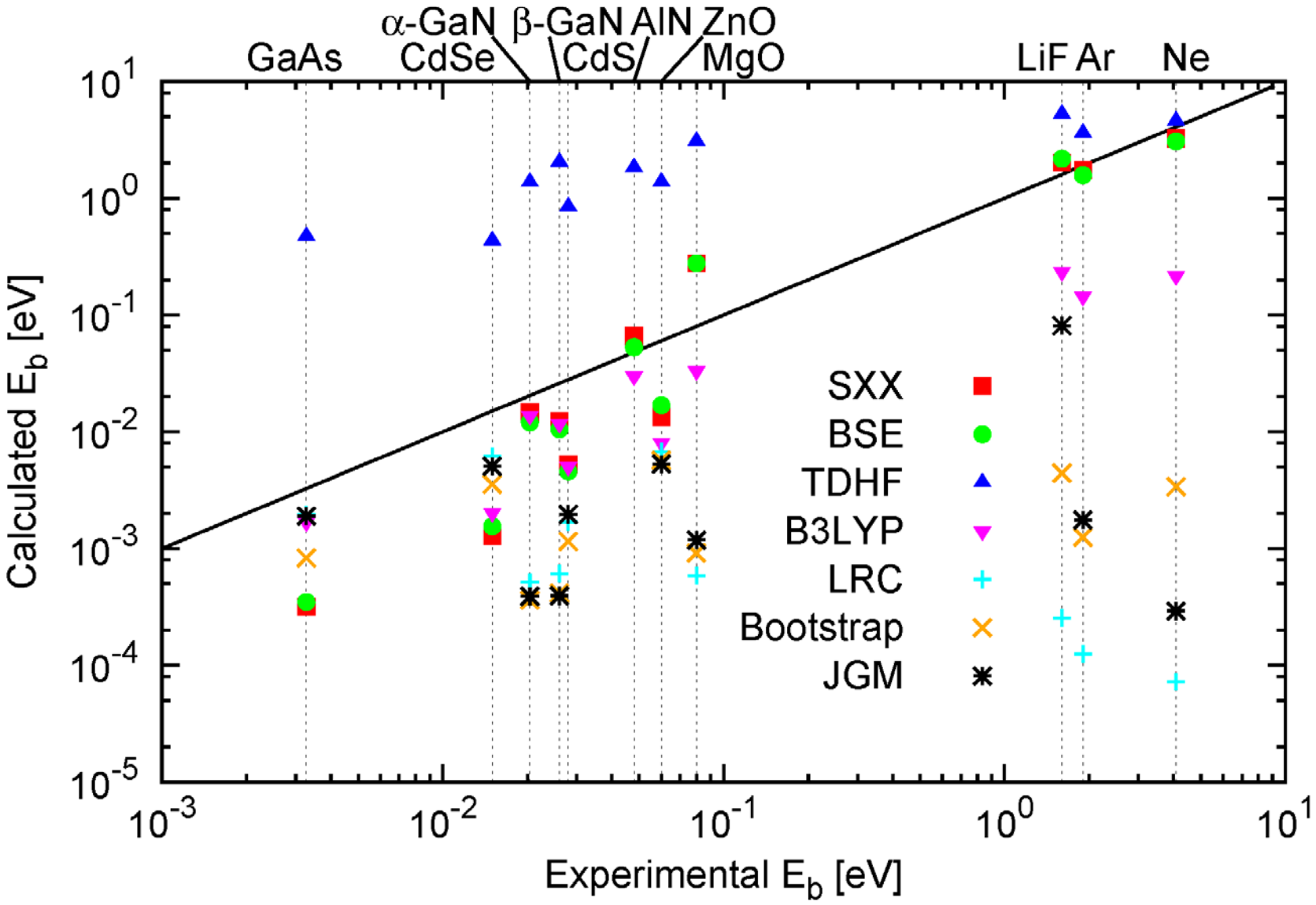
TDHF: $$g_{GG'}(\mathbf{q}) = -4\pi \frac{1}{|\mathbf{q} + \mathbf{G}'|^2} \delta_{GG'}$$ **unscreened**

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

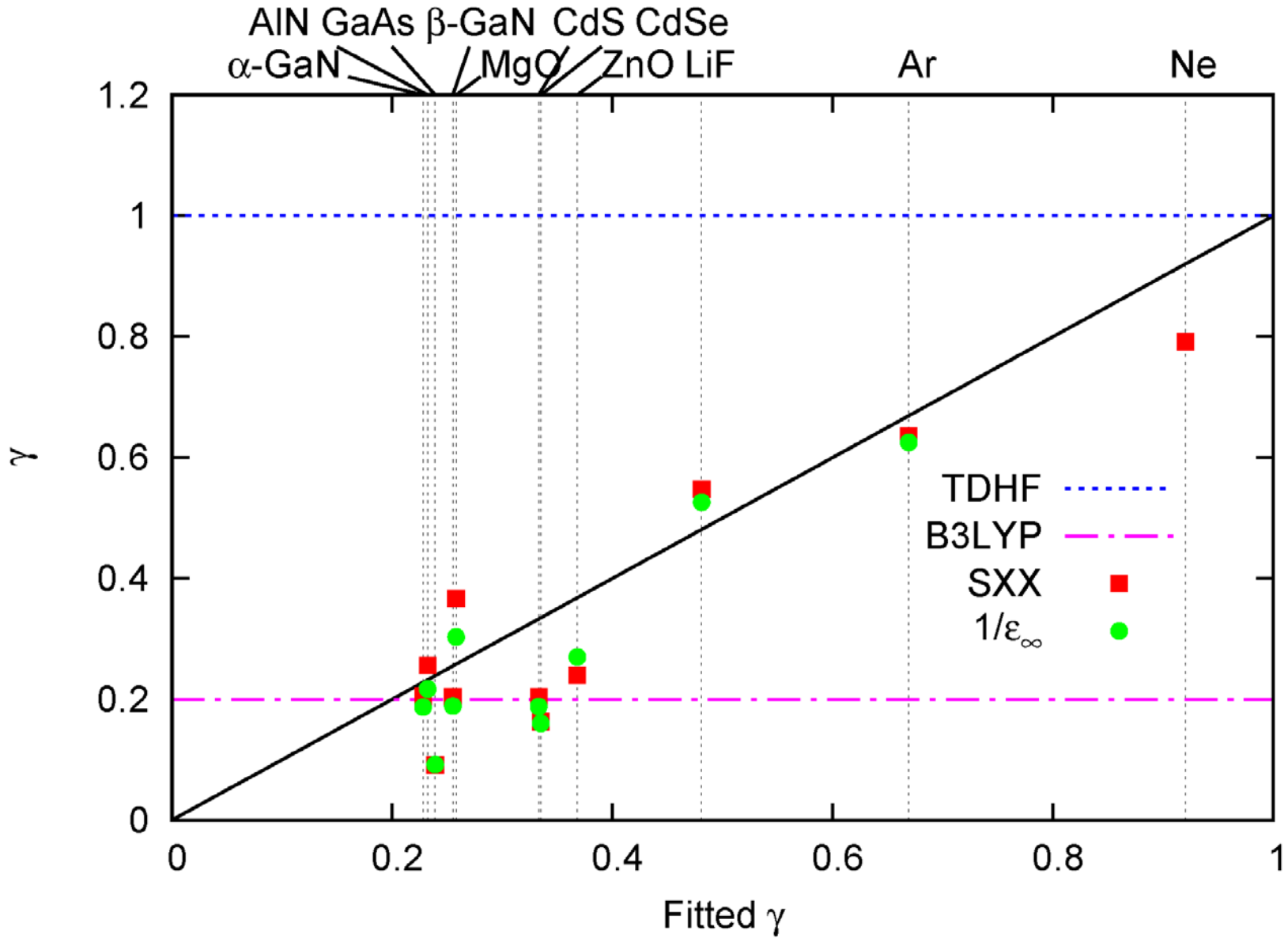
$$\gamma = \varepsilon^{-1}_{00}(0,0)$$ **Calculated with RPA**

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

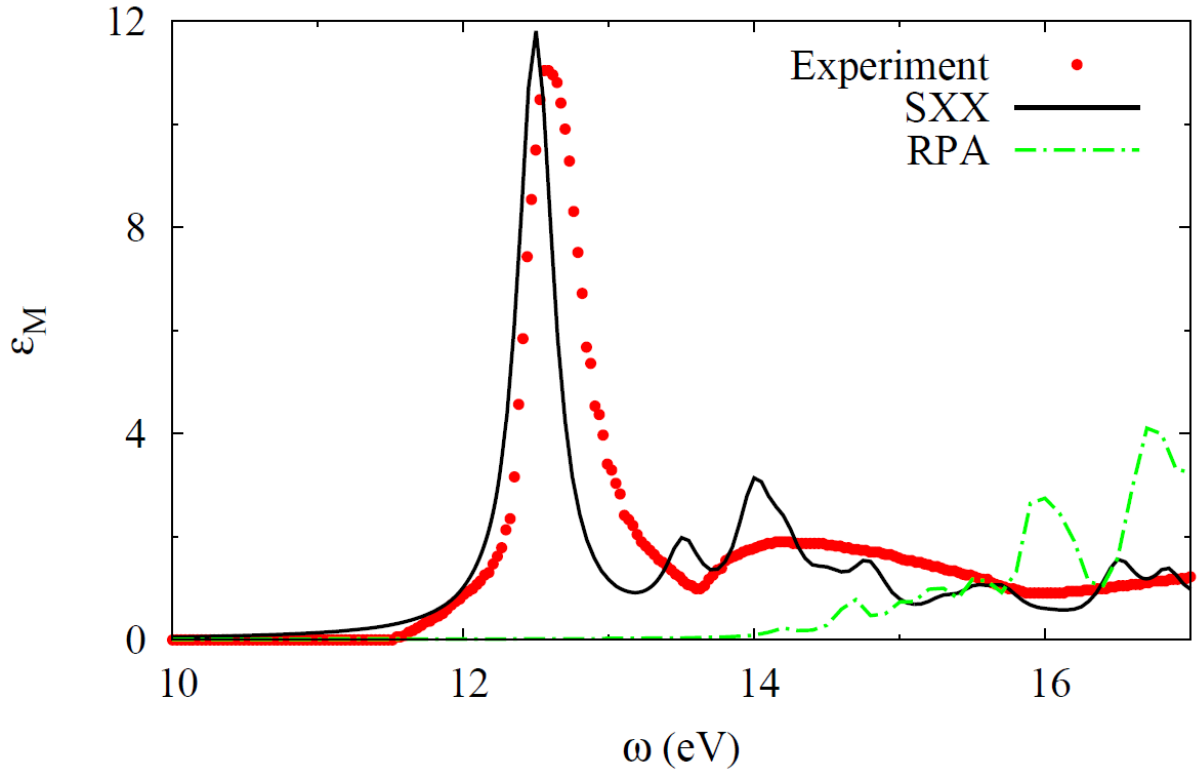
Exciton binding energies (4-band model)



Screening parameter



Absorption spectrum of LiF



- ►good oscillator strength
- ►second excitonic peak

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 – similar accuracy but cheaper. SXX works very well for exciton binding energies for large- and small-gap materials (still room for improvement).

- Probably the best way to describe excitons with TDDFT will be via hybrid functionals.

- Challenge: real-time TDDFT description of excitonic effects, beyond linear response

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)