VASP: BSE

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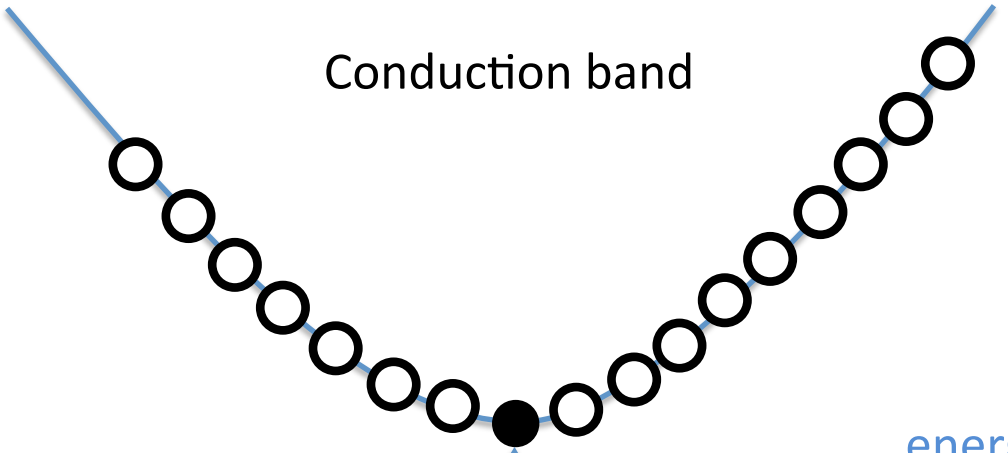
Photo absorption



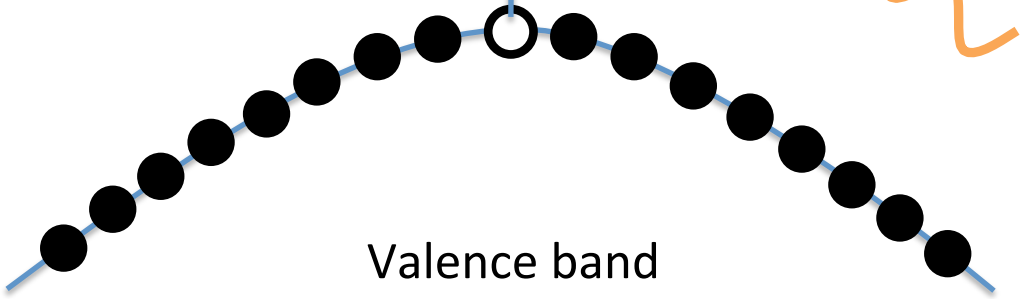
energy and momentum conservation

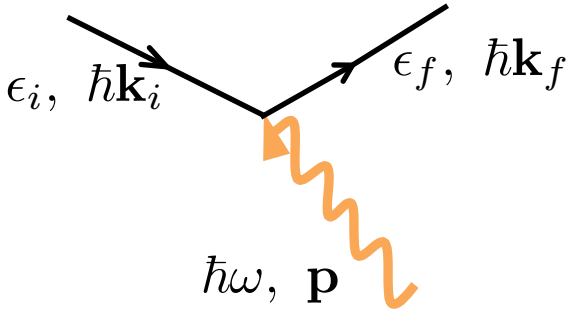
$$\hbar\omega = \epsilon_f - \epsilon_i$$

$$\mathbf{p} = \hbar\mathbf{k}$$

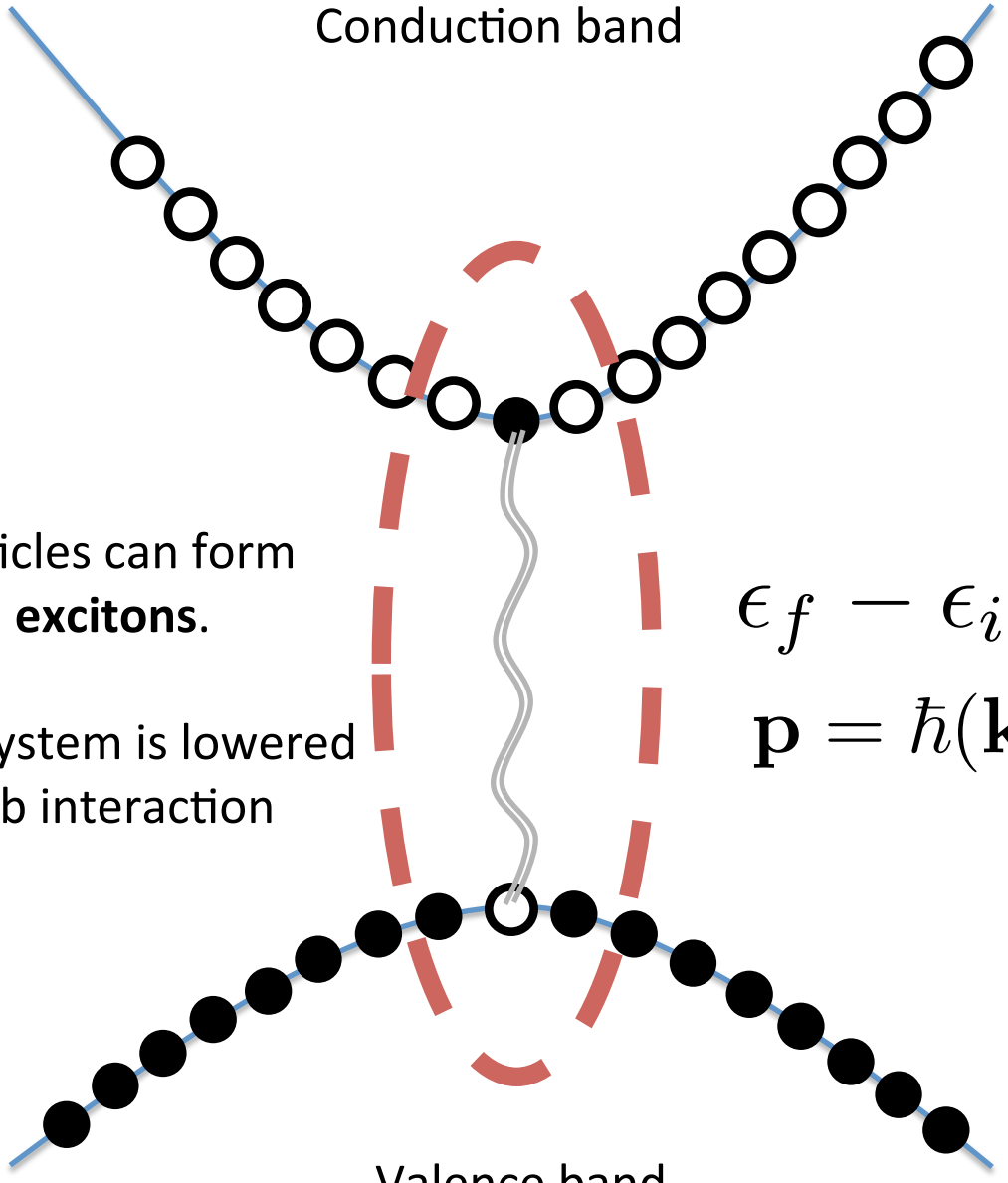
‘Likeliness or intensity’ of the transition is given by the oscillator strength:

$$| < f|\hat{V}_0|i > |^2$$





Excitons



In the excited state, quasiparticles can form with finite lifetimes called **excitons**.

The total energy of the excited system is lowered by the electron-hole Coulomb interaction

$$\epsilon_f - \epsilon_i - E_{eh}$$

$$\mathbf{p} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

Bethe Salpeter Equation (BSE)

$$\hat{H}\Psi(\mathbf{r}_1,...,\mathbf{r}_N) = E\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$$

$$\left(-\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) + \int \Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

$$\Sigma = iGW$$

At this point we have quasiparticle energies and wave functions including many body e-e interactions in the GW approximation.

With the BSE we include e-h interactions into the electronic description. Often necessary to improve the calculated optical spectra w.r.t. experiment.

The Bethe-Salpeter equation is solved for the Polarization propagator in the frequency domain given by a Dyson-like equation:

Independent quasiparticles (IQP)

$$P = P_{\text{IQP}} + P_{\text{IQP}}(2\bar{v} - W)P$$

It introduces higher order interaction diagrams and improves the electronic description systematically on top of GW.

E.E. Salpeter, H.A. Bethe, Phys. Rev. **84**, 1232 (1951), L.J. Sham, T.M. Rice, Phys Rev. **144**, 708 (1966)

BSE continued

Remarks

Physically intuitive picture of interacting e-h pairs.

Instantaneous screening: $W(\omega \to 0)$ (static screening)
(dynamical effects are excluded)

Product basis of occupied and unoccupied orbitals to express the quasiparticle (excitonic) wave function:

$$\Phi^n = \sum_c^{\text{elec}} \sum_v^{\text{hole}} A^n_{cv} \phi_c(\mathbf{r}) \phi^*_v(\mathbf{r}')$$

$$\omega^+_{\text{IP}} = \epsilon_c - \epsilon_v \geq 0$$

$$\omega^-_{\text{IP}} = \epsilon_v - \epsilon_c \leq 0$$

(Tamm-Dancoff approximation)

Overview of BSE theory: G. Onida et al., Rev. Mod. Phys. **74**, 601 (2002)

BSE EVP

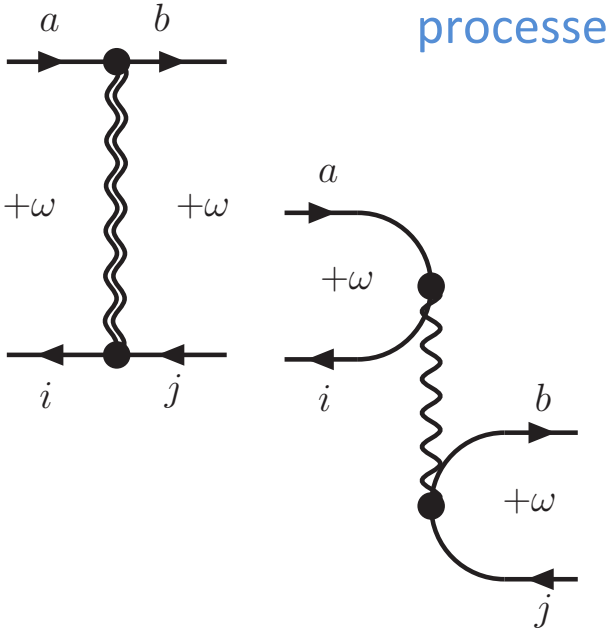
Problem can be formulated as an eigenvalue problem (EVP):

$$\frac{\Omega}{(2\pi)^3}\sum_{c'v'}\int_{\Omega_{\mathrm{BZ}}}\hat{H}^{cv}_{c'v'}(\mathbf{k},\mathbf{k}')A^n_{c'v'}(\mathbf{k}')\mathrm{d}\mathbf{k}' = E^n A^n_{cv}(\mathbf{k})$$

$$\hat{H}^{cv}_{c'v'}(\mathbf{k},\mathbf{k}') = (\epsilon_{c\mathbf{k}}-\epsilon_{v\mathbf{k}})\delta_{cc'}\delta_{vv'}\delta_{\mathbf{k}\mathbf{k}'} - W^{cv\mathbf{k}}_{c'v'\mathbf{k}'} + 2\bar{v}^{cv\mathbf{k}}_{c'v'\mathbf{k}'}$$

Interaction with each other by two terms:

Scattering and annihilation/creation processes



Direct

$$W^{cv\mathbf{k}}_{c'v'\mathbf{k}'} = \int\int \phi^*_{c\mathbf{k}}(\mathbf{r})\phi_{c'\mathbf{k}'}(\mathbf{r})\frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_{v\mathbf{k}}(\mathbf{r}')\phi^*_{v'\mathbf{k}'}(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

Exchange

$$\bar{v}^{cv\mathbf{k}}_{c'v'\mathbf{k}'} = \int\int \phi^*_{c\mathbf{k}}(\mathbf{r})\phi_{v\mathbf{k}}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{c'\mathbf{k}'}(\mathbf{r}')\phi^*_{v'\mathbf{k}'}(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

S. Albrecht et al. PRL **80**, 4510 (1998) | G. Onida et al., Rev. Mod. Phys. **74**, 601 (2002) |F. Fuchs et al., Phys. Rev .B **78**, 085103 (2008)

BSE EVP

Discretization on (some) grid gives the generalized eigenvalue problem to solve:

$$\frac{\Omega}{(2\pi)^3}\int_{\Omega_{\mathrm{BZ}}} f(\mathbf{k})\mathrm{d}\mathbf{k} \longrightarrow \sum_{\mathbf{k}\in\Omega_{\mathrm{BZ}}} w_{\mathbf{k}} f(\mathbf{k})$$

$$\sum_{c'v'\mathbf{k}'} \sqrt{w_{\mathbf{k}} w_{\mathbf{k}'}} H^{cv\mathbf{k}}_{c'v'\mathbf{k}'} \sqrt{w_{\mathbf{k}'}} A^n_{c'v'\mathbf{k}'} = (E^n - (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}))\sqrt{w_{\mathbf{k}}} A^n_{cv\mathbf{k}}$$

$$H^{cv\mathbf{k}}_{c'v'\mathbf{k}'} = -W^{cv\mathbf{k}}_{c'v'\mathbf{k}'} + 2\bar{v}^{cv\mathbf{k}}_{c'v'\mathbf{k}'}$$

Build matrix based on $\{E_{IQP}, \psi_{DFT}, \epsilon_{RPA}(\mathbf{r}, \mathbf{r}', \omega)\}$, diagonalise and obtain $\{E^n, A^n_{cv\mathbf{k}}\}$.

S. Albrecht et al. PRL **80**, 4510 (1998) | G. Onida et al., Rev. Mod. Phys. **74**, 601 (2002) |F. Fuchs et al., Phys. Rev .B **78**, 085103 (2008)

BSE dielectric function

The obtained $\{E^n, A^n_{cv\mathbf{k}}\}$ are used to construct the dielectric function
In the long wavelength limit (**q** -> 0).

BSE oscillator strength

$$\varepsilon^i(\omega) = 1 - C\frac{|\sum_{c,v,\mathbf{k}}(f_{c\mathbf{k}} - f_{v\mathbf{k}})F^n_{cv\mathbf{k}}w_{\mathbf{k}}A^n_{cv\mathbf{k}}|^2}{\omega - E^n + i\delta}$$

IQP oscillator strength

$$F^n_{cv\mathbf{k}} = \frac{<\psi_c|\hat{p}_i|\psi_v>}{\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}}$$

$\{E^n, A^n_{cv\mathbf{k}}\}$, modify the dielectric function of the IQP description.

Absorption coefficient can be compared to experiment:

$$\alpha(\omega) = \omega\sqrt{\frac{-\Re\varepsilon(\omega) + \sqrt{\Re\varepsilon(\omega)^2 + \Im\varepsilon(\omega)^2}}{2}}$$

Typical BSE calculation

1. Preform a ground state DFT or Hybrid calculation
2. Increase the number of unoccupied orbitals
3. Preform a GW calculation (keeping orbitals fixed) and calculate the quasiparticle energies and screened Coulomb kernel.

   (Keep the Wxxx.tmp and WFULLxxx.tmp files)
4. Preform BSE calculation (dielectric function will be written in vasprun.xml)

All details about the BSE Implementation in VASP 5.4.1:

PHYSICAL REVIEW B **92**, 045209 (2015)

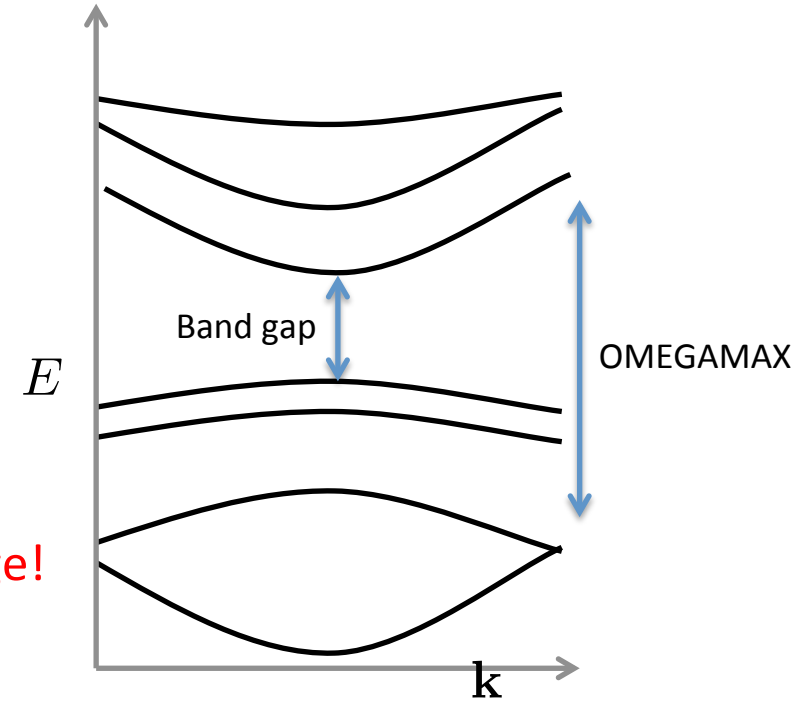
Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization

Tobias Sander, Emanuele Maggio, and Georg Kresse
University of Vienna, Faculty of Physics and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Vienna, Austria
(Received 27 November 2014; revised manuscript received 22 June 2015; published 20 July 2015)

INCAR Tags and links

ALGO = BSE Turn on BSE calculation
ANTIRES = 0/1/2 0: Tamm-Dancoff approximation
1: exact at omega = 0
2: Beyond TD
NBANDSO = n Number of occupied bands included (INTEGER)
NBANDSV = m Number of unoccupied bands included (INTEGER)
OMEGAMAX = x.x Maximal frequency included in BSE basis (REAL [eV])

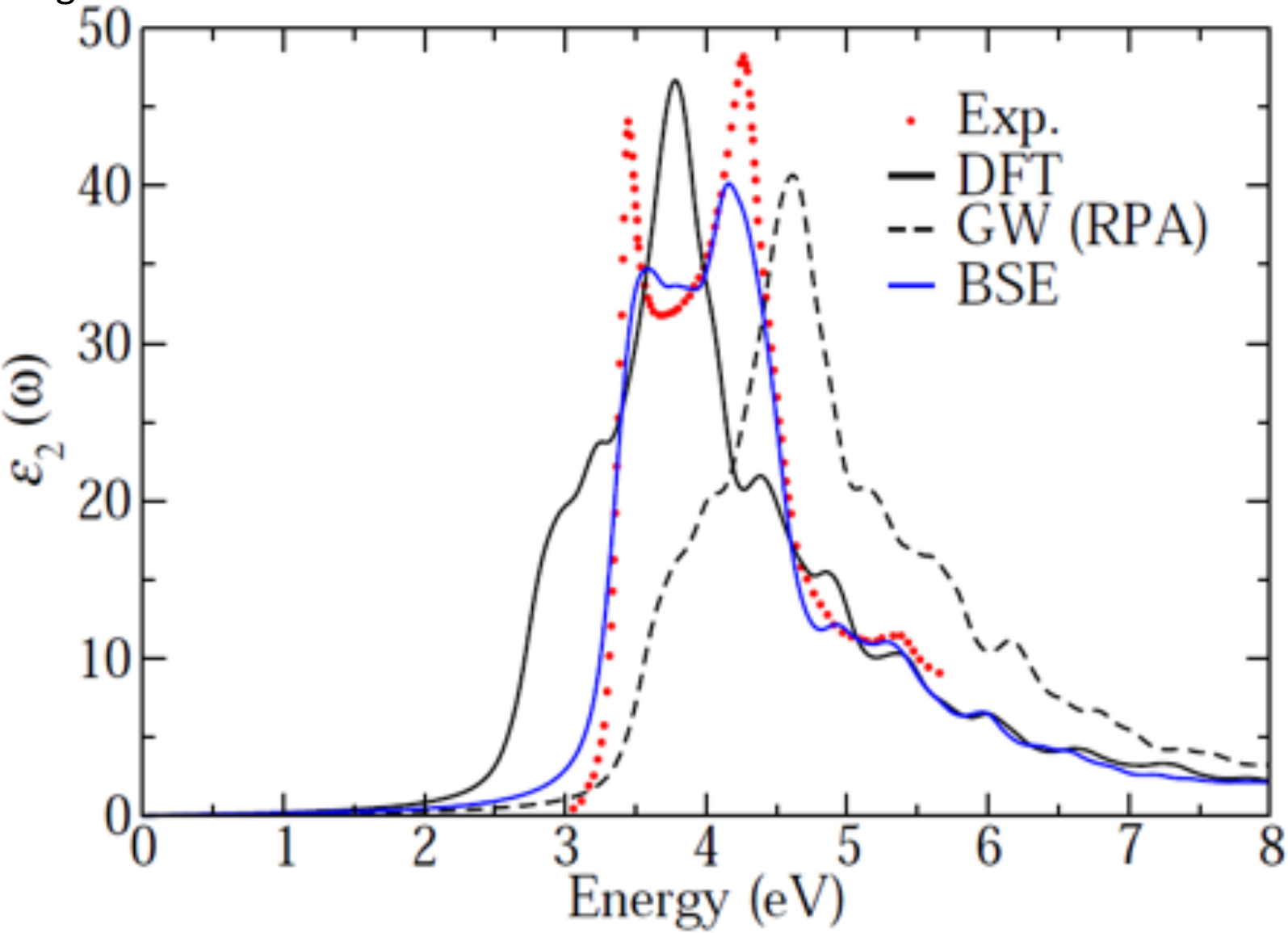
BSE Bethe-Salpeter calculations in the Vasp manual



Truncate your e-h product basis or face MEMORY shortage!

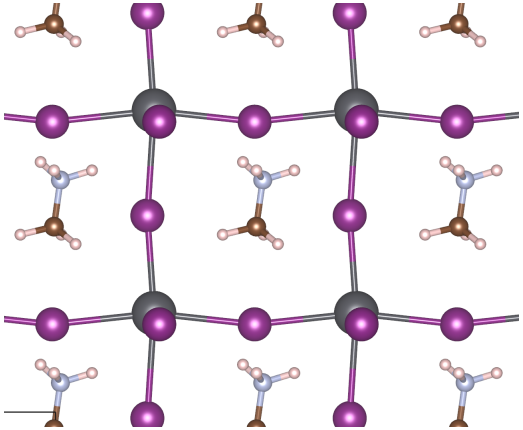
Example Silicon

Absorption spectrum is given by the Imaginary part of the dielectric function $\epsilon(\omega)$ in the long wave length limit.



Example: Exciton in $MAPbI_3$

BSE calculations become more expensive for small gap semi conductors with high dielectric constants. The e-h interaction is heavily screened and the extent of the exciton wave function is large.
-> Large supercells / dense **k**-point meshes are required.



Band gap at different levels of theory:

	Δ_{opt} (eV)	$\Delta_{\mathrm{opt}}^{\mathrm{EXP}}$ (eV)	$\mathrm{E_{xb}}$ (meV)	$E_{\mathrm{xb}}^{\mathrm{EXP}}$ (meV)	Δ_{GW} (eV)	Δ_{DFT} (eV)	$\Delta_{\mathrm{DFT}}^{\mathrm{ws}}$ (eV)	Vol. ($\mathrm{\AA}^3$)
$MAPbI_3$	1.63	1.52-1.67	45	6-55	1.67	0.77	1.69	251.60

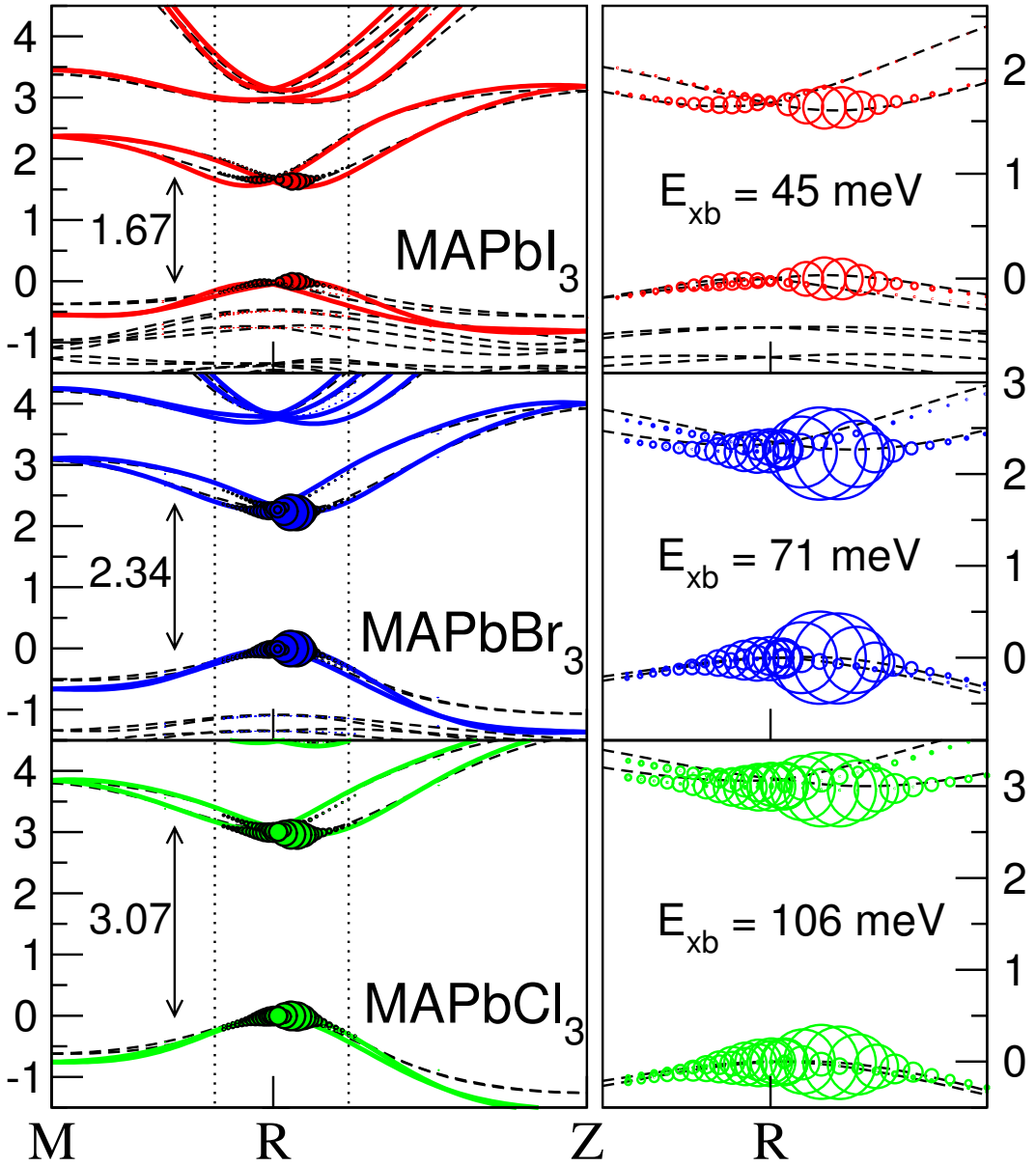
$$\Delta_{\mathrm{opt}} = \Delta_{GW} - E_{\mathrm{xb}} \qquad E_{\mathrm{xb}} = E_{GW} - E_{\mathrm{BSE}}$$

Which quasiparticle energies should be used?

The shift in the onset of absorption is the relevant quantity.

M.Bokdam et al., Scientific Reports, **6**, 28618, (2016)

Example MAPbX_3



$$\Phi^n = \sum_c^{\text{elec}} \sum_v^{\text{hole}} A^n_{cv} \phi_c(\mathbf{r}) \phi^*_v(\mathbf{r}')$$

Even though band gap not at R,

exciton is centered at R:

M.Bokdam et al, Scientific Reports, **6**, 28618, (2016)

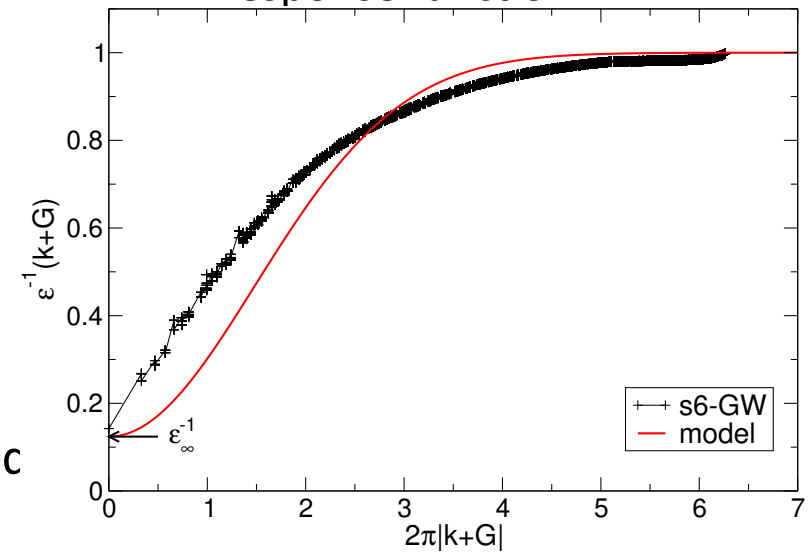
Model BSE calculations: Excitons

1. Start from DFT orbitals + SCISSOR to get GW_0 gap

2. Model Screened Coulomb: $$W^{cv\mathbf{k}}_{c'v'\mathbf{k}} = \frac{4\pi e^2}{\Omega}\sum_{\mathbf{G}} B^{c\mathbf{k}}_{c'\mathbf{k}}(\mathbf{G})\frac{\varepsilon^{-1}(\mathbf{k}+\mathbf{G})}{|\mathbf{k}+\mathbf{G}|^2}B^{v\mathbf{k}}_{v'\mathbf{k}}(\mathbf{G})$$

$\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{k})$ is replaced by local model dielectric response function.

$$\varepsilon^{-1}(\mathbf{k}+\mathbf{G}) = 1-(1-\varepsilon^{-1}_{\infty})e^{\frac{-(2\pi|\mathbf{k}+\mathbf{G}|)^2}{4\lambda^2}}$$

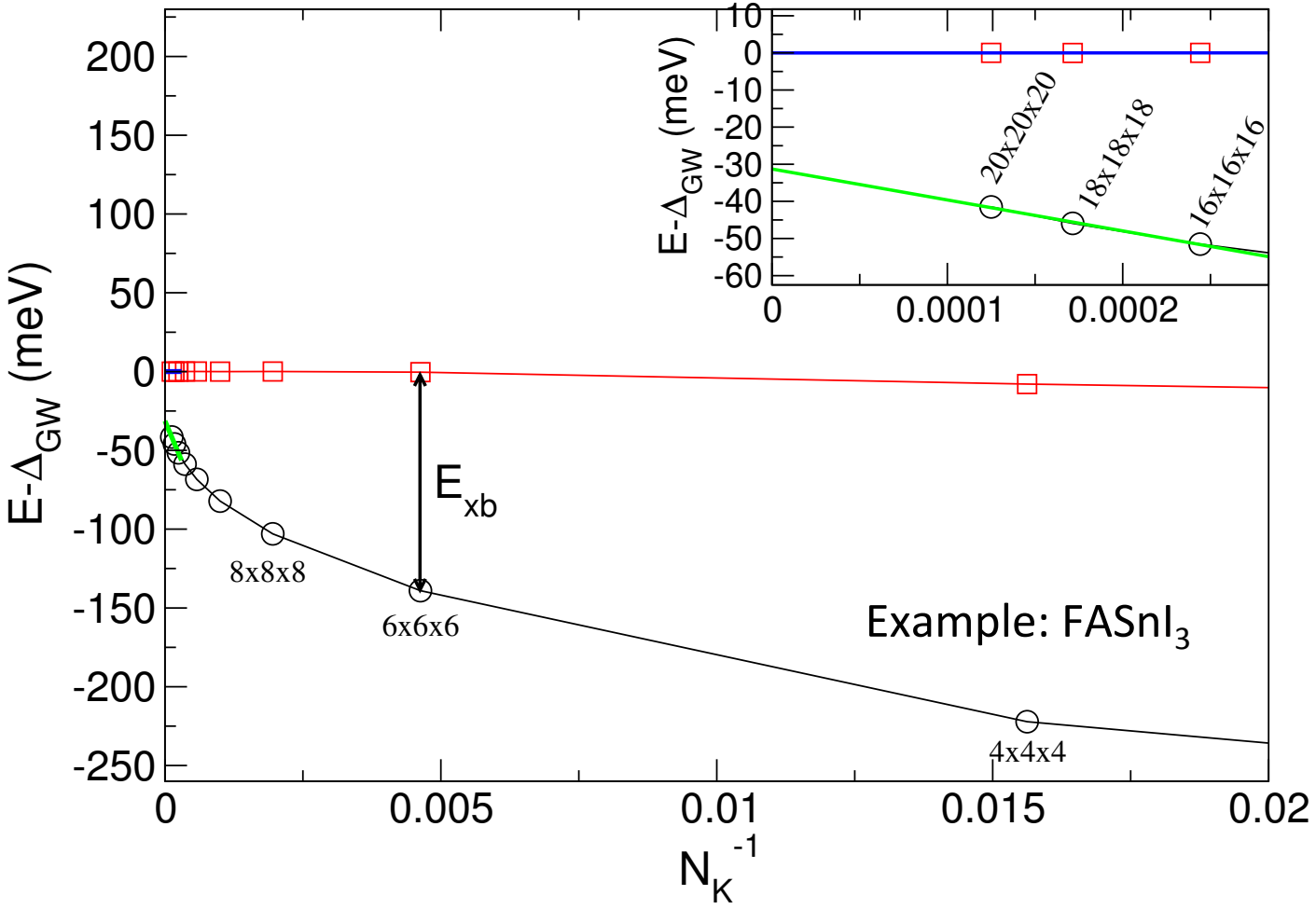


3. Truncate BSE basis:
   - TDA
   - 2 conduction/valence banc
   - **q=k-k'**=0

4. Converge E_{xb} with increasing grid and linearly extrapolate E_{xb} to infinite k-points.

M.Bokdam et al, Scientific Reports, **6**, 28618, (2016)

Model BSE calculations: Excitons



Extrapolate to infinite k-pint grids

F. Fuchs et al. Phys. Rev. B **78**, 085103 (2008)

M.Bokdam et al, Scientific Reports, **6**, 28618, (2016)

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Alternatively, the Cassida Equation or ModelBSE:

ALGO = TDHF Turn on BSE calculation
LHFCALC = .TRUE. Turn on model screening
AEXX = 0.3 ; HFSCREEN = 0.2 (Typical values, for modelBSE these parameters need to be determined by fitting to a preceding RPA calculation.)

BSE Bethe-Salpeter calculations in the Vasp manual

The End

Thank you!