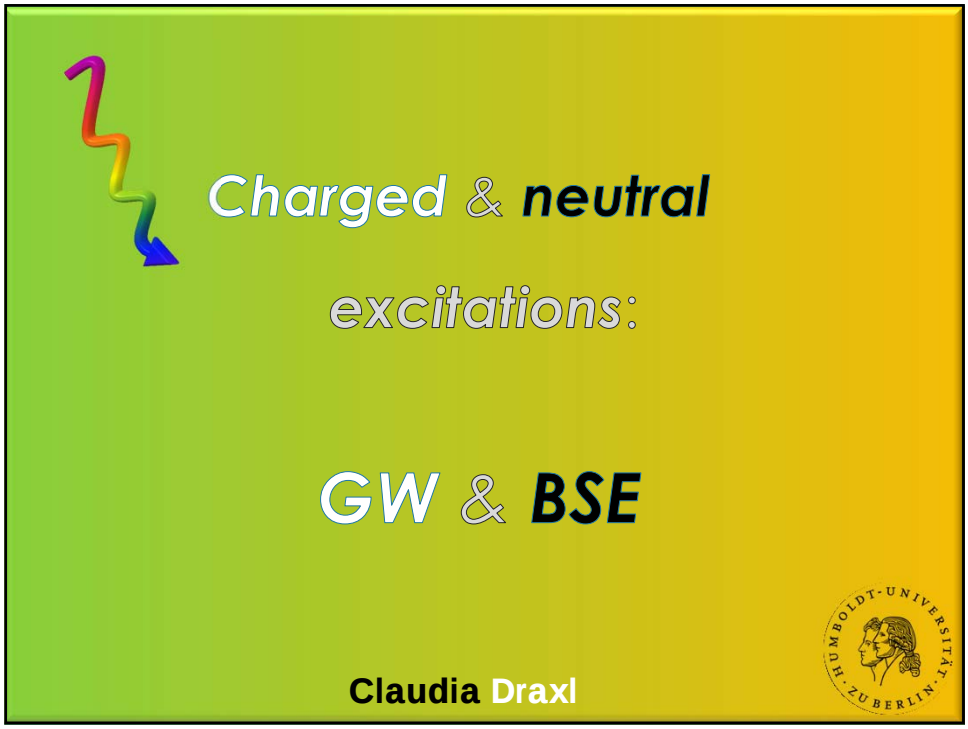
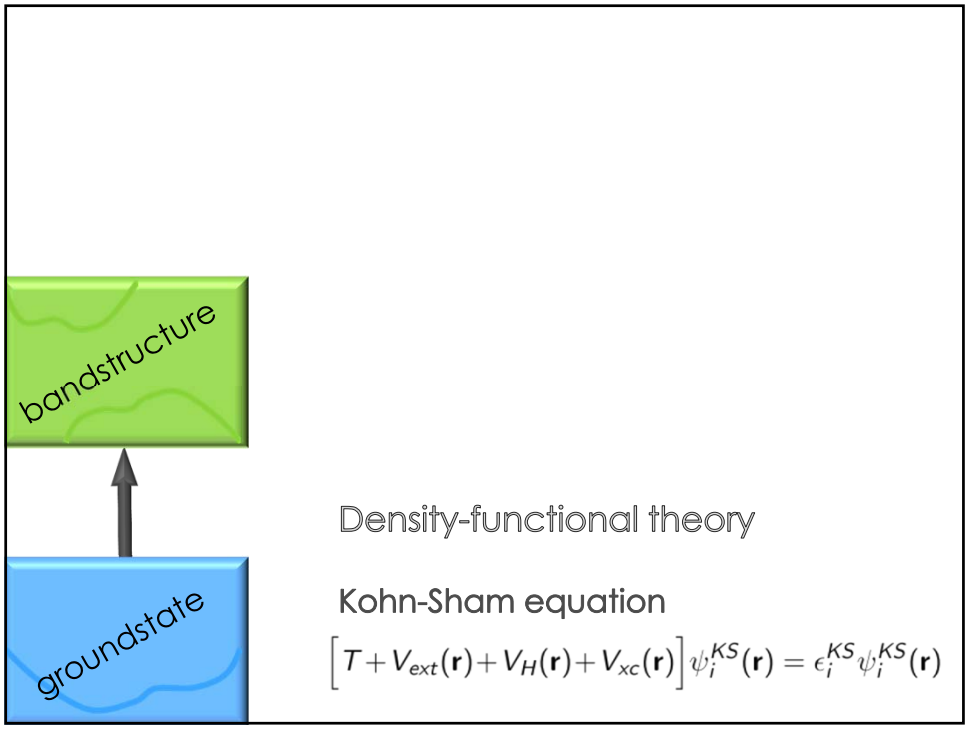
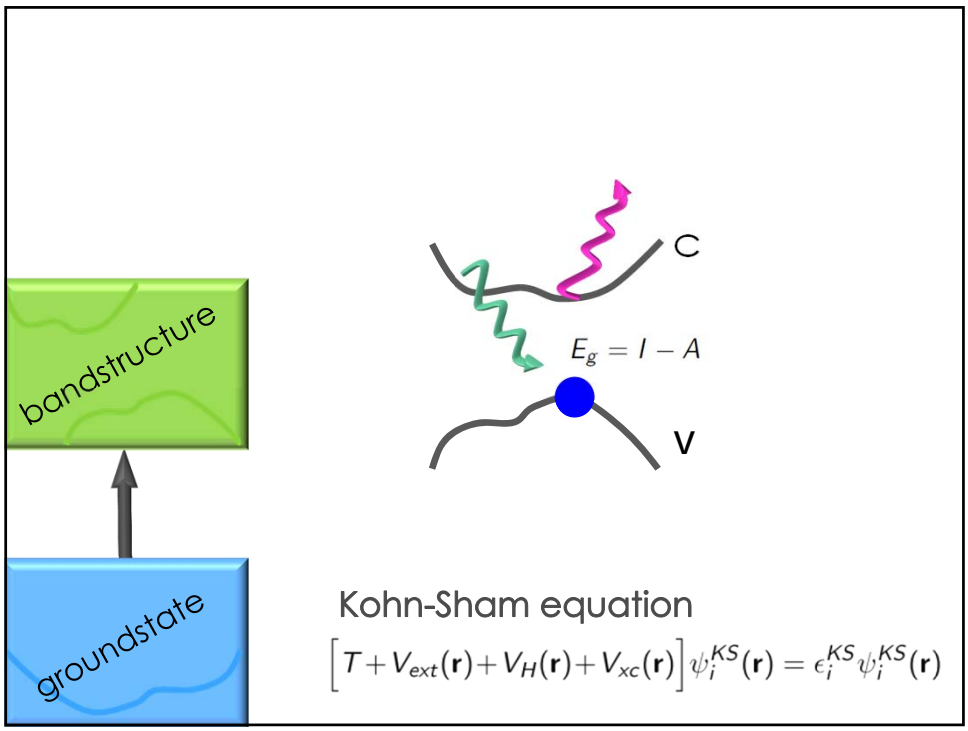
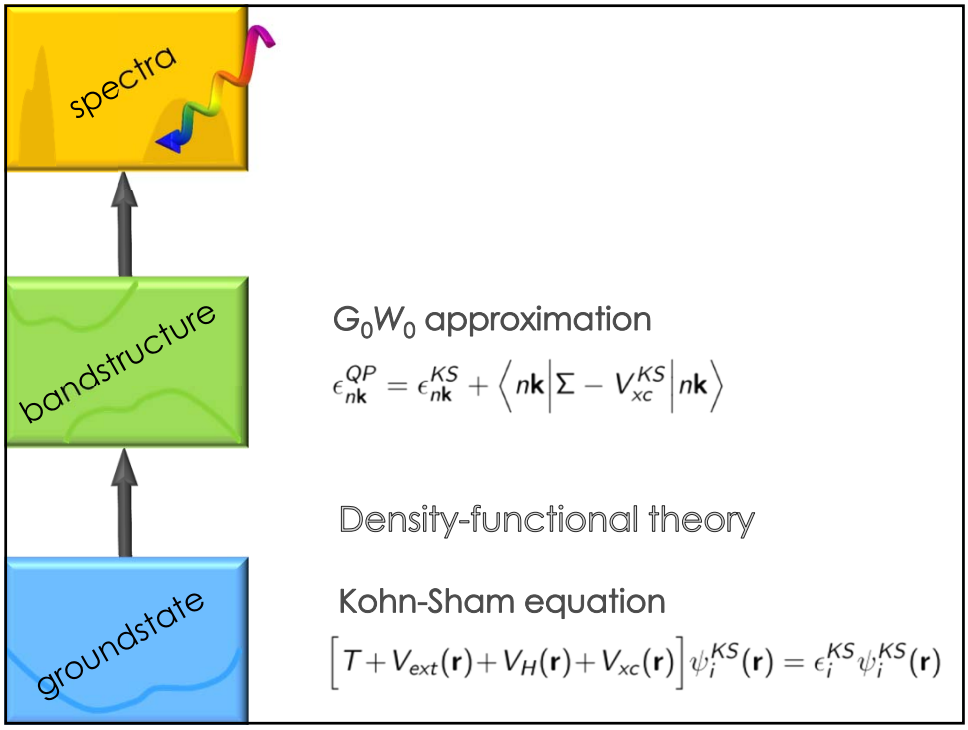
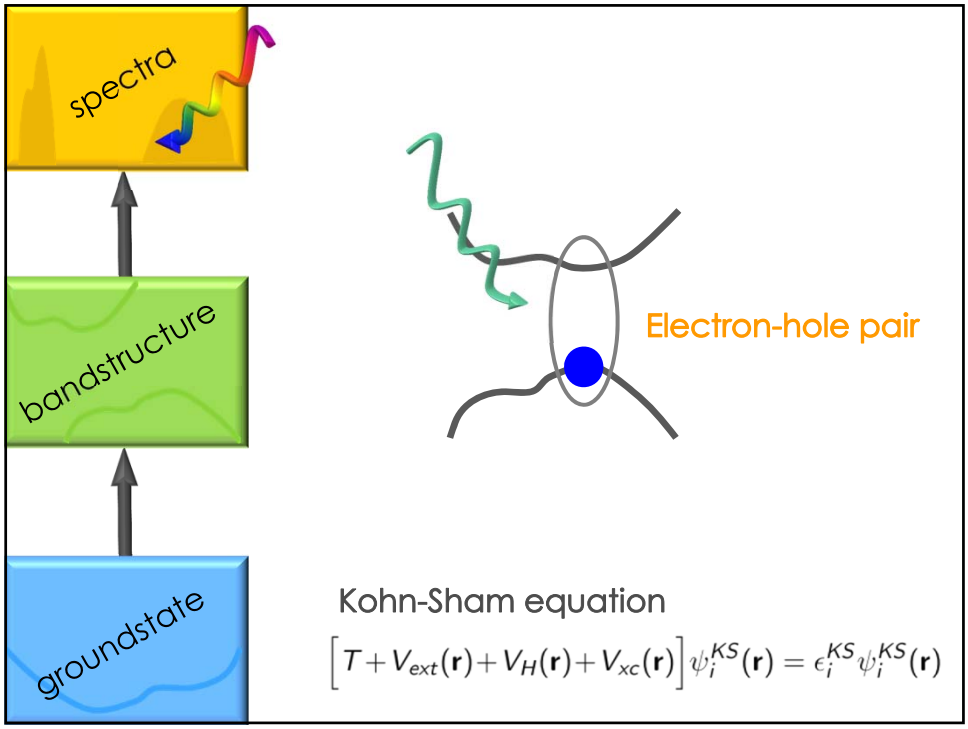
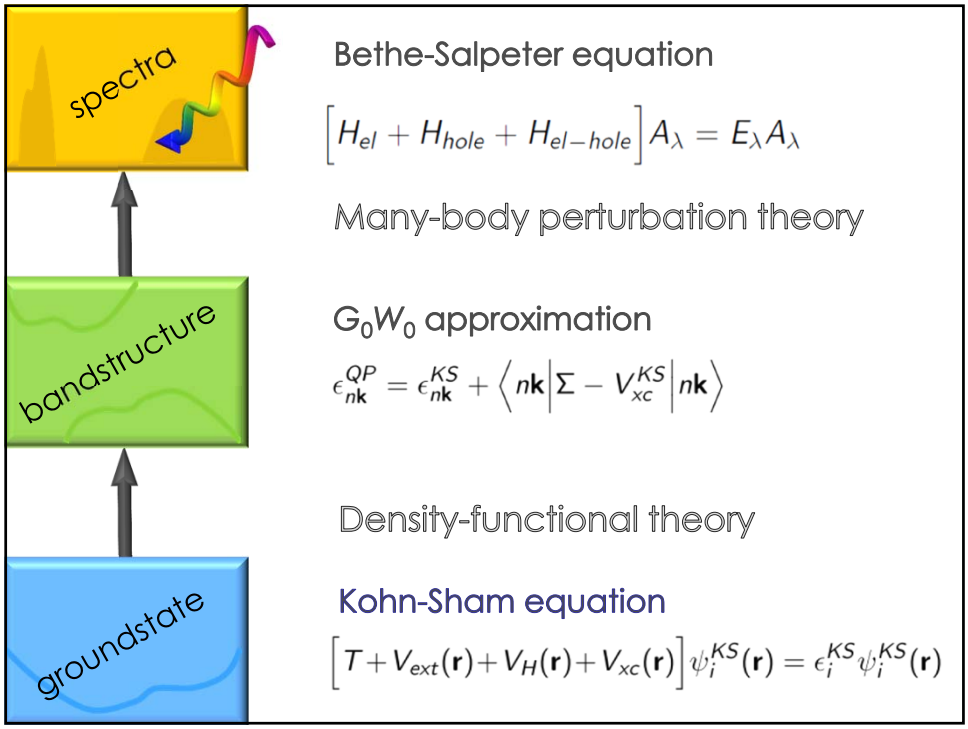

Charged & neutral
excitations:
GW & BSE
Claudia Draxl


bandstructure
groundstate
Density-functional theory
Kohn-Sham equation
$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r})=\epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$


bandstructure
groundstate
C
$E_g = I - A$
V
Kohn-Sham equation
$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$

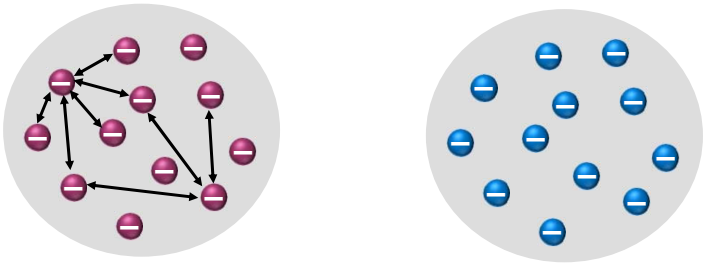

spectra
bandstructure
groundstate
G_0W_0 approximation
$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle n\mathbf{k}\middle|\Sigma - V_{xc}^{KS}\middle|n\mathbf{k}\right\rangle$
Density-functional theory
Kohn-Sham equation
$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$


spectra
bandstructure
groundstate
Electron-hole pair
Kohn-Sham equation
$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r})=\epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$


spectra
bandstructure
groundstate
Bethe-Salpeter equation
$\left[H_{el}+H_{hole}+H_{el-hole}\right]A_\lambda=E_\lambda A_\lambda$
Many-body perturbation theory
G_0W_0 approximation
$\epsilon_{n\mathbf{k}}^{QP}=\epsilon_{n\mathbf{k}}^{KS}+\left\langle n\mathbf{k}\middle|\Sigma-V_{xc}^{KS}\middle|n\mathbf{k}\right\rangle$
Density-functional theory
Kohn-Sham equation
$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r})=\epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$

Ground state

We have replaced the many-body system of interacting electrons by fictitious non-interacting electrons



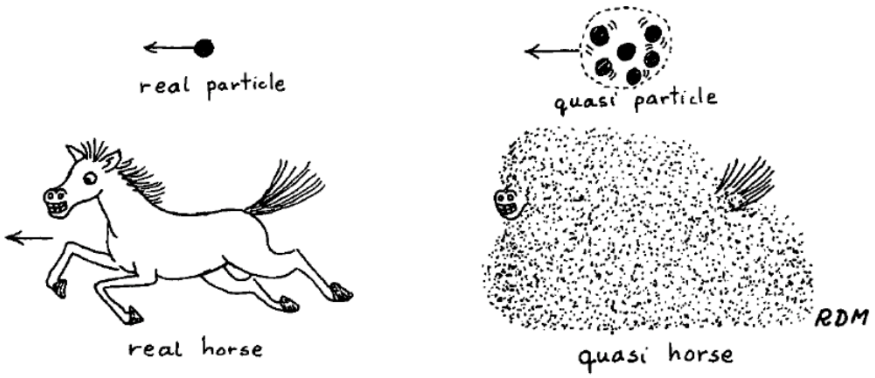
Density-functional theory

groundstate

Kohn-Sham equation

$$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r})=\epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

Quasi-particle concept



The quasi horse according to Richard D. Mattuk

Ideal quasi-particles

Characterized by spectral function

$$A(E) = \frac{\Gamma}{(E - E^{QP})^2 + \Gamma^2}$$

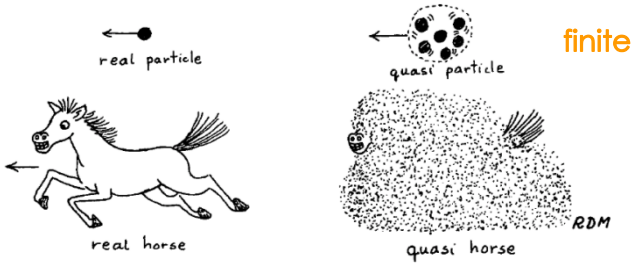
Lorentzian lineshape

Peak position = quasiparticle energy

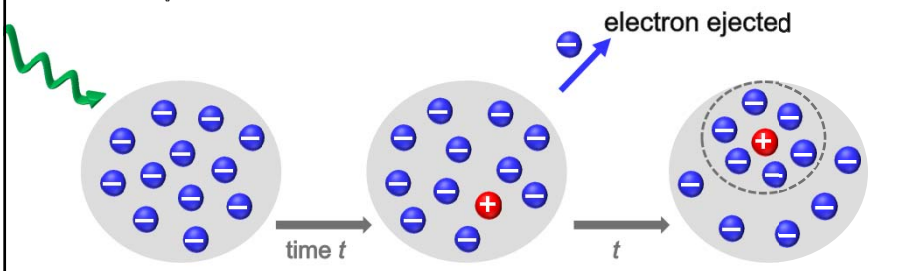
Lifetime $\tau = 1/\Gamma$

renormalized energy, velocity, mass, …

finite lifetime



Quasi-particles



Key quantities

Dielectric function ε

Dynamically screened Coulomb interaction *W(**r**,**r**',t)*

$$W(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',t)}{|\mathbf{r}'' - \mathbf{r}'|}$$

Light-matter interaction

Resonse to external electric field $\mathbf{E}$

Polarizability $$P_\alpha = \sum_\beta \chi_{\alpha\beta} E_\beta + \sum_{\beta\gamma} \chi_{\alpha\beta\gamma} E_\beta E_\gamma + \dots$$

Linear approximation

Susceptibility χ	$\mathbf{P} = \chi \mathbf{E}$
Conductivity σ	$\mathbf{J} = \sigma \mathbf{E}$
Dielectric tensor ε	$\mathbf{D} = \epsilon \mathbf{E}$

$$D_\alpha(\mathbf{r}, t) = \sum_\beta \int_{\mathbf{r}'} \int_{t'} \epsilon_{\alpha\beta}(\mathbf{r}, \mathbf{r}', t - t') E_\beta(\mathbf{r}', t')$$

Fourier transform

$$D_\alpha(\mathbf{q} + \mathbf{G}, \omega) = \sum_\beta \sum_{\mathbf{G}'} \epsilon_{\alpha\beta}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}', \omega) E_\beta(\mathbf{q} + \mathbf{G}', \omega)$$

Green-function approach

Propagation of particles described by Green function

Dyson equation to obtain the QP energies

$$G(z) = \frac{1}{z - \epsilon^0 - \Sigma(z)}$$

Bare energy ϵ^0 of non-interacting electron

Self-energy Σ carries information about interactions

Spectral function

$$A(E) = -\frac{1}{\pi} \mathrm{Im} G(E + i0)$$

Hedin's equations

$$\Sigma = i \int GW\Lambda$$

$$W = v + \int vPW$$

$$P = -i \int G\Lambda G$$

$$\Lambda = \delta + \int \partial\Sigma/\partial G \; GG\Lambda$$

GW approximation

$$\Sigma = i\, GW$$

$$W = v + \int vPW$$

$$P = -i\, GG$$

$$\Lambda = \delta$$

Hedin (1965)

W screened Coulomb potential
v bare Coulomb potential
P polarizability
Λ vertex

iterative

$$G = G_{Hartree} + G_{Hartree}\Sigma G$$

Where to start from?

$$G = G_{KS} + \ldots$$

The quasiparticle equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\psi_i^{QP}(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i)\psi_i^{QP}(\mathbf{r})d^3\mathbf{r}' = \epsilon_i^{QP}\psi_i^{QP}(\mathbf{r})$$

The Kohn Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

G_0W_0

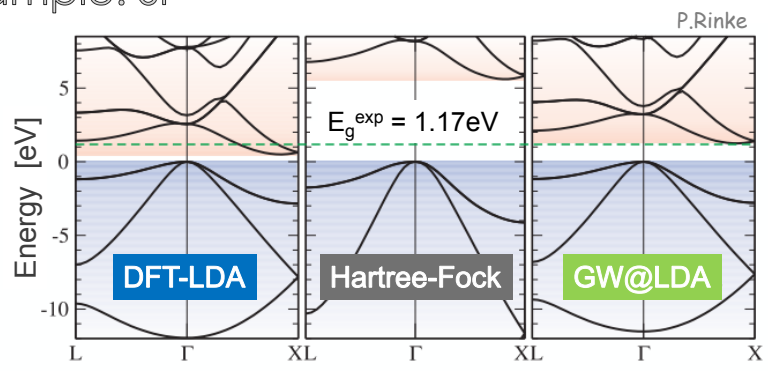
$$G_0 = G_{KS} + \ldots$$

non-iterative

$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{DFT} - \left\langle n\mathbf{k}\left|\Sigma(\epsilon_{n\mathbf{k}}^{QP}) - V_{xc}^{DFT}\right|n\mathbf{k}\right\rangle$$

Materials …

Example: Si



DFT-LDA underestimates gap

Hartree-Fock overestimates gap

Coulomb interaction not screened

GW corrects to a great extent

G_0W_0 band gaps

	Experiment	LDA	exciting	VASP
C	5.48	4.40	6.25	6.21
Si	1.17	0.65	1.29	1.22
SiC	2.4	1.33	2.45	2.43
BN	6.1-6.4	4.35	6.46	6.37
AlP	2.45	2.24	2.37	2.42
GaAs	1.52	0.30	1.15	1.08
GaN	3.2	1.57	2.89	2.88
MgO	7.83	4.65	7.61	7.55
ZnO	3.44	0.62	2.70	2.46
ZnS	3.91	1.75	3.34	3.36
CdS	2.42	0.86	2.08	2.05
LiF	14.2	8.47	14.13	13.27
Ar	14.2	8.18	13.25	13.28
Ne	21.7	11.44	20.69	19.59

D. Nabok, A. Gulans, and CD, in preparation

exciting

Klimeš, et al.
PRB 90, 075125 (2014)

Shishkin and Kresse,
PRB 75, 235102 (2007)

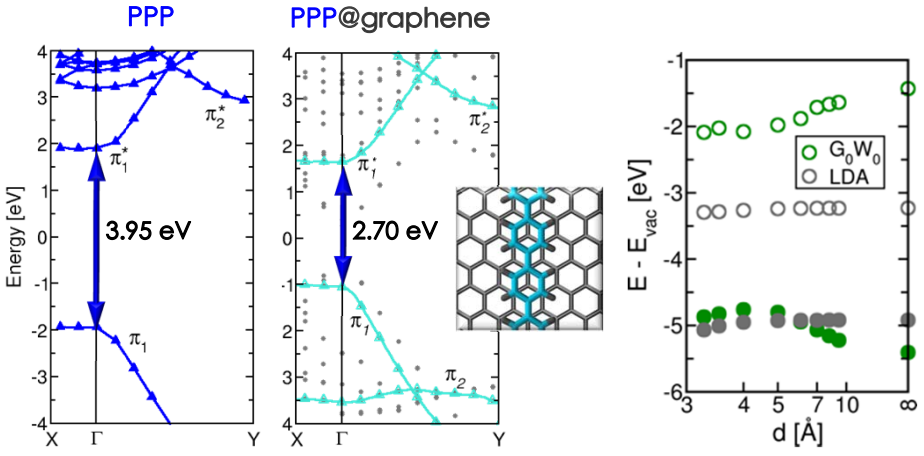
Polarization effect

G_0W_0@LDA

Decrease of gap on adsorption

P. Puschnig, P. Amiri & CD
PRB 86, 085107 (2012).

FWF



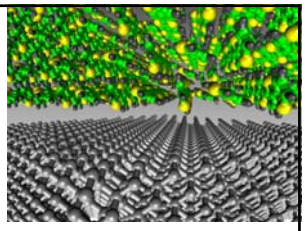
Issues …

GW

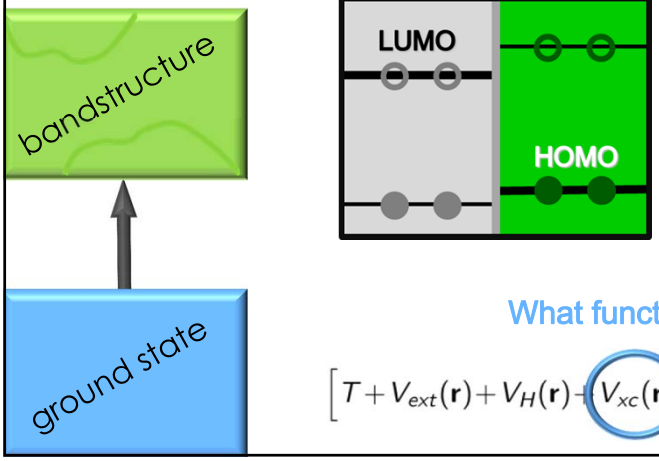
- Starting point
  - DFT ground state
- Self-consistency?
  - Vertex correction
- Approximations
  - All-electron vs pseudopotentials
  - Plasmon-pole approximation
  - Convergence with empy bands
- Comparison with experiment
  - Matrix-element and final-state effects
  - Electron-phonon coupling

Interfaces

Starting point



inorganic organic



What functional ?

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

Neutral excitations

Many-body perturbation theory

Bethe-Salpeter equation

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E_\lambda A^{\lambda}_{vc\mathbf{k}}$$

Two-body wavefunction

$$\phi^{\lambda}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vc\mathbf{k}} A^{\lambda}_{vc\mathbf{k}} \psi^{*}_{v\mathbf{k}}(\mathbf{r}_h)\, \psi_{c\mathbf{k}}(\mathbf{r}_e)$$

from ground state

Dielectric function

$$\mathrm{Im}\,\epsilon \sim \sum_{\lambda} \sum_{vc} \left| \frac{\langle c|\nabla|v\rangle A^{\lambda}_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E_\lambda - \omega)$$

Two-particle eigenvalue problem

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E_\lambda A^{\lambda}_{vc\mathbf{k}}$$

Diagonal term

$$H^{\text{diag}}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

Direct term - attractive

$$H^{\text{dir}}_{cv\mathbf{k},c'v'\mathbf{k}'} = \int \mathrm{d}^3r\, \mathrm{d}^3r' \frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\epsilon^{-1}(\mathbf{r},\mathbf{r}')\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Exchange term - repulsive

$$H^{\text{x}}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \mathrm{d}^3r\, \mathrm{d}^3r'\, \psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r})\, \bar{v}(\mathbf{r},\mathbf{r}')\, \psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi_{c'\mathbf{k}'}(\mathbf{r}')$$

Two-particle eigenvalue problem

Spin singlets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{\text{x}}$$

Spin triplets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{\text{x}}$$

Random-phase approximation

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{\text{x}}$$

Independent-particle approximation

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{\text{x}}$$

Role of electron-hole interaction

Dielectric function in IPA

$$\mathrm{Im}\,\epsilon \sim \sum_{cv} \left| \frac{\langle c|\nabla|v\rangle}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(\varepsilon_c - \varepsilon_v - \omega)$$

Dielectric function from BSE

$$\mathrm{Im}\,\epsilon \sim \sum_{\lambda} \sum_{vc} \left| \frac{\langle c|\nabla|v\rangle A^{\lambda}_{cv}}{\varepsilon_c - \varepsilon_v} \right|^2 \delta(E_{\lambda} - \omega)$$

Peaks at electron-hole pair energies

Redistribution of osczillator strength

Experimental counterparts

Optical absorption

X-ray spectroscopy

Electron-loss spectroscopy

Raman scattering

Photoluminescense

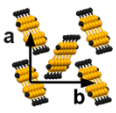
…

Materials …

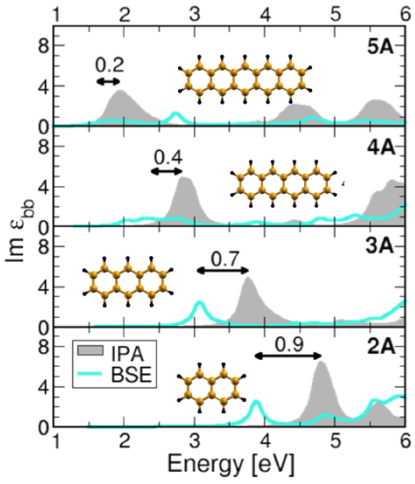
Organic semiconductors: oligoacenes

Electron-hole binding energy depends on

- molecular size
- molecular packing
- polarization of light



Exciton binding energies
Singlet ~1 eV – 0.1 eV
Triplet ~2 eV – 1 eV



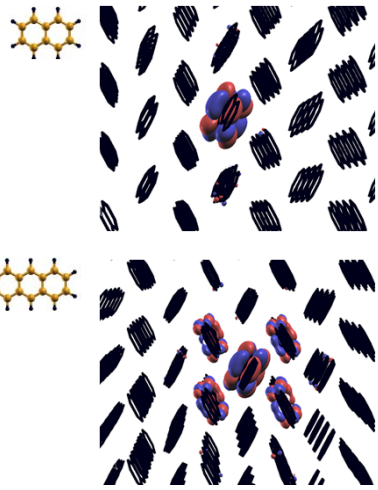
K. Hummer, P. Puschnig, & CD, PRL 92, 147402 (2004).
K. Hummer & CAD, PRB 71, 081202(R) (2005).

Organic semiconductors: oligoacenes

Size of electron-hole pairs depends on

- molecular size
- molecular packing
- polarization of light

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e)\ \psi_v(\mathbf{r}_h)$$



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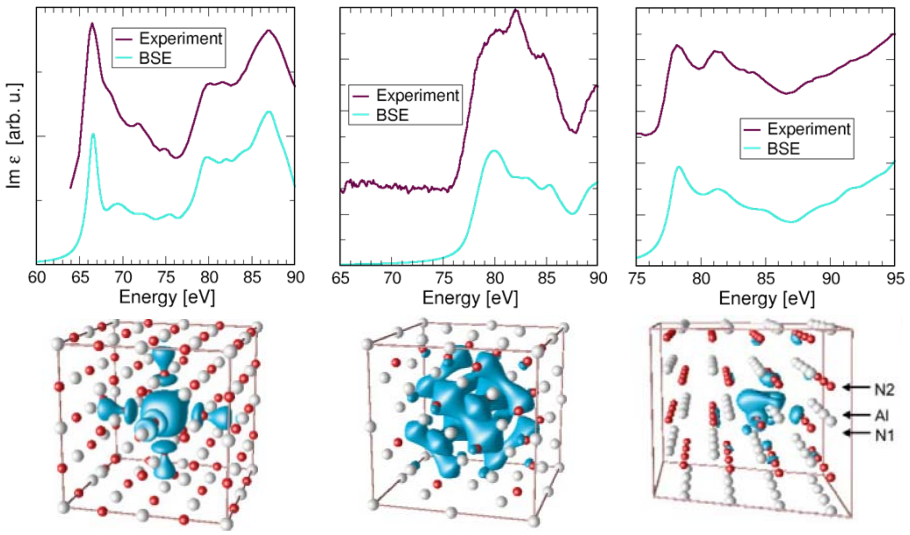
K. Hummer & CAD, PRB 71, 081202(R) (2005).

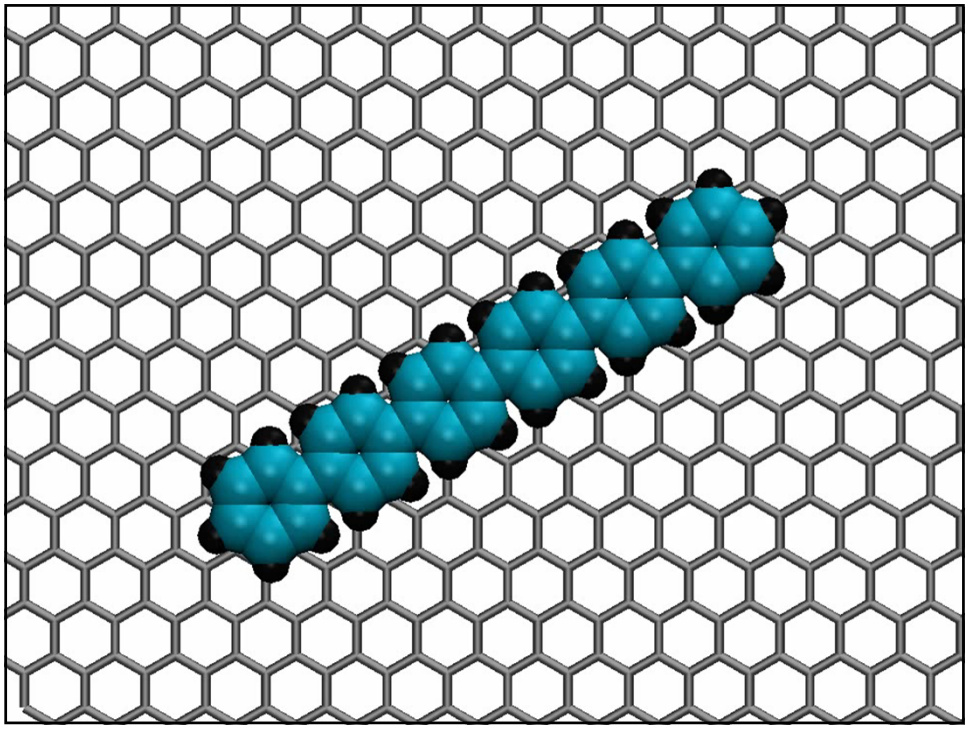
Core excitations by BSE: AlN

Al $L_{2,3}$-edge

rocksalt | zincblende | wurtzite



W. Olovsson et al., PRB **83**, 195206 (2011).



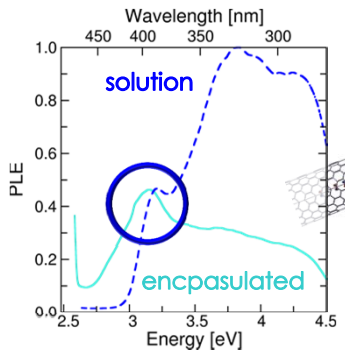
Optical spectroscopy

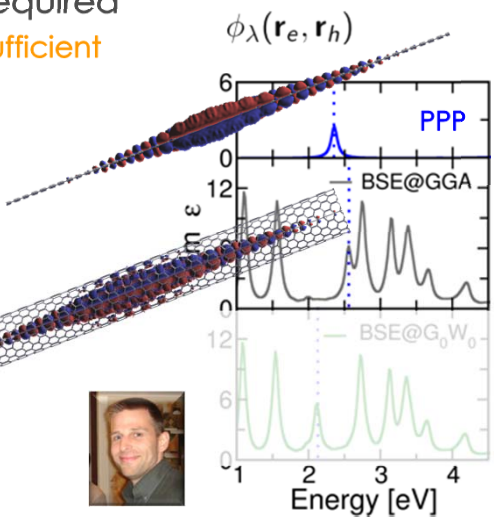
FWF

Highest-level theory required

Scissors correction insufficient

PPP@(14,0)





M. A. Loi, et al., Adv. Mater. 22, 1635 (2010).
J. Gao, et al., Small 7, 1721 (2011).

M. Milko, P. Puschnig, and CD
J. Phys. Chem. Lett. 4, 2664 (2013).

Issues …

Starting point

- GW and BSE level

Comparison with experiment

- What is the exciton binding energy?

Approximations

- All-electron vs pseudopotentials
- Feasibility

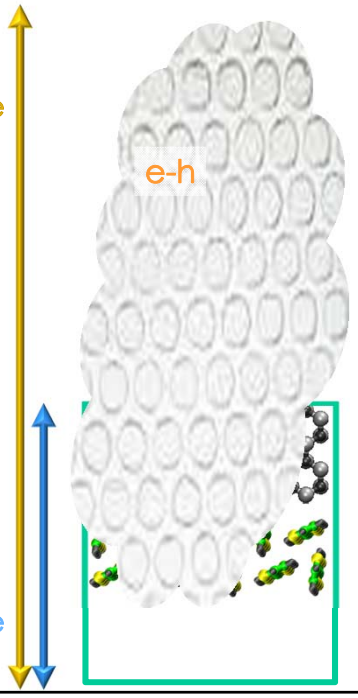
Interfaces

Huge cell size required

Large vacuum size

- Unoccupied states

Challenge: feasibility




THANKS !!
Claudia Draxl
HUMBOLDT-UNIVERSITÄT ZU BERLIN