# Density functional theory in solid state physics

Lecture 14

Organisation

- Exam: September 14th, project-based

- I will send those who want to participate a project to work in the morning of the 14th, you do the calculations including convergence tests etc

- Use a provided template to write a report, explain theoretical background, approximations used and why, parameters used, results

- HPC accounts are valid until the end of September and should be used for the simulations

- A challenge for theoretical methods: excitation spectra

- Time-independent DFT cannot really deal with time-varying external potentials, only independent particle approximation possible

- Extension the the time-domain: time-dependent DFT, time-dependent Kohn-Sham equation

- Technically exact if exact exchange-correlation potential $v_{xc}(r,t) = \frac{\delta A_{xc}[n]}{\delta n(r,t)}$ is known

- In practice usually use the adiabatic approximation $v_{xc}(r,t) \approx \left.\frac{\delta E_{xc}[\tilde{n}]}{\delta \tilde{n}(r)}\right|_{\tilde{n}(r)=n(r,t)}$

- Adiabatic LDA (ALDA) and similar local approximations are often used
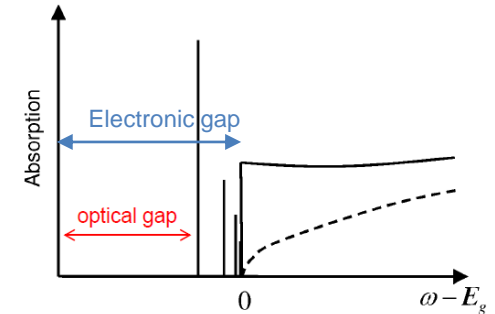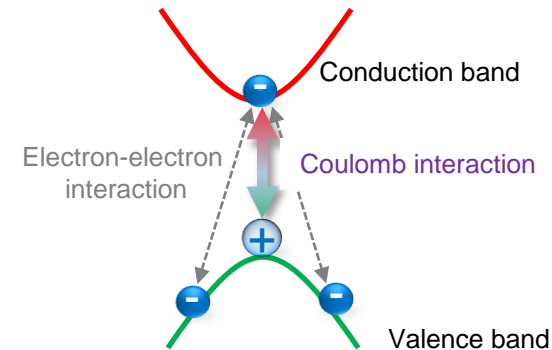
- Linear response: small potential $\delta v_{ext}(r', t')$ induces density fluctuations at point r, t,

$$\chi(r, r', t, t') = \frac{\delta n(r, t)}{\delta v_{ext}(r', t')}$$

- Poles of $\chi(r, r', \omega)$ are the excitation energies of the system for δv_{ext}

- Solve Dyson equation $\chi = \chi_0 + \chi_0(v_c + f_{xc})\chi$ instead of TD-KS equations

  Non-interacting response function, from DFT

  Coulomb potential

  Exchange-correlation kernel

- ALDA works well for EEL spectra, plasmon dispersions etc., but cannot properly describe excitons

- ALDA suffers from band gap problem inherited from time-independent DFT

- Long-range corrected XC kernels have been proposed, another option is using non-local adiabatic kernels, such as time-dependent Hartree-Fock or time-dependent hybrid functionals

- The state-of-the-art approaches for the excited state properties of solid materials are rooted in many-body theory.

- Measurement of electronic band gaps usually through addition or removal of electrons, e.g. PES or inverse PES, „charged excitations"
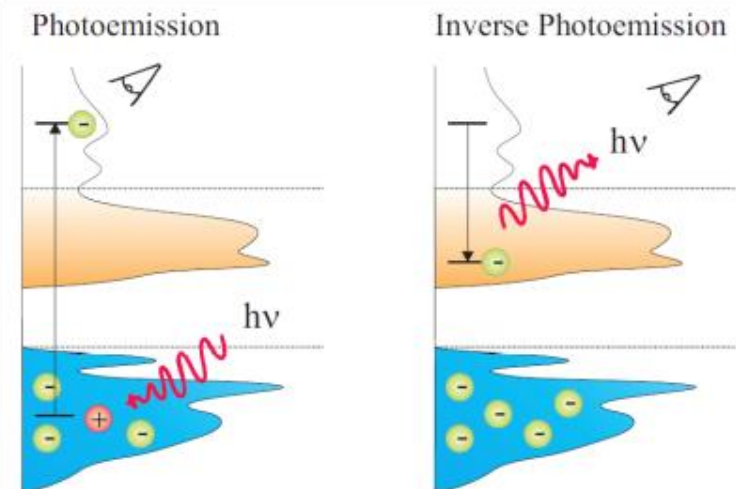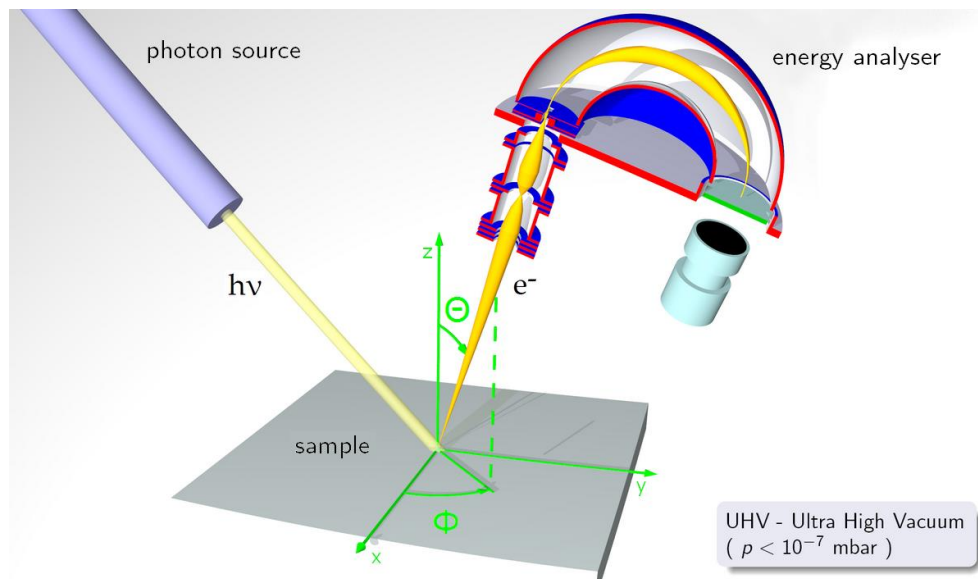
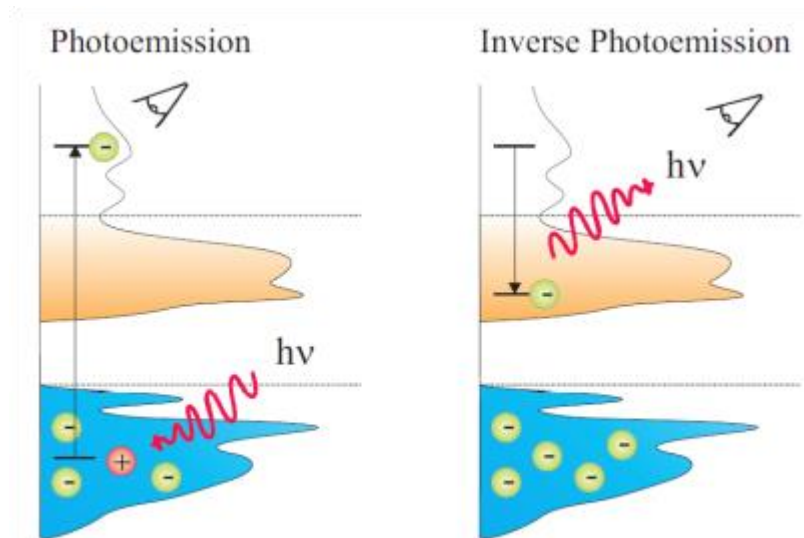New J. Phys. 7, 126 (2005)

- Energy to remove an electron from state i:

$$\varepsilon_i = E(N-1, i) - E(N)$$
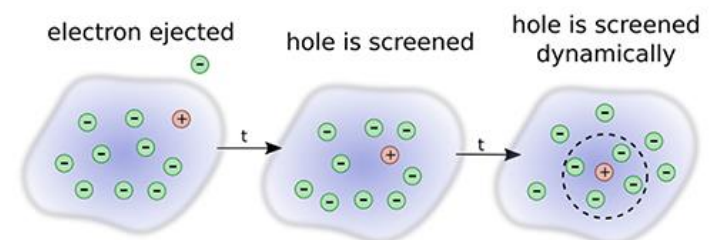
- Energy to add an electron to state i:

$$\varepsilon_i = E(N+1, i) - E(N)$$

Excited state   Groundstate

- Excited states are not single Slater determinants, but quasiparticles due to electron-electron interaction

- Reason for why KS-DFT band energies are usually bad

- Still: Can use equations above for relatively accurate band gaps from DFT (ΔSCF method)

Photoemission   Inverse Photoemission

hv

hv

New J. Phys. 7, 126 (2005)

electron ejected   hole is screened   hole is screened dynamically

- How to calculate quasiparticle energies of charged excitations from many-body theory?

- Central quantity: Green function $G(r, r'; t, t') = -i \langle N | \hat{T} [\hat{\Psi}(r, t) \hat{\Psi}^+(r', t')] | N \rangle$ ← N-electron ground state

Propagation of an extra electron (or hole) between r, t to r', t'

Time-ordering operator so that earlier time acts on N first.

Annihilate an electron at r' and t'

- Energy form: $G(r, r'; \varepsilon) = \lim_{\eta \to 0} \sum_i \frac{\psi_i(r) \psi_i^*(r\prime)}{\varepsilon - \varepsilon_i - i\eta(E_F - \varepsilon_i)}$

ψ_i : Transition amplitude between ground and excited state i

- Recast many-body Hamiltonian into single-particle Hamiltonian

$$\left(-\frac{1}{2}\nabla^2 + v(r) + v_H(r) \right) \psi_i(r) + \int \Sigma_{xc}(r, r'; \varepsilon) \psi_i(r') dr' = \varepsilon_i \psi_i(r)$$

Self-energy, contains all electron-electron and electron-hole interactions (apart from Hartree). We want this

- In principle can obtain exact self-energy through solution of Hedin's Equations: (*Phys. Rev. 139, A796 (1965)*)

Non-interacting Green function $1 = r_1, t_1$

$$G(1,2) = G_0(1,2) + \int G_0(1,3)\big(v_H(3) + \Sigma_{xc}(3,4)\big)G(4,2)d34$$

Green function

$$\Sigma_{xc}(1,2) = i\int G(1,3)W(1,4)\Gamma(4,2,3)d34$$

Self-energy

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}G(4,6)G(5,7)\Gamma(6,7,3)d4567$$

Vertex function

$$P(1,2) = -i\int G(1,3)G(4,1)\Gamma(3,4,2)d34$$

Polarizability

$$\epsilon(1,2) = \delta(1,2) - \int v_c(1,3)P(3,2)d3$$

Dielectric matrix

$$W(1,2) = \int \epsilon^{-1}(1,3)v_c(3,2)d3$$

Screened Coulomb interaction

- Self-consistent solution until converged

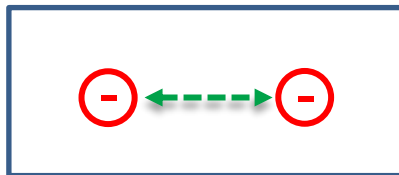- External potential enters through the Dyson Eq, all other Eqs. are universal

- The picture: dynamically screened interation between electrons due to charge cloud gives rise to modified self-energy
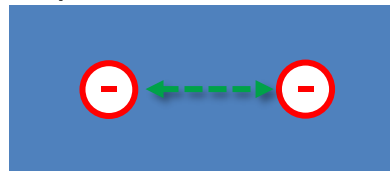
Screened Coulomb interaction

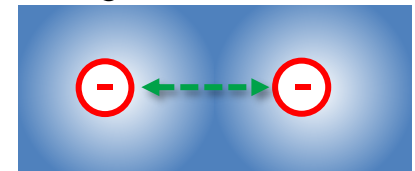$W(r,r';\omega)$
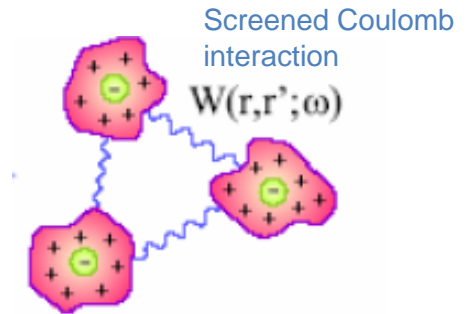
- What is W?

Interactions in vacuum

$$v_c(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|}$$

Screening in homogenous polarizable medium

$$W(\vec{r}, \vec{r}') = \frac{1}{\epsilon|\vec{r} - \vec{r}'|}$$

Dynamical screening in general medium

$$W(\vec{r}, \vec{r}', \omega) = \int \frac{\epsilon^{-1}(\vec{r}, \vec{r}'', \omega)}{|\vec{r}'' - \vec{r}'|} dr''$$

→ self-energy is not instantaneous

- Exact theory, but Hedin's equations impossible to solve in practice

- A big problem is evaluation of the three-particle vertex function

$$G(1,2) = G_0(1,2) + \int G_0(1,3)\big(v_H(3) + \Sigma_{xc}(3,4)\big)G(4,2)d34$$

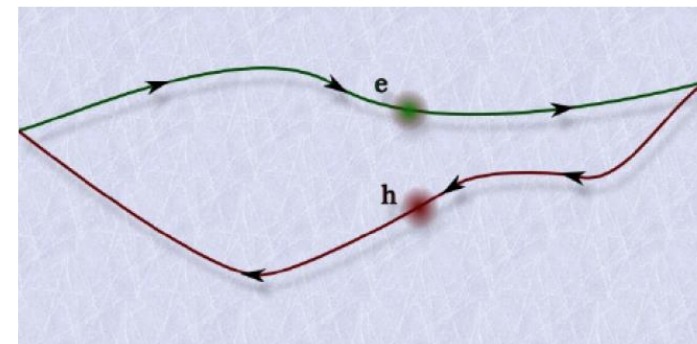$$\Sigma_{xc}(1,2) = i\int G(1,3)W(1,4)\Gamma(4,2,3)d34 = {\color{red}iG(1,2)W(1,2)}$$

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}G(4,6)G(5,7)\Gamma(6,7,3)d4567$$

$$P(1,2) = -i\int G(1,3)G(4,1)\Gamma(3,4,2)d34 = {\color{red}-iG(1,2)G(2,1)}$$

$$\epsilon(1,2) = \delta(1,2) - \int v_c(1,3)Pd3$$

$$W(1,2) = \int \epsilon^{-1}(1,3)v_c(3,2)d3$$

- No vertex → non-interating e-h pairs

- Vertex also removes „self-screening"

- „GW approximation"

- The following self-consistent updates miss the effect of vertex corrections, can have effects on results

- Typically: no self-consistent update, truncation after first iteration

- G_0W_0 approximation (in spectral representation):

Kohn-Sham orbitals

$$G_0(r, r'; \varepsilon) = \lim_{\eta \to 0} \sum_i \frac{\varphi_i(r)\varphi_i^*(r')}{\varepsilon - \varepsilon_i - i\eta(E_F - \varepsilon_i)}$$

Non-interacting Green function

$$P_0(r, r'; \varepsilon) = -\frac{i}{2\pi} \int G_0(r, r', \varepsilon - \varepsilon')G_0(r, r'; \varepsilon') \, d\varepsilon'$$

Polarizability in RPA

$$\epsilon(r, r'; \varepsilon) = \delta(r - r') - \int v_c(r, r'')P_0(r'', r'; \varepsilon)dr''$$

Dielectric matrix

$$W_0(r, r'; \varepsilon) = \int \epsilon^{-1}(r, r''; \varepsilon)v_c(r'', r')dr''$$

Screened Coulomb interaction

$$\Sigma_{xc}^{GW}(r, r'; \varepsilon) = \frac{i}{2\pi} \int G_0(r, r'; \varepsilon + \varepsilon')W_0(r, r'; \varepsilon')d\varepsilon'$$

Self-energy

- DFT exchange-correlation can be seen as a special case of quasiparticle self-energies

$$\Sigma_{xc}^{GW}(r, r'; \varepsilon) = \qquad \Sigma_x^{GW} \qquad + \qquad \Sigma_c^{GW}$$
$$= \frac{i}{2\pi} \int G_0 v_c d\varepsilon' \quad + \qquad \frac{i}{2\pi} \int G_0 [W_0 - v_c] d\varepsilon'$$

bare (exact) exchange   non-local correlation

- Hartree-Fock: $\Sigma_{xc}^{HF}(r, r') = \Sigma_x^{GW}(r, r')$

- Local density approximation: $\Sigma_{xc}^{LDA}(r, r'; \varepsilon) = v_{xc}^{LDA}(r)\delta(r - r')$

- Hybrid functionals: $\Sigma_{xc}^{hyb}(r, r'; \varepsilon) = \Sigma_x^{GW} + (1 - a)(v_x^{DFT}\delta(r - r') - \Sigma_x^{GW}) + v_c^{DFT}\delta(r - r')$

- $G_0 W_0$ is essentially a dynamically screened Hartree-Fock exchange (like a fifth rung XC functional)

- Useful, because

Don't know this yet

quasiparticle equations: $\left[-\frac{1}{2}\nabla^2 + v + v_H + \Sigma_{xc}^{GW}\left(\varepsilon_{nk}^{GW}\right) \right]\varphi_{nk}^{GW} = \varepsilon_{nk}^{GW}\varphi_{nk}^{GW}$
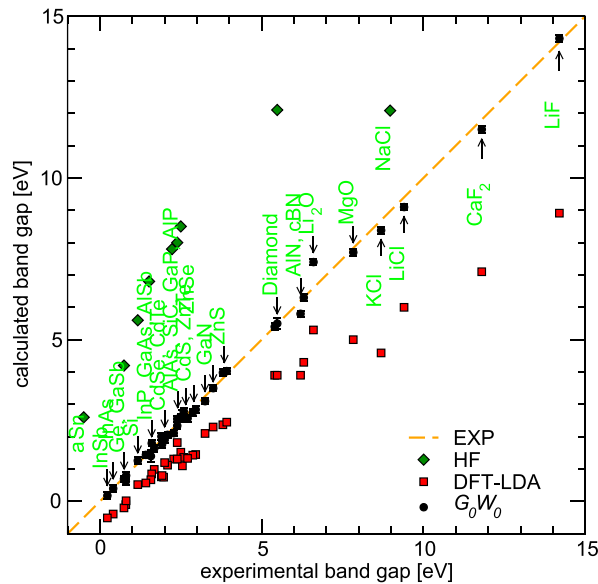
Kohn-Sham equations: $\left[-\frac{1}{2}\nabla^2 + v + v_H + v_{xc}^{DFT} \right]\varphi_{nk}^{DFT} = \varepsilon_{nk}^{DFT}\varphi_{nk}^{DFT}$

- GW energies can be derived from self-consistent solution of GW quasiparticle equation
  → expensive, as non-local self-energy has to be evaluated at each step

- Typical approach: Approximation $\varphi_{nk}^{GW} \approx \varphi_{nk}^{DFT}$ (often, this approximation is quite valid)

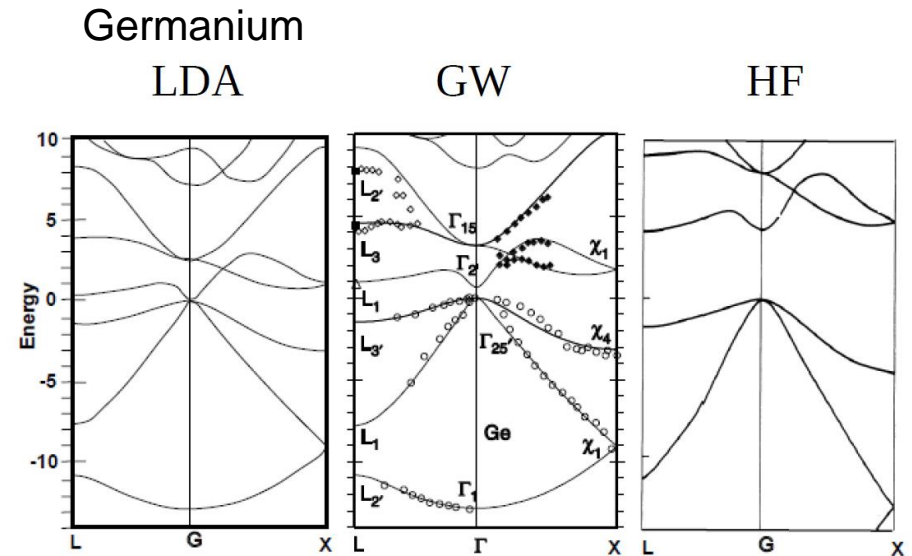- Use Σ_{xc}^{GW} to do „one-shot" correction of DFT band energies

$$\varepsilon_{nk}^{GW} = \varepsilon_{nk}^{DFT} + Z_{nk}\left\langle \varphi_{nk}^{DFT} \middle| \Sigma_{xc}^{GW}\left(\varepsilon_{nk}^{DFT}\right) - v_{xc} \middle| \varphi_{nk}^{DFT} \right\rangle$$

with $\Sigma_{xc}^{GW}\left(\varepsilon_{nk}^{GW}\right) \approx \Sigma_{xc}^{GW}\left(\varepsilon_{nk}^{DFT}\right) + \left(\varepsilon_{nk}^{GW} - \varepsilon_{nk}^{DFT}\right)\frac{\partial\Sigma_{xc}^{GW}(\varepsilon)}{\partial\varepsilon}$, $Z_{nk} = 1/\left(1 - \frac{\partial\Sigma_{xc}^{GW}(\varepsilon)}{\partial\varepsilon}\right)$

- GW based methods are very accurate but also very expensive (N^4 -N^5)

http://perso.neel.cnrs.fr/valerio.olevano/gw/gw.html

Germanium

LDA   GW   HF

Phys. Rev. B. 48, 17791 (1993)

Band alignment at Si/SiO$_2$ interface

Phys. Rev. Lett. 100, 186401 (2008)

SiO$_2$

Si

G$_0$W$_0$: 2.9 eV
Exp: 3.1 eV

G$_0$W$_0$: 4.1 eV
Exp: 4.1 eV

- GW based methods are very accurate but also very expensive (N^4 -N^5)

  - Dielectric matrix ϵ is energy/frequency dependent and needs to be inverted
    at each frequency → „plasmon-pole approximation", model ϵ^{-1} by single peak at
    plasma frequency

  - Non-local, all k-points in the calculation are coupled

  - The correlation component and the polarizability in principle require integration
    up to high energies ε to achieve sufficient accuracy (often several 1000 empty bands)
    → „effective energy" techniques, approximate contribution of high energies

- Further increase in accuracy at rather small additional cost can be achieved by updating
  G (GW_0 approximation)

- Hybrid functionals often of similar accuracy as G_0W_0 but lower computational cost

- More details about GW at Front. Chem. 7, 377 (2019) and other review articles

- Another type of excitation: charge neutral excitations of electrons into conduction band
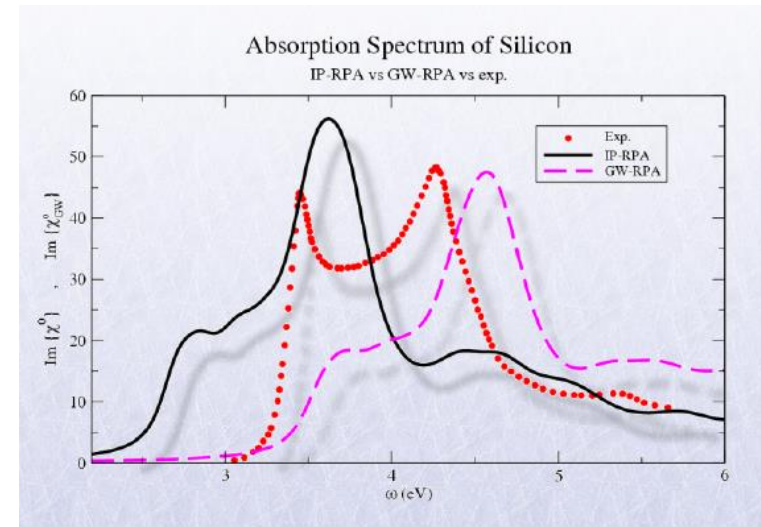

Conduction band

Conduction band

Electron-electron
interaction

Coulomb interaction

Valence band

Valence band

$h\nu$

Optical absorption
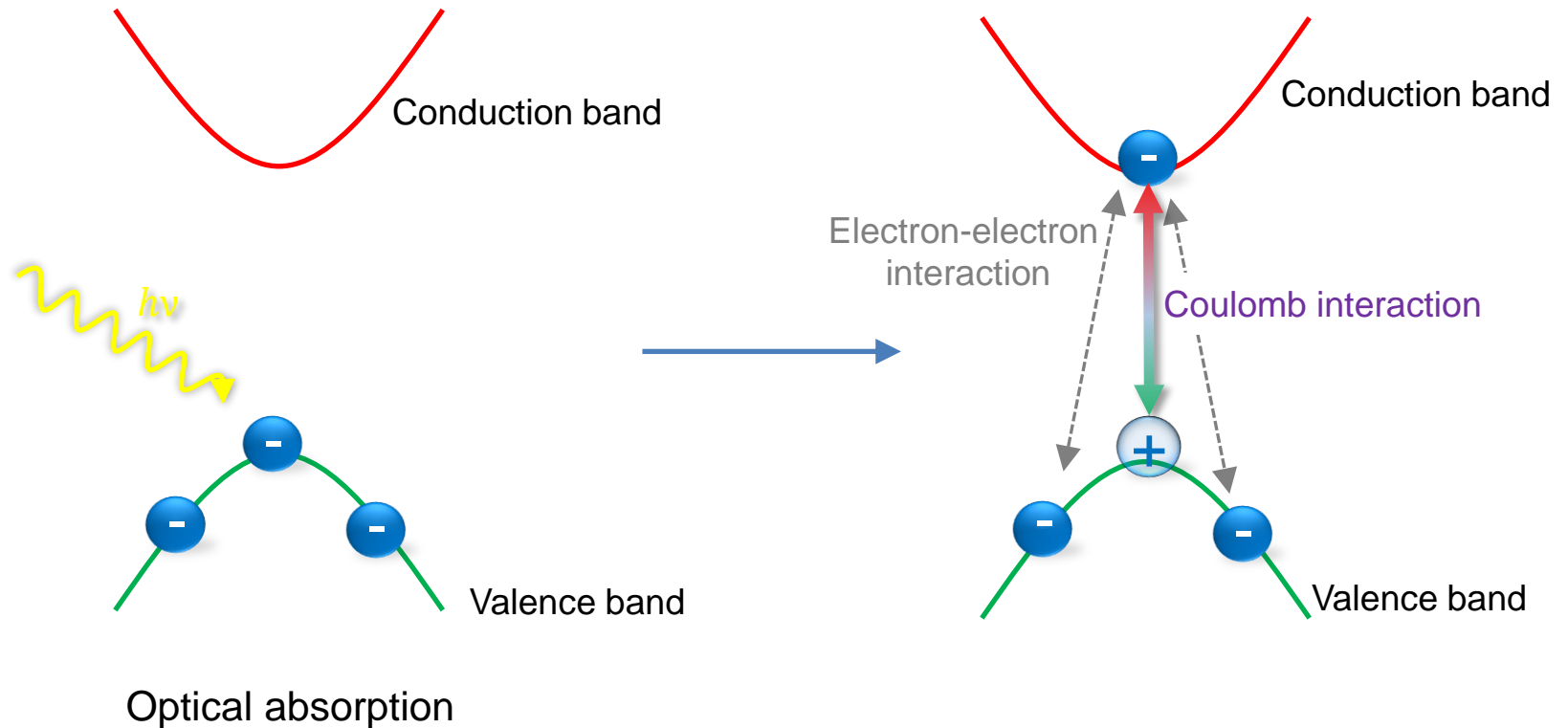
- Electron-electron interaction causes „dressing" of electrons and holes → GW approximation

$$\chi_0^{GW} = P = -i \int G(1,3)G(4,1)d34$$

$$= \sum_{m,n} \frac{\varphi_m(r)\varphi_n^*(r)\varphi_m^*(r')\varphi_n(r')}{\omega - (\varepsilon_m^{GW} - \varepsilon_n^{GW})}$$

Absorption Spectrum of Silicon
IP-RPA vs GW-RPA vs exp.

- Absorption onset is corrected compared to RPA, but excitonic properties are absent

- We need interaction between dressed electrons and holes for excitons

Dressed hole

e-h interaction

Dressed electron
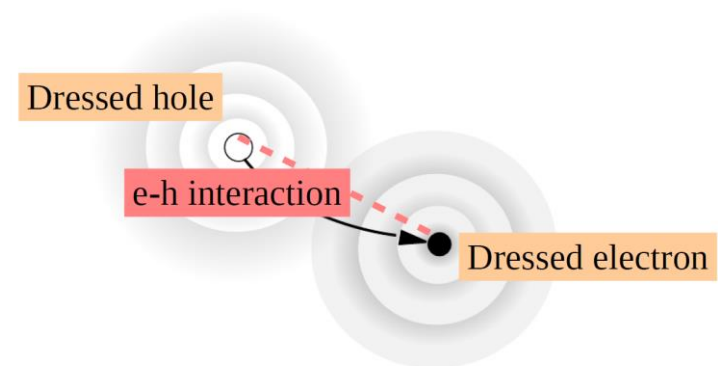
- Hedin equations: electron-hole interactions are included in the vortex function

$$P(1,2) = -i \int G(1,3)G(4,1)\Gamma(3,4,2)d34$$

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)} G(4,6)G(5,7)\Gamma(6,7,3)d4567$$

Vertex contribution

- Observations:

    - $\frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}$ defines the electron-hole coupling

    - Σ_{xc} is a generalized XC potential

    - G is related to the one-particle density matrix $\gamma(r,r',t) = G(r,r';t,t)$ and the electron density, $n(r,t) = G(r,r;t,t)$
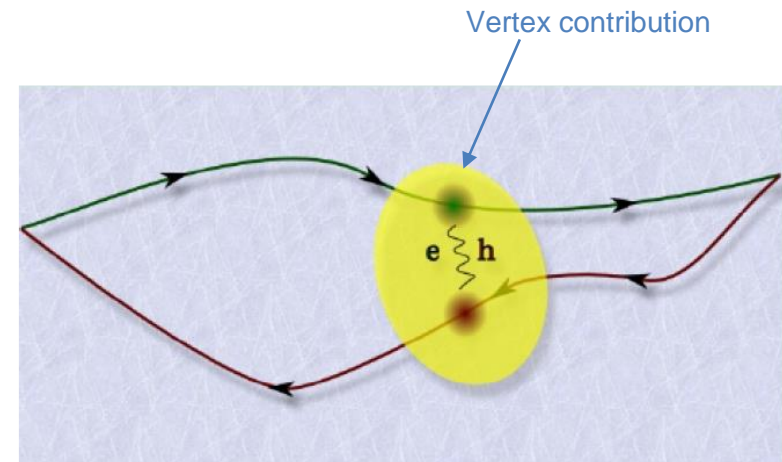
- Idea: Use the linear response approach from TDDFT, with $\frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}$ as a generalized time-dependent xc kernel

- The generalized response picture: Apply a non-local „potential" $\tilde{v}(r, r', t, t')$ to the system, describe the generalized response by the two-particle Green function

$$L(1,2,1',2') \equiv \frac{\delta G(1,1')}{\delta \tilde{v}(2',2)} \qquad \left(\text{TDDFT: } \chi \equiv \frac{\delta n(r,t)}{\delta \tilde{v}(r\prime,t\prime)}\right)$$

- This yields the *excitonic Bethe-Salpeter equation*

$$L = L_0 + L_0\underbrace{(-iv_c + \Xi_{xc})}_{\text{Bethe−Salpeter kernel } K}L \qquad (\text{TDDFT: } \chi = \chi_0 + \chi_0(v_c + f_{xc})\chi)$$

with the generalized XC kernel $\Xi_{xc} = \frac{\delta\Sigma_{xc}(1,2)}{\delta G(4,5)}$ $\qquad \left(\text{TDDFT: } f_{xc} = \frac{\delta A_{xc}(r,t)}{\delta n(r',t\prime)}\right)$

and the *uncorrelated generalized response* $L_0(1.2.1',2') = G(1,2')G(2,1')$

Obtained from solution of the
Dyson Eq. for G

- The excitonic BSE describes the propagation of a correlated electron-hole pair

- More details: https://www.cond-mat.de/events/correl16/manuscripts/reining.pdf (or similar)

- GW approximation ($\Sigma_{xc}^{GW} = iGW$)): $\Xi^{GW}(1,2,3,4) = i\delta(1,4)\delta(2,3)W(1,2) + iG(1,3)\frac{\delta W(1,3)}{\delta G(4,2)}$
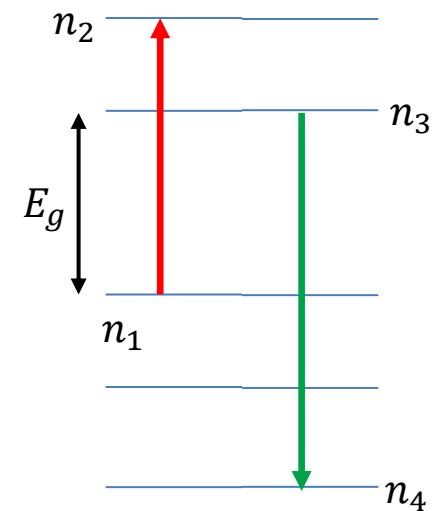
$$\approx i\delta(1,4)\delta(2,3)W(1,2)$$

- Static approximation: $W(1,2) = W(r,r')\delta(t - t')$

- How to solve BSE? Usually transform to transition space

$$L_{(n_1 n_2)}^{(n_3 n_4)} = \int L(1,2,3,4,)\varphi_{n_1}(1)\varphi_{n_2}^*(2)\varphi_{n_3}^*(3)\varphi_{n_4}(4)d1234$$

$$L(1,2,3,4,\omega) \Rightarrow L_{(n_1 n_2)}^{(n_3 n_4)}(\omega) = L_{0,(n_1 n_2)}^{(n_5 n_6)}(\omega)K_{(n_5 n_6)}^{(n_7 n_8)}L_{(n_7 n_8)}^{(n_3 n_4)}(\omega)$$

$$= [H_{exc} - \omega]^{-1}$$

with an effective two-particle excitonic Hamiltonian

$$H_{exc} = \left(\varepsilon_{n_2}^{QP} - \varepsilon_{n_1}^{QP}\right)\delta_{n_1 n_3}\delta_{n_2 n_4} + \left(f_{n_2} - f_{n_1}\right)\left(2v_{c,(n_1 n_3)}^{(n_2 n_4)} - W_{(n_1 n_2)}^{(n_3 n_4)}\right)$$ (for non-spinpolarized system)

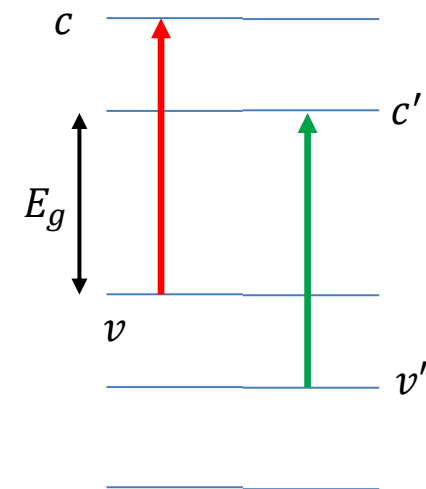- Optical transitions happen between occupied and empty bands

- Tamm-Dancoff approximation: neglect „non-resonant" transitions from unocc $\rightarrow$ occ states

$$H_{exc} = \left(\varepsilon_c^{QP} - \varepsilon_v^{QP}\right)\delta_{vv'}\delta_{cc'} + (f_c - f_v)\left(2v_{c,(vv')}^{(cc')} - W_{(vc)}^{(v'c')}\right)$$

Transition energies without electron-hole coupling effects

Electron-hole „exchange" term
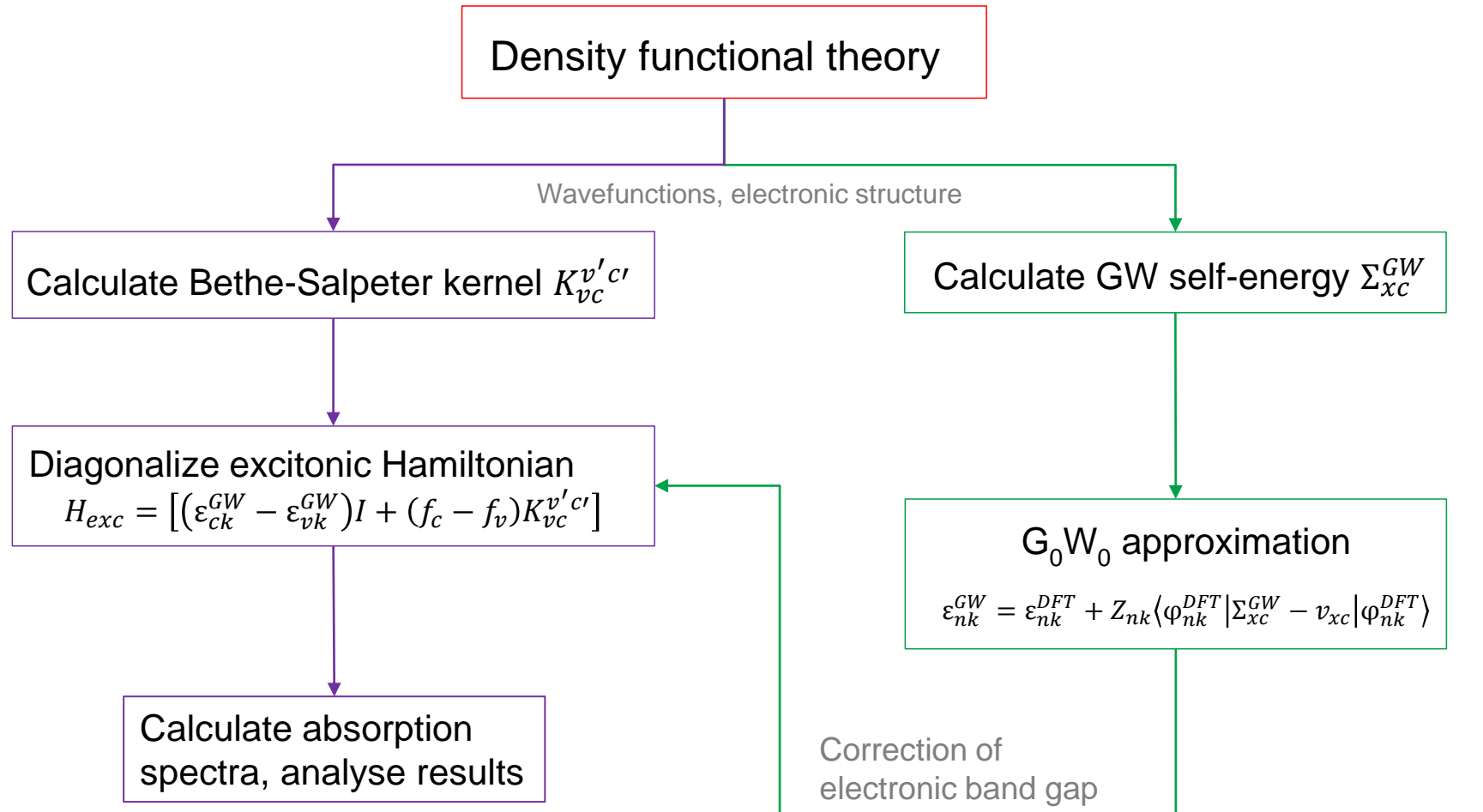
„direct" term, variation of the GW self-energy

- Useful, because this leads to the spectra representation

$$L_{(vc)}^{(v'c')} = \sum_\lambda \frac{|A_\lambda\rangle\langle A_\lambda|}{E_\lambda - \omega} \quad \text{with } H_{exc}A_\lambda = E_\lambda A_\lambda$$

(this is the idea behind the Casida equations as well)

- Dielectric function: $\epsilon_M(\omega) \propto \sum_\lambda \left|\sum_{vc} A_\lambda^{(vc)}\langle c|\hat{r}|v\rangle\right|^2 \delta(E_\lambda - \omega)$

- Problem is reduced to an eigenvalue problem of H_{exc}, eigenvalues give excitation energies, eigenvectors give „exciton wavefunctions"

- Note how the eigenvalue equation is similar to the Wannier equation, but much complexer

- BSE calculation scheme for solids

Density functional theory

Wavefunctions, electronic structure

Calculate Bethe-Salpeter kernel $K_{vc}^{v'c'}$

Calculate GW self-energy Σ_{xc}^{GW}

Diagonalize excitonic Hamiltonian
$$H_{exc} = \left[\left(\varepsilon_{ck}^{GW} - \varepsilon_{vk}^{GW}\right)I + (f_c - f_v)K_{vc}^{v'c'}\right]$$

G_0W_0 approximation
$$\varepsilon_{nk}^{GW} = \varepsilon_{nk}^{DFT} + Z_{nk}\langle\varphi_{nk}^{DFT}|\Sigma_{xc}^{GW} - v_{xc}|\varphi_{nk}^{DFT}\rangle$$

Calculate absorption spectra, analyse results

Correction of electronic band gap

Yields: simulated spectra with e-h effects

Yields: accurate electronic bandstructure

- The BSE ansatz works very well for excitonic spectra (for single excitations)

- For low-energy absorption:

SiO$_2$
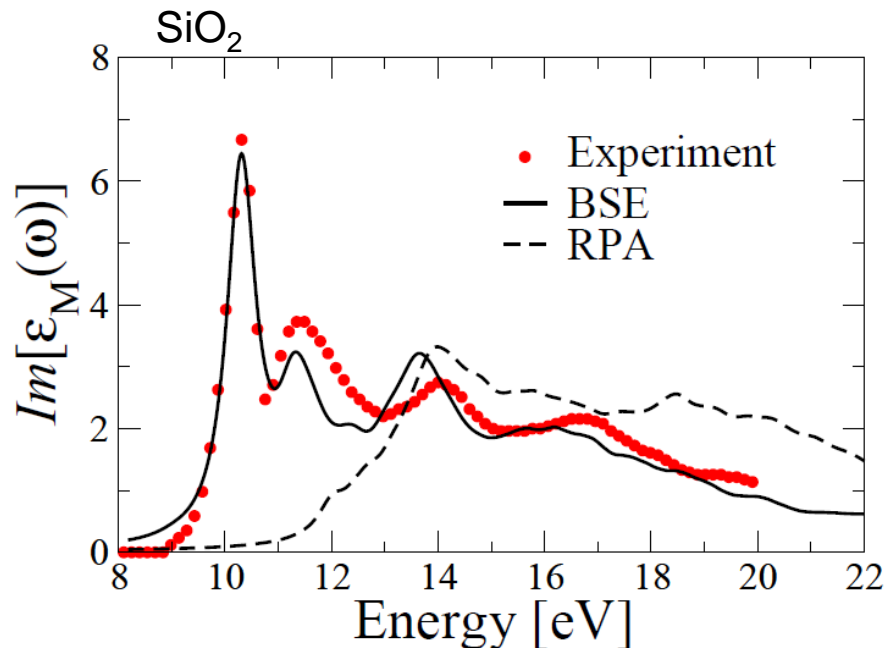
Phys. Rev. Lett.91, 256402 (2003)
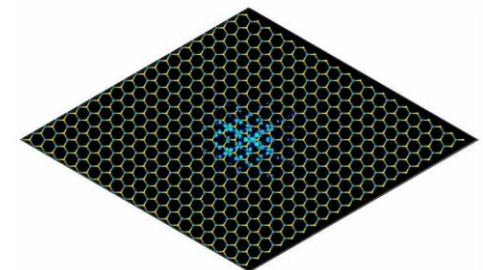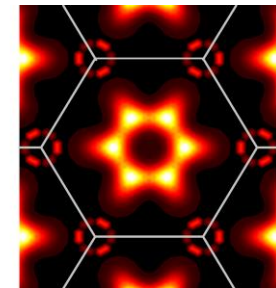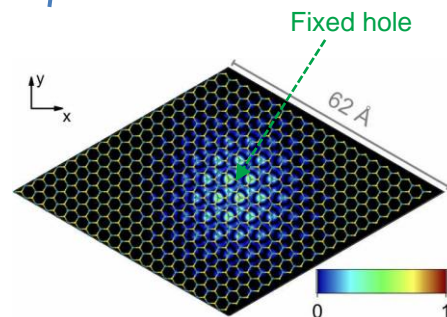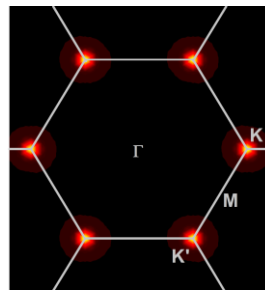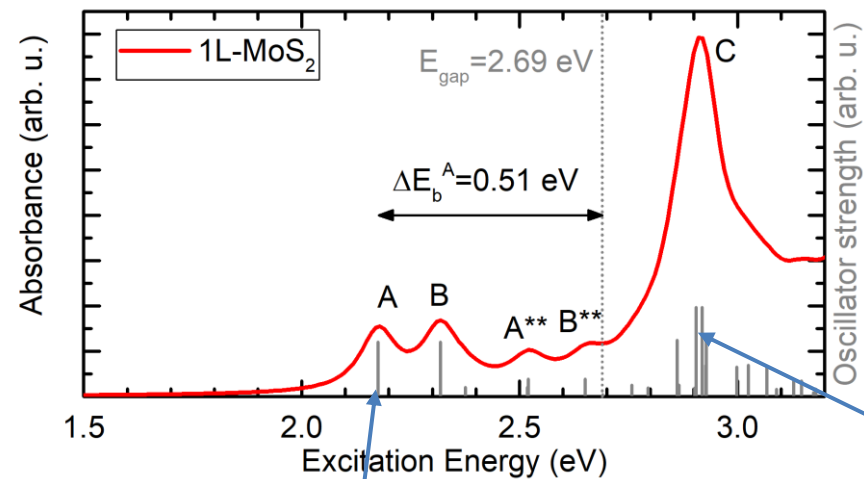

- The BSE also works for x-ray absorption, excitons formed by conduction band electrons and core holes
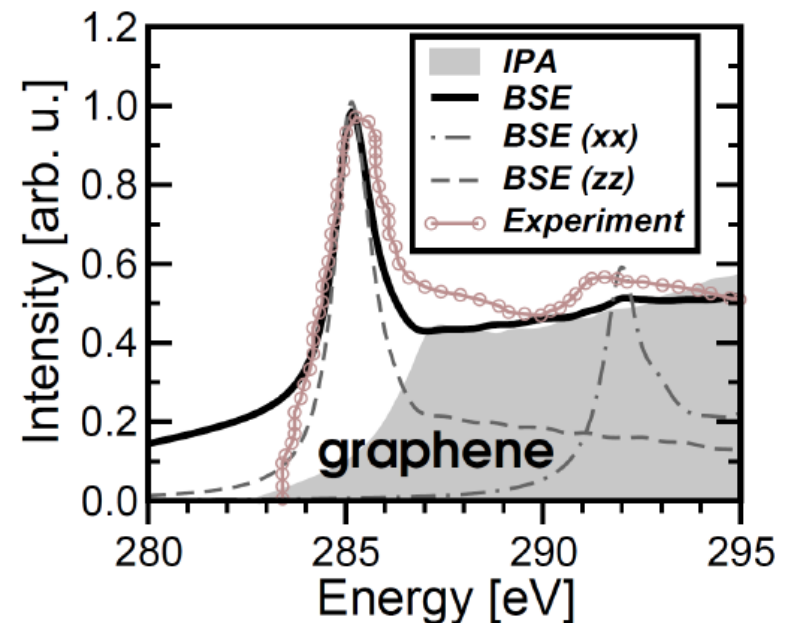
arXiv:1709.02288

- Theoretical spectroscopy gives insight into excitations that make up the optical spectra

Fixed hole

IEEE JSTQE 23, 2604359 (2016)

- Complement experiment with exciton binding energies, wavefunctions, oscillator strengths

- GW and the Bethe-Salpeter Equation are readily available in a variety of code packages nowadays

- Usually use of a planewave basis set for efficient evaluation of the screened Coulomb interaction

- However: High computational cost makes it difficult to use the BSE for larger systems, like GW, things get difficult for more 10-50 atoms (depending on elements) in the system

- Major bottleneck: excitons require very high k-point densities for converged results

- Improvements in computational efficiency of GW&BSE are an active field of research0

- The Bethe-Salpeter Equation and the TDDFT are very similar

- For the self-energy $\Sigma_{xc}(\omega) \approx \Sigma_x$, the BSE reduces to time-dependent Hartree-Fock (TDHF)

- Idea: Can we find a TDDFT XC kernel that mimicks the results of the BSE?

- Yes, we can write the two effective Hamiltonians for TDDFT and BSE

$$H_{exc}^{BSE} = \left(\varepsilon_{ck}^{QP} - \varepsilon_{vk}^{QP}\right)I + (f_{ck} - f_{vk})K_{(vck),(v'c'k')}^{BSE}$$

$$H_{exc}^{TDDFT} = \left(\varepsilon_{ck}^{DFT} - \varepsilon_{vk}^{DFT}\right)I + (f_{ck} - f_{vk})K_{(vck),(v'c'k')}^{TDDFT}$$

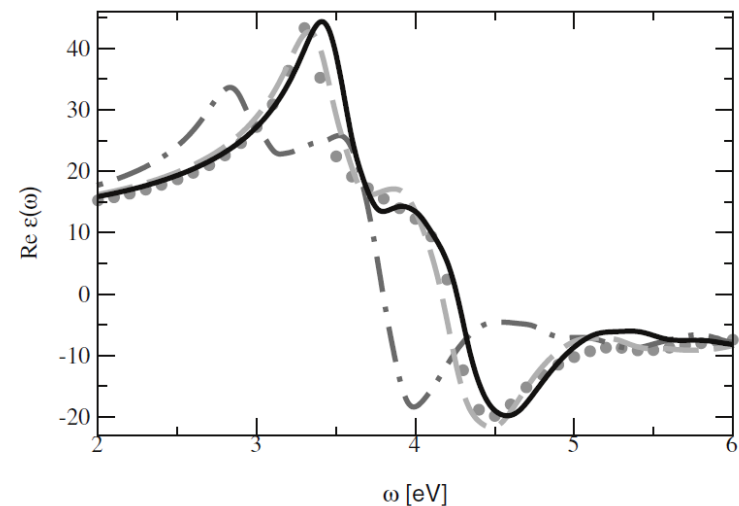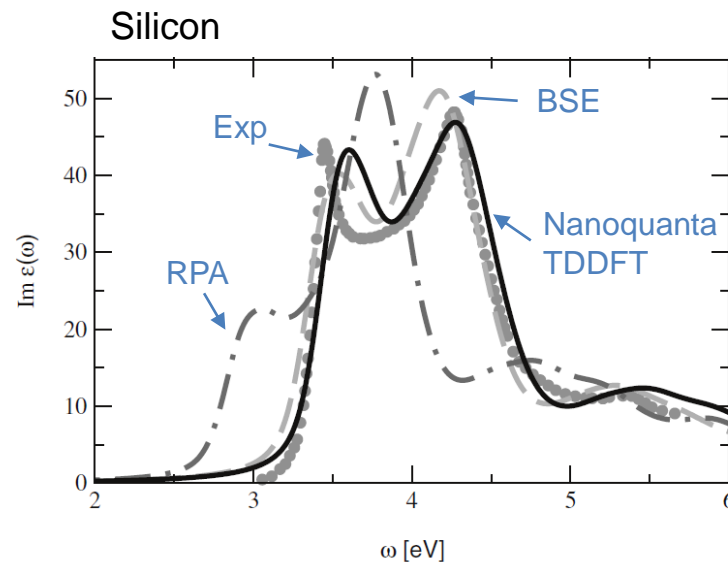- TDDFT kernel f_{xc} yields the same optical spectrum as BSE, if

$$(f_{ck} - f_{vk})K_{(vck),(v'c'k')}^{TDDFT} = \left(\varepsilon_{ck}^{QP} - \varepsilon_{vk}^{QP} - \varepsilon_{ck}^{DFT} + \varepsilon_{vk}^{DFT}\right)I + (f_{ck} - f_{vk})K_{(vck),(v'c'k')}^{BSE} = K_{(vck)}^{(v'c'k')}$$

$$= \int \varphi_{vk}(r)\varphi_{ck}^*(r)f_{xc}(r,r')\varphi_{v'k'}^*(r')\varphi_{c'k'}^*(r')drdr'$$

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$$\rightarrow f_{xc}(q, G, G') = \sum_{v,v',c,c'} \frac{1}{(f_{ck} - f_{vk})} (\widetilde{\varphi}_{vk}(G)\widetilde{\varphi}_{ck}^*(G))^{-1} K_{(vck)}^{(v'c'k')} (\widetilde{\varphi}_{v'k'}^*(G')\widetilde{\varphi}_{c'k'}(G'))^{-1}$$

- „Nanoquanta" kernel maps BSE kernel onto TDDFT XC kernel

- Very similar results to BSE, but also about as expensive

Silicon

- Implemented in dp

- And with that…

Thank you for your attention over the last couple of months