Ab initio Theoretical Optical Spectroscopy and the Bethe-Salpeter Equation (BSE)

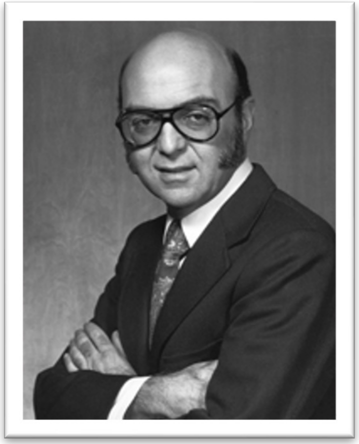
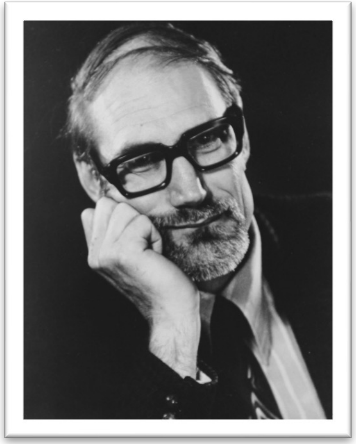
Felipe H. da Jornada
Department of Materials Science and Engineering, Stanford University
Stanford PULSE Institute, SLAC National Laboratory

Los Alamos Computational Condensed Matter Summer School 2025
June 20, 2025

HOW TO UNDERSTAND A SOLID WITH ~10^{23} INTERACTING ELECTRONS?

- Dirac: fundamental laws are known, equations are complicated, need approximations.

- Cohen & Heine:

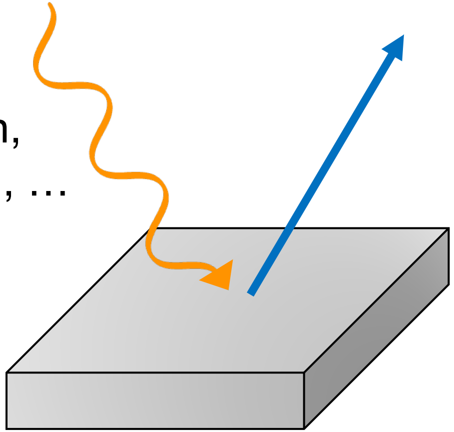
"**To calculate the total wave function** for the ~10^{23} electrons in a solid is an **impossible task** and **would not be of the slightest use** to anyone if one could do it.

Understanding a phenomenon in solid state physics means picking out the few essential factors and expressing them **AS SIMPLY AS POSSIBLE IN TERMS OF THEORETICALLY WELL-FOUNDED CONCEPTS.**"

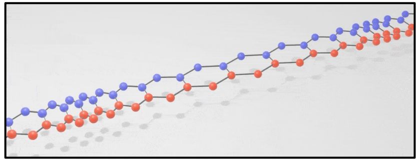
M. L. Cohen and V. Heine, Solid State Physics, 24, 37 (1970).

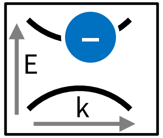
Experimentally inspired approach

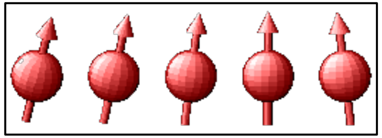
Probe:
photon,
electron,
neutron, …



Elementary excitation:
phonon, quasiparticle,
magnon, plasmon,
polaron, polariton,
exciton, …





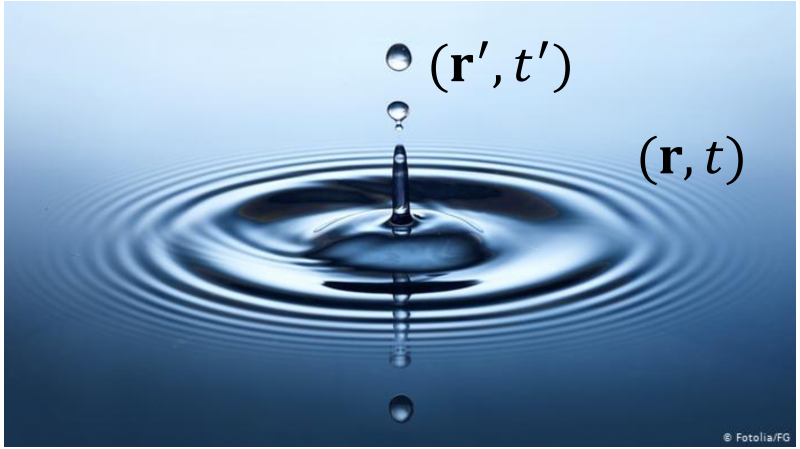


- **Elementary excitations**:
  - Directly related to **experiment**
  - **Intuitive picture** for properties (eg: transport, …)

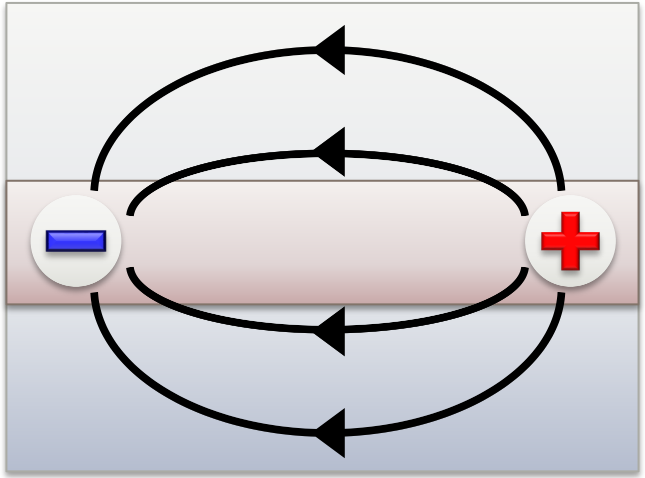
Many-body perturbation theory (MBPT): **powerful and intuitive** way to rationalize excited-state properties of materials

Outline

Theoretical spectroscopy and the Bethe-Salpeter equation (BSE)

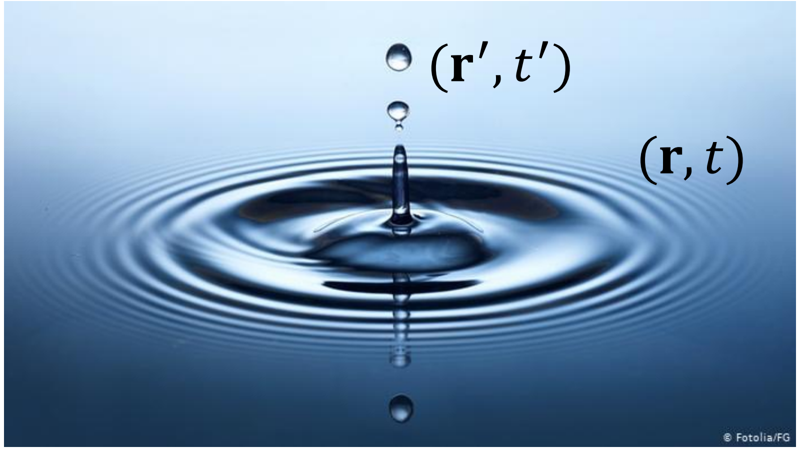


Example: Electronic and optical properties of 2D materials

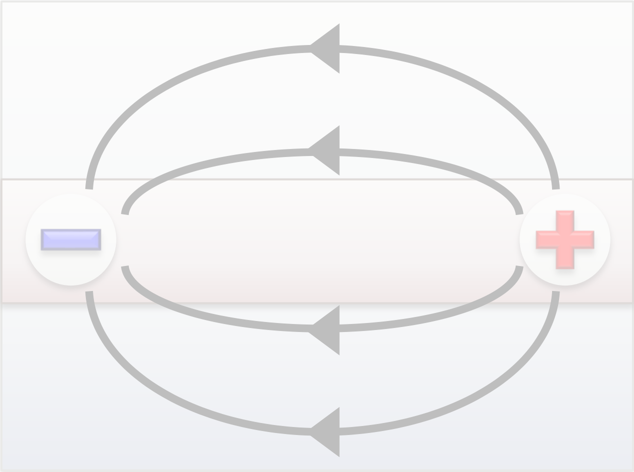


Outline

Theoretical spectroscopy and the Bethe-Salpeter equation (BSE)



Example: Electronic and optical properties of 2D materials

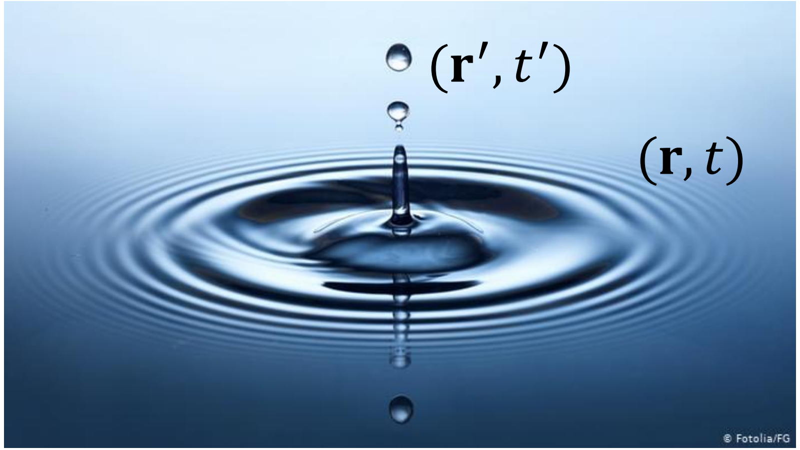


Recap: Green's functions formalism

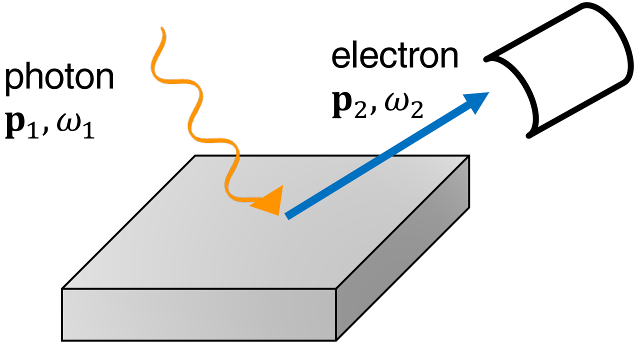
- Quasiparticle excitation from Green's function

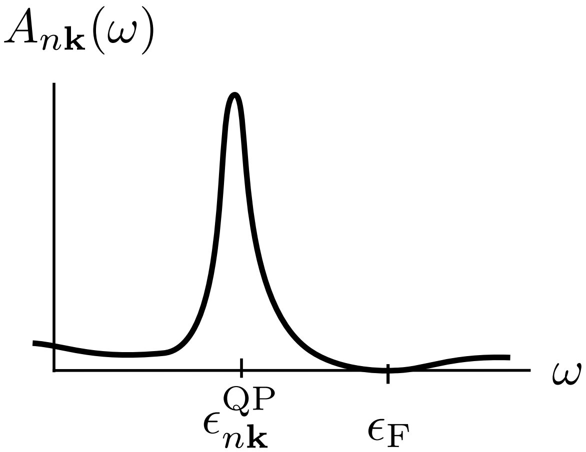
$$G(\mathbf{r},t;\mathbf{r},t') = -i\langle\Psi_0\big|\hat{T}\big[\hat{\psi}(\mathbf{r},t)\hat{\psi}^\dagger(\mathbf{r}',t')\big]\big|\Psi_0\rangle$$

- Add an electron, see the "ripple" it creates



events detected:
spectral function $A(\omega)$





Recap: Green's functions formalism

- Non-interacting Green's function (e.g. DFT)

$$G^0(\mathbf{r},\mathbf{r}';\omega) \sim [\omega - H^0(\mathbf{r},\mathbf{r}')]^{-1}$$

- Interacting Green's function

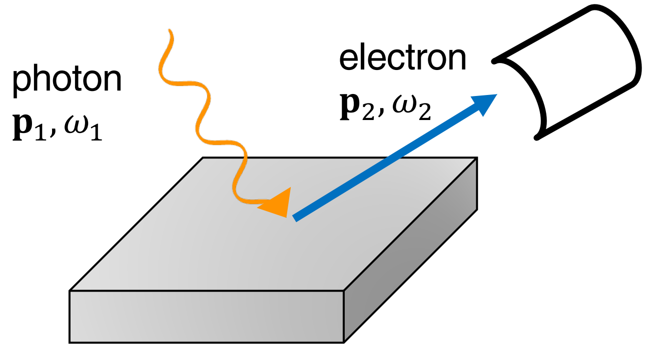
$$G_{n\mathbf{k}}(\omega) = [\omega - H^0 - \Sigma_{n\mathbf{k}}(\omega)]^{-1}$$

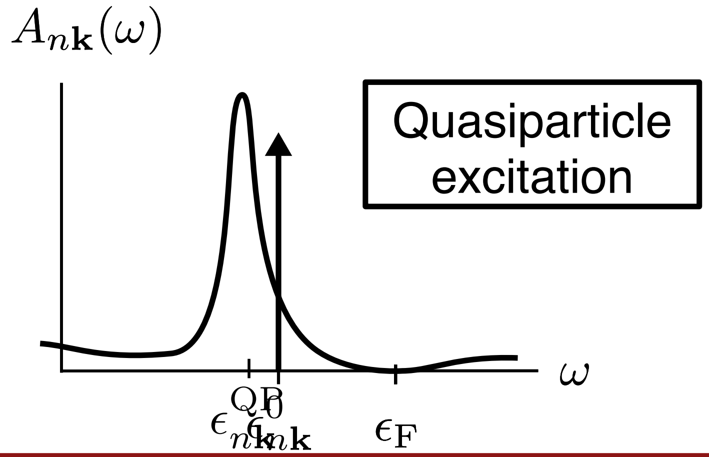
Self-energy

  - Exact, in principle.
  - No need to deal with many-body Hamiltonian.

Peaks of Green's functions:
long-lived elementary excitations.

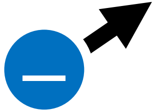
events detected:
spectral function $A(\omega)$

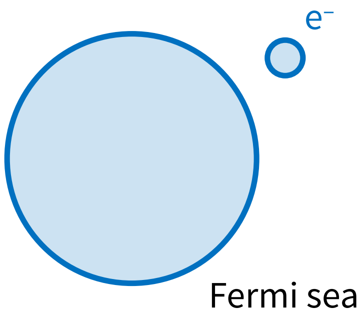




Spectroscopic properties = behavior of excited particles

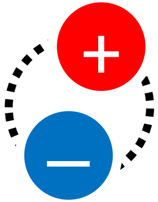
Quasiparticle (QP) properties

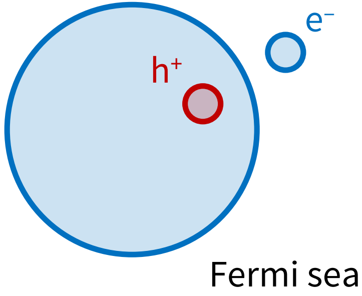




- “N+1” particle problem (add elec. or hole)
- Photoemission, tunneling, etc.
- Quasiparticle approach & GW approximation

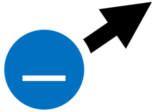
Optical properties





- “N” electron (or “+2” particle) problem
- Electron-hole interaction & excitonic effects
- Optical absorption, EELS, etc.

Spectroscopic properties = behavior of excited particles

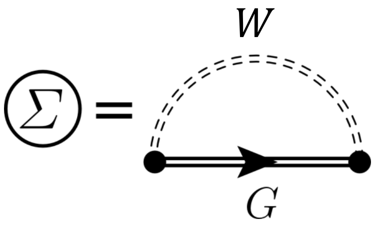


Quasiparticle (QP) properties via single-particle Green's function:

$$G(1;1') = -i\langle\Psi_0|\hat{T}[\hat{\psi}(1)\hat{\psi}^\dagger(1')]|\Psi_0\rangle$$

Add electron at $(\mathbf{r}';t')$, measure amplitude at $(\mathbf{r};t)$

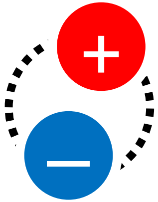
GW approximation to Σ



Dyson's equation:

$$G^{-1}(\mathbf{r},\mathbf{r}';\omega) = G_0^{-1}(\mathbf{r},\mathbf{r}';\omega) - \Sigma(\mathbf{r},\mathbf{r}';\omega)$$

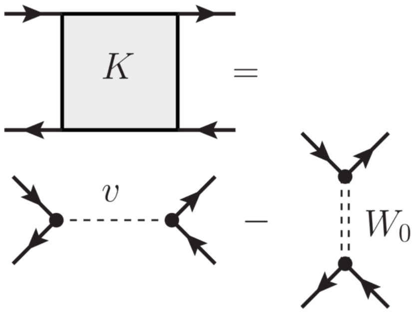
Inverse interacting Green's function | Inverse noninteracting Green's function | QP self-energy



Optical properties via eh correlation function L:

$$L(1,2;1',2') = -i\langle\Psi_0|\hat{T}[\hat{\psi}(1)\hat{\psi}^\dagger(2)\hat{\psi}(2')\hat{\psi}^\dagger(1')]|\Psi_0\rangle_{\mathrm{joint}}$$

eh interaction kernel K



Bethe-Salpeter equation (BSE):

$$L^{-1} = L_0^{-1} - K$$

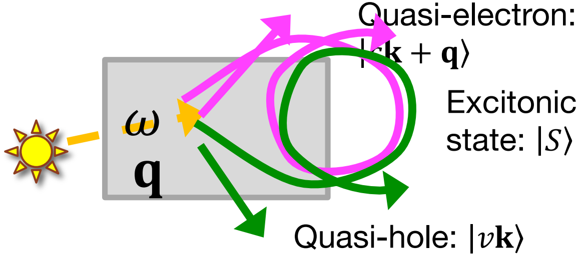
Inverse (non-)interacting eh propagator

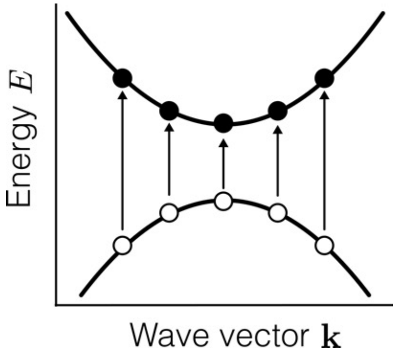
Kernel of the BSE = e-h self-energy

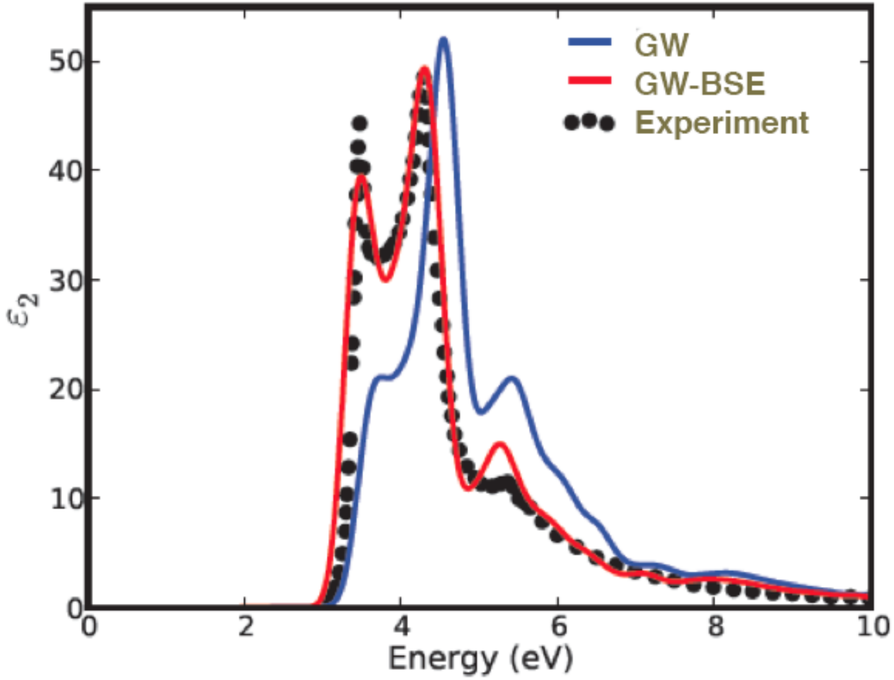
Add eh pair $(\mathbf{r}_1',\mathbf{r}_2';t')$, measure amplitude at $(\mathbf{r}_1,\mathbf{r}_2;t)$

Optical spectrum & excitonic effects

No electron-hole
With electron-hole
interactions

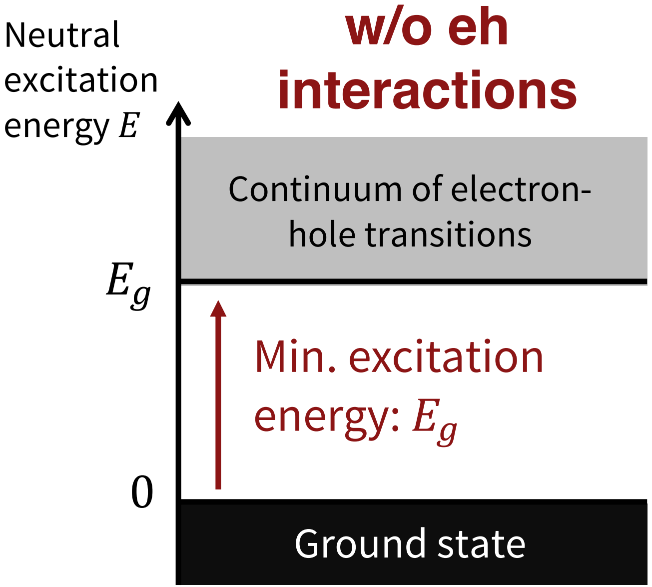


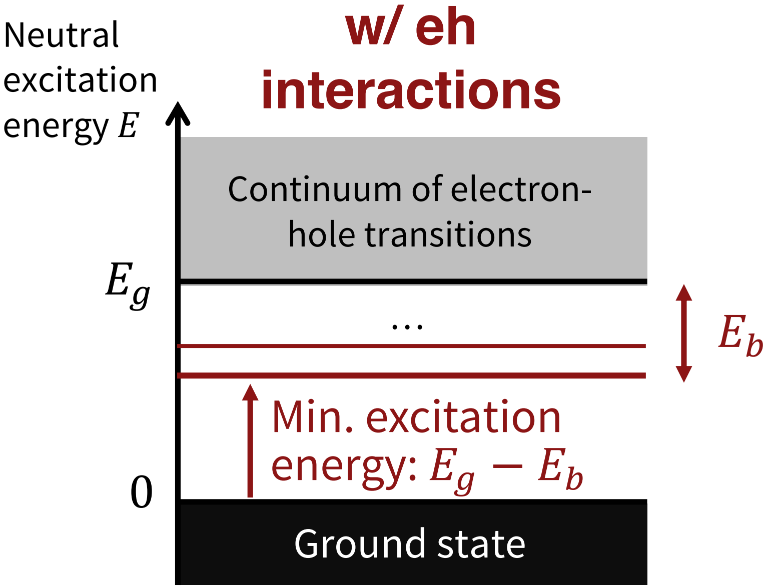




S. Albrecht, L. Reining, R. Del Sole, and G. Onida, PRL 80, 4510 (1998)
M. Rohlfing and S. G. Louie, PRL 81, 2312 (1998)
L. X. Benedict, E. L. Shirley, and R. B. Bohn, PRL 80, 4514 (1998)
J. R. Deslippe et al., CPC. 183, 1269 (2012)

Representing excited states & excitonic effects

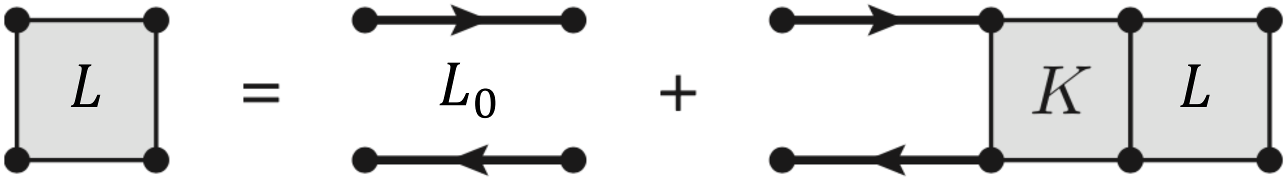




- Lowest-energy excitation: electron at CBM, hole at VBM
- Excitation energy: E_g
- Only continuum of states in bulk materials

- There's a finite e-h binding (E_b)
- Lowering of the excitation energy: $E_g - E_b$
- Presence of <u>discrete</u> sub-bandgap excitations → **excitons**!

The Bethe-Salpeter equation (BSE)



$$L(11';22') = L_0(11';22') + \int \mathrm{d}(33';44')\, L_0(11';33')K(33';44')L(44';22')$$

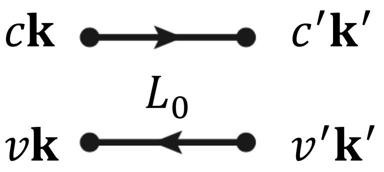
e-h correlation function

kernel of the BSE

$1 \equiv (\mathbf{x}, t)$

- Express quantities in quasiparticle basis $\quad L(\omega) = L_{vc\mathbf{k},v'c'\mathbf{k}}(\omega), \;\; \cdots$
- Assume static kernel K $\quad L^{-1}(\omega) = L_0^{-1}(\omega) - K$

The BSE effective Hamiltonian



- L^0 is already diagonal in the QP basis

$$L^0_{v c\mathbf{k}, v' c' \mathbf{k}'}(\omega) = \left[\omega - \left(E^{\mathrm{QP}}_{c\mathbf{k}} - E^{\mathrm{QP}}_{v\mathbf{k}}\right)\delta_{cc'}\delta_{vv'}\delta_{\mathbf{k}\mathbf{k}'}\right]^{-1}$$

D: diagonal term = kinetic energy of free e-h pairs

- Define the BSE effective Hamiltonian H_{BSE}

$$\boxed{L^{-1}(\omega) =} L_0^{-1}(\omega) - K \; = \omega - D - K := \boxed{\omega - H_{\mathrm{BSE}}}$$

$$\boxed{H_{\mathrm{BSE}} := \; D + K}$$

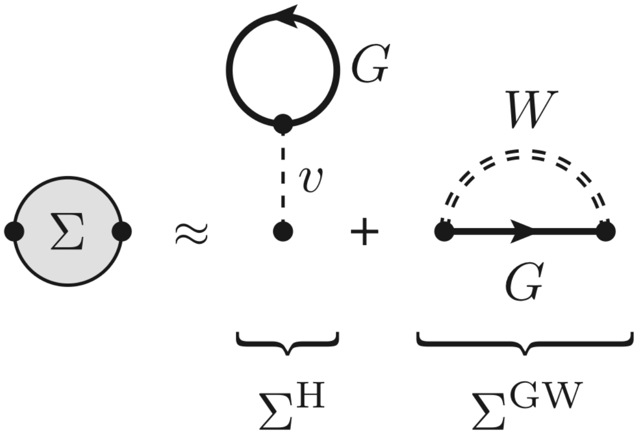
Poles of $L(\omega)$ = collective, neutral excitations
= eigenstates of H_{BSE}

$$H_{\mathrm{BSE}}|S\rangle = \Omega_S|S\rangle$$

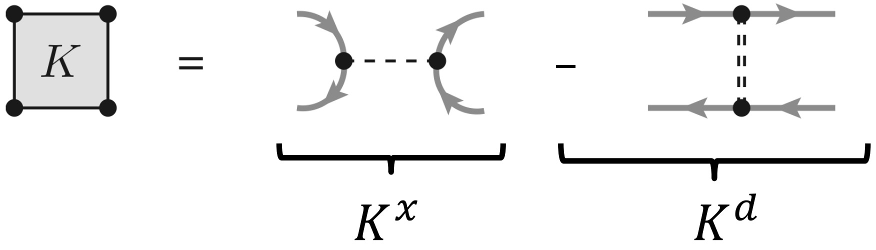
The electron-hole interaction kernel K

- K is related to the single-particle self-energy Σ $\quad K = \dfrac{\delta \Sigma}{\delta G}$

GW approximation

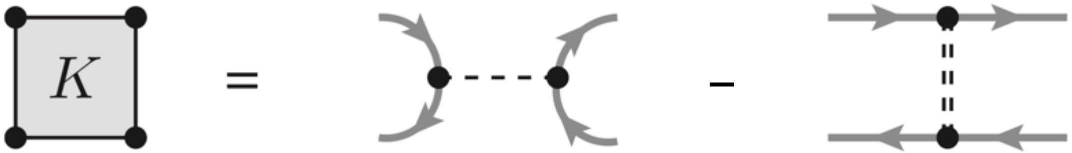


Corresponding K
(neglect $\delta W / \delta G$)



The electron-hole interaction kernel K

$\sim J_x(\mathbf{Q}_{\mathrm{COM}})\delta(\mathbf{r}_e - \mathbf{r}_h)$



$\sim -\varepsilon^{-1}\dfrac{e^2}{|\mathbf{r}_e - \mathbf{r}_h|}$

K^x K^d

Exchange interaction K^x

- **Repulsive**, density-density interaction
- Involves **bare** Coulomb interaction (v)
- Requires overlap. e-h pairs in space & spin
- Can couple two e-h pairs far apart
- Responsible for splitting of spin-singlet & triplet excitons, plasmons, Föster-like coupling, etc.

Direct interaction K^d

- **Attractive**, orbital-dependent interaction
- Involves **screened** Coulomb interaction (W)
- Requires overlap. initial+final electrons & initial+final holes
- Does not require e-h to overlap
- Responsible **binding of excitons**, Rydberg-like solutions, etc.

Physical picture & Wannier equations

- Assuming 2-band model, smooth WFNs, constant screening, effective mass dispersion

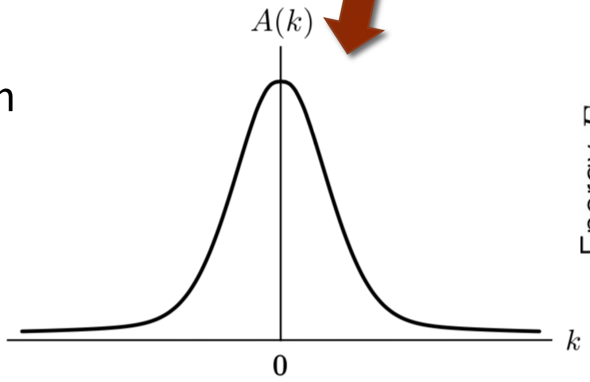
$$H_{\text{BSE}} = D - K^d + K^x$$

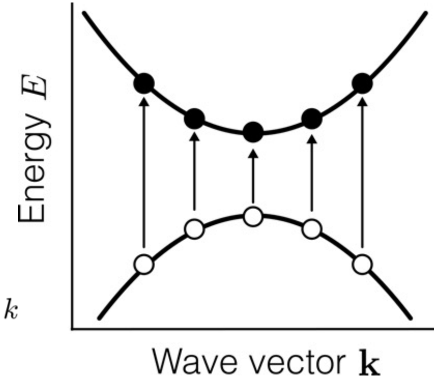
$$\left[\left(E_g - \frac{\nabla^2}{2\mu}\right) - \frac{e^2}{\varepsilon|\mathbf{r}_e - \mathbf{r}_h|} + \delta_{M_S,0}\, J_x\, \delta(\mathbf{r}_e - \mathbf{r}_h)\right] F_S(\mathbf{r}_e - \mathbf{r}_h) = \Omega_S\, F_S(\mathbf{r}_e - \mathbf{r}_h)$$

Fourier pairs!

- Hydrogenic equation!
  - Bound excitonic states ⟷ bound electronic states in a hydrogenic atom

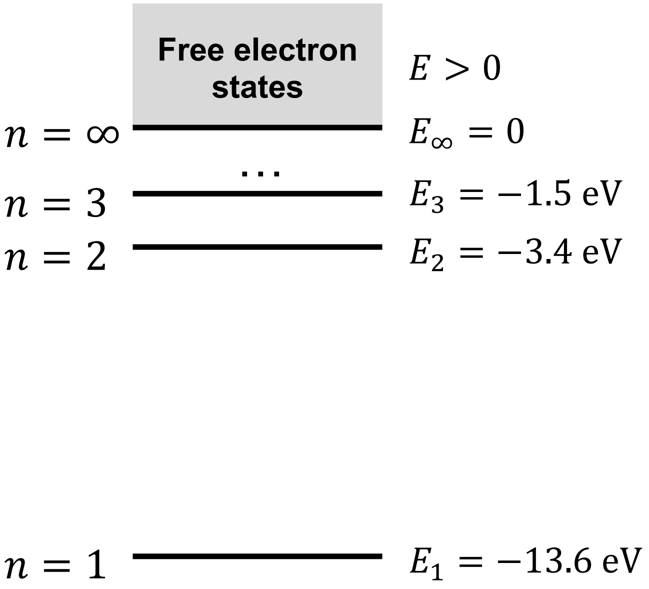
- K^x often small in solids (~meV), but important in localized excitons (e.g., Frankel excitons)



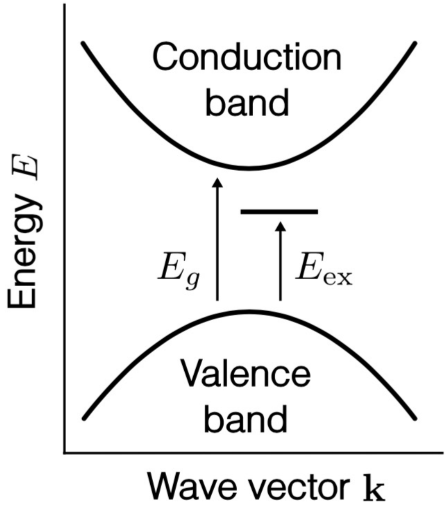


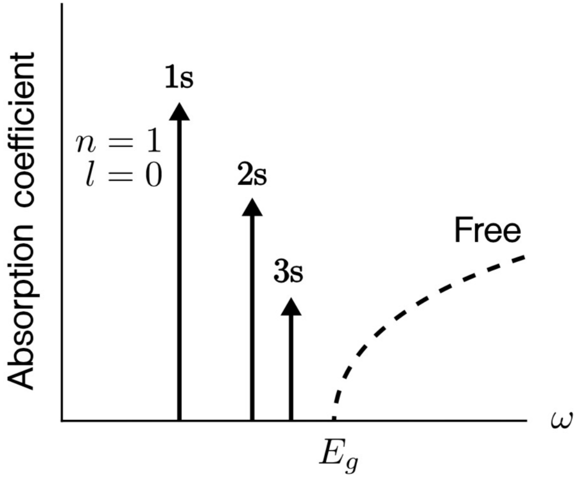
Physical picture & Wannier equations

Hydrogen atom



(Wannier-Mott) excitons





The BSE & optical absorption spectrum

- Couple electron-hole excitations

$$|S\rangle = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}}\, c^\dagger_{c\mathbf{k}} c_{v\mathbf{k}}\, |0\rangle$$

  - $|0\rangle$: ground state of the N-electrons, many-body problem
  - $c^\dagger_{c\mathbf{k}}$: electron creation operator at
  - $A^S_{vc\mathbf{k}}$: exciton electron-hole expansion coefficients

- BSE as an eigenvalue problem

$$\left(E^{\mathrm{QP}}_{c\mathbf{k}} - E^{\mathrm{QP}}_{v\mathbf{k}}\right) A^S_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'} \langle vc\mathbf{k}|K|v'c'\mathbf{k}'\rangle A^S_{v'c'\mathbf{k}'} = \Omega^S A^S_{vc\mathbf{k}}$$

- Optical properties ~ $H_{\mathrm{el-ph}} \sim \mathbf{A} \cdot \mathbf{v}$

$$\varepsilon(\omega) \propto \sum_S \underbrace{|\langle 0|\mathbf{v}\cdot\hat{e}|S\rangle|^2}_{\text{Oscillator strength}} \delta(\omega - \underbrace{\Omega_S}_{\text{Opt. excitation energy}})$$

  - $\mathbf{v}$: velocity matrix elements

- K can be very large $> 10^6$!
- Need fine k-point sampling to resolve fine spatial features of excitons features

The Bethe-Salpeter equation calculation in practice

Desired expressions

$$\left(E^{\mathrm{QP}}_{c\mathbf{k}} - E^{\mathrm{QP}}_{v\mathbf{k}}\right) A^{S}_{vc\mathbf{k}} + \sum_{v'c'\mathbf{k}'} \langle vc\mathbf{k}|K|v'c'\mathbf{k}'\rangle A^{S}_{v'c'\mathbf{k}'} = \Omega^{S} A^{S}_{vc\mathbf{k}}$$

$$\varepsilon(\omega) \propto \sum_{S} |\langle 0|\mathbf{v}\cdot\hat{e}|S\rangle|^{2} \delta(\omega - \Omega_{S})$$

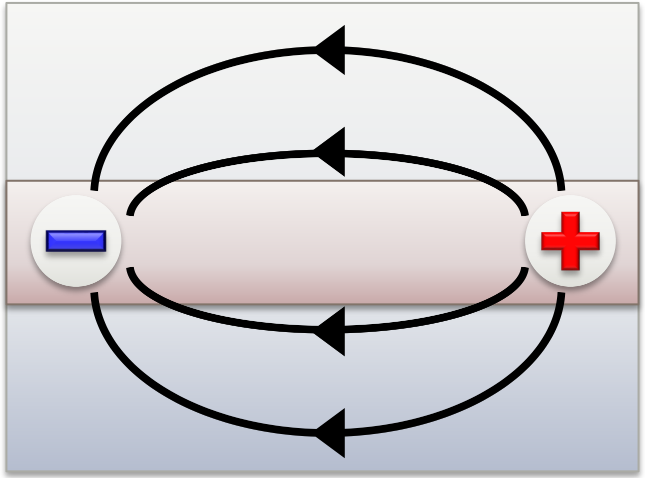
Main ingredients/ steps

- **Quasiparticle** states on a dense set of k-points [**`sigma`** code]
  - In practice, use WFNs from DFT
  - Only correct QP energies with a GW calculation
- Evaluation of **K** [**`kernel`** code]
  - Requires screened Coulomb interaction W → dielectric screening ε^{-1} [**`epsilon`** code]
- Diag. of H_{BSE} [**`absorption`** code]

Outline

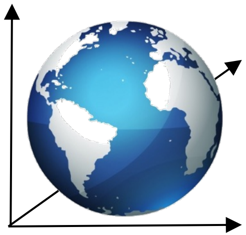
Many-body perturbation theory

Electronic and optical properties of 2D materials

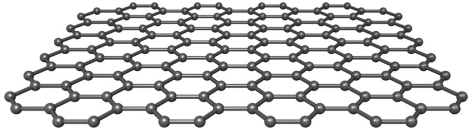


Low-dimensional materials: a theoretician's dream

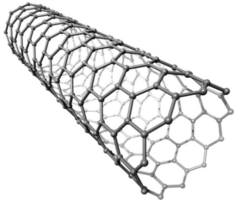
3D



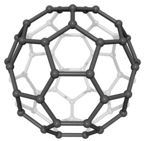
Quasi-2D



Quasi-1D

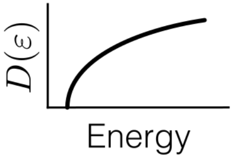


Quasi-0D

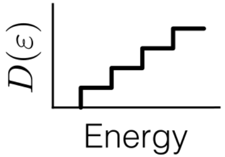


- Low-energy excitation spectrum strongly modified by dimensionality

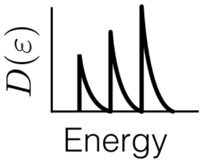
3D



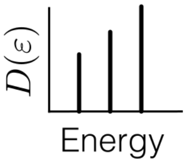
2D



1D



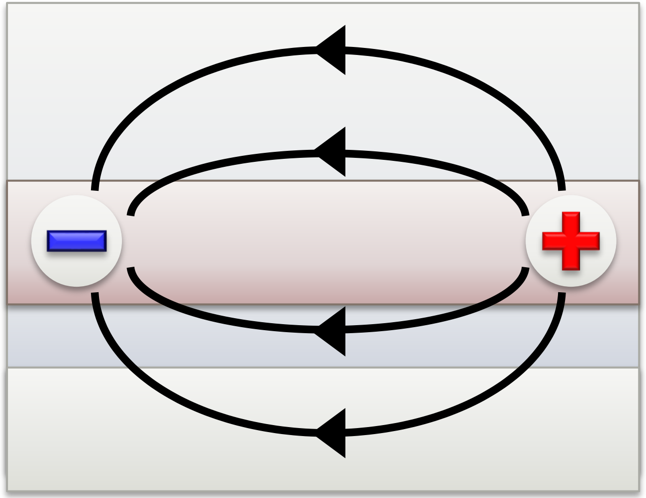
0D

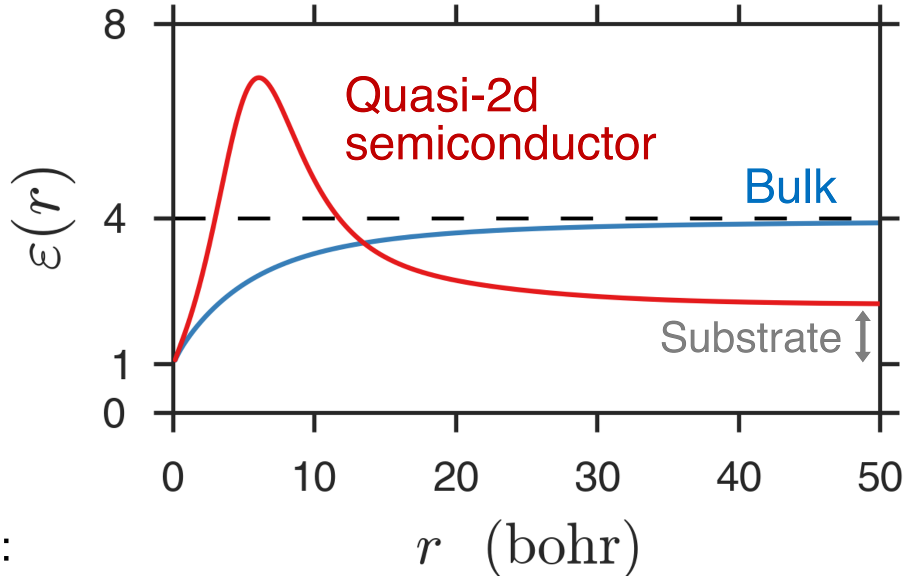


Qualitatively different electronic and optical properties in **low-dimensional** materials!

Low-dimensional materials and reduced screening

Screening is highly **spatially dependent** in semicond. with reduced dimensionality.



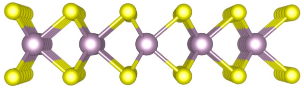


Spatial dependence of screening leads to:

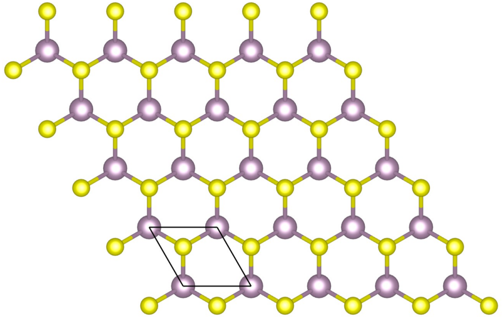
- Enhancement of **many-electron effects**.
- **Breakdown of simpler continuum models** (non-hydrogenic excitonic series, etc.)
- **Environment-dependent** results (substrate, etc.).

Monolayer TMDCs

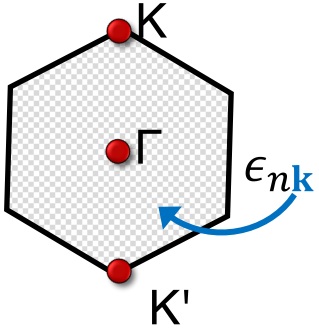
Monolayer TMD/MX_2 – side view:



Monolayer TMD/MX_2 – top view:



Brillouin zone



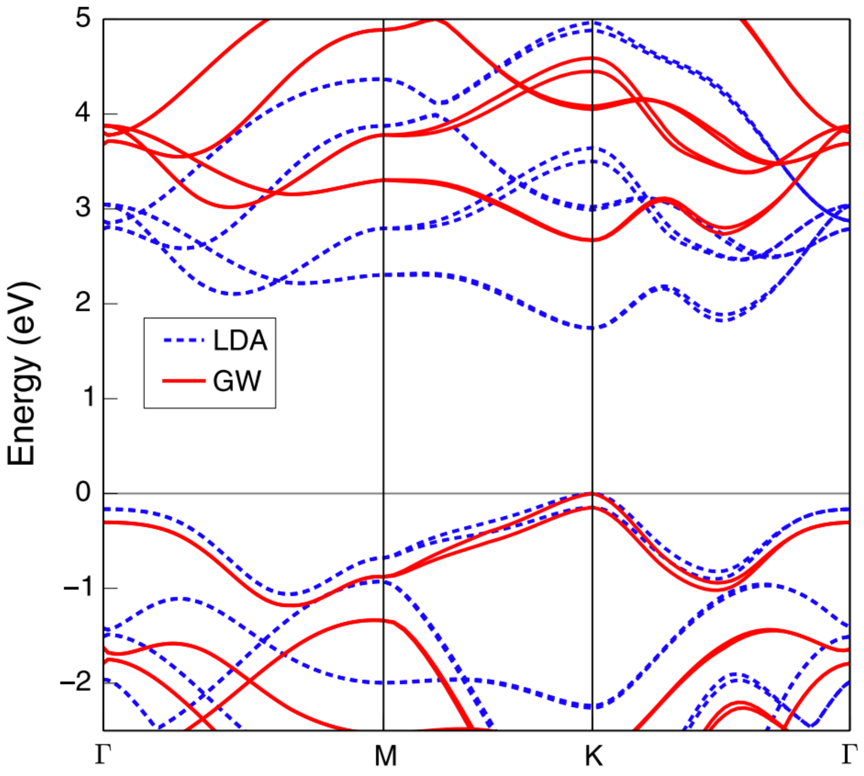
M = Mo, W, etc. (transition metal)

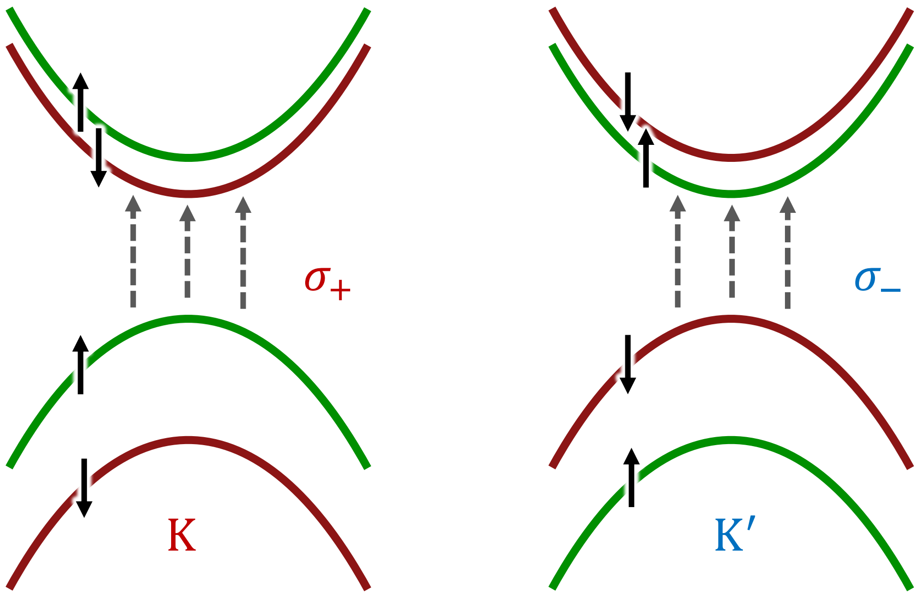
X = S, Se, etc. (chalcogen)

- Unusual/exciting properties:
  - Large optical absorption; [1-3]
  - Locked spin/valley degrees of freedom / valley Hall effect; [4]
  - Tunable electronic screening, non-hydrogenic excitonic physics;
  - Large catalytic activity (H_2 evolution reaction) [5]; etc.

[1] Mak, Lee, Hone, Shan, Hein, PRL 105, 136805 (2010); [2] Qiu, **da Jornada**, Louie, PRL 111, 216805 (2013).
[3] Bernardi, Palummo, Grossman, Nano Lett 13, 3664 (2013);
[4] D. Xiao, et al. PRL (2012); T. Cao,et al. Nat. Comm. (2012); K. F. Mak, et al. Science (2014).
[5] Jaramillo, et al., Science 317, 100 (2007).

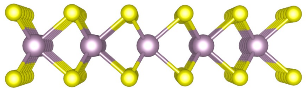
MoS_2 quasiparticle band structure





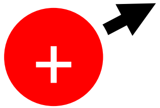
Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

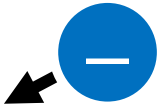
Example: optical excitations in 1L MoS_2



No electron-hole interactions (GW-RPA)

Quasi-hole: $|v\mathbf{k}\rangle$

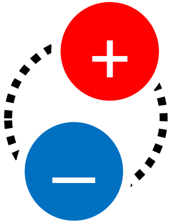




Quasi-electron: $|c\mathbf{k}+\mathbf{q}\rangle$

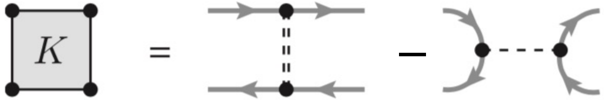
With electron-hole interactions (GW-BSE)

Exciton: $|S\rangle$



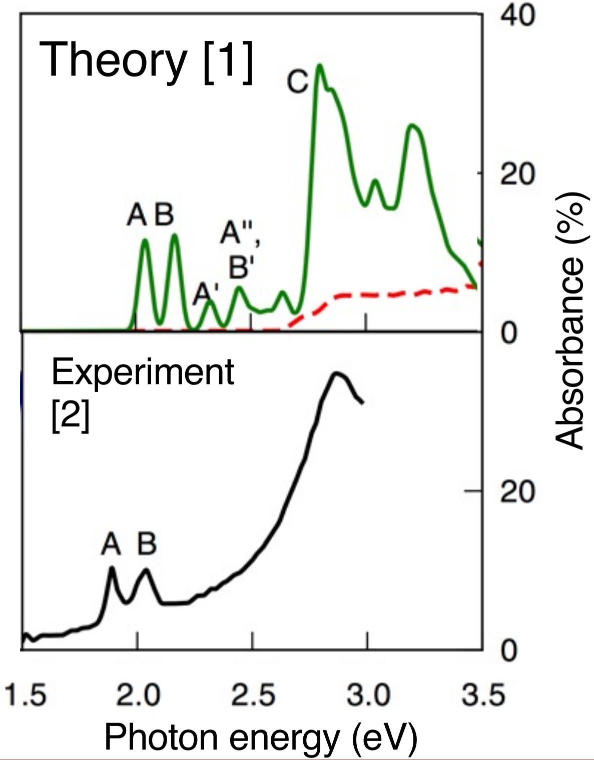
Bethe-Salpeter equation (BSE)

$$L^{-1} = L_0^{-1} - K$$



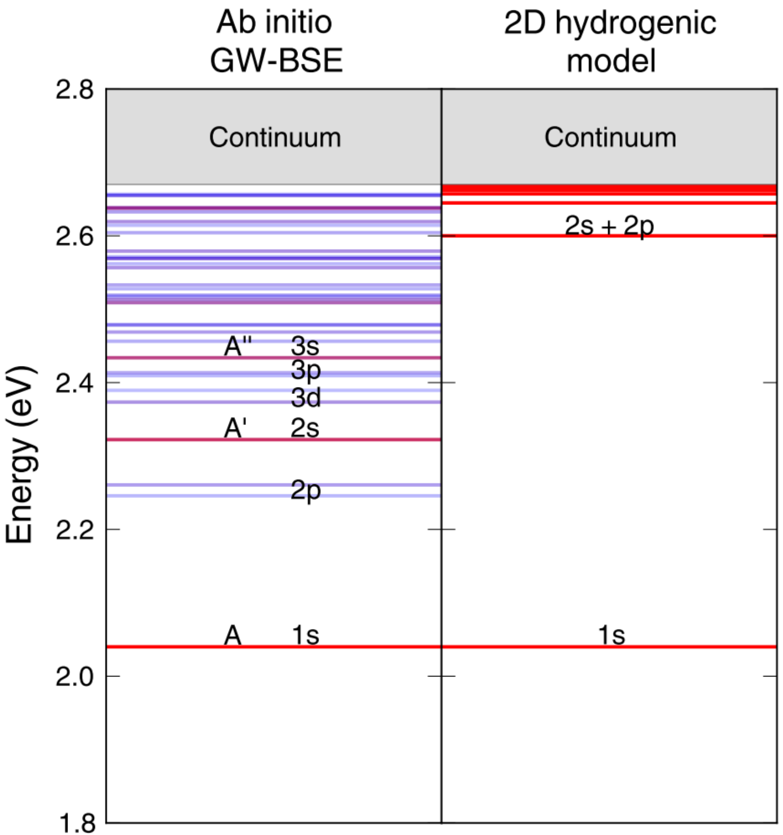
$$\sim \frac{1}{\varepsilon|\mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{h}|} \qquad \sim \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

Optical absorption spectrum (monolayer MoS_2)

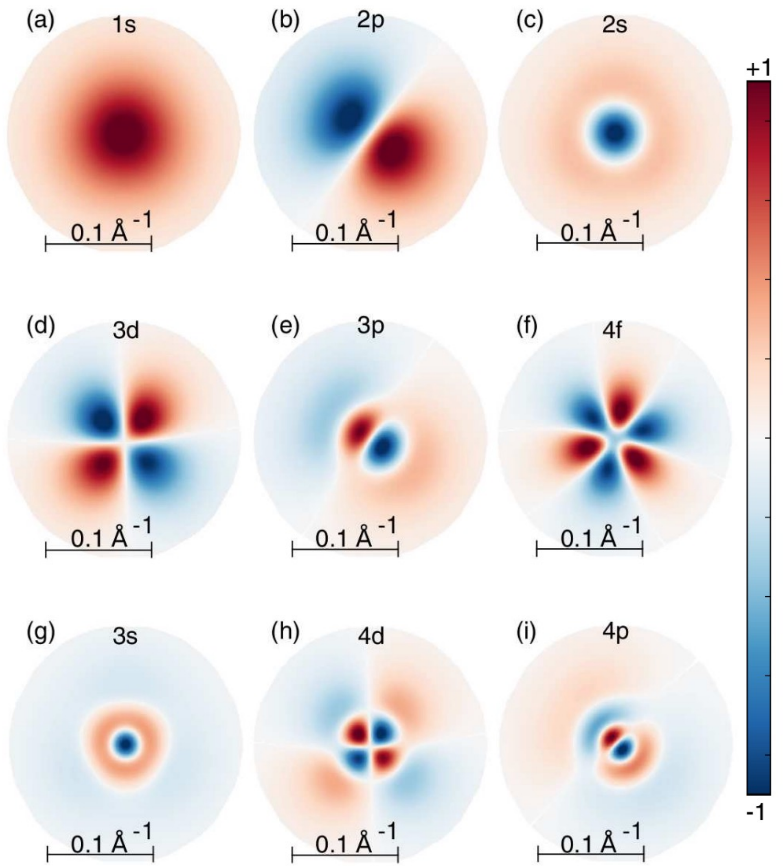


[1] Qiu, da Jornada, Louie, PRL 111, 216805 (2013).
[2] Mak, Lee, Hone, Shan, Heinz, PRL 105, 136805 (2010).
[3] Rohlfing, Louie, PRB 62, 4927 (2000).

Excitons in monolayer TMDCs

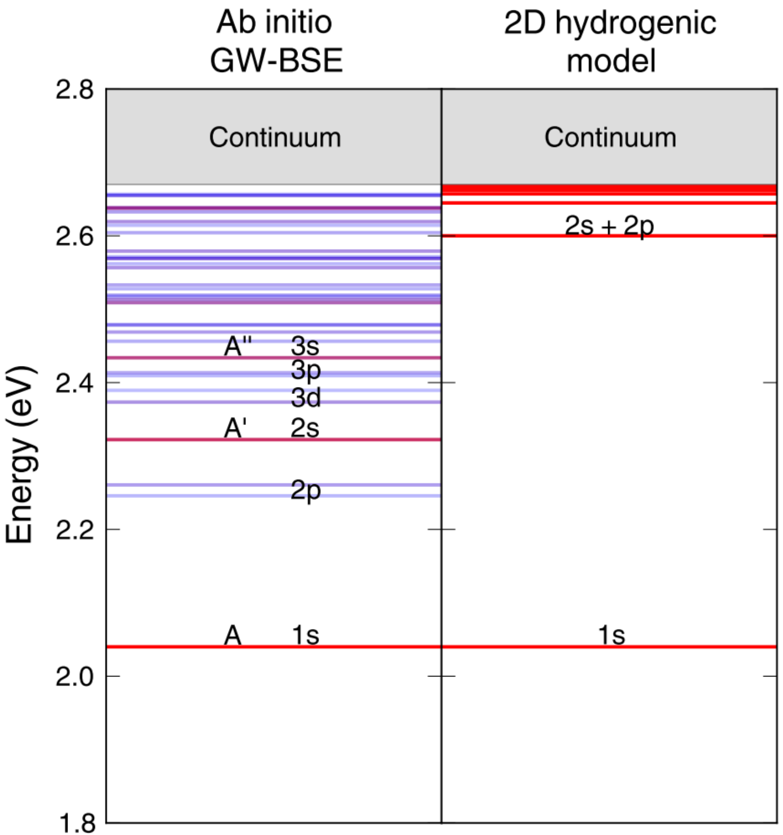


$A^{S}_{vc\mathbf{k}}$

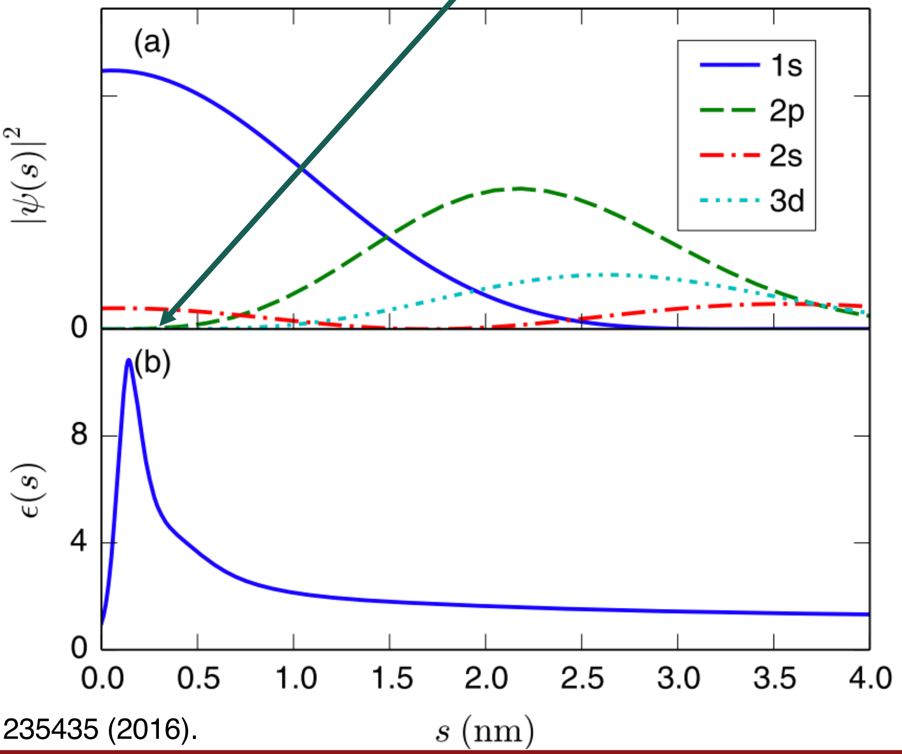


Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

Excitons in monolayer TMDCs

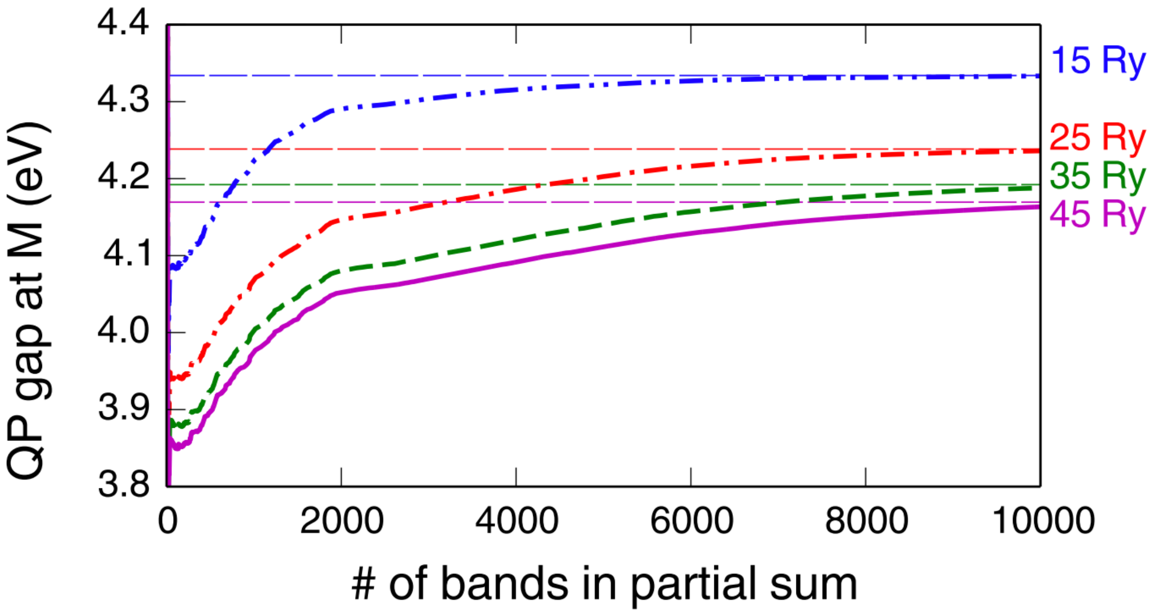


Wavefunction is small where screening is strongest!
2p has stronger binding energy than 2s



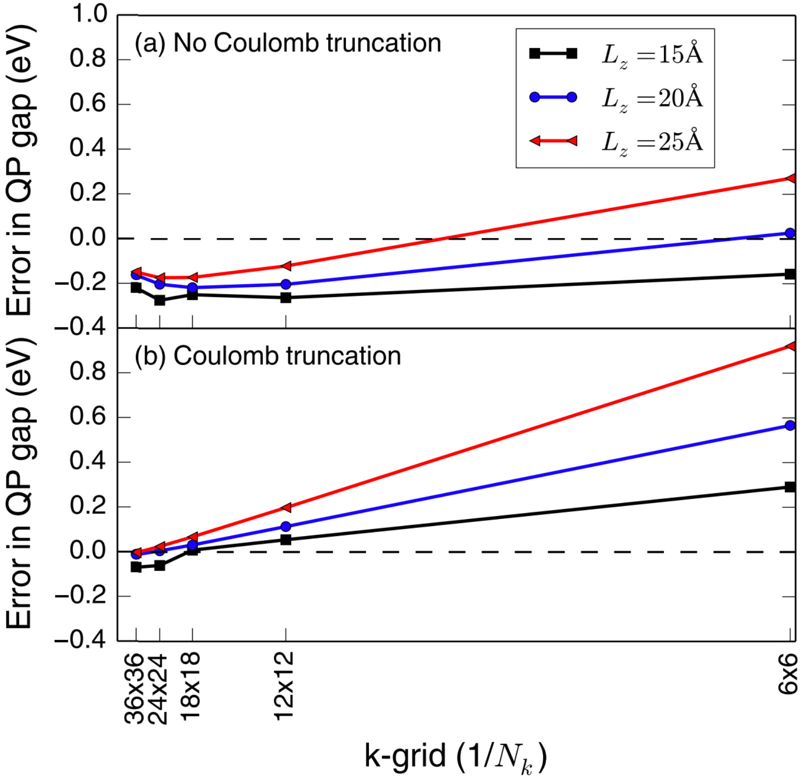
Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

TECHNICAL DETAIL #1: Convergence wrt energy cutoff for QP energies



Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

TECHNICAL DETAIL #2: convergence wrt k-point sampling & cell size



Calculations are hard to converge wrt **k-point sampling** (at least 36x36 at GW vs. 6x6 @ DFT)

In GW calculations on a supercell arrangement (out-of-plane sep. L_z):

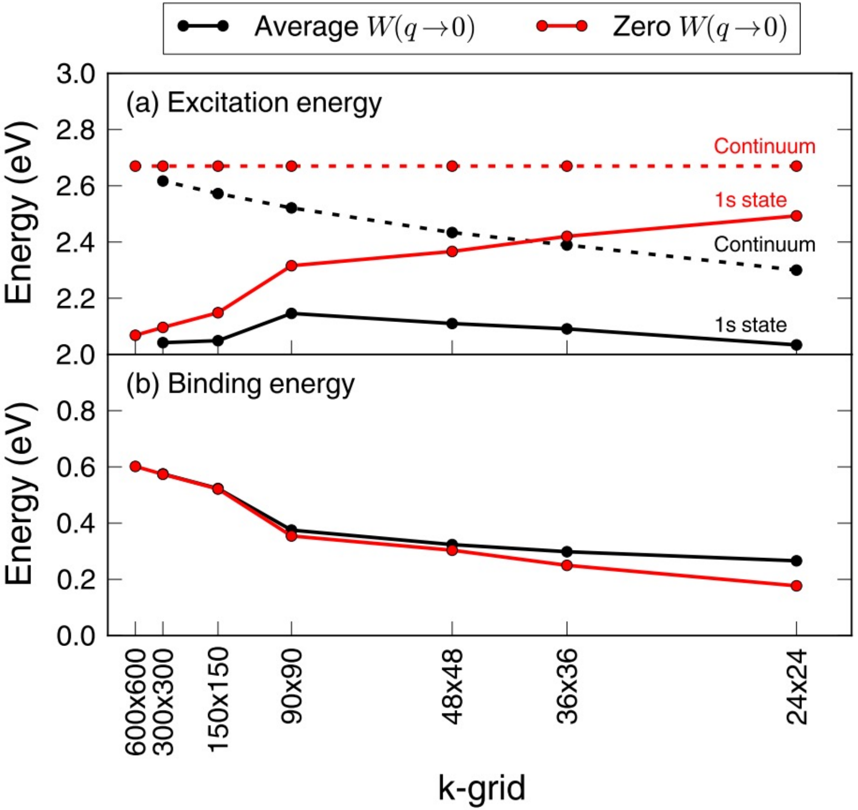
- Polarizability from repeated cells leads to an **overscreening**!
- This effect is hard to converge: decays as $1/L_z$, and couples to k-point sampling.
- Proper solution: truncate the Coulomb interaction:

$$\frac{1}{r} \rightarrow \frac{1}{r}\theta(z_c - |z|)$$

Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

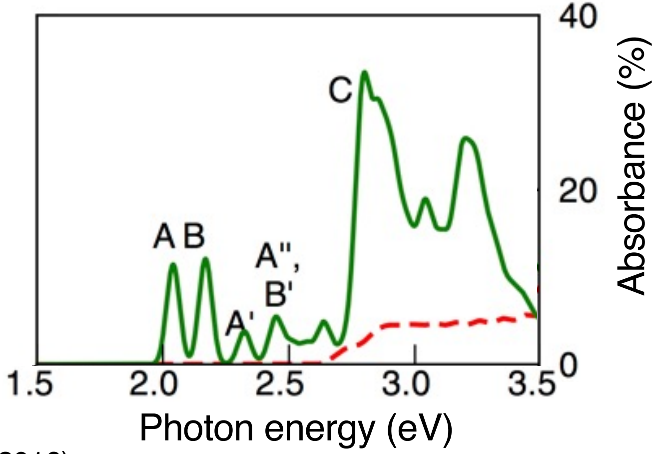
S. Ismail-Beigi, Physical Review B **73**, (2006).

TECHNICAL DETAIL #3: k-point sampling



Even harder to converge exitonic properties!

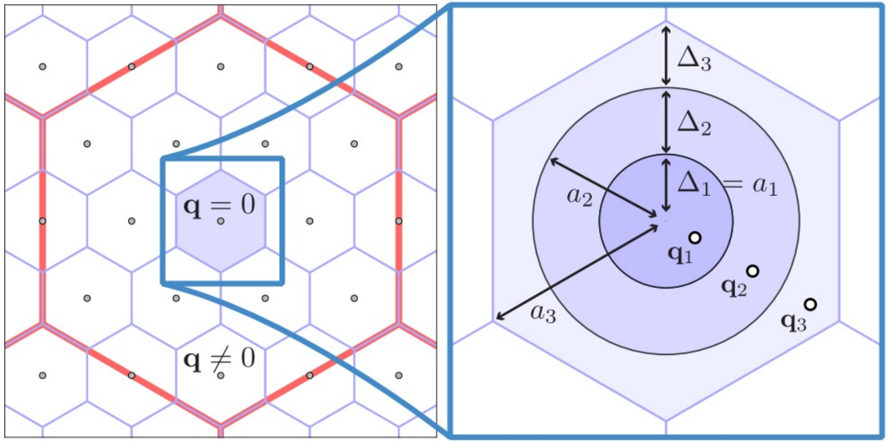
- At least **300x300 k-point sampling** to converge energy difference from 1s to continuum!
- Cancellation of errors if only interested in the binding energy.

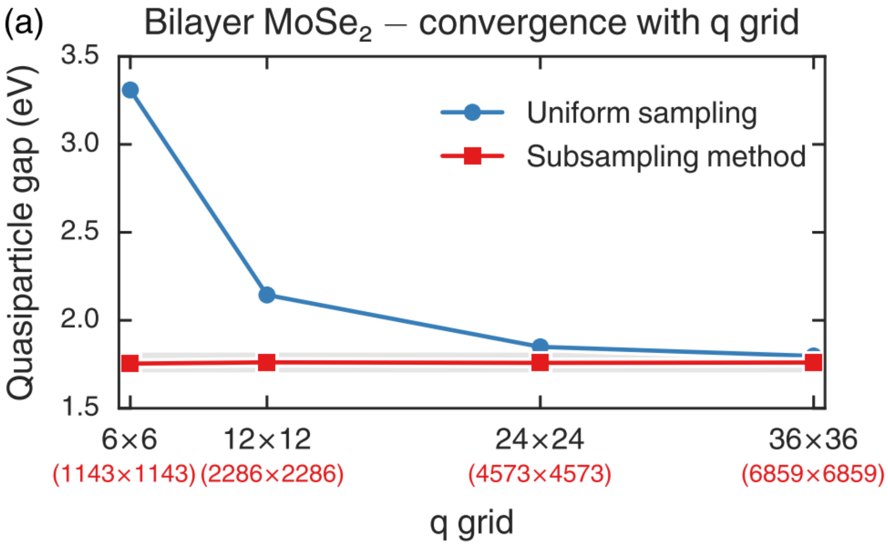


Qiu, Jornada, Louie, PRL 111, 216805 (2013); Qiu, Jornada, Louie, PRB 93, 235435 (2016).

Solution: non-uniform k-point sampling of the BZ

Simple idea: sample more finely (and only radially) $\varepsilon(\mathbf{q})$ for $\mathbf{q}$ close to Γ.
Order of magnitude savings in CPU resources!

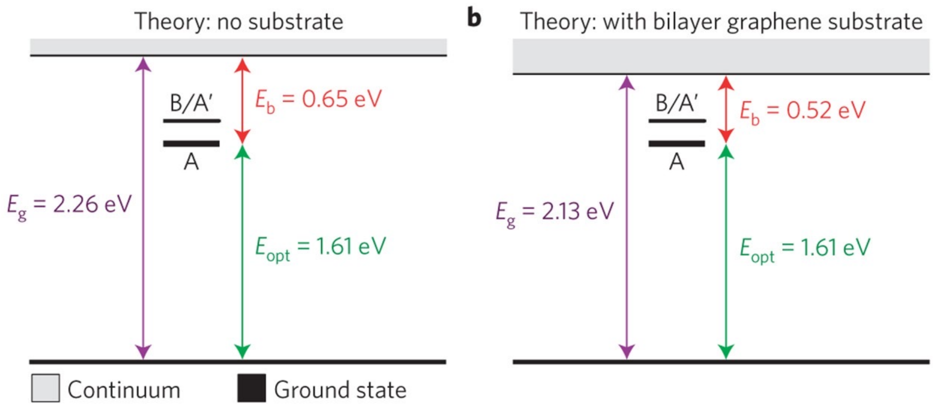




Jornada*, Qiu*, Louie, PRB 95, 035109 (2017).

Screening cloud is important and nonlocal!

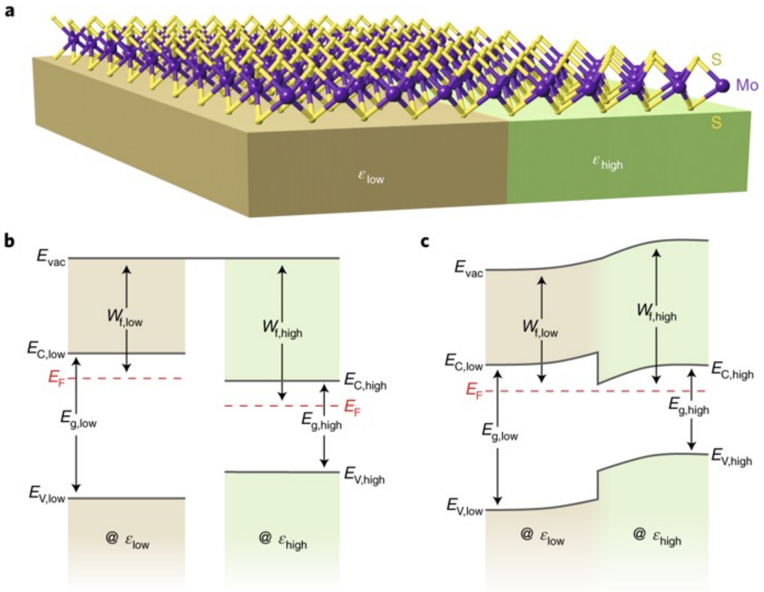
Electronic and optical properties of materials **depend on the supporting substrate**!



Ugeda, Bradley, Shi, **Jornada**, …,. Louie, Crommie, Nature Materials 13, 1091 (2014).

Bradley*, Ugeda*, **Jornada***, …, Louie, Crommie, Nano Letters 15, 2594 (2015).

Can create a **pn junction without** a semiconductor **interface**!

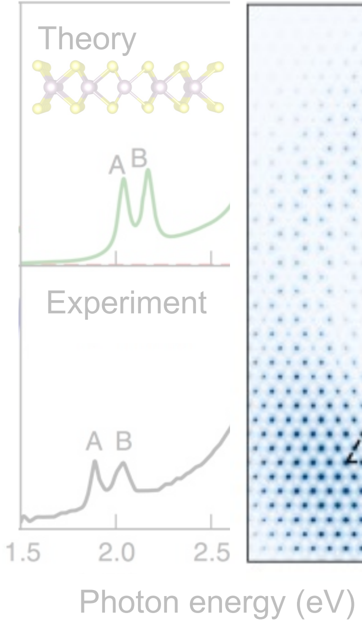


Utama, …, **Jornada**, … Nature Electronics (2019).

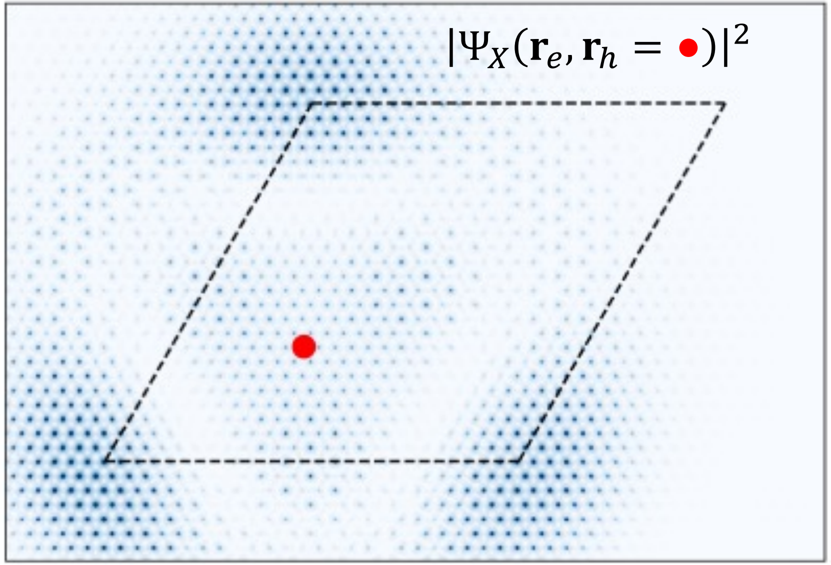
Final examples:
Optical absorption spectrum in moiré systems
Exciton-phonon interactions

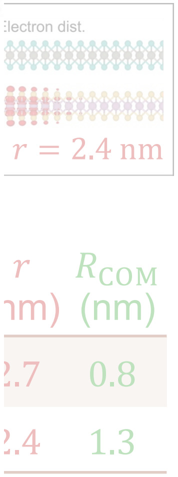
MBPT can predict optical properties of various TMDCs

Monolayer MoS_2

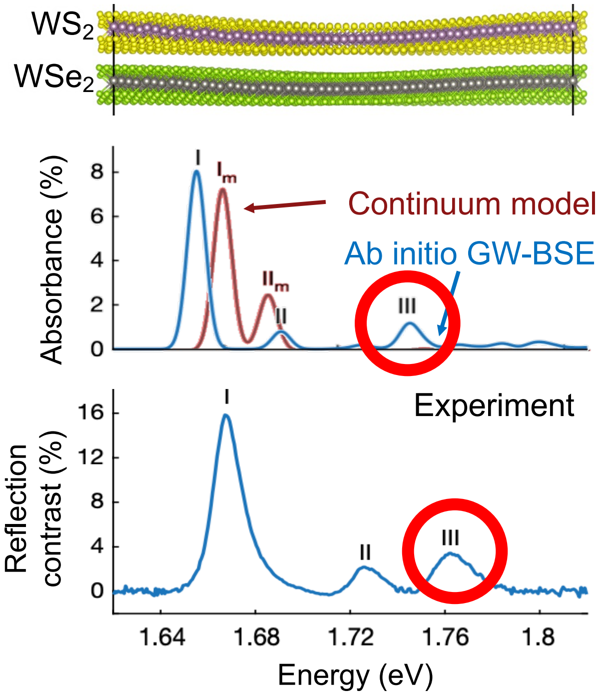


Bilayer MoS_2/WSe_2





Bilayer WS_2/WSe_2



Qiu, Jornada, Louie, PRL 111, 216805 (2013).

Mak, Lee, Hone, Shan, Heinz, PRL 105, 136805 (2010).

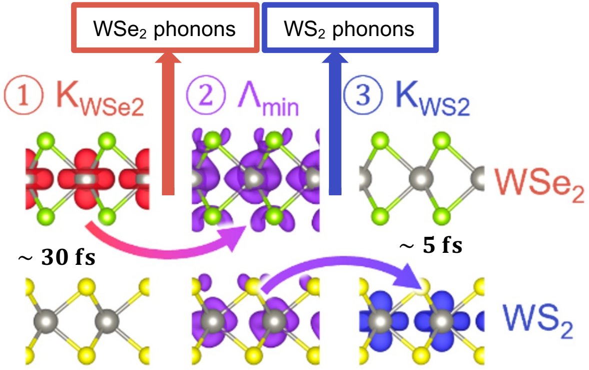
Karni*, …, Jornada, Heinz, Dani, Nature 603, 247 (2022).

Barré, …, R.-Abramson, Jornada, Heinz, Science 376, 406 (2022).

Naik*, …, Jornada, Wang, Louie, Nature 609, 52 (2022).

Example: exciton dynamics in TMDC mono- and bilayers

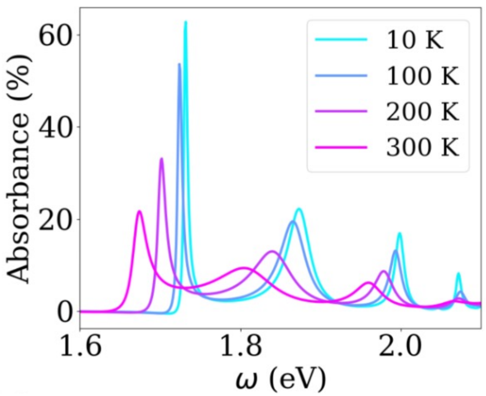
Coupled exciton & phonon dynamics & nonequilibrium thermal transport



Sood et al, Nat. Nanotechnol. 18, 29 (2022).
A. C. Johnson et al., Sci. Adv. 10, (2024).

Exciton linewidth & asymmetry: need for coherent, 2nd-order formalism

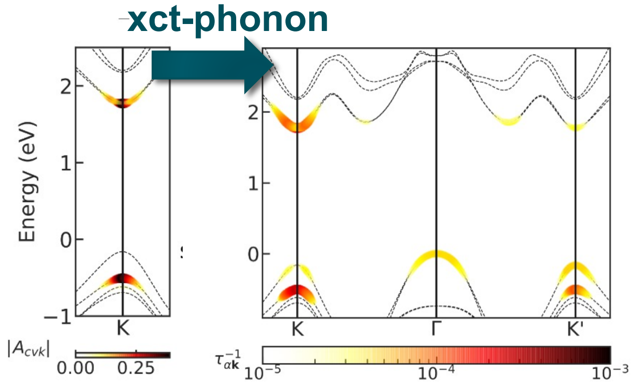
See also: Toyozawa(1958), Toyozawa(1964), Knorr(2016)



Theory: Chan*, Haber, Naik, Neaton, Qiu*, Jornada*, Louie*, Nano Lett. 23, 3971 (2023).

Exciton dynamics in complex TMDC heterostructures

Intralayer exciton: Fano resonance! Need:
~200 excitonic bands
~100 TB for matrix elements!



Chan*, Naik, Haber, Neaton, Louie, Qiu*, Jornada*, Nano Lett. 24, 7972 (2024).

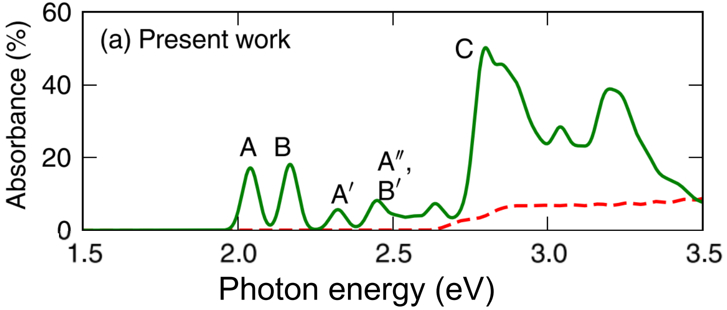
Quiz

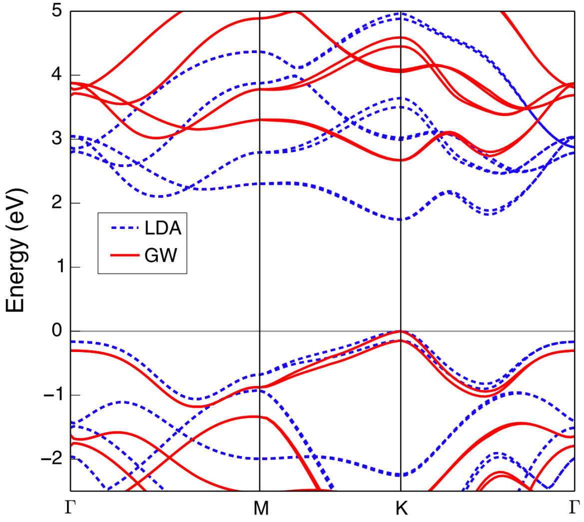
1. Bound excitons can originate from transitions involving bands other than the VBM to the CBM.
2. For a semiconductor described within a 2-band model, the exciton binding energy cannot exceed the quasiparticle bandgap.
3. Excitonic effects are typically negligible in bulk metals.
4. There is a continuous of bound exciton states
5. Excitons are detrimental for the performance of PV devices (need to "waste" binding energy to break-up excitons into free carriers).

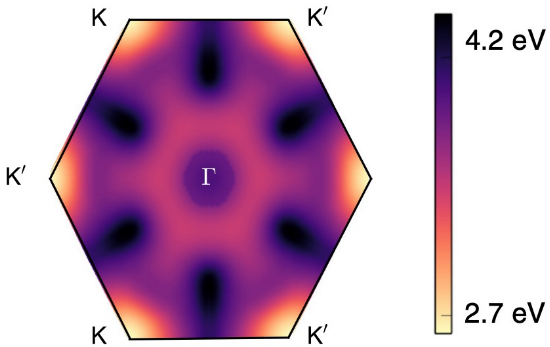
Quiz

1. Bound excitons can originate from transitions involving bands other than the VBM to the CBM.

Example: monolayer MoS_2







Qiu, Jornada, Louie, PRL (2013)
Qiu, Jornada, Louie, PRB (2016)

Quiz

1. Bound excitons can originate from transitions involving bands other than the VBM to the CBM.

2. For a semiconductor described within a 2-band model, the exciton binding energy cannot exceed the quasiparticle bandgap.

3. Excitonic effects are typically negligible in bulk metals.

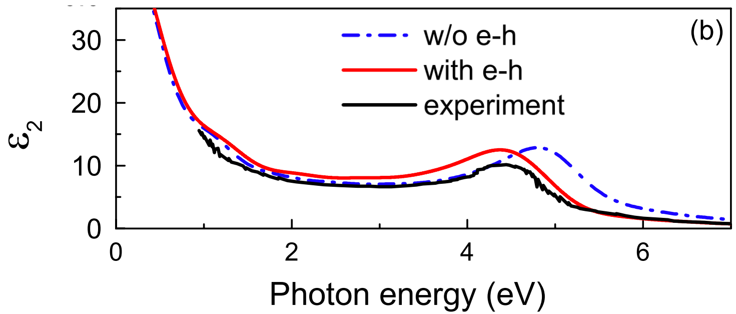
4. There is a continuous of bound exciton states

5. Excitons are detrimental for the performance of PV devices (need to "waste" binding energy to break-up excitons into free carriers).

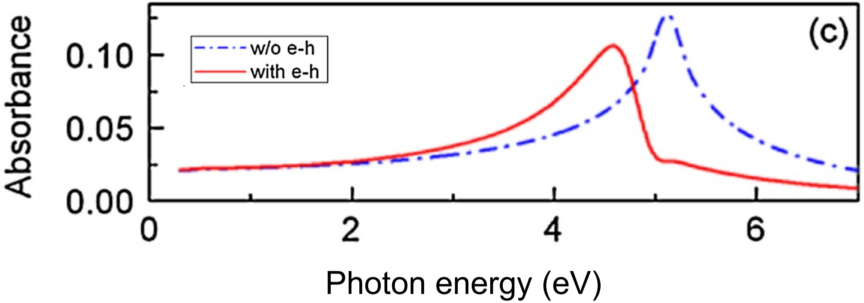
Quiz

3. Excitonic effects are typically negligible in bulk metals.

Graphite



Graphene



Yang, Deslipe, Park, Cohen, Louie (2009)

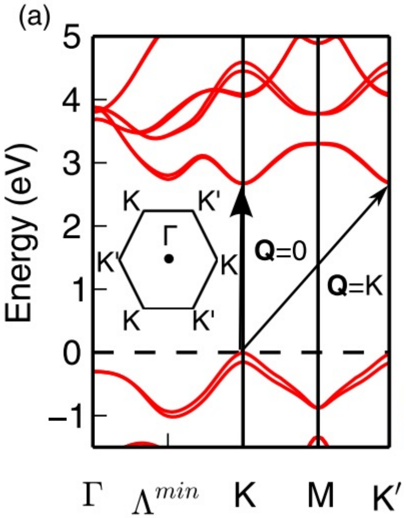
Quiz

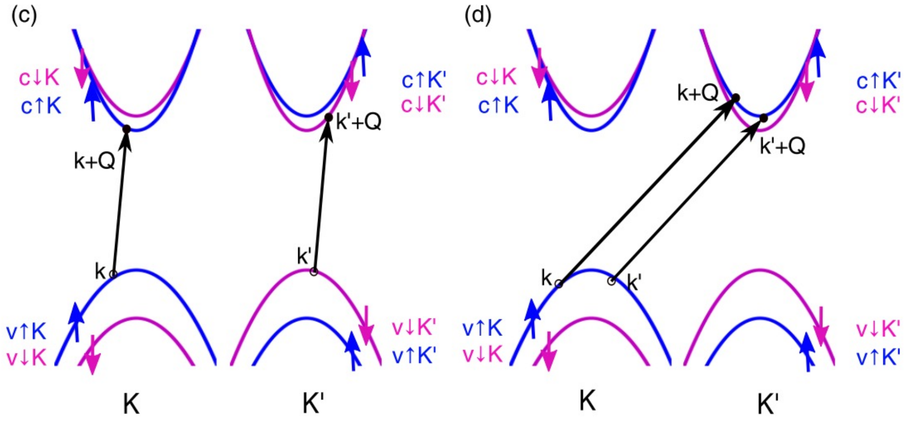
1. Bound excitons can originate from transitions involving bands other than the VBM to the CBM.
2. For a semiconductor described within a 2-band model, the exciton binding energy cannot exceed the quasiparticle bandgap.
3. Excitonic effects are typically negligible in bulk metals.
4. There is a continuous of bound exciton states
5. Excitons are detrimental for the performance of PV devices (need to "waste" binding energy to break-up excitons into free carriers).

Quiz

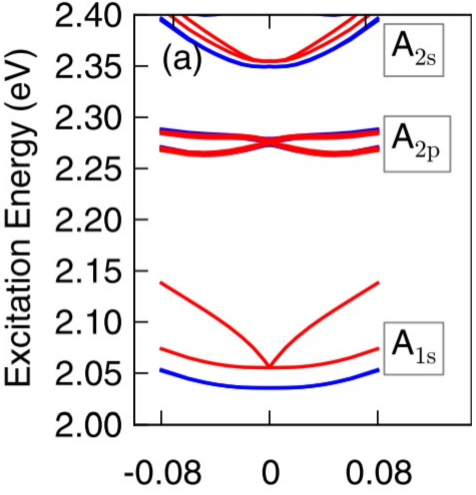
Excitons form bands!
But only $\mathbf{Q} \approx \mathbf{0}$ states are optically accessible.

4. There is a continuous of bound exciton states





Exciton band structure



Exciton center-of-mass (COM) wavevector

Qiu, Cao, Louie, PRL 115, 176801 (2015); Cudazzo et al, PRL 116, 066803 (2016), …

Quiz

1. Bound excitons can originate from transitions involving bands other than the VBM to the CBM.
2. For a semiconductor described within a 2-band model, the exciton binding energy cannot exceed the quasiparticle bandgap.
3. Excitonic effects are typically negligible in bulk metals.
4. There is a continuous of bound exciton states
5. Excitons are detrimental for the performance of PV devices (need to "waste" binding energy to break-up excitons into free carriers).

Acknowledgments

BerkeleyGW

www.berkeleygw.org

C2SEPEM

U.S. DEPARTMENT OF ENERGY

Office of Science