2023 Virtual School on Many-Body Calculations using EPW and BerkeleyGW

June 5-9 2023

Many-body Green's function approach to excited states: Quasiparticle excitations, optical responses, and field-driven time-dependent phenomena

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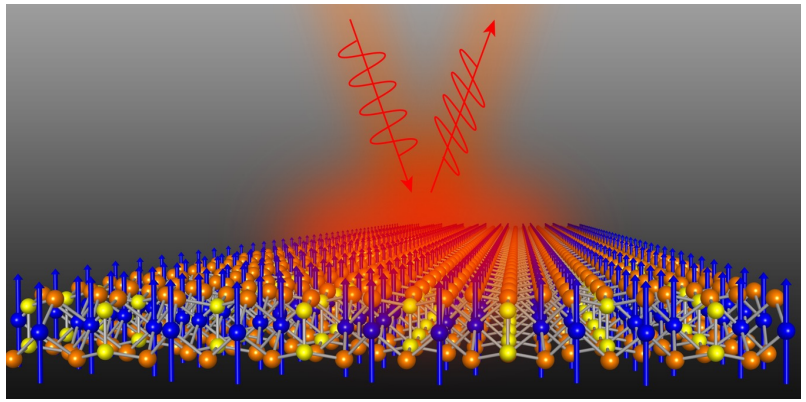
National Science Foundation



Virtual School on Many-Body Calculations using EPW and BerkeleyGW
June 8, 2023

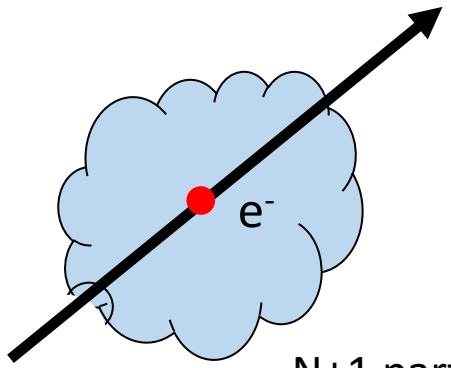
Study of Material Properties – A N-Particle Quantum Problem

$$H_T = \sum_i \frac{p_i^2}{2m} + \sum_n \frac{p_n^2}{2M_n} + \frac{1}{2}\sum_{ij}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{nn'}{}' \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} + \sum_{n,i} V_n(\mathbf{r}_i - \mathbf{R}_n) + H_R,$$

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 ... \mathbf{r}_N, t)$$

For large N (~10^{22}/cc),

- impossible to solve exactly
- often not desirable to get full solutions



N+1 particle problem

E.g., single-particle behaviors:

$$G(\mathbf{r}, \mathbf{r}', \tau) = -i\langle 0 \left| T\{\psi(\mathbf{r}, \tau)\psi^\dagger(\mathbf{r}', 0)\} \right| 0\rangle$$

Interacting single-particle Green's function

Optical properties – N+2 particle problem

Excited States in Materials

- Excited-state phenomena (transport, optical, energy transfer, charge/spin dynamics...) in a material often give rise to its ***defining attributes*** and determine its usefulness.

- *Ab initio* calculations of excited states ⟺ different and higher-level treatment of many-electron interaction effects

- Existing ***ab initio*** methods and community codes for solids: predict & understand 1-particle or 2-particle excitation phenomena in increasingly complex materials. *(BerkeleyGW, WEST, Yambo, VASP, ABINIT, FHI-aims, Exciting, stochasticGW, nanoGW,* FlapwMBPT, *QMCPACK, EPW,...)*

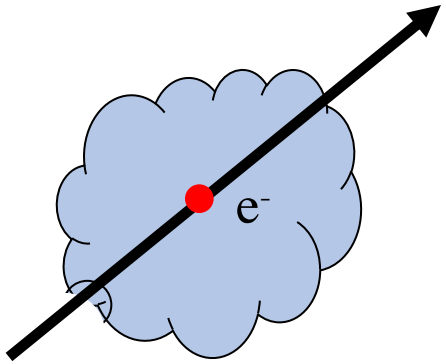
- Key phenomena – 3- or 4-particle correlated excitations, non-linear spectroscopies, field-driven time-dependent processes, excited-state dynamics, etc. -- to be addressed by *ab initio methods & public domain* software that include **relevant** many-electron interactions **accurately**.

Outline of talk

- Introduction -- many-body interactions and excited-state phenomena in materials
- Quasiparticle excitations, optical responses, and correlated multiparticle excitations
- Time-dependent and high-field phenomena
- Correlation enhanced electron-phonon interaction
- Photophysics of moiré 2D heterostructures

Ab initio Studies of Quasiparticle Excitations in Tunneling and ARPES

1-particle excitations
(N+1 particle problem)



$$E(\mathbf{k}) = E^0(\mathbf{k}) + \Sigma(\mathbf{k},E)$$

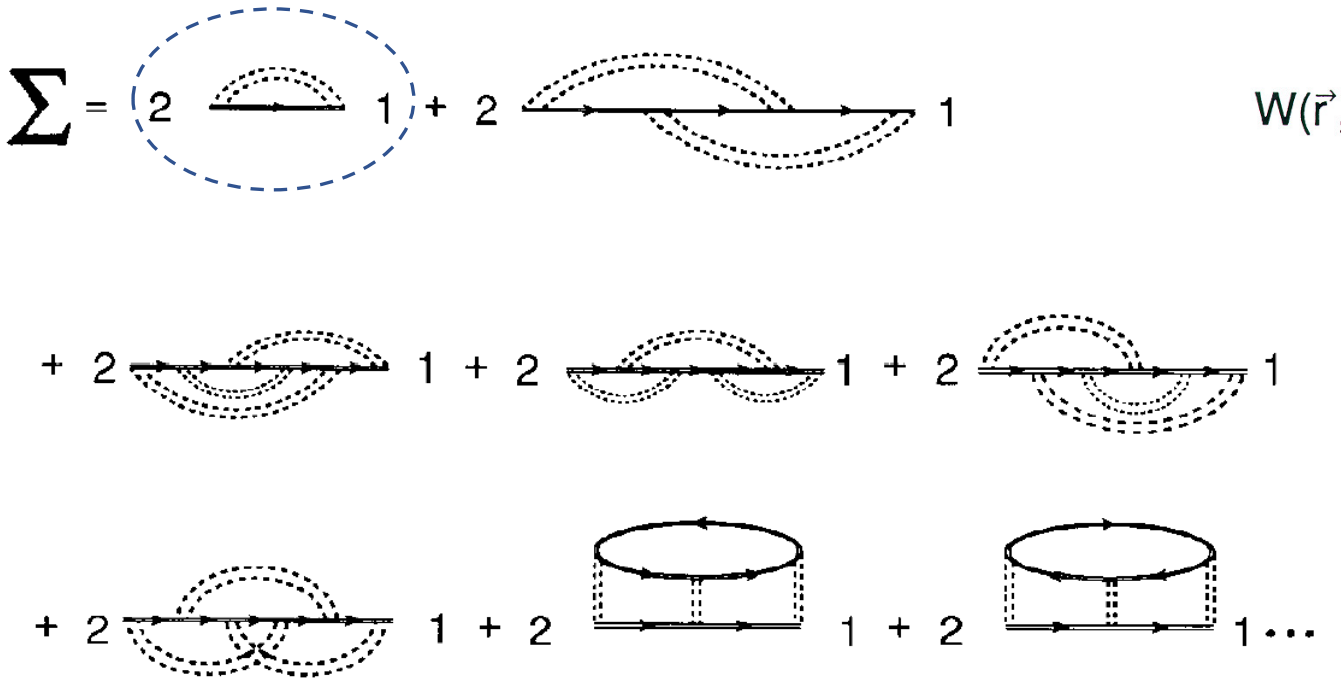
- renormalizes energy dispersion
- gives rise to finite lifetime
- satellite structures

$$A(\mathbf{k},\omega) = \frac{2}{\pi}\frac{-\mathrm{Im}\Sigma(\mathbf{k},\omega)}{[\omega - \varepsilon_{\mathbf{k}} - \mathrm{Re}\Sigma(\mathbf{k},\omega)]^2 + [\mathrm{Im}\Sigma(\mathbf{k},\omega)]^2}$$

$$\Sigma = \Sigma_{\text{e-e}} + \Sigma_{\text{e-ph}} + \ldots$$

Quasiparticle (electron or hole) excitations in solids: the GW approach

Interacting 1-particle Green's Functions: $E(\mathbf{k}) = E^0(\mathbf{k}) + \Sigma(\mathbf{k},E)$



$$W(\vec{r},\vec{r}',\omega) = \int v(\vec{r},\vec{r}'')\varepsilon^{-1}(\vec{r}'',\vec{r}',\omega)d^3r''$$

Screened Coulomb interaction

Hubbard (1957)
Phillips (1961)

Interacting 2-particle Green's function via the Bethe-Salpter equation (GW-BSE): linear optical properties including excitonic effects

GW approximation:
Electron gas - Hedin, PR (1965)
Real materials - Hybertsen and Louie, PRL (1985)

Quasiparticle Band Structure Calculations

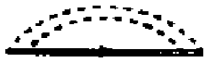
- Density-functional theory:

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + V_{\text{xc}}\right\}\psi_{\mathbf{nk}}^{\text{DFT}} = \varepsilon_{\mathbf{nk}}^{\text{DFT}}\psi_{\mathbf{nk}}^{\text{DFT}}$$

Hohenberg, Kohn, and Sham 1965

- Green-function approach

$$\left\{-\nabla^2 + V_{\text{ext}} + V_{\text{Coul}} + \Sigma(\varepsilon_{\mathbf{nk}}^{\text{QP}})\right\}\psi_{\mathbf{nk}}^{\text{QP}} = \varepsilon_{\mathbf{nk}}^{\text{QP}}\psi_{\mathbf{nk}}^{\text{QP}}$$



$\Sigma = iG_1W$ GW approximation for the self energy

G_1 one-particle Green function

$W = \epsilon^{-1}v$ screened Coulomb interaction

Hedin 1965, Hybertsen and Louie 1985

- $\Sigma(\mathbf{r}, \mathbf{r'}, \omega)$ - nonlocal, energy-dependent nonHermitian operator
- Large complex eigenvalue problem

The GW approximation for Σ

$$\Sigma(\vec{r},\vec{r}';E) = \frac{i}{2\pi}\int W(\vec{r},\vec{r}',\omega)G(\vec{r},\vec{r}',E+\omega)e^{i\delta\omega}d\omega$$

with

$$W(\vec{r},\vec{r}',\omega) = \int v(\vec{r},\vec{r}'')\varepsilon^{-1}(\vec{r}'',\vec{r}',\omega)d^3r''$$

$$G(\vec{r},\vec{r}',\omega) = \sum_{n\vec{k}} \frac{\psi_{n\vec{k}}(\vec{r})\psi^{*}_{n\vec{k}}(\vec{r}')}{\omega - E_{n\vec{k}} - i\delta_{n\vec{k}}}$$

Require:

(1) Full dielectric matrix (local fields)

$$\varepsilon^{-1}(\vec{r}',\vec{r},\omega) \text{ or } \varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)$$

(2) Good starting $\psi_{n\vec{k}}$ and $E_{n\vec{k}}$ to construct the Green's function G.

$H = H_o + (H - H_o)$

H_o: LDA/GGA
LDA+U
exact exchange
hybrid functionals
iterative scheme
…

Calculation of Optical Absorption Spectrum

- Coupled electron-hole excitations:

$$|S\rangle = \sum_{v}^{\text{elec}} \sum_{c}^{\text{hole}} A^{S}_{vc}\, \hat{a}^{\dagger}_{v}\, \hat{b}^{\dagger}_{c}\, |0\rangle$$

$|0\rangle$ ground state of many-electron system

$\hat{a}^{\dagger}_{v}$, $\hat{b}^{\dagger}_{c}$ creates quasi-hole, -electron

A^{S}_{vc} coupling coefficients

v = n**k** (occupied)

c = n'**k** (unoccupied)

- The Bethe-Salpeter Equation for the two-particle Green's function G_2 yields:

$$(\varepsilon^{\text{QP}}_{c} - \varepsilon^{\text{QP}}_{v}) A^{S}_{vc} + \sum_{v'c'} \langle vc|K^{eh}|v'c'\rangle A^{S}_{v'c'} = \Omega^{S} A^{S}_{vc}$$

M. Rohfling and S. G. Louie, PRL (1998)

$\varepsilon^{\text{QP}}_{c}$, $\varepsilon^{\text{QP}}_{v}$ single-quasiparticle energies

K^{eh} electron-hole interaction

$\Longrightarrow \Omega^{S}$ excitation energies

Also:
S. Albrecht, et al, PRL (1998)
L. Benedict, et al, PRL (1998)

- Electron-hole interaction kernel:

$$K^{eh} = \frac{\delta V_{\text{Coul}}}{\delta G_1} + \frac{\delta \Sigma}{\delta G_1}$$

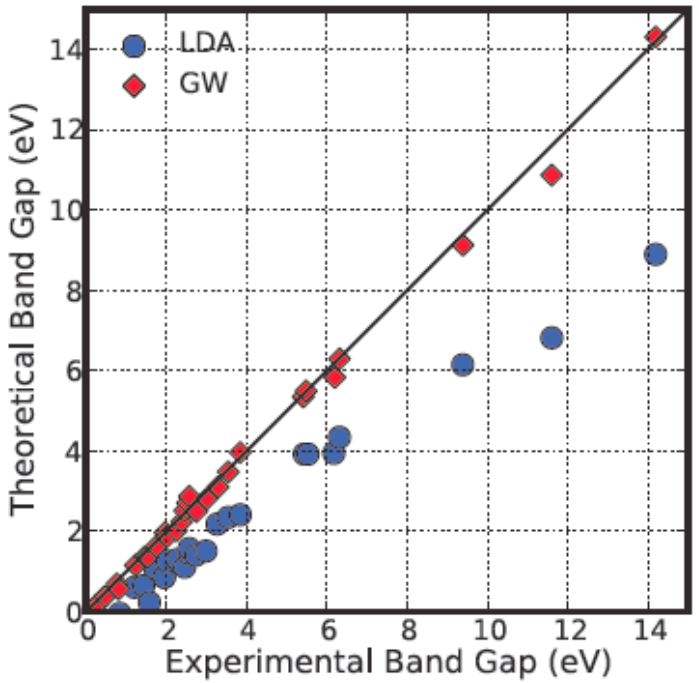
$\delta G_1 \searrow v$; $\delta G_1 \searrow -W$

- $\Longrightarrow$ Optical absorption spectrum: $\epsilon_2(\omega)$

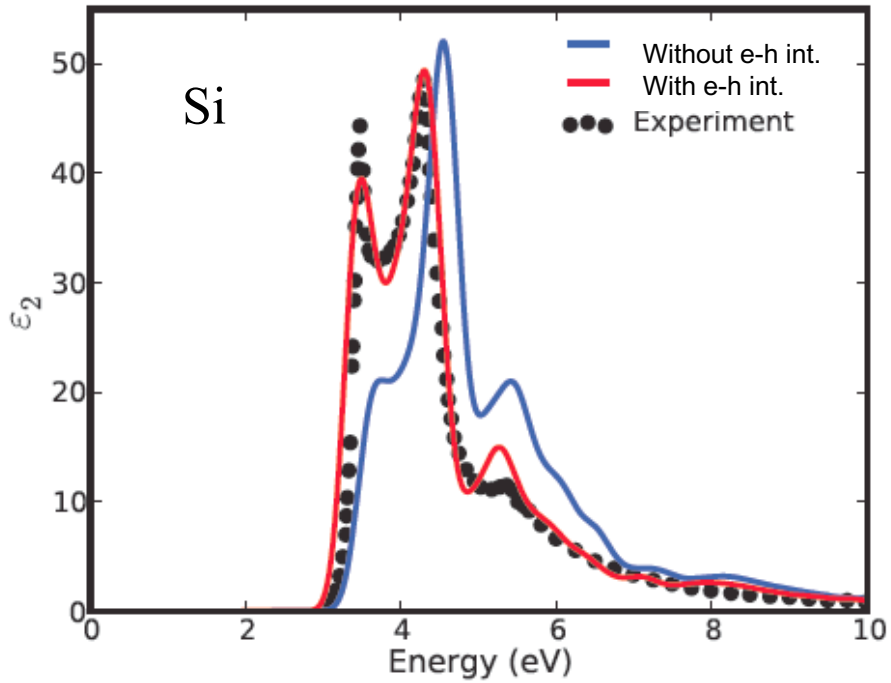
- K - large, nonHermitian matrix with very fine **k** sampling
- K can have dimensions as large as ~10^6

Ab initio GW and GW-BSE Approaches: Theory vs. Experiment

Materials:
InSb, InAs, Ge,
GaSb, Si, InP,
GaAs, CdS,
AlSb, AlAs,
CdSe, CdTe,
BP, SiC, C_{60},
GaP, AlP,
ZnTe, ZnSe,
c-GaN, w-GaN,
InS, w-BN,
c-BN,
diamond,
w-AlN, LiCl,
Fluorite, LiF



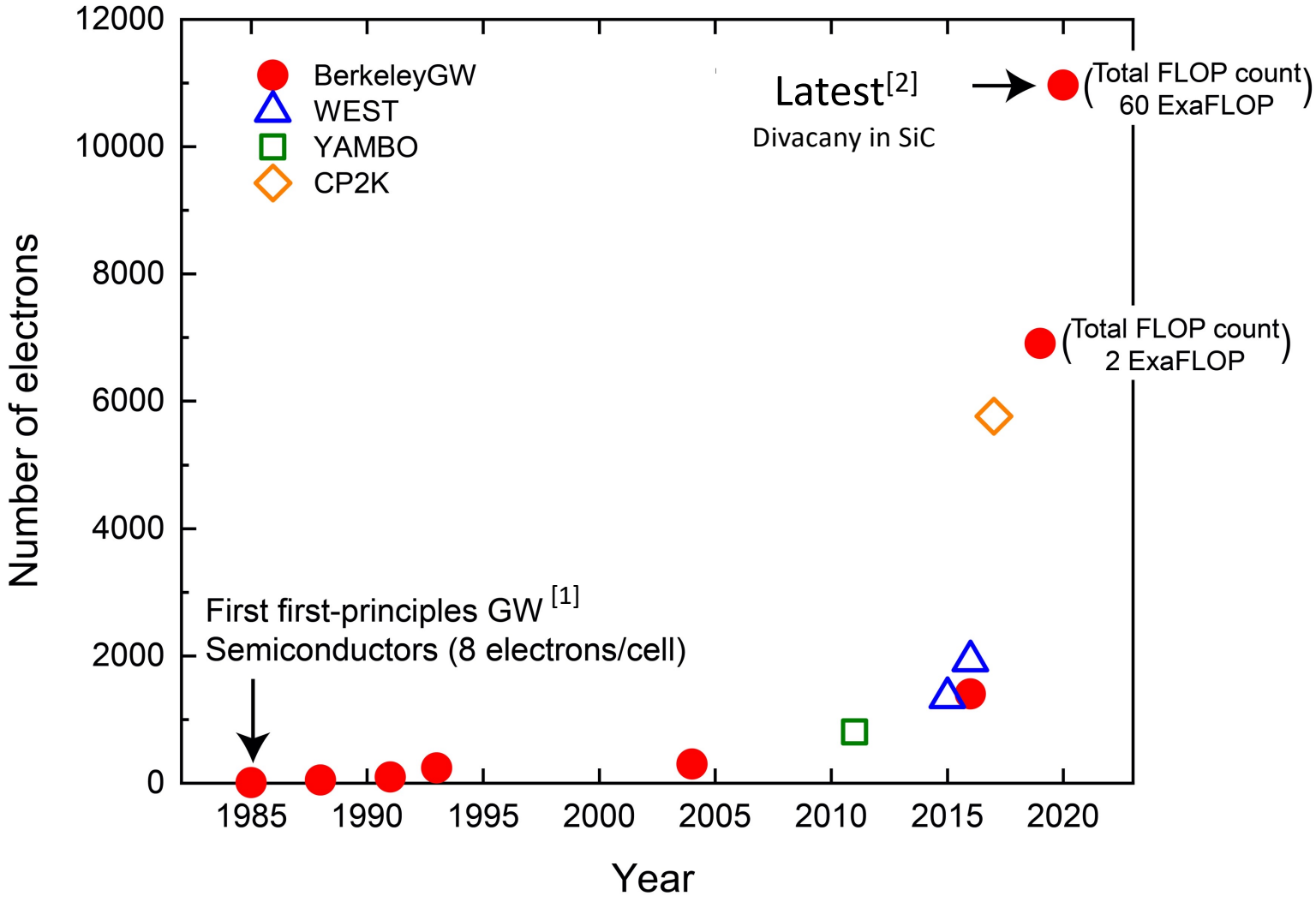
Quasiparticle Gap[1]



Optical absorption[2]

1) Hybertsen and Louie, PRL (1985); Louie, Topics in Comput. Mat. Sci. (1997)
2) Rohlfing and Louie, PRL (1998); Deslippe, Samsonidze, Strubbe, Jain, Cohen, and Louie, Comput. Phys. Commun. (2012)

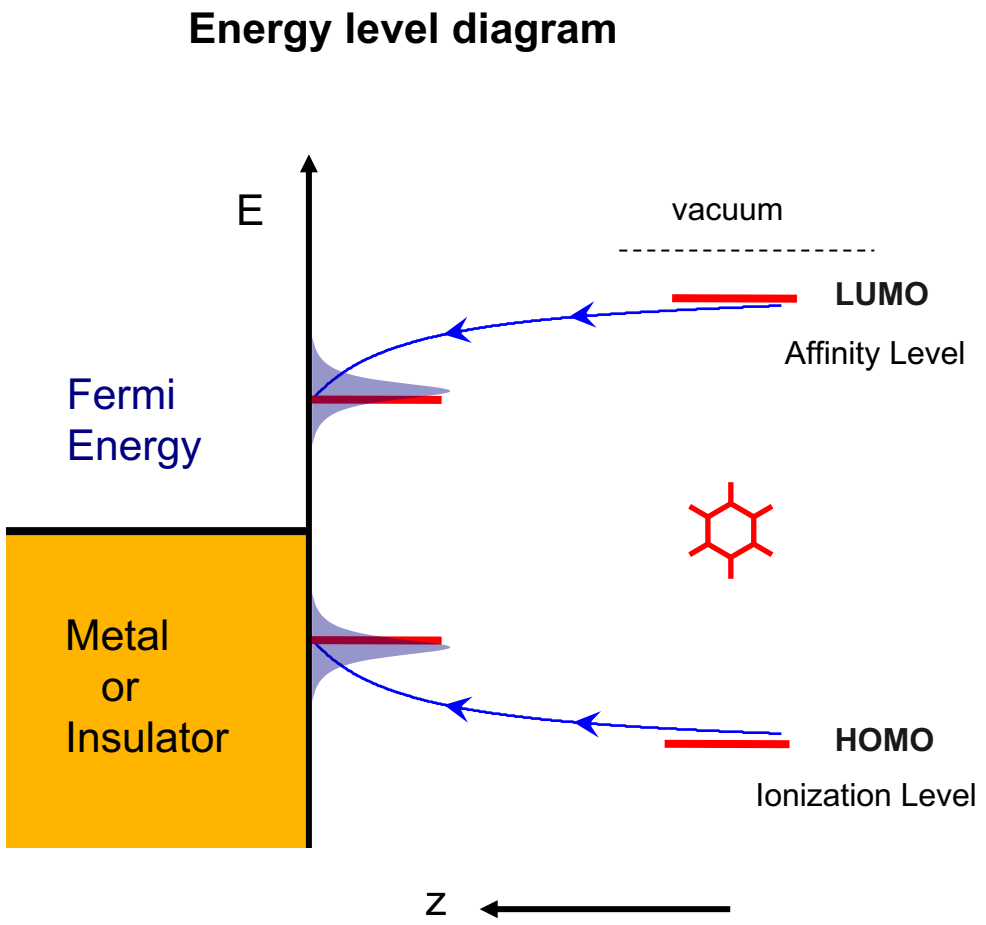
Large-scale ab initio GW Calculations over the Years



[1] Hybertsen and Louie, PRL 55, 1418 (1985).

[2] Del Ben, Yang, Li, Jornada, Louie, Deslippe, in 2020 SC20: International Conference for High Performance Computing, Networking, Storage and Analysis (SC), Atlanta, GA, US, 2020 pp. 36-46

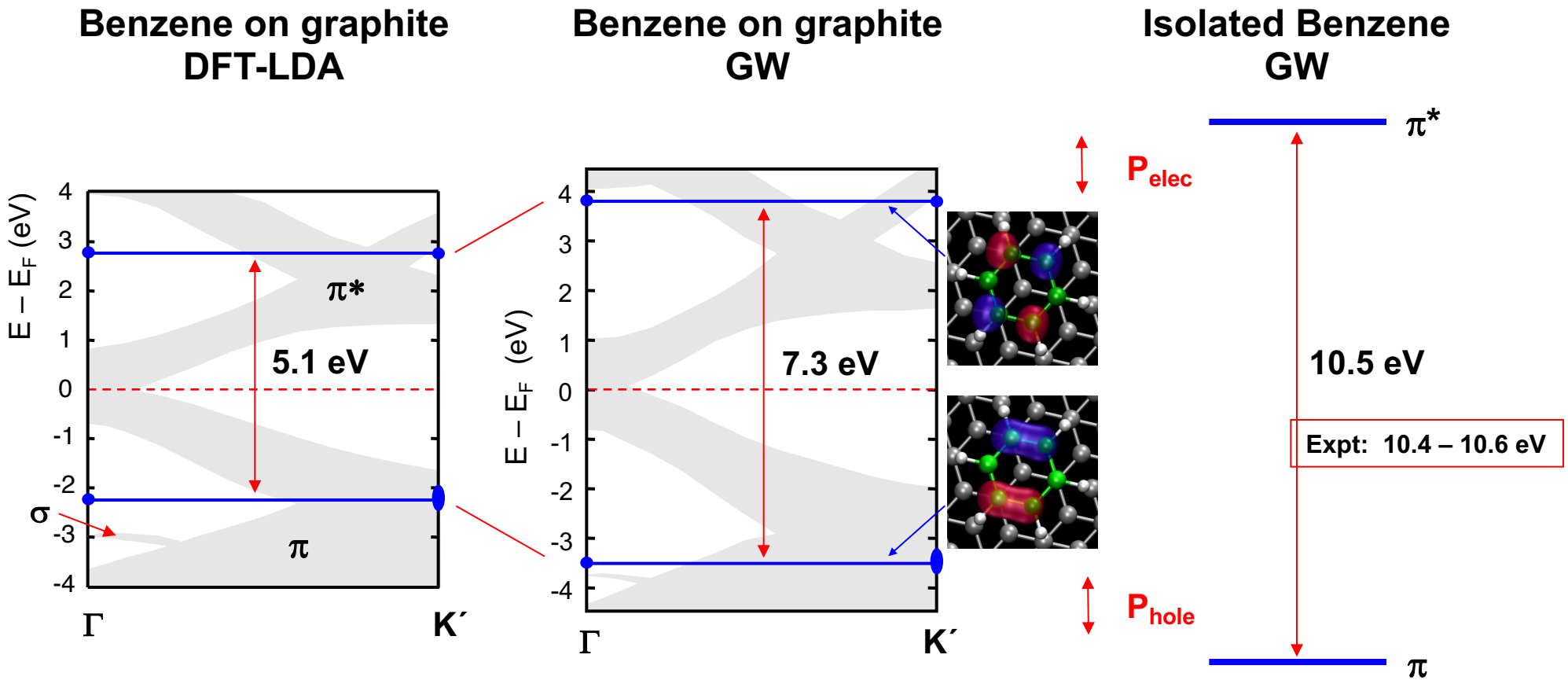
Quantum level alignment at interface – importance of nonlocal screening/correlations



Physical effects

- Interfacial charge transfer (dipoles)
- Quantum mechanical (electronic) coupling
- Electron correlation (**self energy**) effects

Benzene orbital energies on graphite

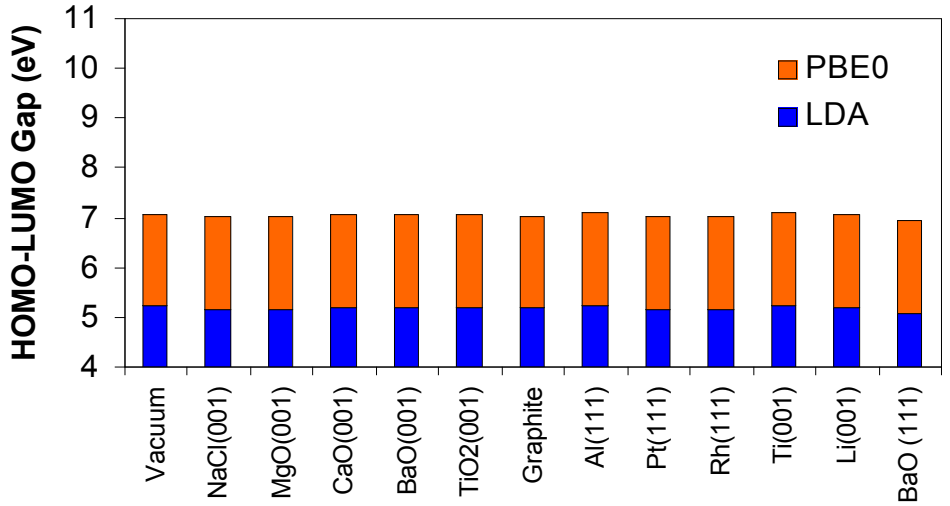


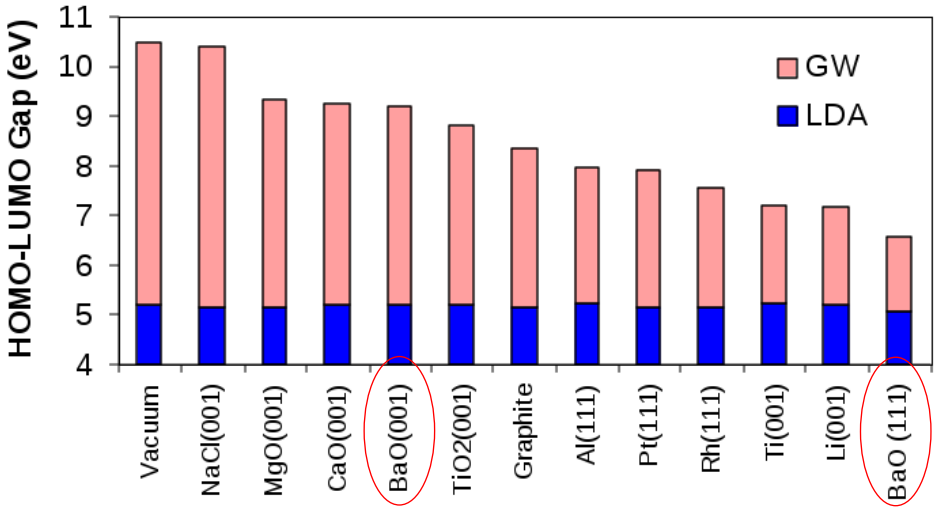
- DFT-LDA gap: ~2 eV error

- Relative to gas phase: Gap narrows by ~3.2 eV
- Kohn-Sham energies do not capture the change
- *In general*, change in self energy: large (~ 2 eV) and environmental dependent

Neaton, Hybertsen, Louie, PRL **97**, 216405 (2006)

HOMO - LUMO Quasiparticle Gap of Benzene on Surfaces



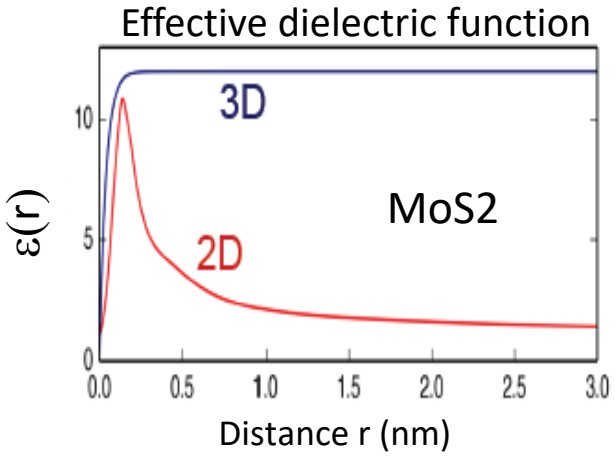


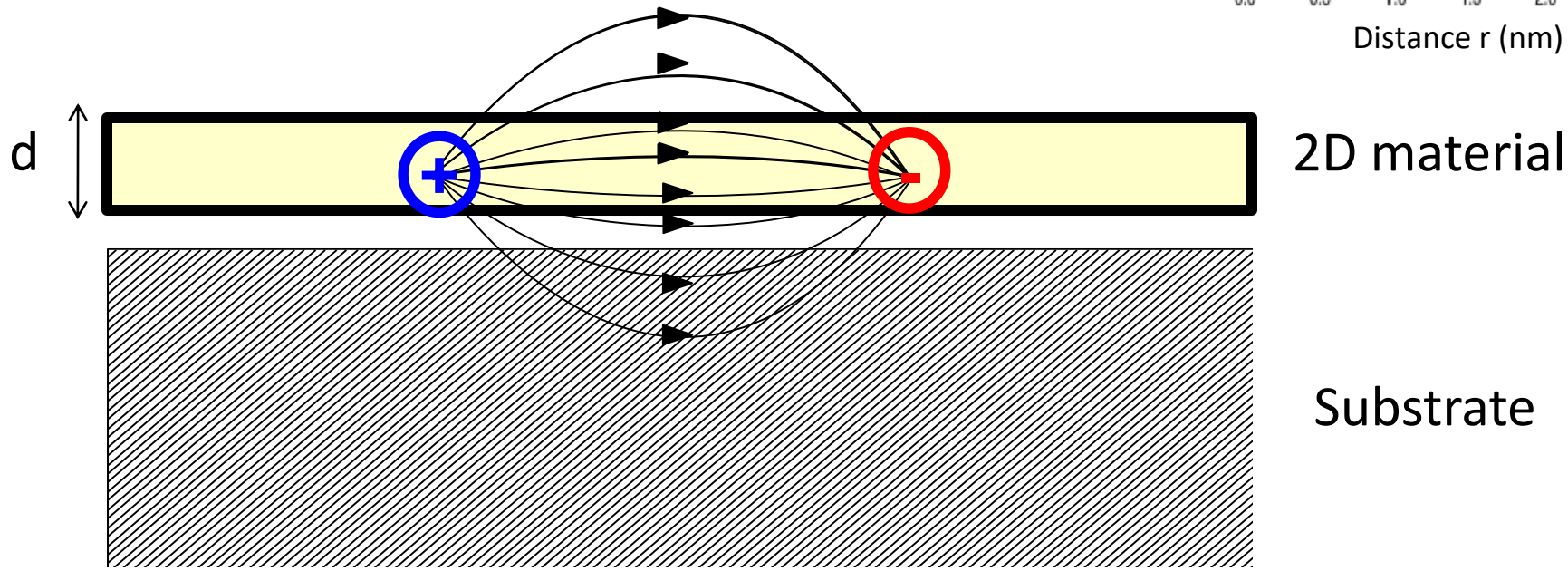
J. Garcia-Lastra, et al, PRB (2009)

Strong & *different* renormalization of molecular levels with different contacts are *absent* in the Kohn-Sham orbital energies -- LDA, GGA or hybrids!!

Electron-Electron & Electron-Hole Interactions in Quasi 2D Systems

- Enhanced Coulomb interaction – reduced dimensionality/phase space
- Strange/strong spatial screening dependence

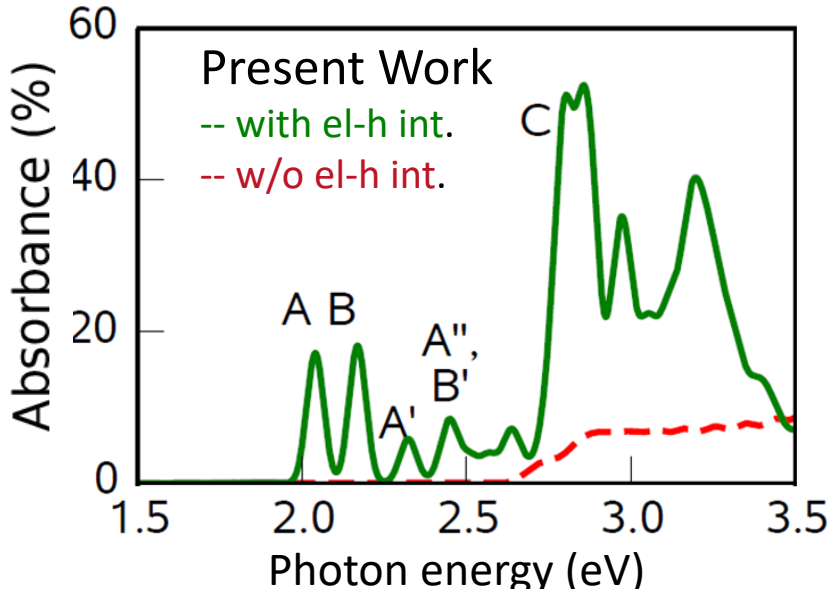




Substrate/environmental screening are important!

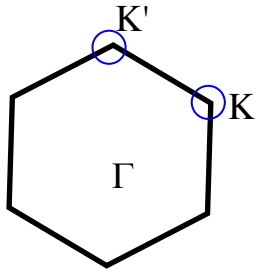
Optical Spectrum of Monolayer MoS2: GW-BSE Theory vs Experiment

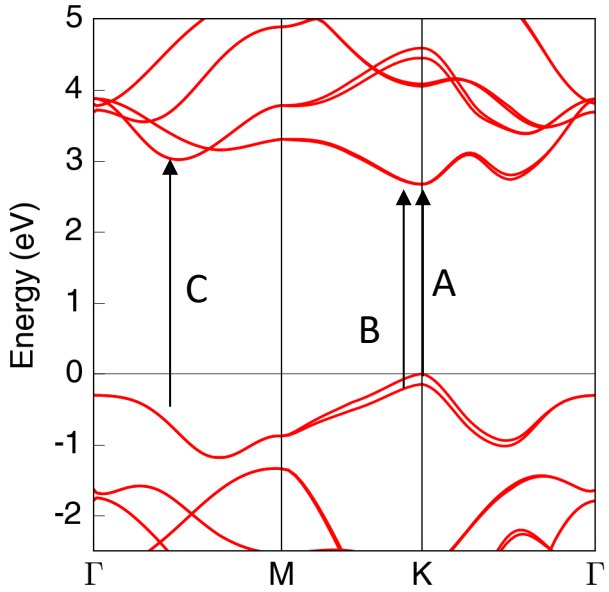
Qiu, da Jornada, and Louie, PRL (2013)

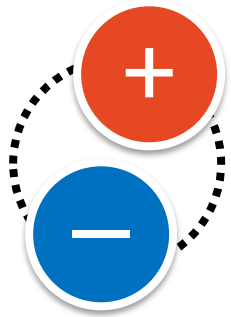


Exciton E_b =0.65 eV!

Bulk semiconductors E_b is two orders of magnitude smaller





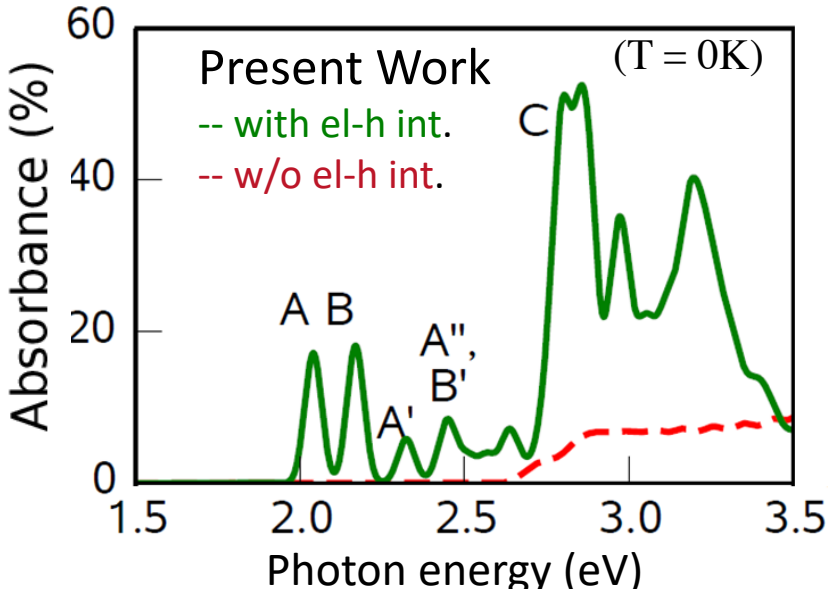


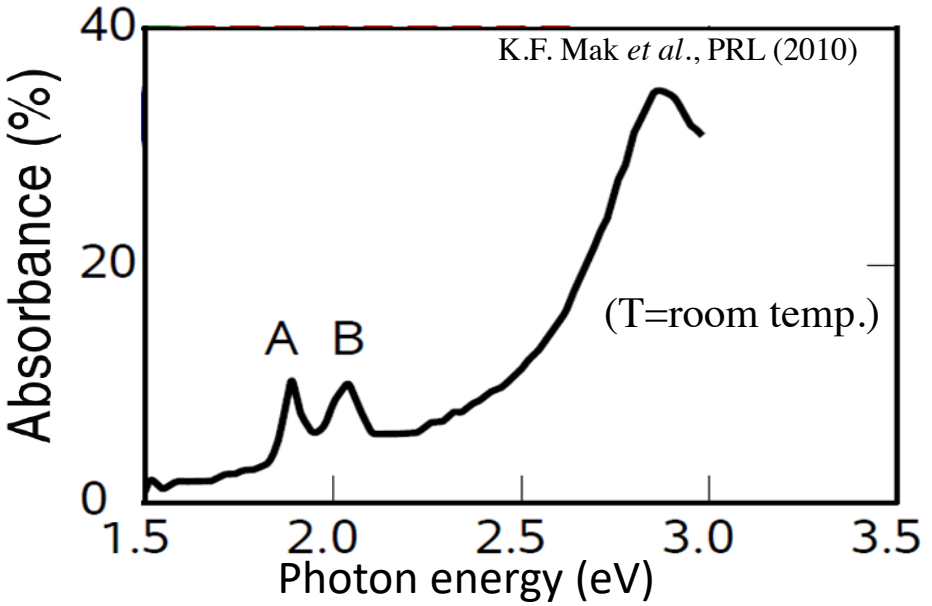
Exciton: $|S\rangle$

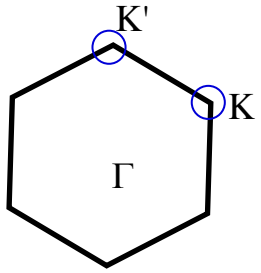
(correlated 2-particle state)

Optical Spectrum of Monolayer MoS2: GW-BSE Theory vs Experiment

Qiu, da Jornada, and Louie, PRL (2013)

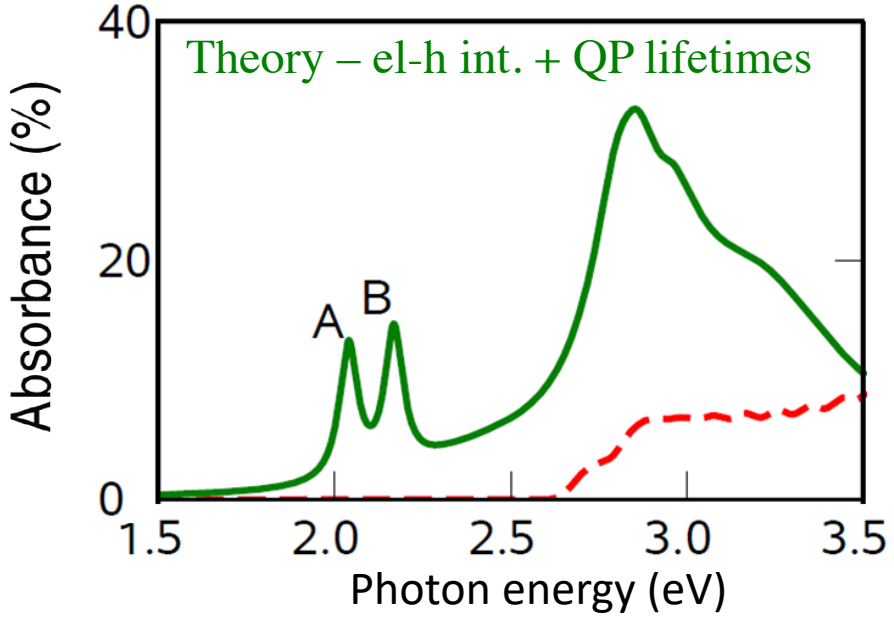




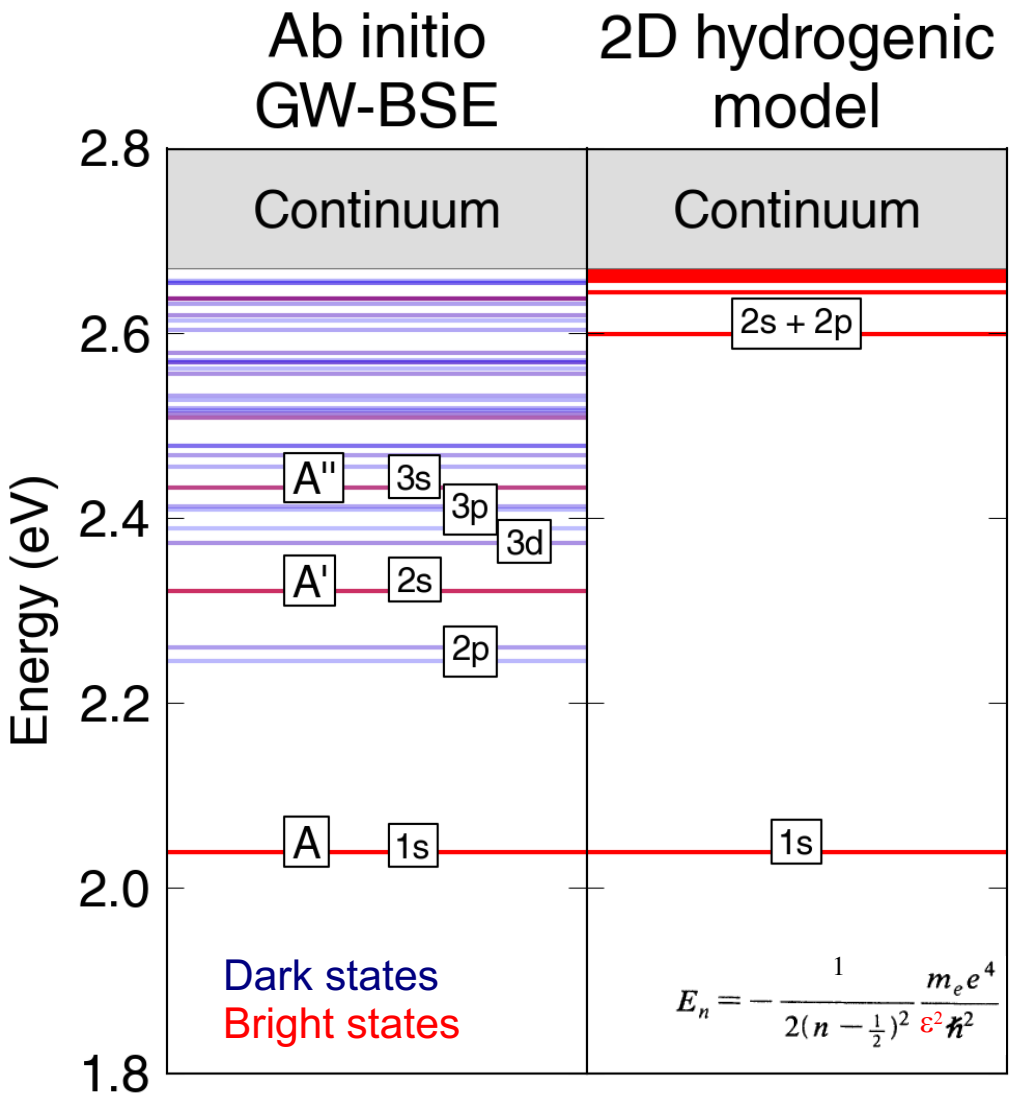


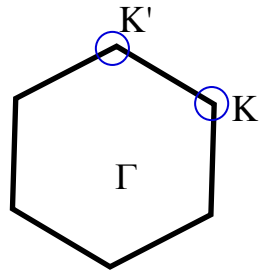
Absorbance per ½ nanometer of material at 2.0 eV :

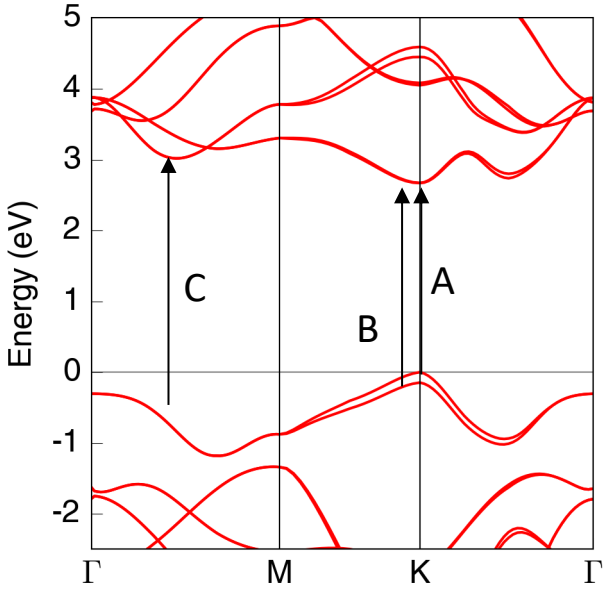
Monolayer MoS2 -- ~ 20%
Bilayer graphene -- ~ 5%
Silicon – ~ 0.02%!

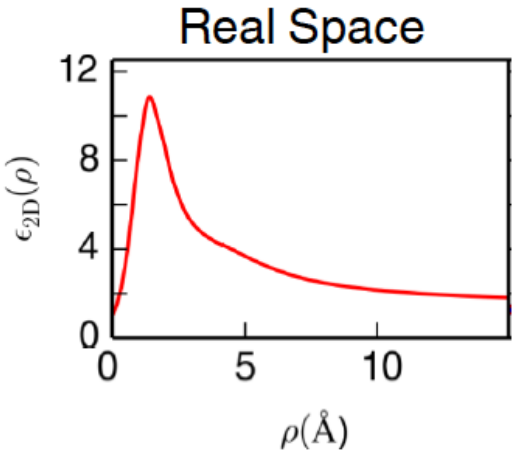


Excitons in Monolayer MoS_2



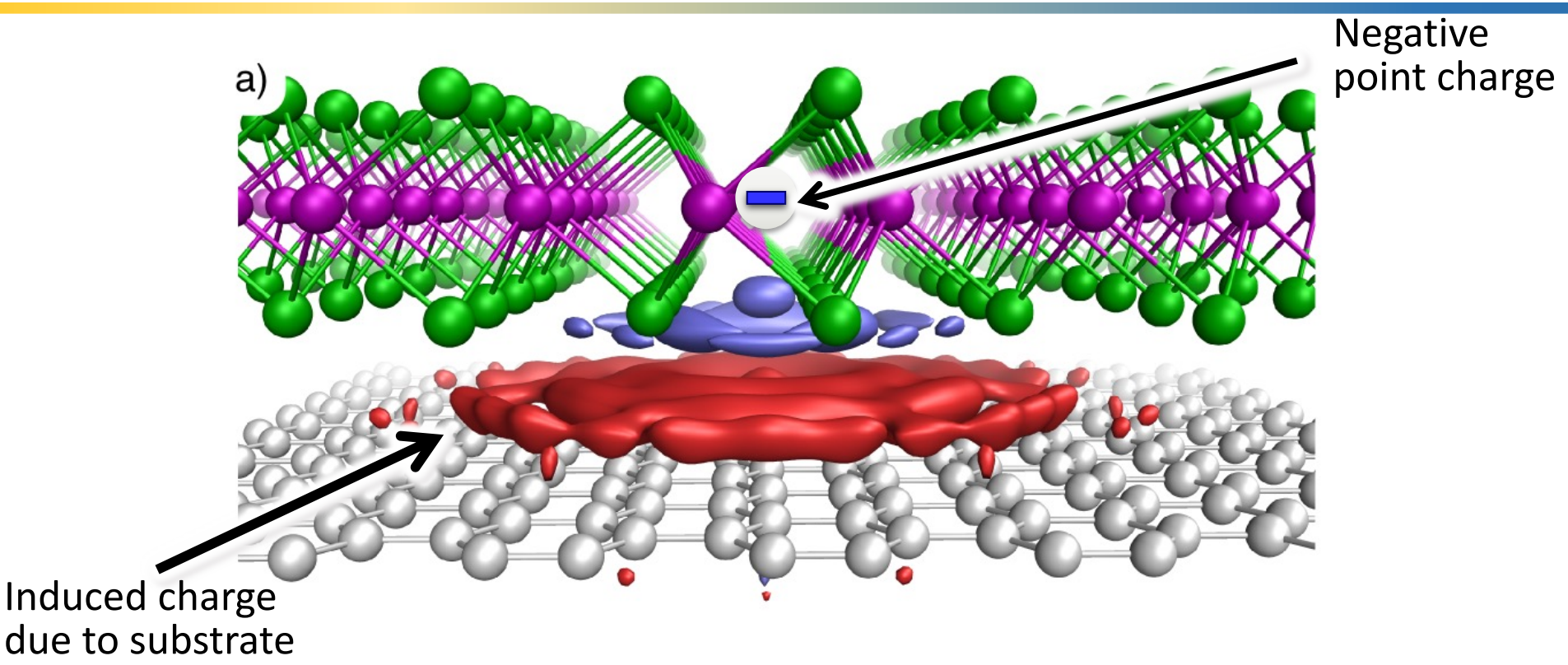






Qiu, da Jornada, and Louie, PRL (2013)

Substrate Screening: Monolayer $MoSe_2$ on bilayer graphene

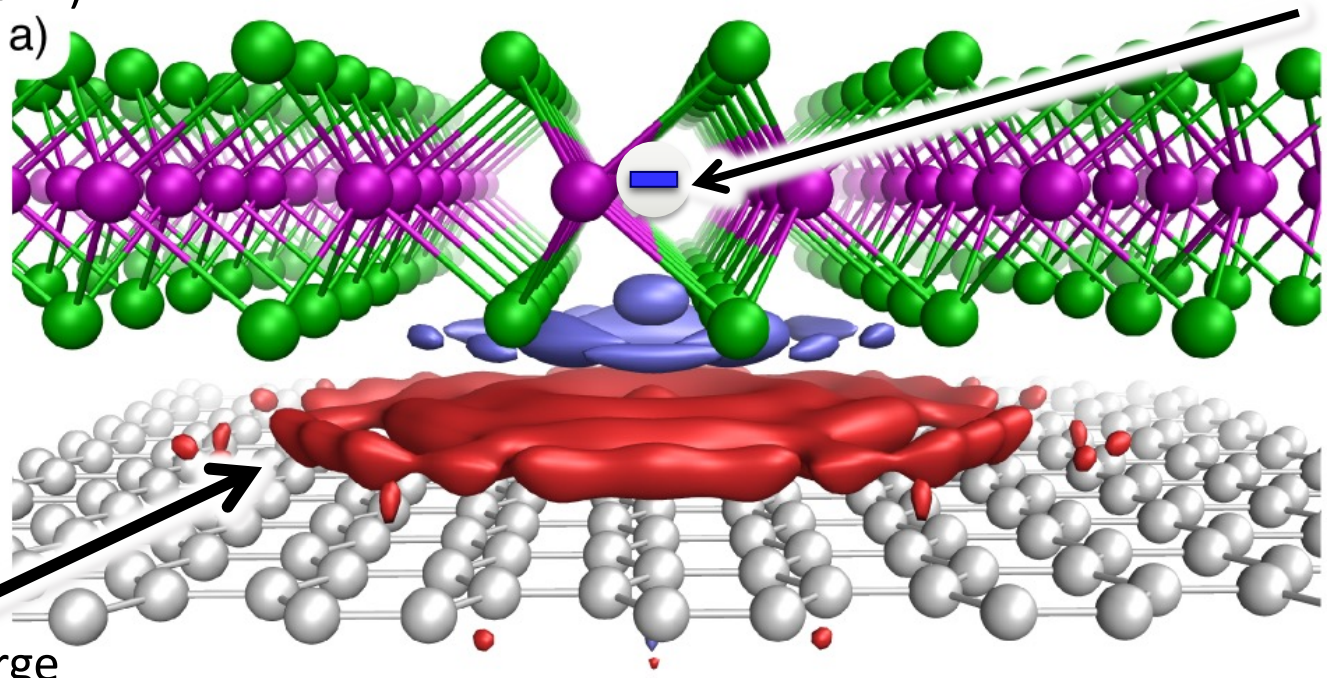


- Screening is nonlocal, frequency dependent
- Incorporate screening of *substrate* by via substrate dielectric matrix $\varepsilon_{Gz,Gz'}(\mathbf{q},\omega)$

Jornada, Qiu and Louie (2014)

Substrate Screening: Monolayer $MoSe_2$ on bilayer graphene

Jornada, Qiu and Louie (2014)



For some systems, substrate/encapturation can

- renormalize the band gap by **>50%**
- change the exciton binding energies by **factor of 2 or more**
- tune the energy (~ 1eV) and dispersion of long-live plasmons in monolayer metallic TMDs by an order of magnitude

E.g., Ugeda, Crommie, Wang, Louie, et al, Nat. Mat. (2014); Li, et al, Nat. Nanotech., (2017), …

da Jornada, Xian, Rubio, Louie (2018)

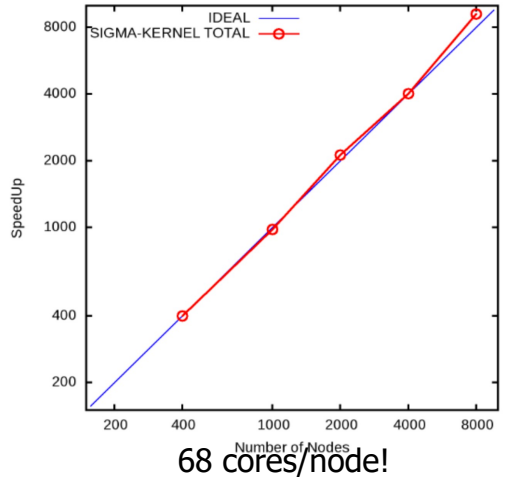
Current BerkeleyGW package - *www.berkeleygw.org*

General excited-state phenomena code that supports:

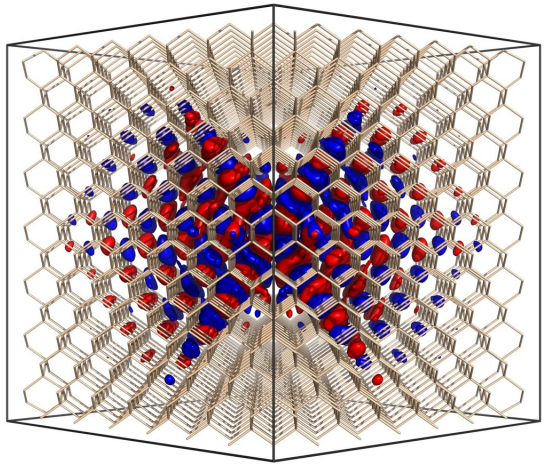
- GW & GW-BSE: 3D, 2D, 1D and molecular systems
- Insulating, metallic and semi-metallic systems
- Interface with a large set of DFT and other mean-field codes: PARATEC, Quantum Espresso, PARSEC, SIESTA, Octopus, ABINIT, RMGDFT, …
- Massively parallel with MPI, OpenMP and SIMD parallelism
- Linear scales to ***500,000*** *CPUs* @ NERSC's Cori2, & to **27,648** GPUs @ OLCF's Summit
- Efficient accurate solution to the BSE via **k**-point interpolation (up to *1,000,000* ***k****-points* – *important for excitons!*)

- Example of recent large-system studies
  - QP states & optical excitations of defects in Si and SiC with **>2,740-atoms** (or **10,900-electrons**) supercell

BerkeleyGW scales linearly up to ***512,000*** CPU cores!



68 cores/node!



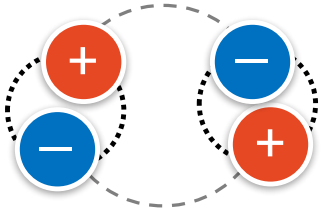
Non-equilibrium
and
beyond 1- & 2-particle excitations

New Phenomena ⟷ New *ab initio* formalisms

Beyond ab initio GW and GW-BSE

Correlated Higher-number-particle Excitations:

- Trions, bi-excitons, exciton-exciton interactions, decay of excited state, …
- Interacting 3- and 4-particle Green's functions, …



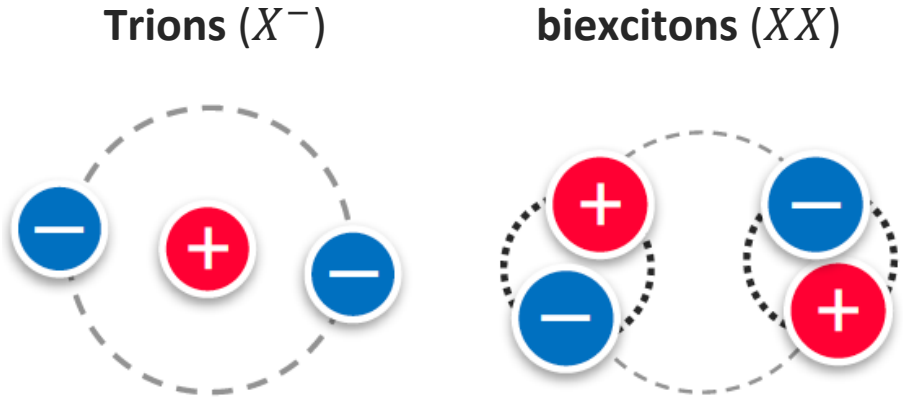
Time-dependent & High-field Phenomena

- Pump-probe experiments, nonlinear optics, field-driven transformations, …
- Explicit time propagation of Green's function (time-dependent GW, non-equilibrium Green's function formalism, …)

$$i\hbar \frac{\partial}{\partial t_1} G^{\gtrless}_{n_1 n_2 \mathbf{k}}$$

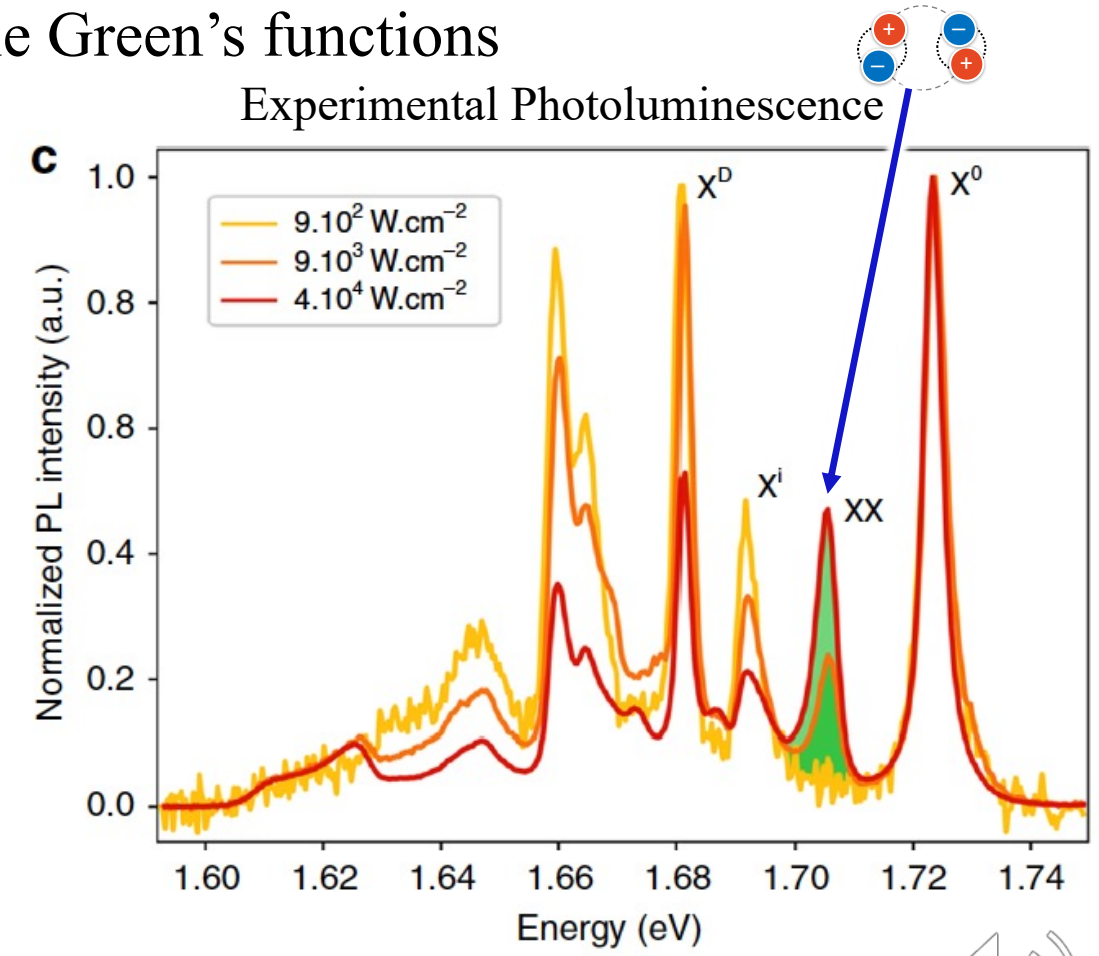
Correlated Multi-particle Excitations in 1D & 2D

- Multi-particle excitations prominent in atomically thin 1D & 2D systems
- Example: biexcitons on monolayer WSe_2
- Trions & biexcitons - interacting 3- and 4-particle Green's functions



Other fundamental and practical interests:

- Exciton condensates/insulators
- Singlet fission in organic crystals



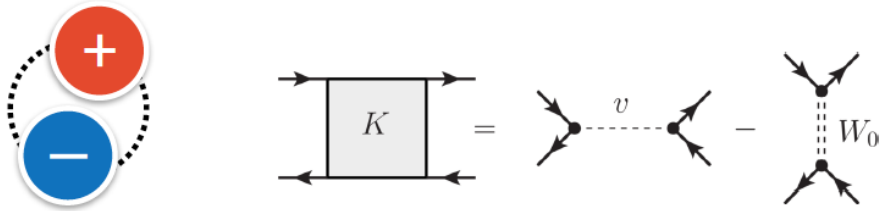
(Monolayer WSe2 encap. w/ hBN)

Z. Ye, T. Heinz, et al., Nat. Commun. (2018)

Correlated Multi-particle Excitations

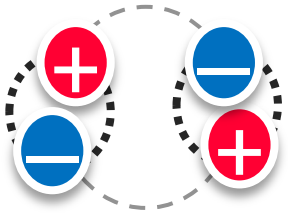
- Quasiparticle excitations -- GW approach (1 diagram)

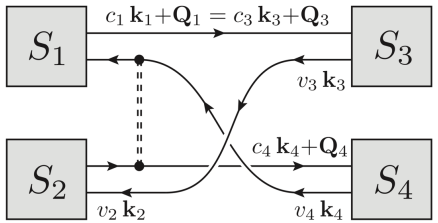
- Optical (electron-hole) excitations – GW-BSE approach (2 diagrams)



Exciton: $|S\rangle$

- Bi-excitons (4-particles excitations) – present approach (36 diagrams!)



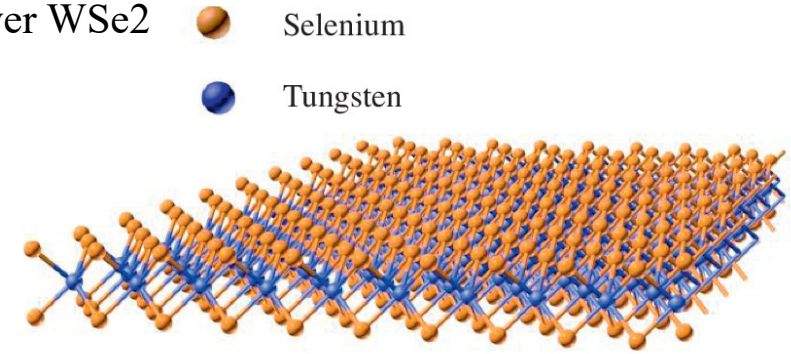


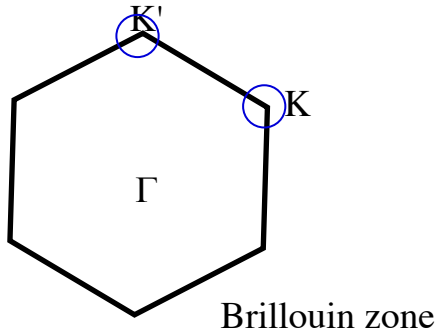
+ 35 other ones

da Jornada, Cepellotti & Louie (2020)

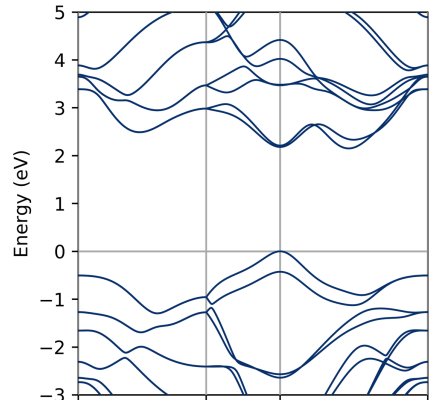
Photophysics of Atomically Thin 2D TMD Materials

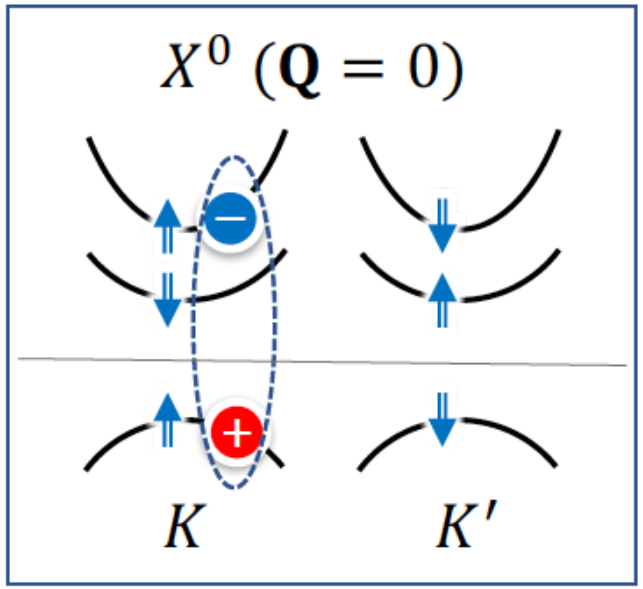
Monolayer WSe2



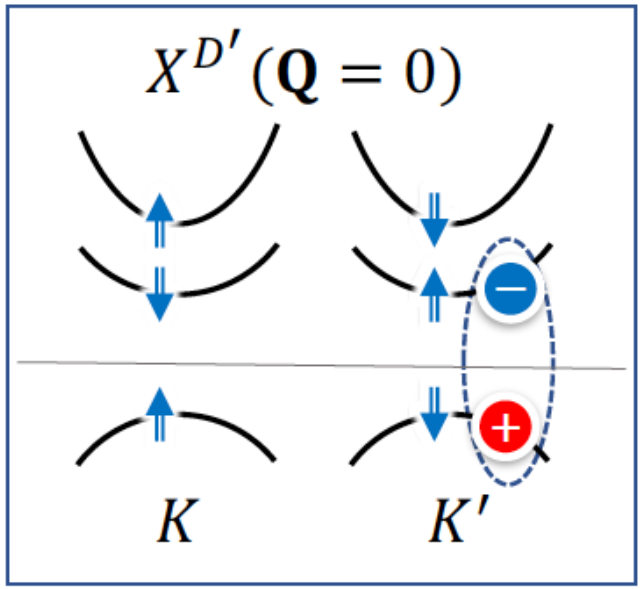


Brillouin zone

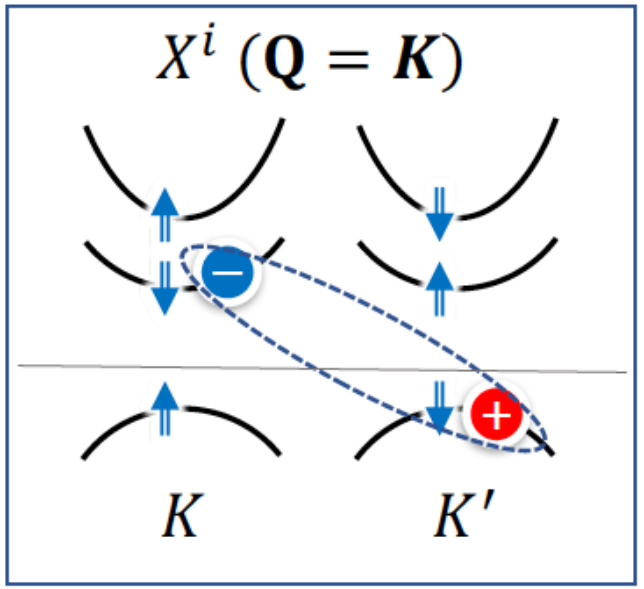




Bright K-valley exciton

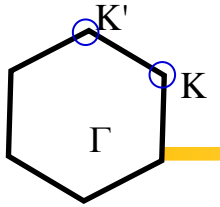


Dark K'-valley exciton



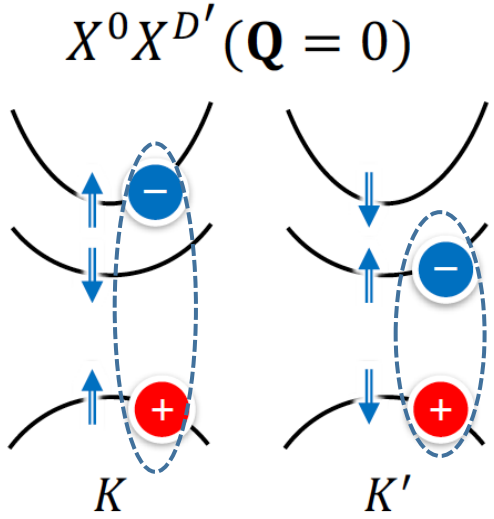
Dark inter-valley exciton

Dark excitons have lower energy then the bright excitons.

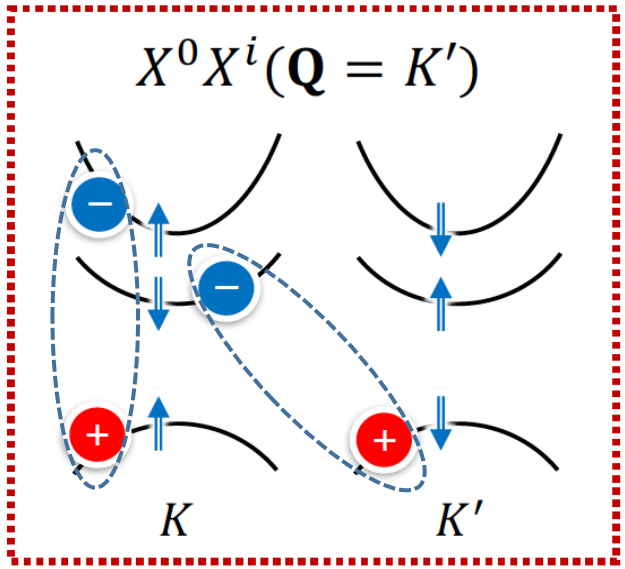


Trions and Biexcitons in Monolayer WSe2: Theory vs. Experiment

$X^0X^{D\prime} \rightarrow X^{D\prime} + \omega_1$



$X^0X^i \rightarrow X^i + \omega_2$



Ignored previously owing to neglect of important e-h exchange effects

	Our Theory*	Experiment
$E_b(X^-)$ Trion binding energy (meV)	(Type 1) 34	34 [2], 35 [3]
	(Type 2) 28	30 [2], 28 [3]
$E_b(XX)$ Biexciton effective binding energy (meV)	22	20 [2] 16-18 [3]

- First fully *ab initio* many-body (N+3 & N+4 particles) calculations
- Very rich energy and spin/valley level structures (high temp phenomena)
- Elucidate experimental observations + new predictions

*da Jornada, Cepellotti & Louie, to be published (2022).

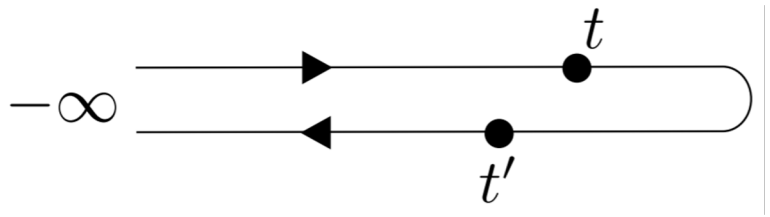
[1] He, Shan, et al, PRL 113, 026803 (2014).
[2] Ye, Heinz, et al, Nat. Commun. 9, 3718 (2018).
[3] Li,, Shi, et al, Nat. Commun. 9, 3719 (2018).
[4] Yong, Wang, et al, Nat. Phys. 14, 1092 (2018).

Field-driven Time-dependent Phenomena: TD-GW

- Non-equilibrium Green's function on Keldysh contour[1]

$1 = (\boldsymbol{r}\, t)$
$2 = (\boldsymbol{r}'t')$

$$G(1,2) = -i\langle T_C[\hat{\psi}_H(1)\hat{\psi}_H^{\dagger}(2)]\rangle$$



$$[i\partial_{t_1} - h(1)]G(1,2) = \delta(1,2) + \int_C d3\Sigma(1,3)G(3,2)$$

- Time propagation ⇒ linear/nonlinear responses and time-resolved phenomena with self-energy and exciton effects

- Use an *ab initio* time-dependent adiabatic GW (TD-aGW) approach with real-time propagation of the density matrix[2]

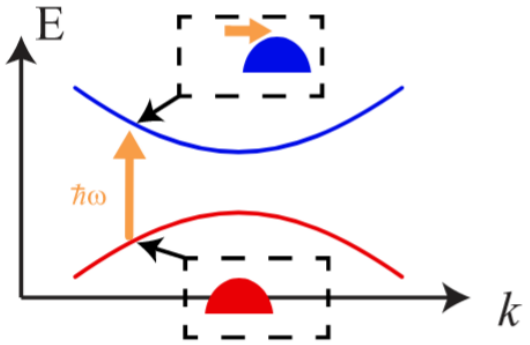
[1]Kadanoff and Baym, Quantum Statistical Mechanics; Keldysh, Zh. Eksp. Teor. Fiz. 47, 1515 (1964)
[2]Chan, Qiu, da Jornada, and Louie, Proc. Natl. Acad. Sci. U.S.A. **118**, e1906938118 (2021)

Shift Currents

- Photo-induced DC current in noncentro-symmetric crystals without p-n junction (bulk photovoltaic effect)
- Second-order optical response (related to band topology)

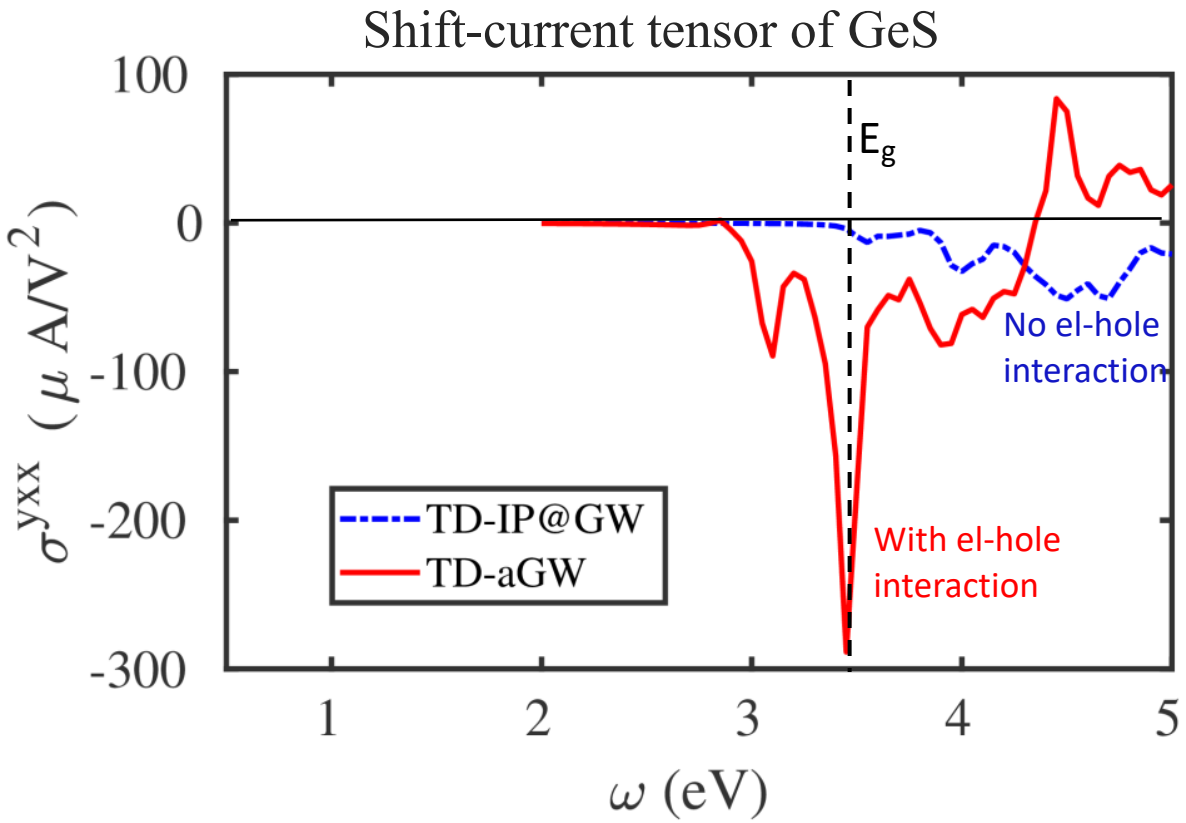
$$\mathbf{j}(0) = \sigma_{\text{shift}}\, \mathbf{E}(\omega)\mathbf{E}^*(\omega)$$

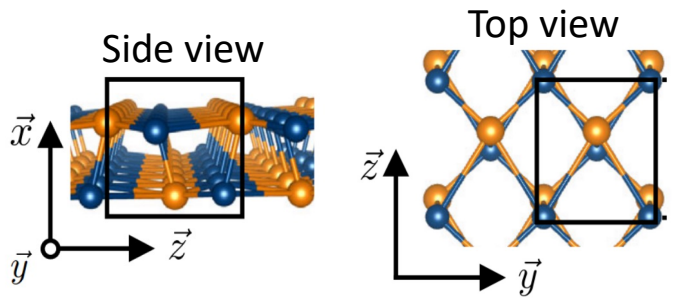
Shift of intracell coordinates from optical transitions



W. Kraut and R. von Baltz, PRB 19, 1548 (1979)
B. S. I. Sturman and V.M. Fridkin, Photovoltaic and photorefractive effects in noncentrosymmetric materials (1992)

TD-aGW Approximation: Shift Currents in Monolayer GeS





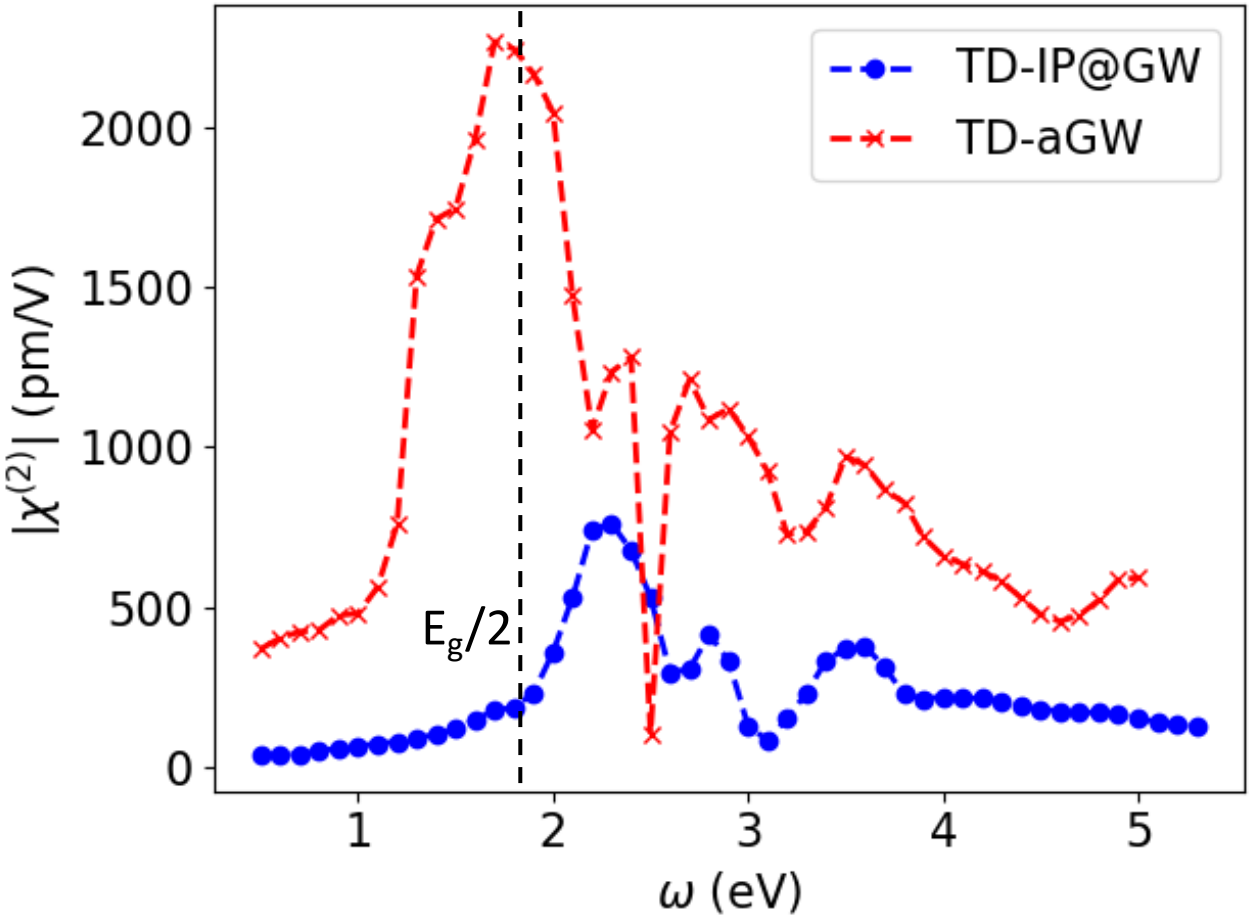
$$\mathbf{j}(0) = \boldsymbol{\sigma}_{\text{shift}}\, \mathbf{E}(\omega)\mathbf{E}^*(\omega)$$

- **Real-time propagation of Green's function on Keldysh contour within aGW**
- **First *ab initio* study including el-hole interactions**
- **Excitons enhance shift currents; effect is *huge – orders of magnitude higher* (also SHG)**
- **DC charge transport with CW in-gap excitations!**

Chan, Qiu, da Jornada and Louie, Proc. Natl. Acad. Sci. U.S.A. **118**, e1906938118 (2021)

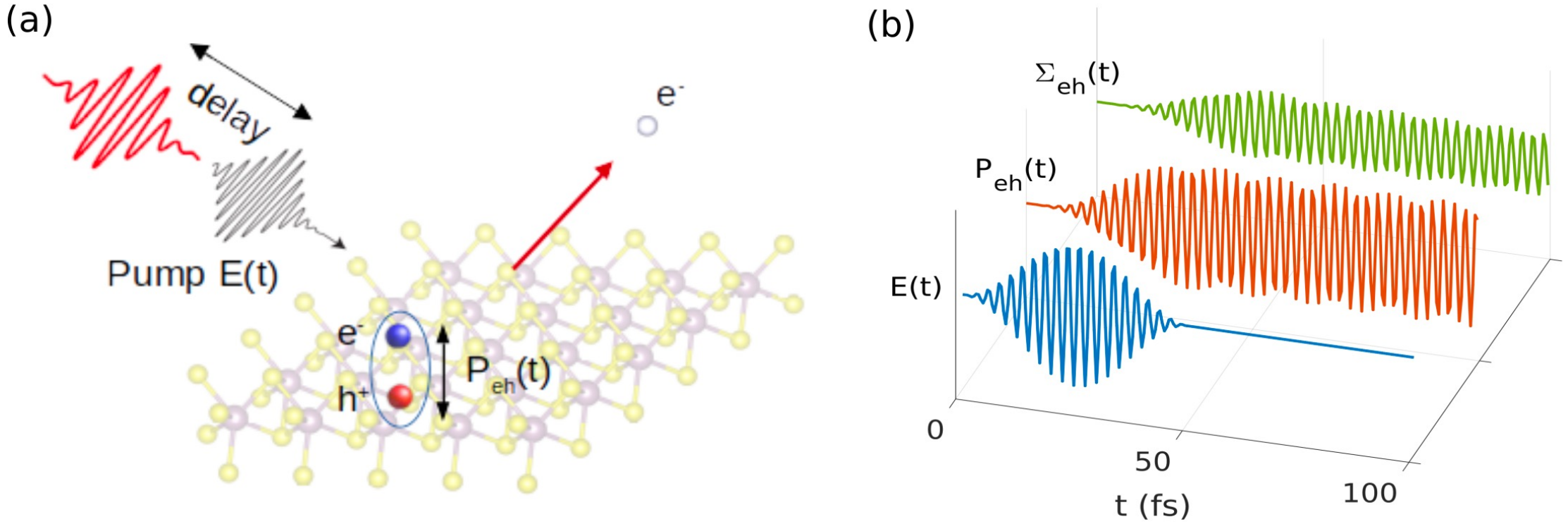
Second Harmonic Generation in Monolayer GeS

Absolute value of $\chi^{(2)yyy}$



Chan, Qiu, da Jornada and Louie, PNAS **118**, e1906938118 (2021)

Field-driven phenomena in tr-ARPES



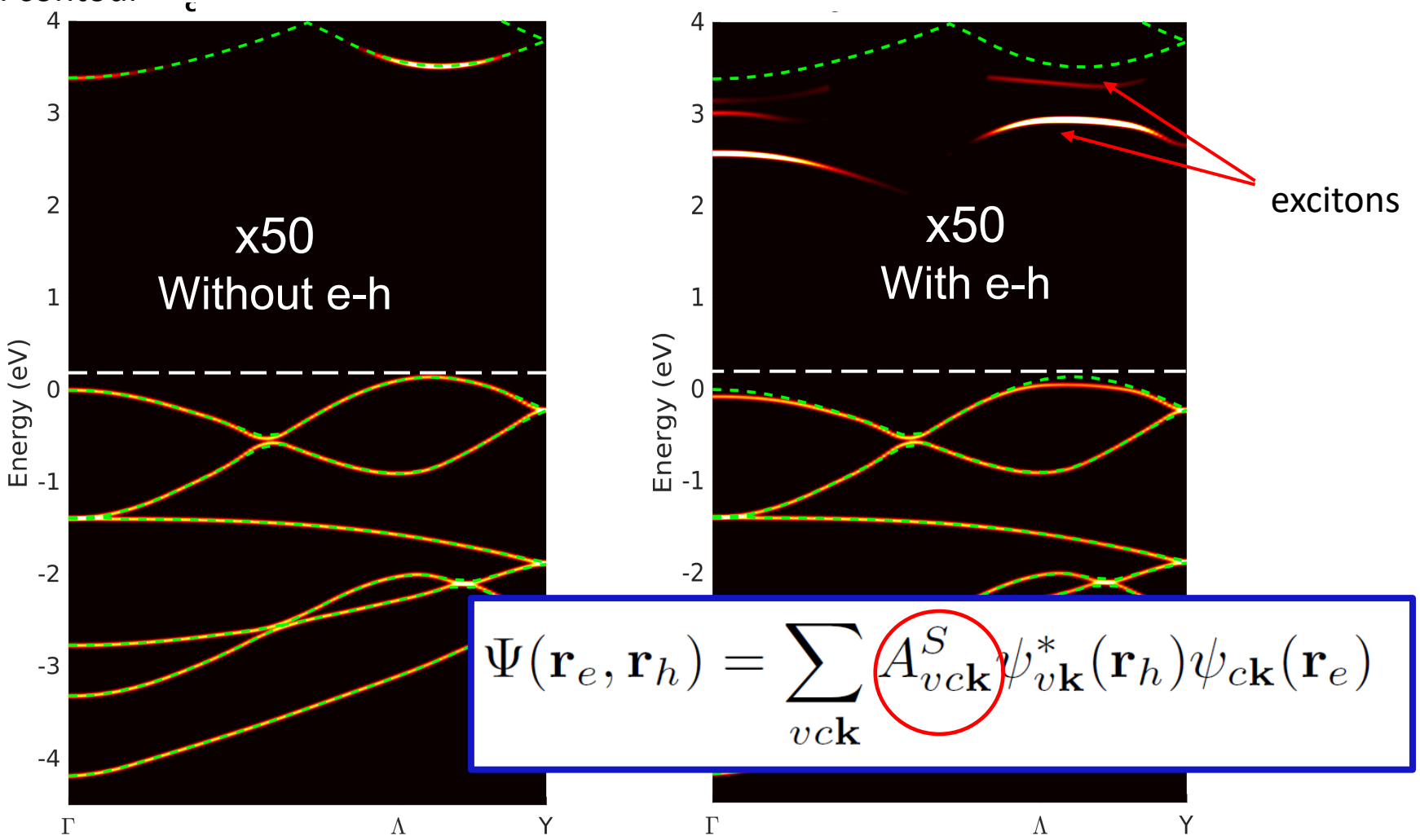
Optical-Field Driven Spectral Function: Monolayer GeS

Ab initio time-dependent GW on Keldysh contour

Pump: $\hbar\omega$ = 2.5 eV, τ = 5 fs,
350 μJ/cm^2
Probe: τ = 100 fs
Delay time: 5 fs

- Two series of excitons observed.
- Direct read out of excitation energies & k-space distribution of hole of exciton (exciton wfn)
- QP band renormalization at larger pump field.

J. K. Freericks, H. R. Krishnamurthy, and Th. Pruschke, PRL 102, 136401 (2009)



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

Without e-h interaction

With e-h interaction

Chan, Qiu, da Jornada & Louie (2021)

Ab initio Electron-phonon coupling

Electron-phonon (*e*-ph) coupling plays a key role in many phenomena

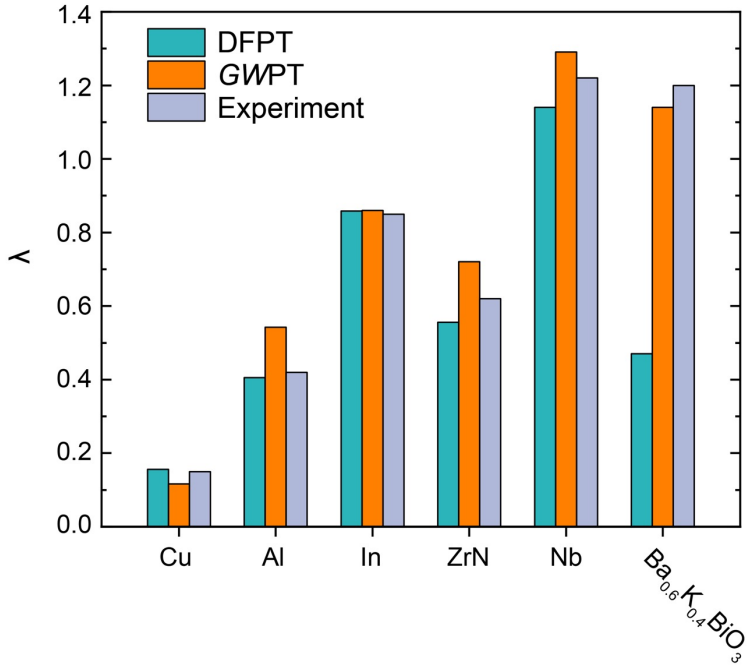
- Electrical and thermal transport
- Bardeen-Cooper-Schrieffer theory for superconductivity
- Optical spectra (phonon-assisted)
- Charge-density wave
- Hot carrier dynamics
- …

Electron-phonon Coupling in GW perturbation theory (GWPT)

- Standard DFT e-ph matrix elements fail in some materials.
- GW level e-ph matrix element: (GWPT)

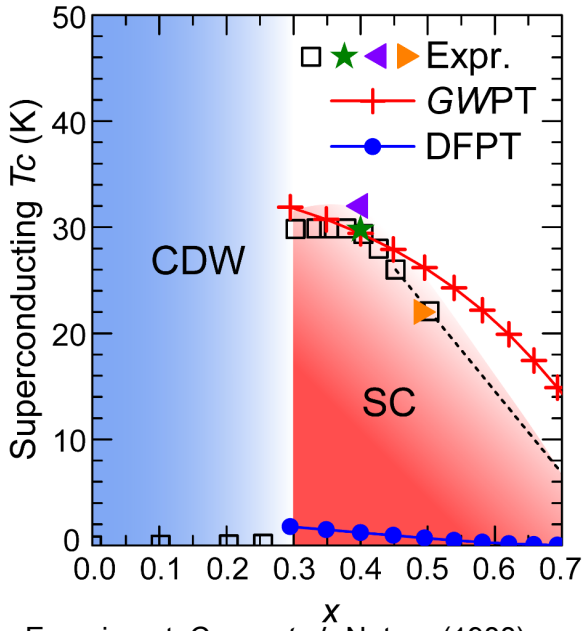
$$g^{GW}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathrm{DFT}}_{mn\nu}(\mathbf{k},\mathbf{q}) - \underbrace{\langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V_{\mathrm{xc}} | \psi_{n\mathbf{k}} \rangle}_{\text{LDA/GGA single-electron XC}} + \underbrace{\langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} \Sigma | \psi_{n\mathbf{k}} \rangle}_{\text{GW many-electron self-energy}}$$

- Correlation renormalization of *g* can be as large as a factor of 2!



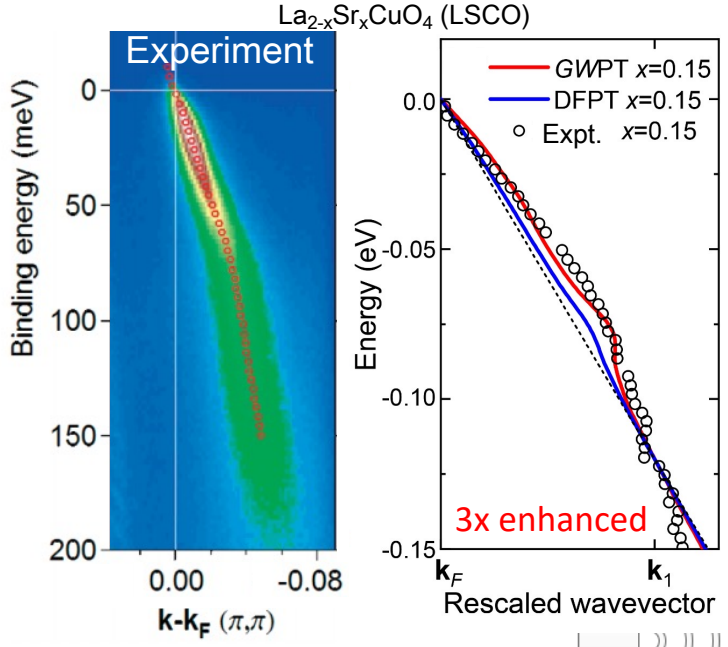
Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)
Li, Wu, Chan, Louie, PRL 126, 146401 (2021)

Superconductivity in $Ba_{1-x}K_xBiO_3$



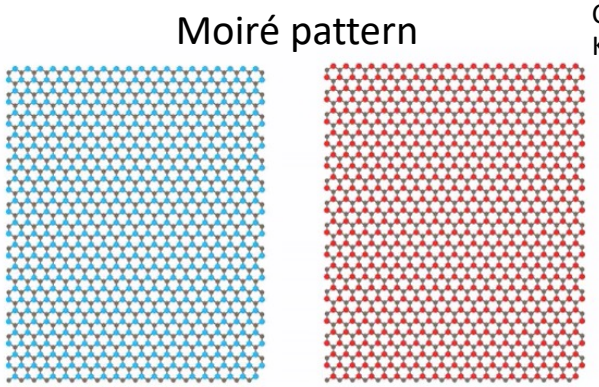
Experiment: Cava *et al.*, Nature (1988), Kumar *et al.*, PRL (1999), Pei *et al.*, PRB (1990), Wen *et al.*, PRL (2018)

Photoemission kink in cuprates



Experiment: Lanzara *et al.*, Nature (2001), Koralek *et al.*, (2006)

Moire Superlattices of Twisted Bilayer 2D Materials



Credit:
Kyle Seyler

Twisted bilayer TMDs

Many exciting new physical phenomena

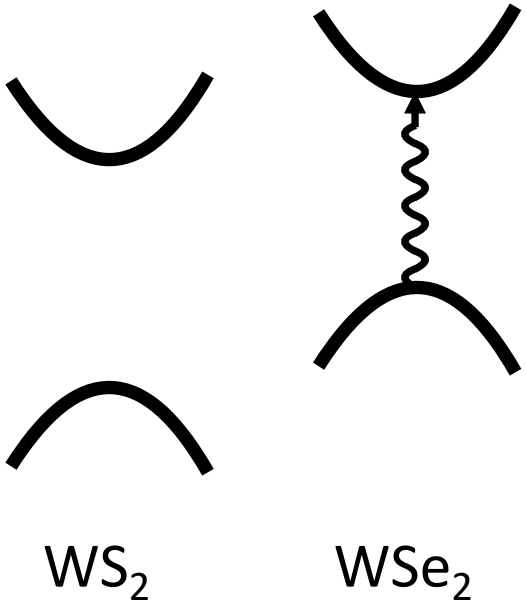
- Flat bands
- Unconventional superconductivity
- Correlated insulating states – Mott insulators, Wigner electron crystals…
- Novel moiré excitons in TMD heterobilayers

…

Excitons in twisted bilayer transition metal dichalcogenides (TMD)

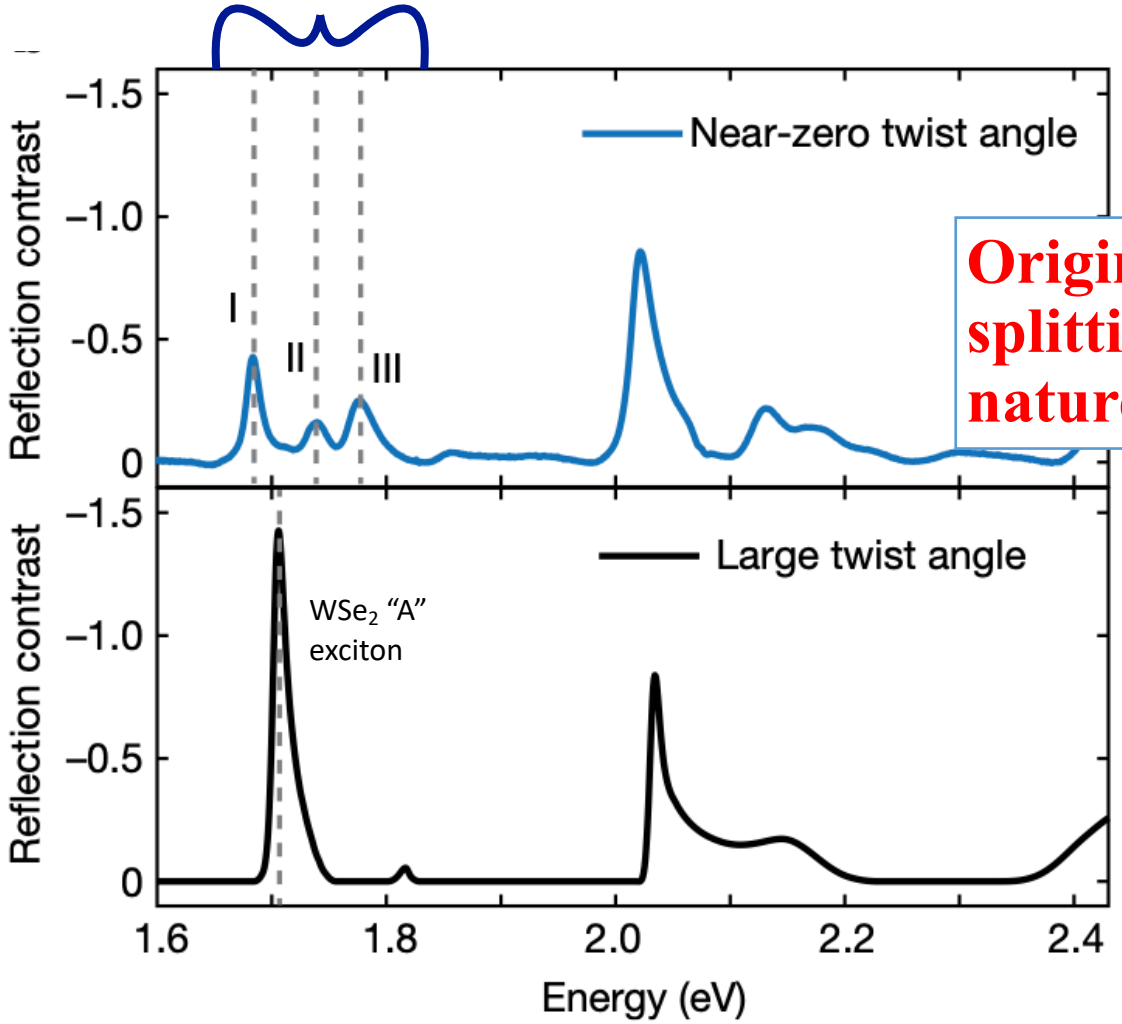
Intralayer moiré excitons in WSe_2/WS_2

Type II band alignment



*C. Jin, E. C. Regan, A. Yan,…, S.Tongay, A. Zettl and F. Wang, Nature, **567**, 76–80 (2019)*
Also, Y. Tang, L. Li, T. Li, …, A. H. MacDonald, J. Shan and K.F. Mak, Nature 579, 253 (2020)

WSe_2 intralayer excitons



Origin of these splittings and nature of excitons?

Early theoretical understanding of moiré intralayer excitons

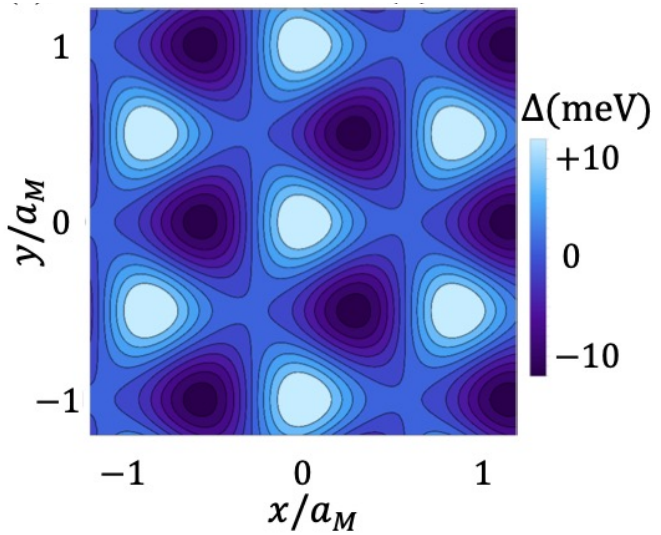
- Effective potential for excitons - modeled as the spatial variation in *intra*layer band gap as a function of changing bilayer stacking:

$$H_m = H_0 + \Delta(\boldsymbol{R})$$

Assumptions of continuum model:

- Neglects structural reconstruction of moiré superlattice
- Assumes internal structure of exciton as identical to that of pristine monolayer

Moiré, $\Delta(\boldsymbol{R})$



Moiré potential for excitons

F. Wu, T. Lovorn, and A. H. MacDonald, Phys. Rev. Lett. 118, 147401 (2017)

C. Jin, E. C. Regan, A. Yan,…, S.Tongay, A. Zettl and F. Wang, Nature, 567, 76–80 (2019)

K. Tran, G. Moody, F. Wu,…, L. Yang, A. H. MacDonald and X. Li, Nature 567, 71–75 (2019)

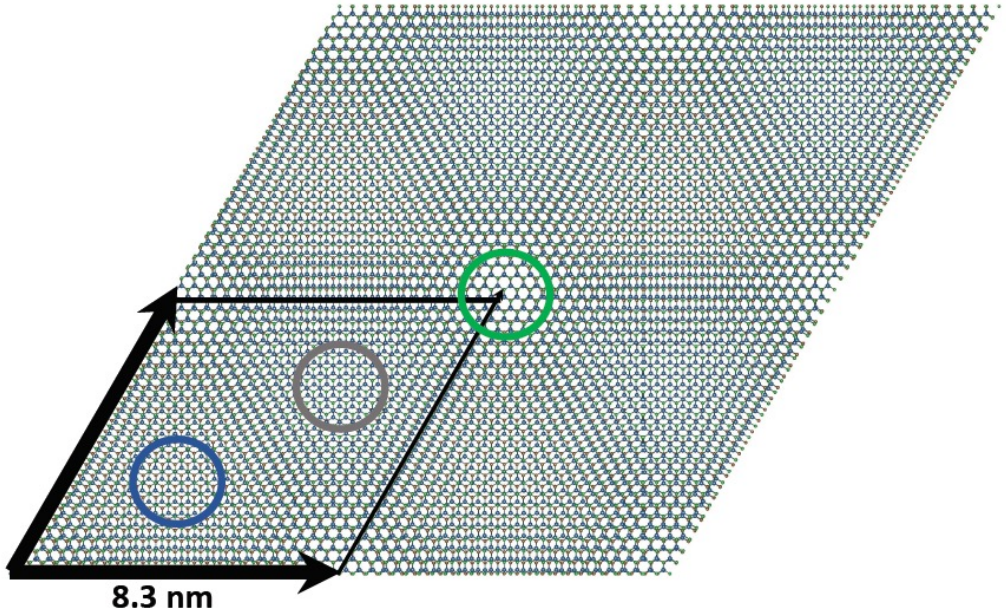
S. Brem, C. Linderälv, P. Erhart, and E. Malic, Nano Lett. 20, 12, 8534–8540 (2020)

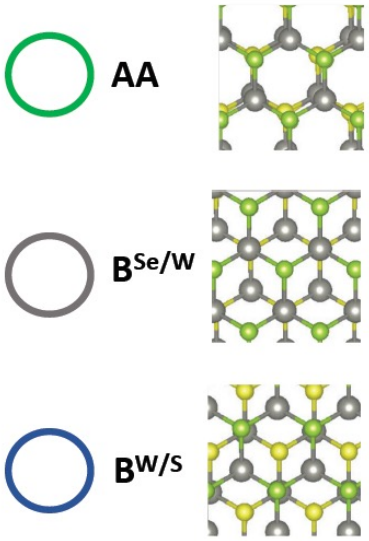
WSe_2/WS_2 moiré superlattice

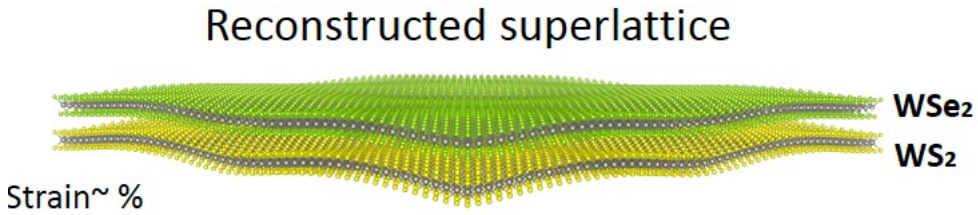
Moiré superlattice for 0° twist angle:

Lattice constants: WS_2 - 3.19 Å; WSe_2 - 3.32 Å

3903 atoms/supercell
~26,000 electrons





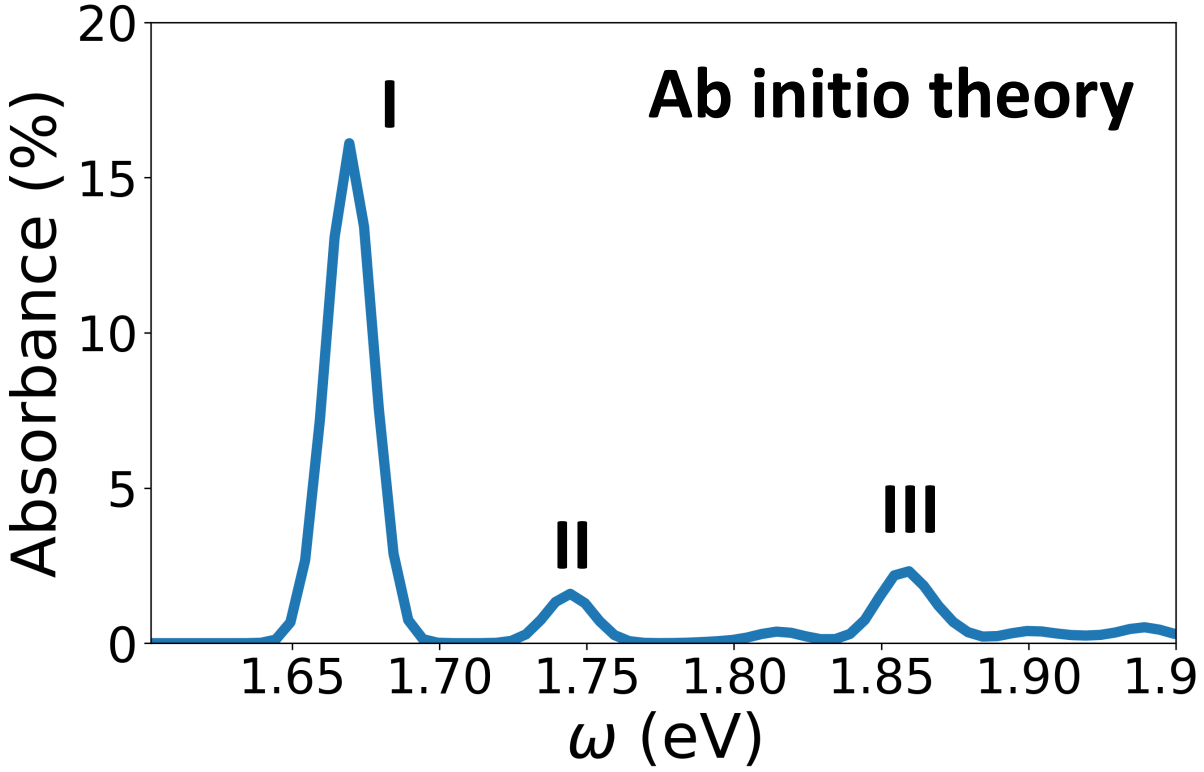


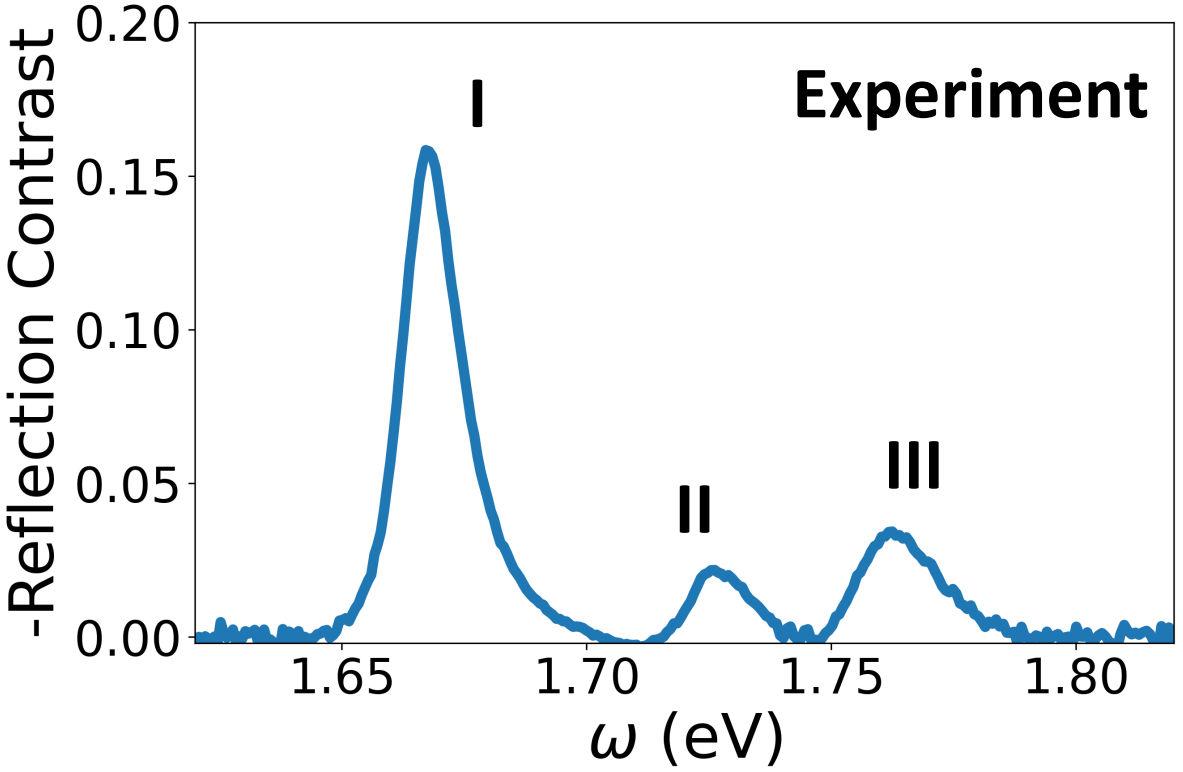
Flat, gapped moire subbands with different characters (e.g., different location of quasiparticles)

H. Li, S. Li*, M. H. Naik*, …, **S. G. Louie**, F. Wang and M. F. Crommie, Nature Materials (2021)*

Absorption spectrum of WSe2 intralayer moire excitons: Theory vs experiment

Ab initio GW-BSE calculation of moire superlattice (1875 atoms) via a new matrix projection formalism – the Pristine Unit-cell Matrix Projection (PUMP) method [1]

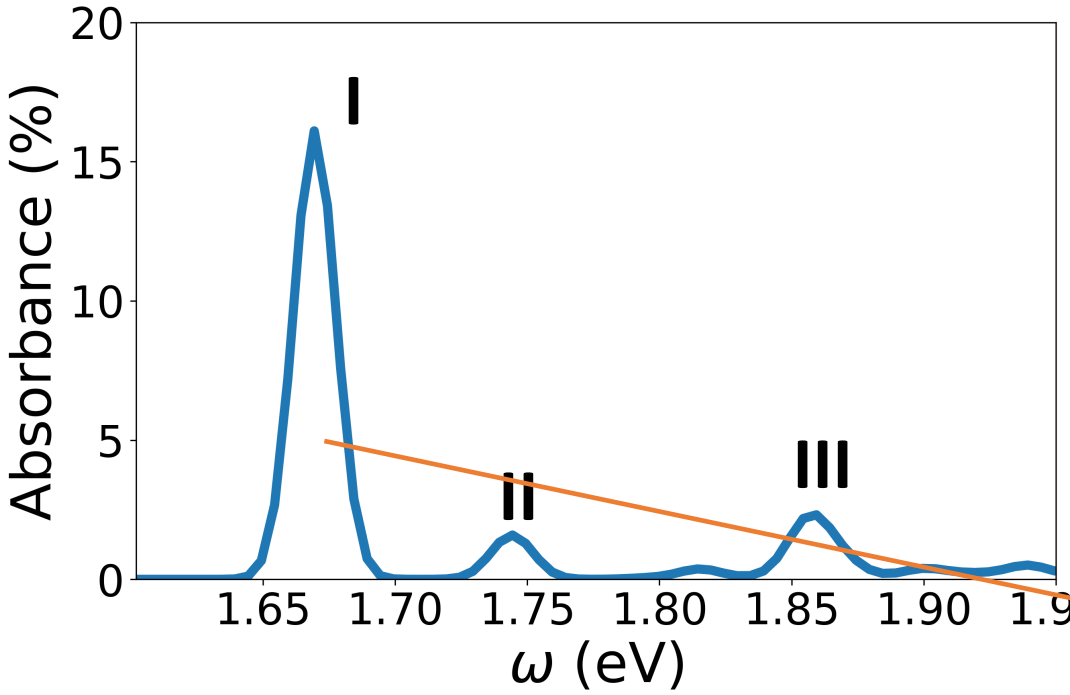




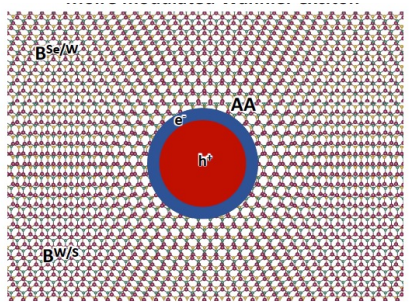
[1] M. H. Naik, E. C. Regan, Z. C. Zhang, … , F. Wang, and **S. G. Louie**, *Nature* **609**, 52 (2022)

*C. Jin, E. C. Regan, A. Yan,…, S.Tongay, A. Zettl and F. Wang, Nature, **567**, 76–80 (2019)*

Nature of intralayer excitons in the moiré superlattice



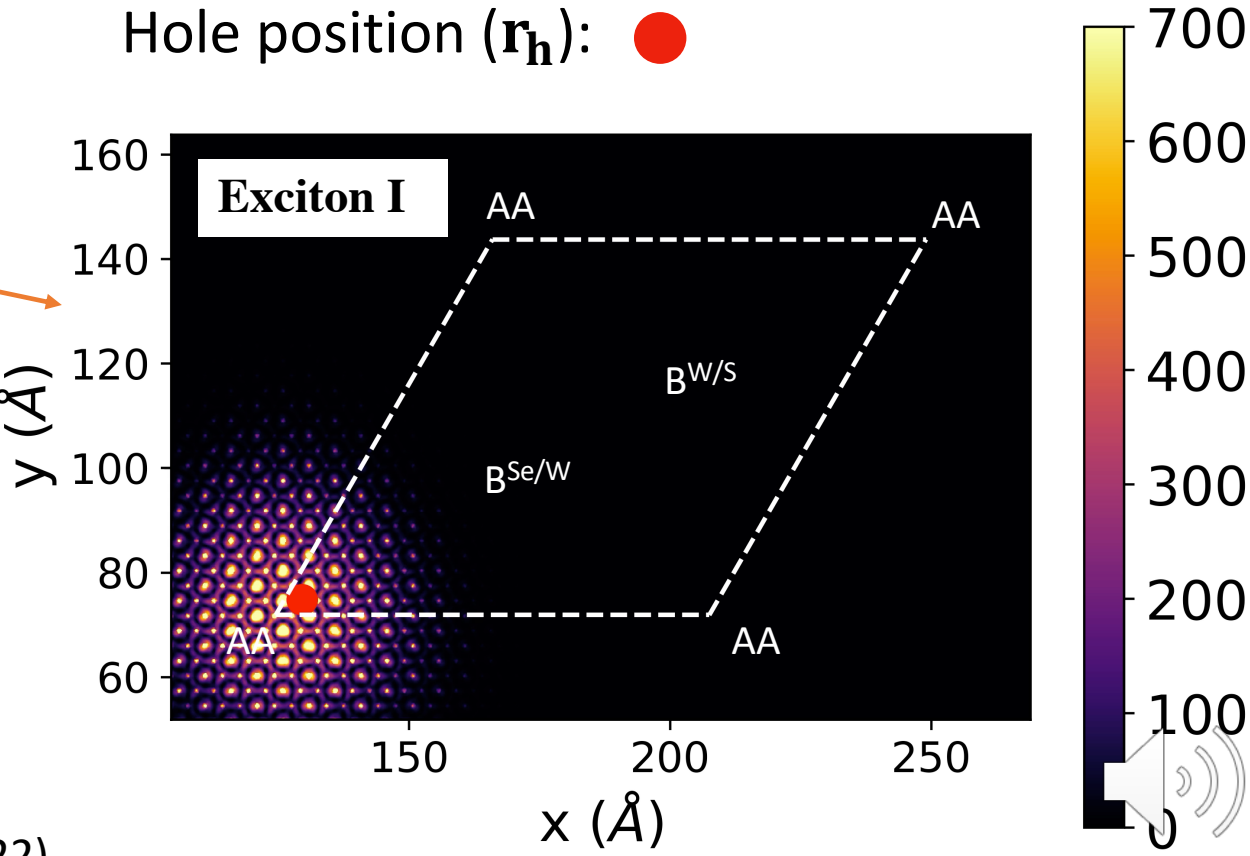
Modulated Wannier exciton



Exciton wave function:

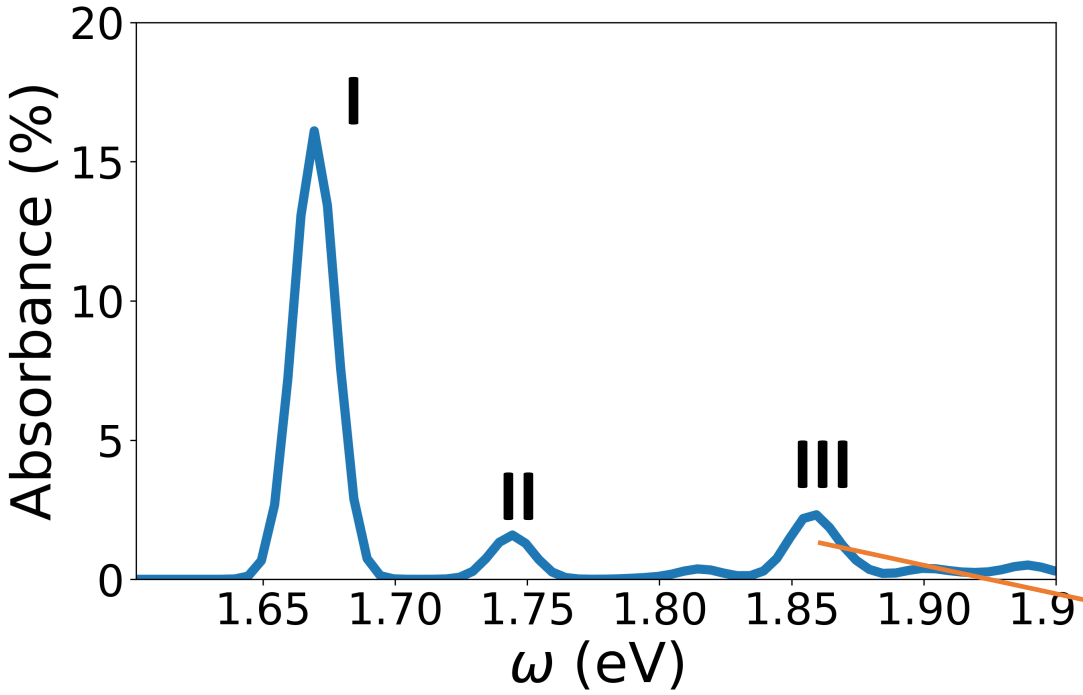
$$\chi_S(\mathbf{r_e}, \mathbf{r_h}) = \sum_{vc\mathbf{k}} A^S_{cv\mathbf{k}} \psi_{v\mathbf{k}}(\mathbf{r}) \psi^*_{v\mathbf{k}}(\mathbf{r_h})$$

Hole position ($\mathbf{r_h}$):



Naik, Regan, Zhang, … , Wang, and **Louie**, *Nature* **609**, 52 (2022)

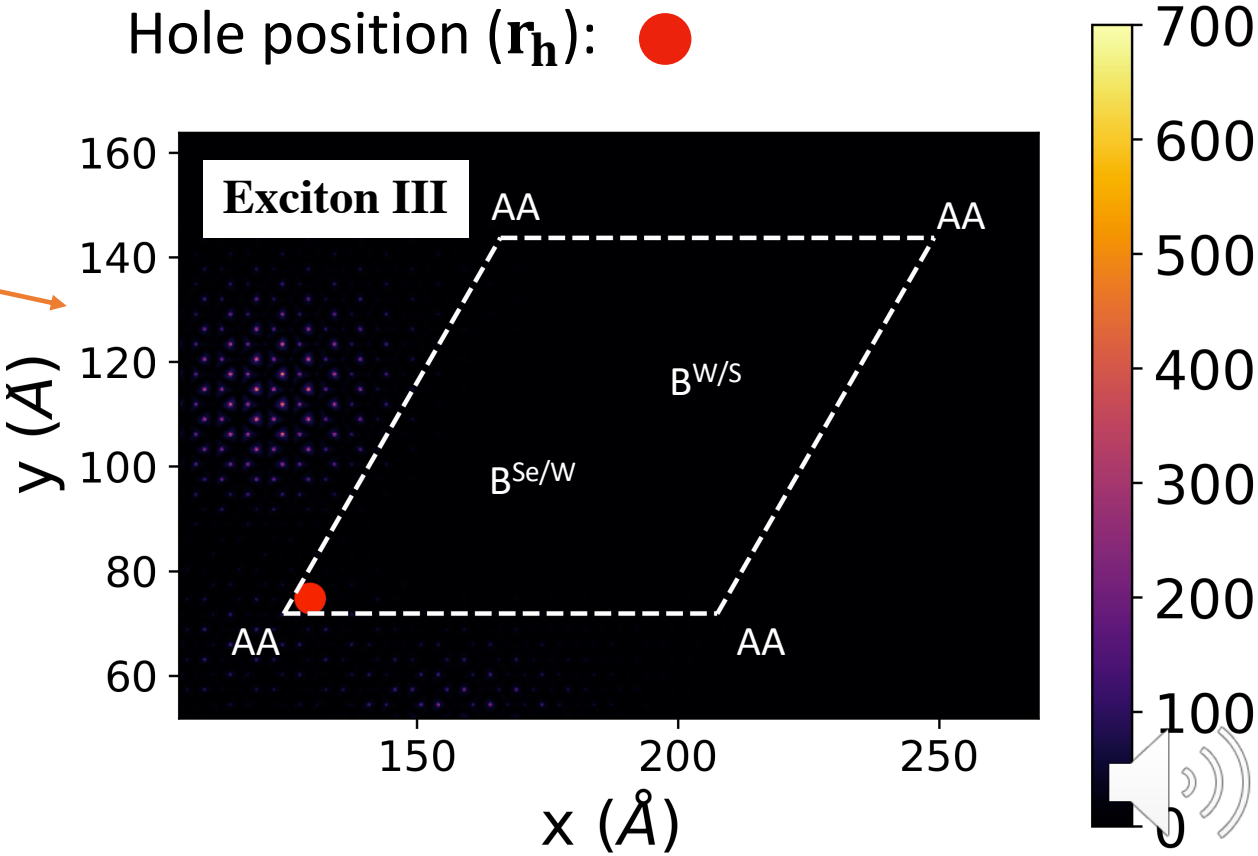
Nature of intralayer excitons in the moiré superlattice



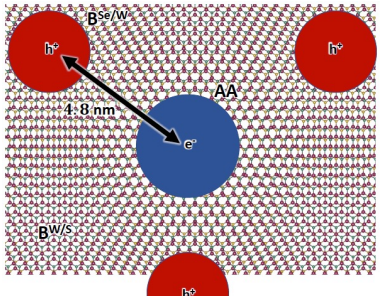
Exciton wave function:

$$\chi_S(\mathbf{r_e}, \mathbf{r_h}) = \sum_{vc\mathbf{k}} A^S_{cv\mathbf{k}} \psi_{v\mathbf{k}}(\mathbf{r}) \psi^*_{v\mathbf{k}}(\mathbf{r_h})$$

Hole position ($\mathbf{r_h}$): ●



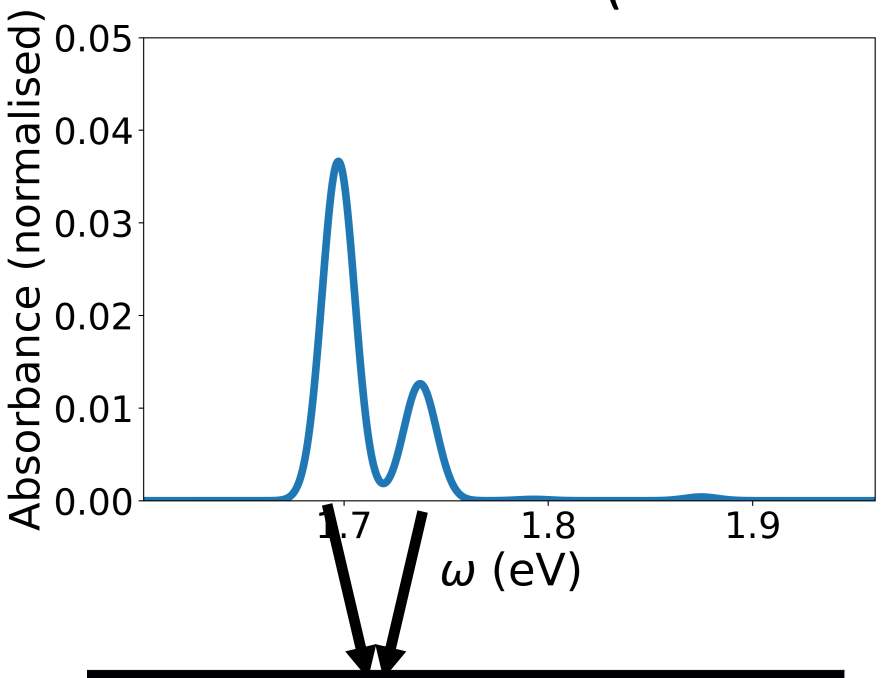
Novel Charge-transfer exciton
(Very large radius -- 5 nm)



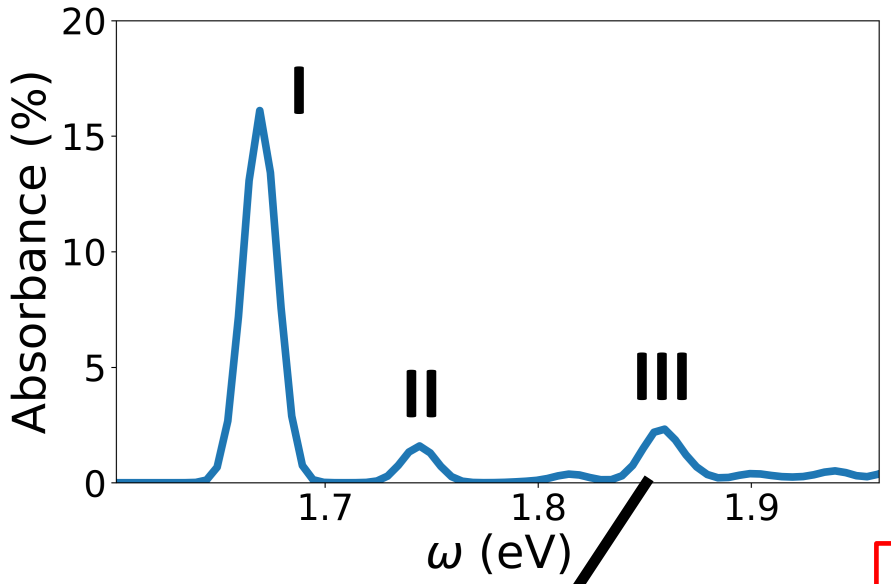
Naik, Regan, Zhang, … , Wang, and Louie, *Nature* **609**, 52 (2022)

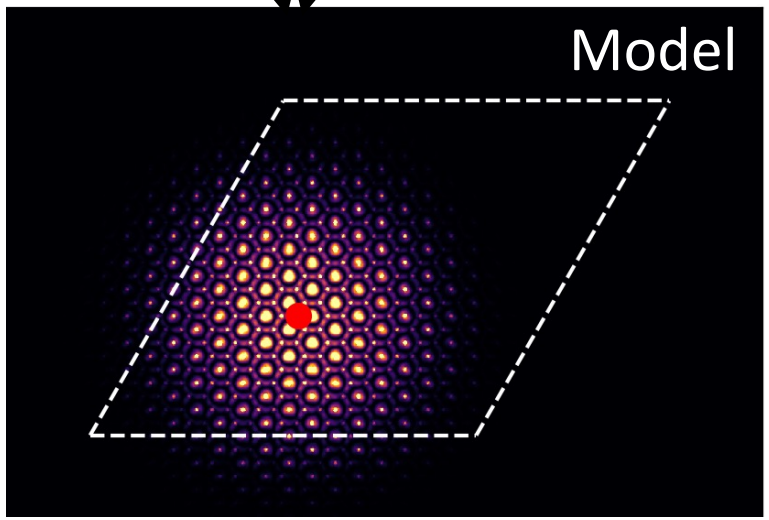
Continuum model vs. ab initio

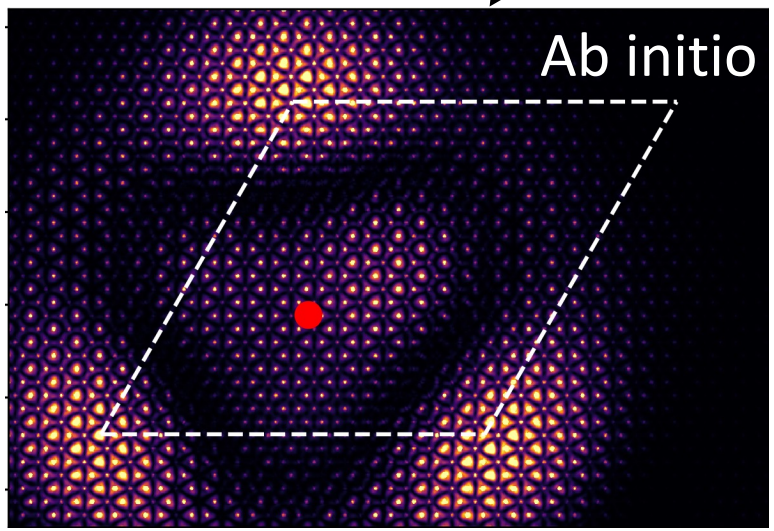
Continuum Model (with strains)



Ab initio GW-BSE







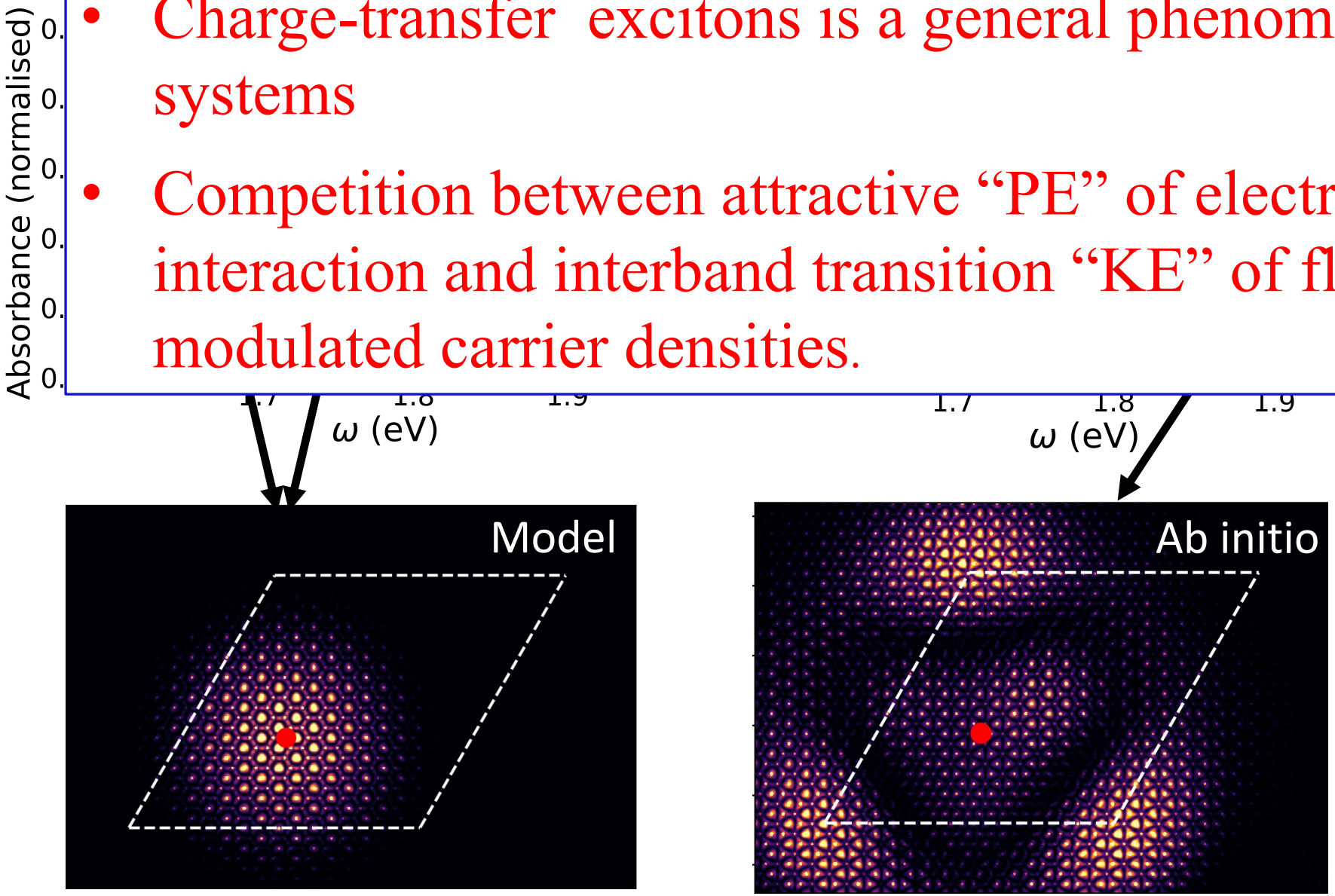
Naik, Regan, Zhang, … , Wang, and Louie, *Nature* **609**, 52 (2022)

Experimental signatures of the nature of moiré excitons:

- Change in absorption spectrum due to doping of electrons or holes to specific stacking sites.
- Exciton III should have a **enhanced** diamagnetic shift as compared to excit I !

Continuum model vs. ab initio

- Charge-transfer excitons is a general phenomenon in moire systems
- Competition between attractive "PE" of electron-hole interaction and interband transition "KE" of flat bands with modulated carrier densities.



Experimental signatures of the nature of moiré excitons:

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Few take-home messages

- Many-body interactions are centrally important in materials properties and phenomena.

- Treatment of interaction effects at the appropriate level is essential, especially for excited states and lower dimensional systems.

- Many-body perturbation theory with screened Coulomb interaction to *n*-particle Green's functions has proven to be a powerful & versatile approach for *ab initio* understanding and prediction of a variety of spectroscopic properties and field-driven, time-dependent phenomena in real materials.

Thank you!