GW, GW-BSE, and beyond: Quasiparticle excitations, optical responses, and field-driven time-dependent phenomena

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School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows
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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 $\Longleftrightarrow$ 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 – correlated 3- or 4-particle excitations, field-driven time-dependent processes, non-linear spectroscopies, excited-state dynamics, etc. – remain to be addressed efficiently by ab initio methods & public domain software, including relevant & accurate many-electron interactions.

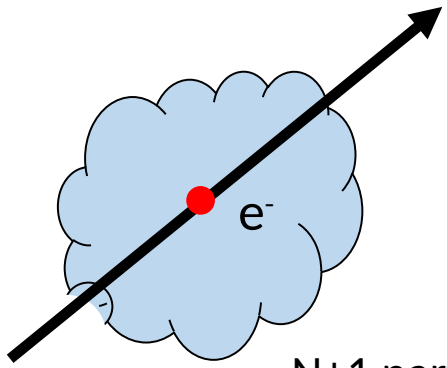
Study of Material Properties – A N-Particle Quantum Problem

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

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

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

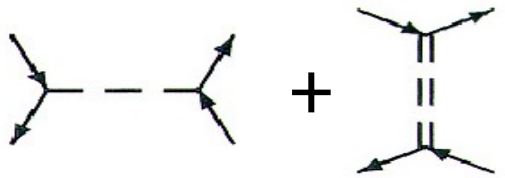
Electrons in Crystals

- **Interacting many-electron problem**

  - Need many-body techniques for electronic, transport and optical properties

  - Moderately correlated systems may be solved numerically from *first principles* using many-body perturbation theory (e.g., GW and GW-BSE approaches, and beyond)

1-particle excitations
(N+1 particle problem)



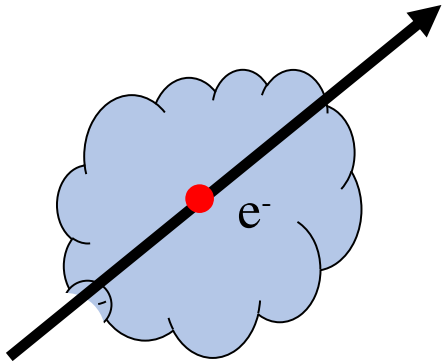
Optical excitations
(N+2 particle problem)

Outline of talk

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

Ab initio Studies of Quasiparticle Excitations in Tunneling and ARPES

1-particle excitations
(N+1 particle problem)



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

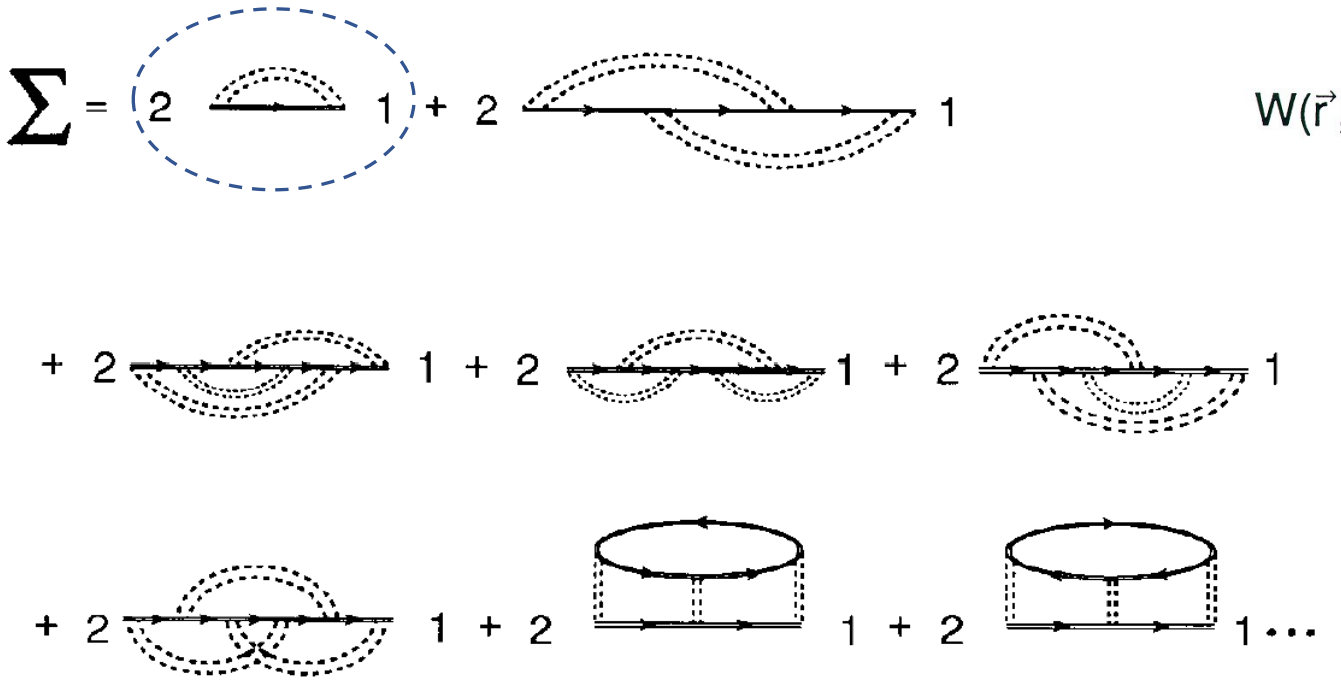
- renormalizes energy dispersion
- gives rise to finite lifetime
- satellite structures

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

Σ $\approx$ $\Sigma_{e\text{-}e}$ + $\Sigma_{e\text{-}ph}$ + …

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

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



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

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

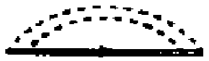
- Density-functional theory:

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

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)

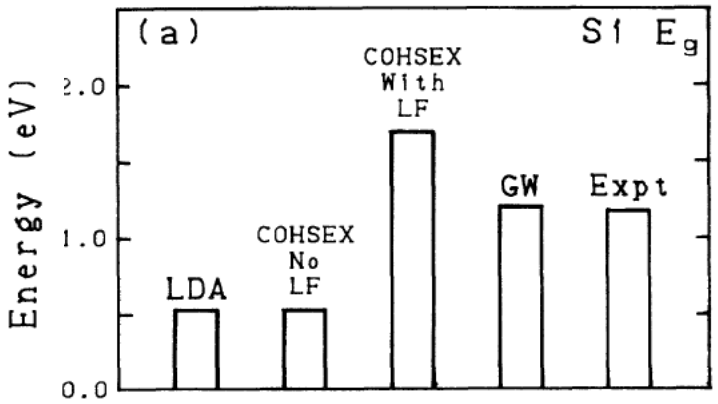
$$\varepsilon^{-1}(\vec{r}',\vec{r},\omega) \text{ or } \varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)$$

(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
…

Band gap of Si



Hybertsen and Louie (PRL 1985)

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

- Electron-hole interaction kernel:

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

$\delta V_{\text{Coul}}/\delta G_1 \rightarrow v$

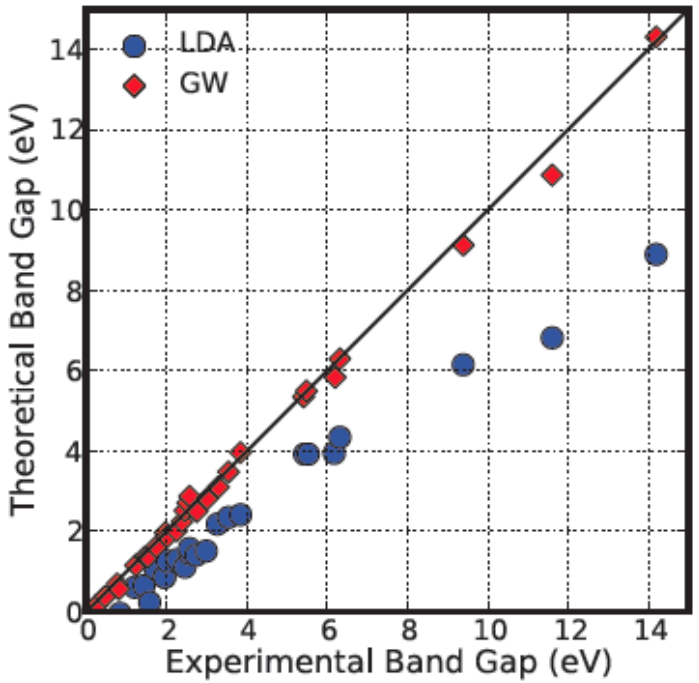
$\delta\Sigma/\delta G_1 \rightarrow -W$

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

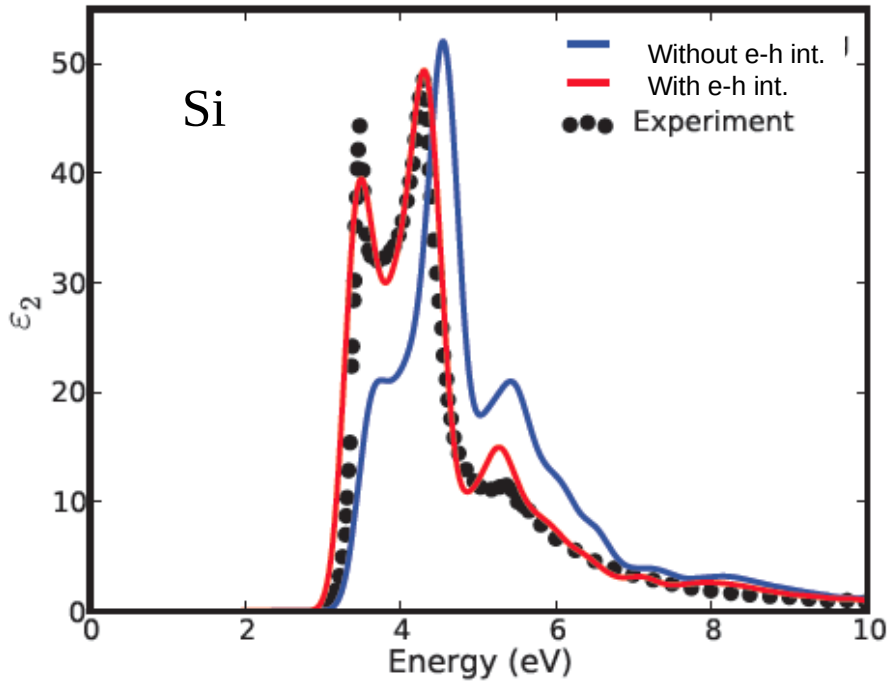
- K - large, nonHermitian matrix with very fine **k** sampling
- K can have dimensions as large as ~10^6

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



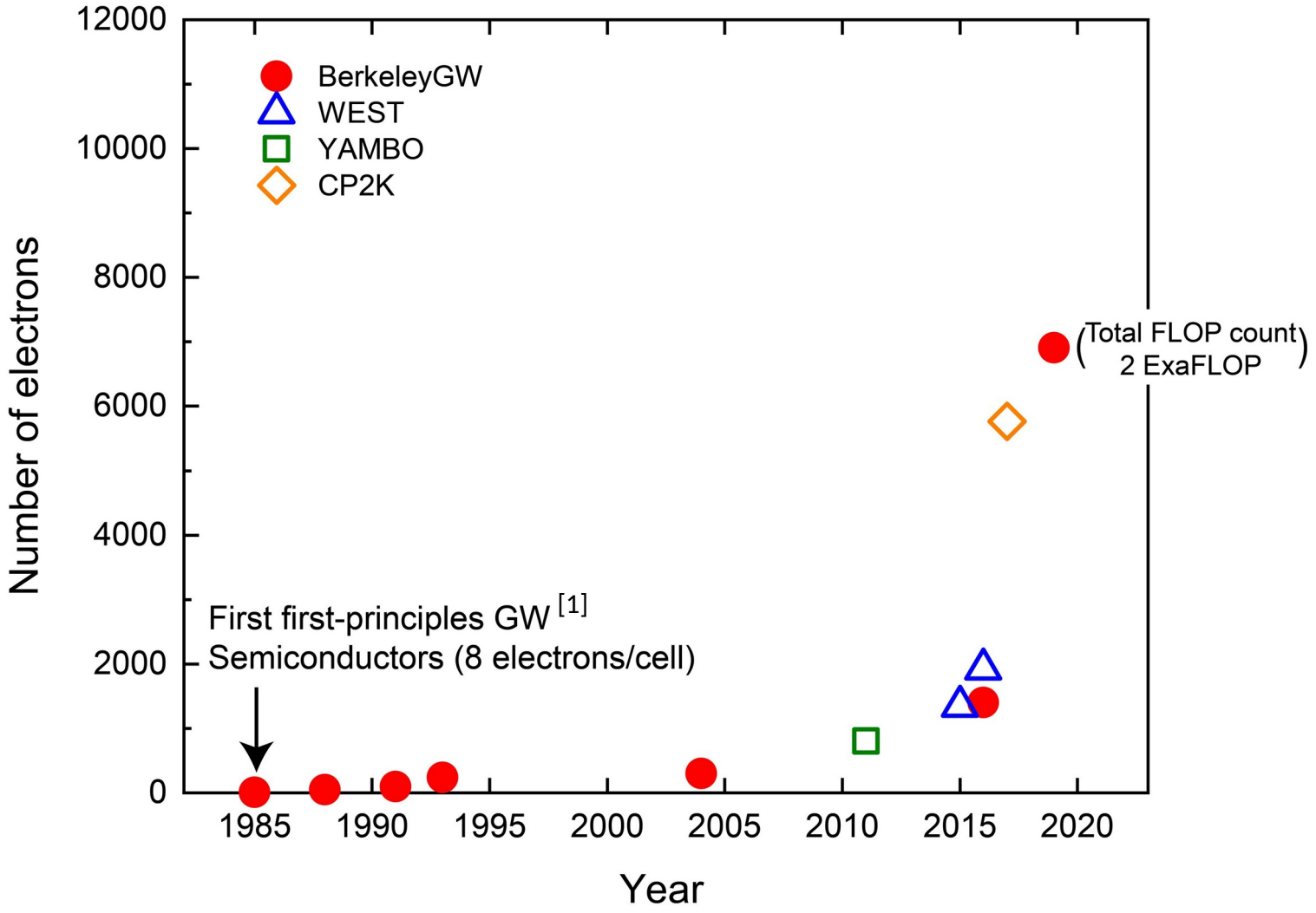
Quasiparticle Gap[1]



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).

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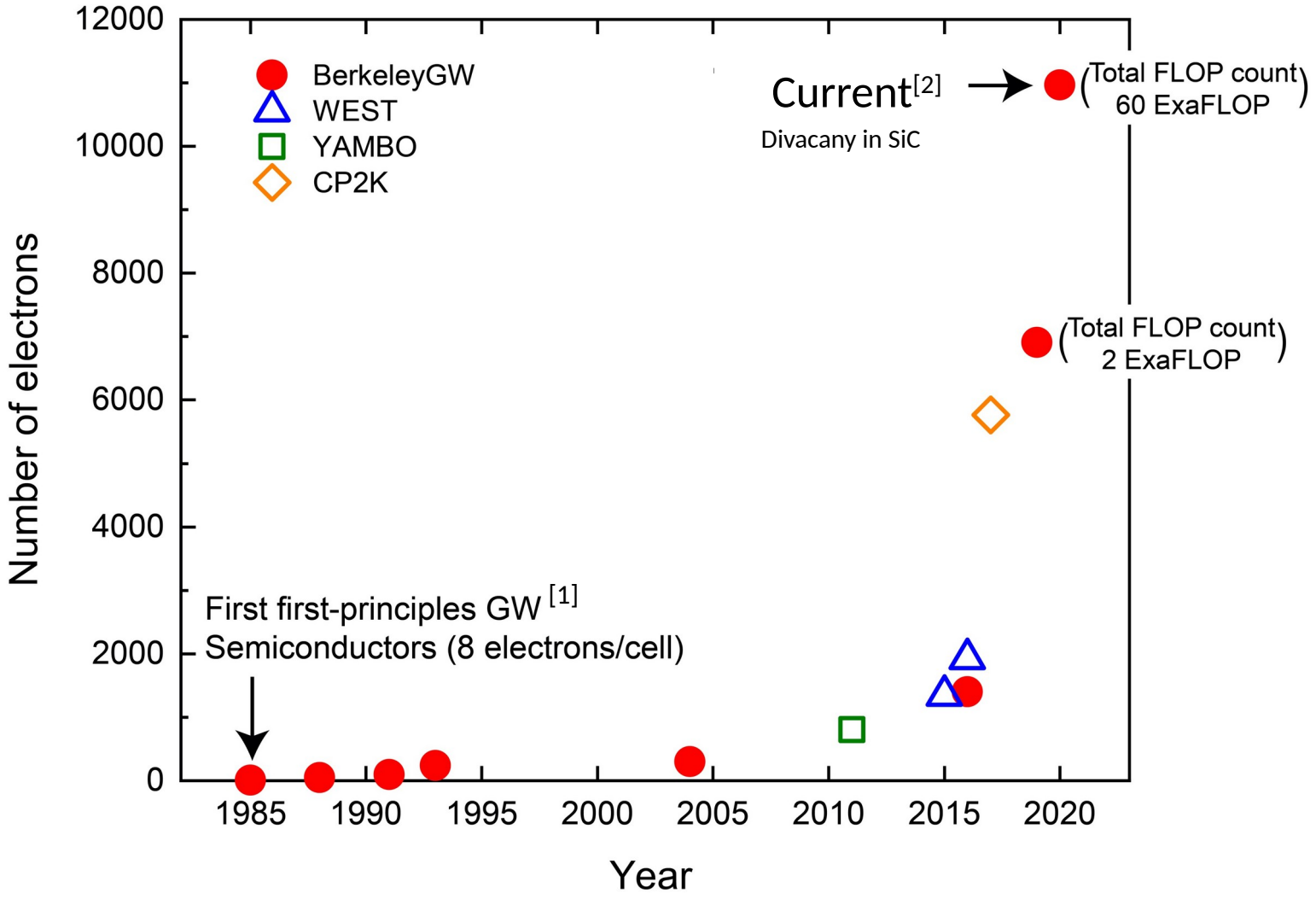
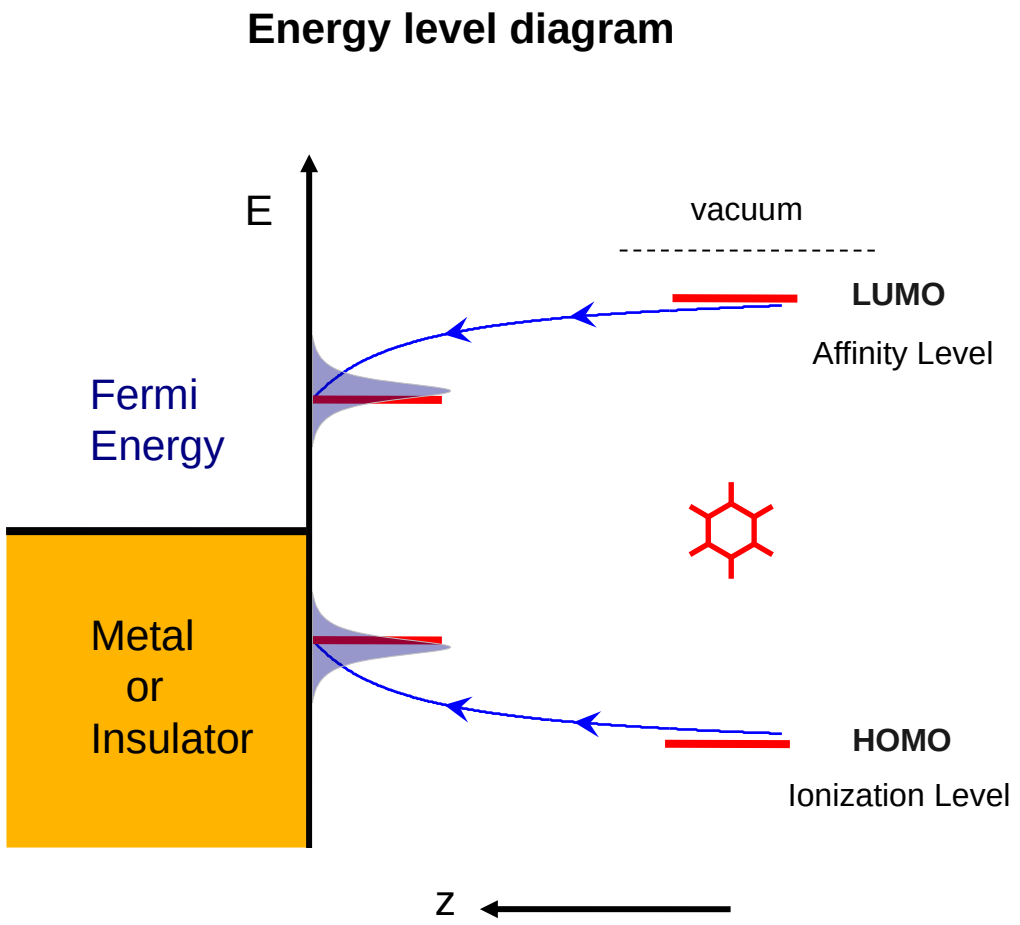


[1] Hybertsen and Louie, PRL 55, 1418 (1985).

[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

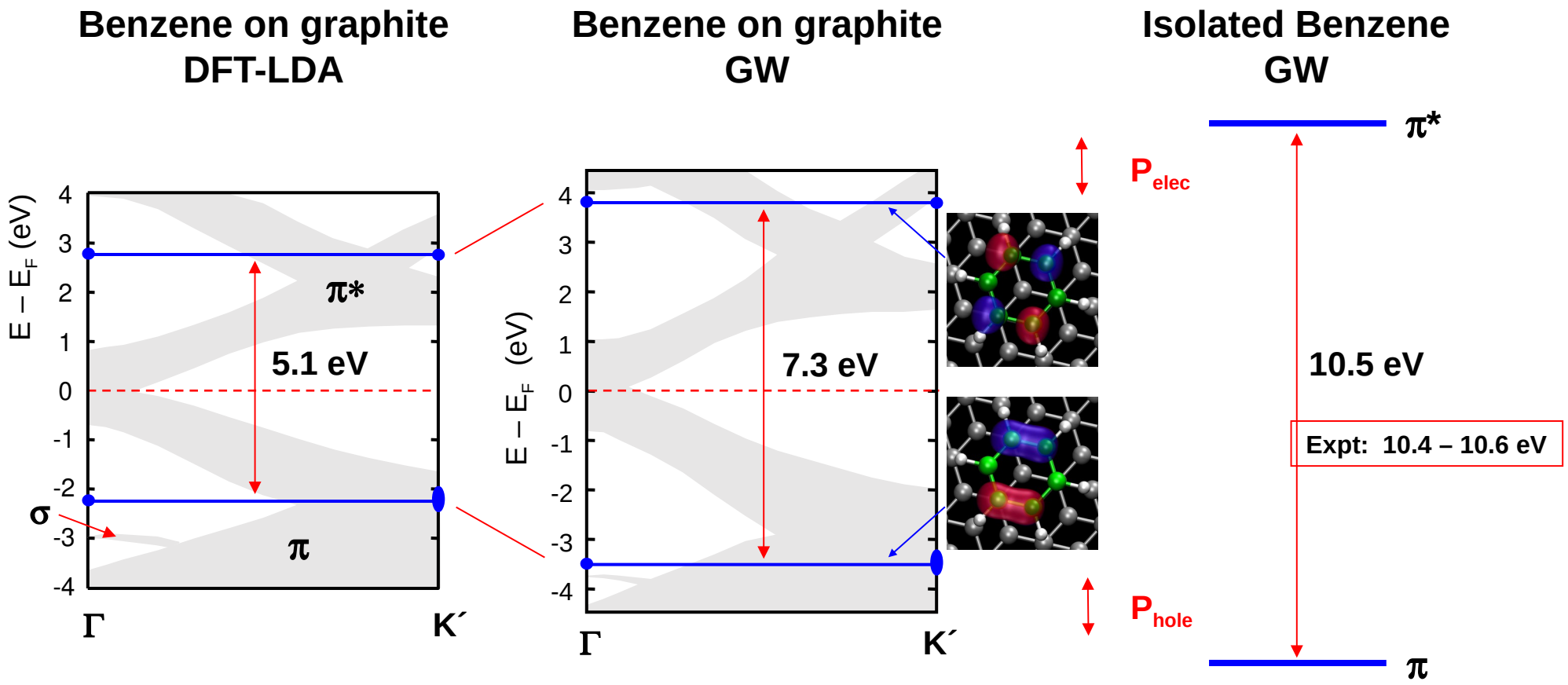
Quantum level alignment at interface – importance of nonlocal screening/correlations



Physical effects

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

Benzene orbital energies on graphite

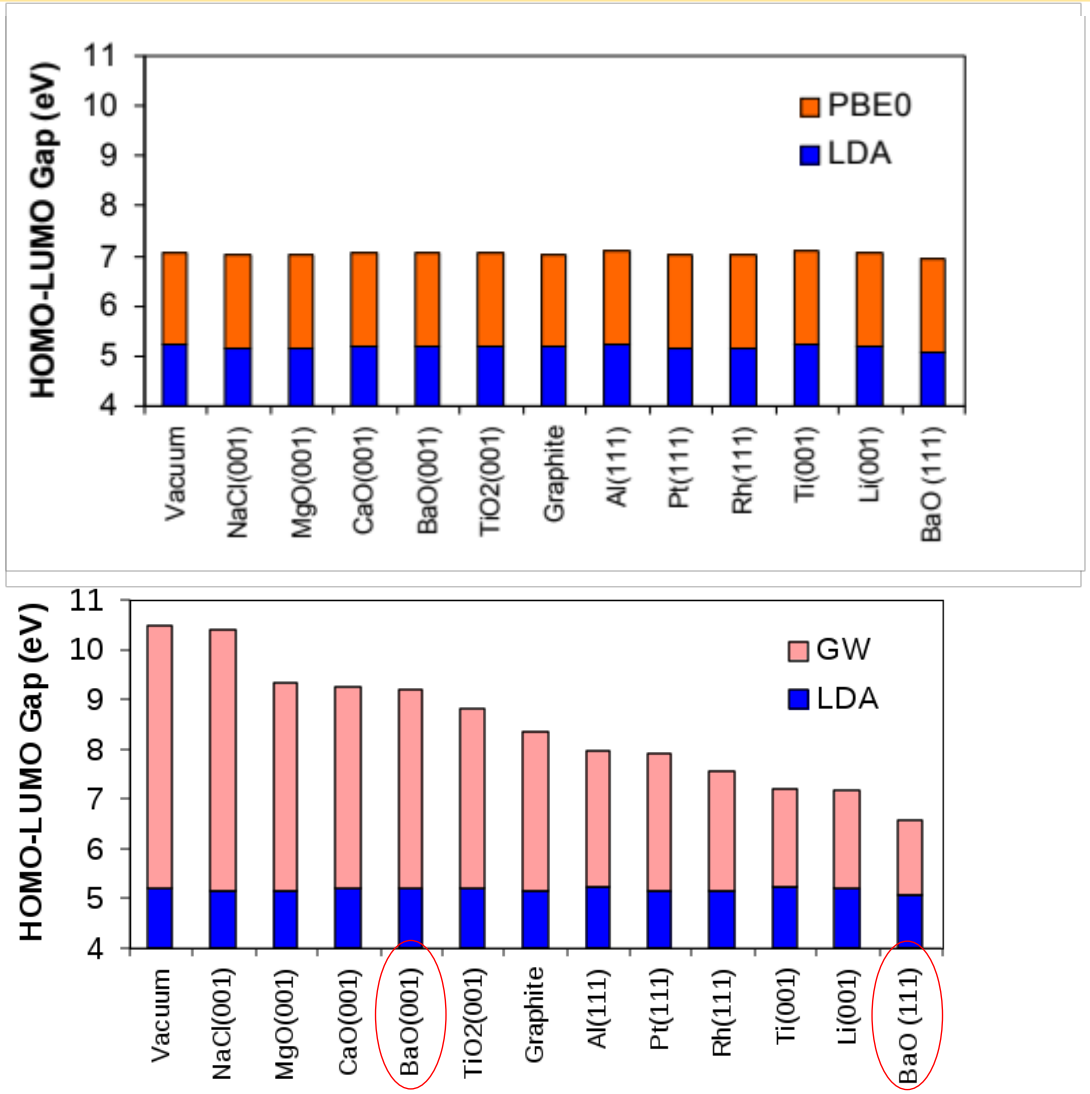


- DFT-LDA gap: ~2 eV error

- 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

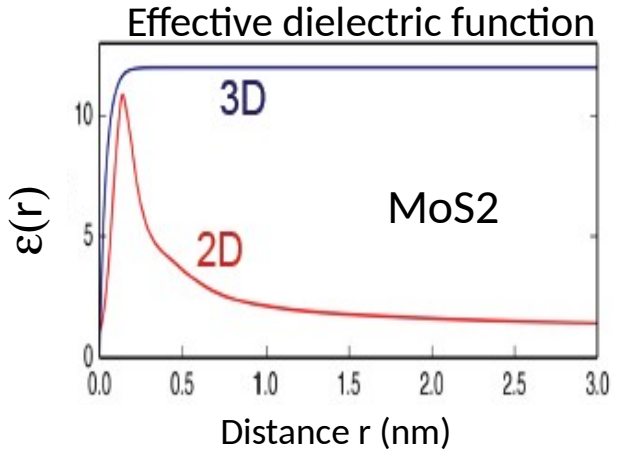


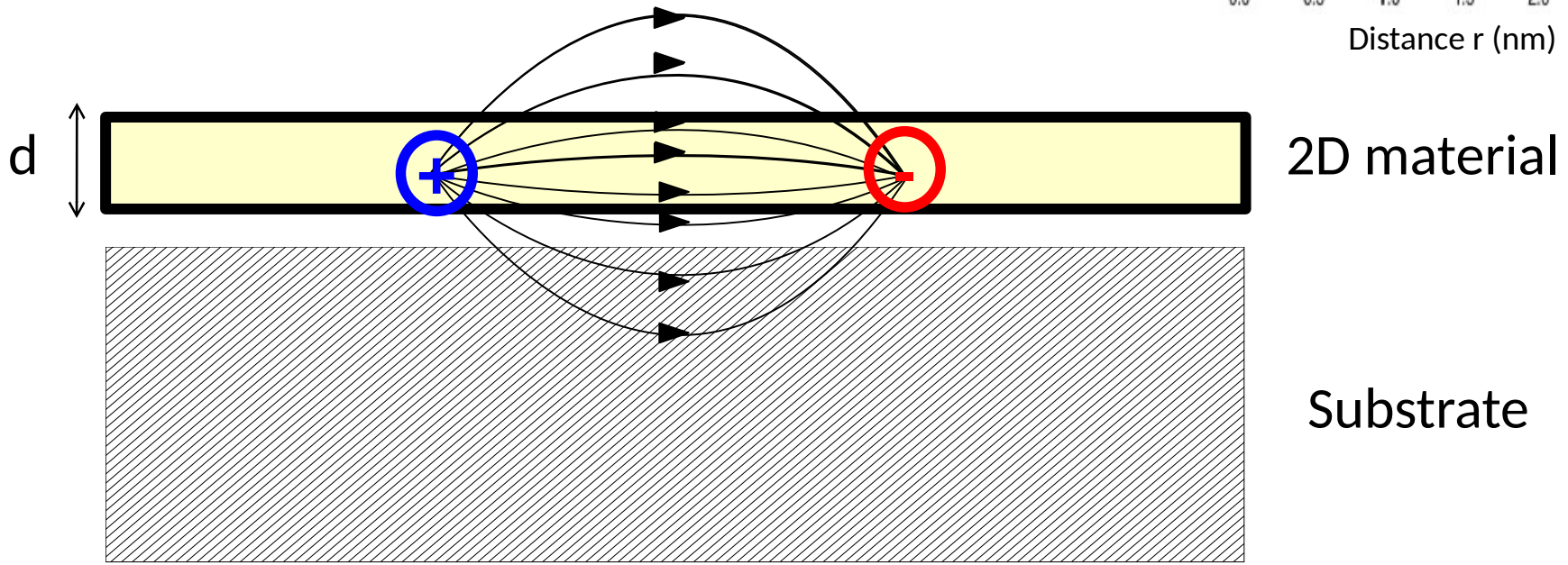
J. Garcia-Lastra, et al, PRB (2009)

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

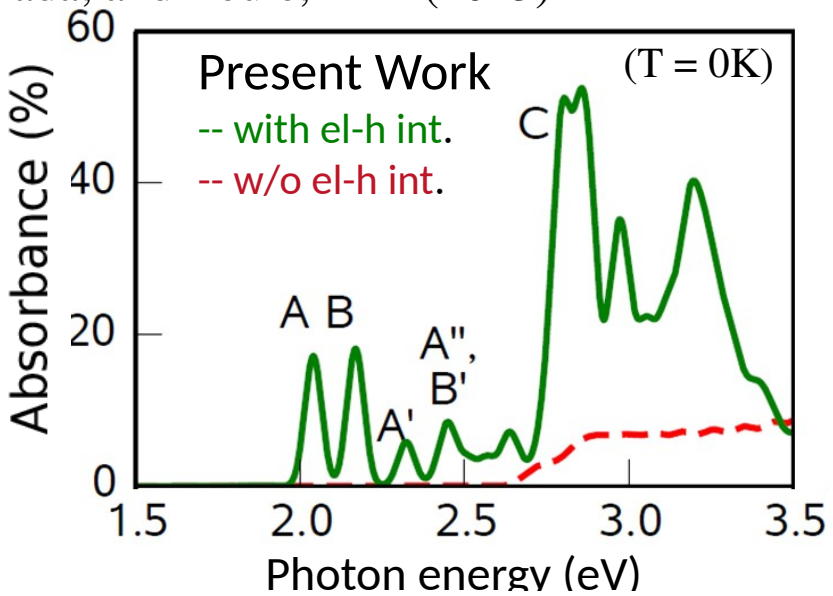


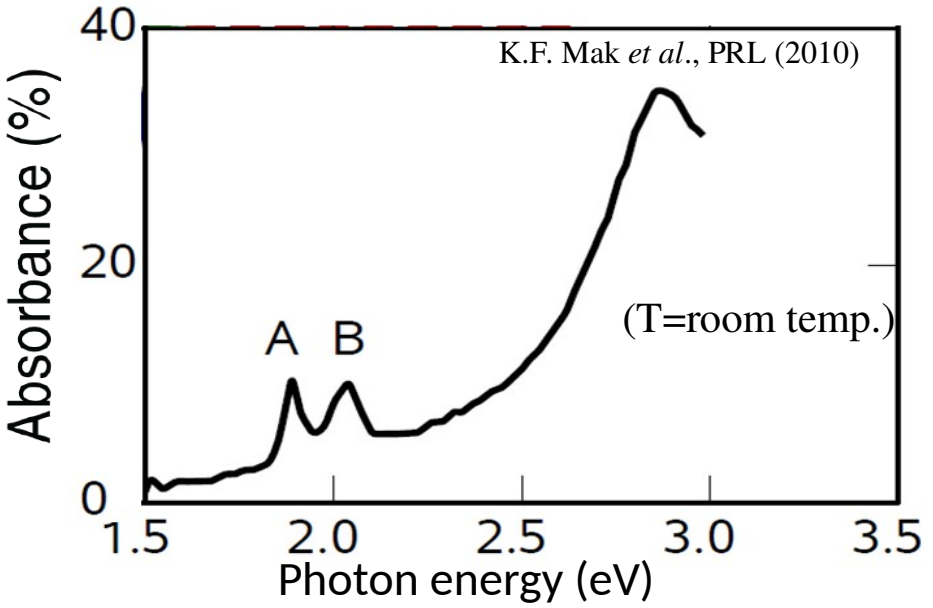


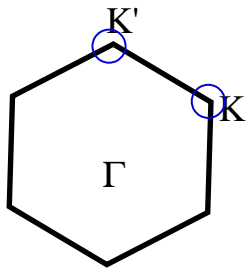
Substrate/environmental screening are important!

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

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

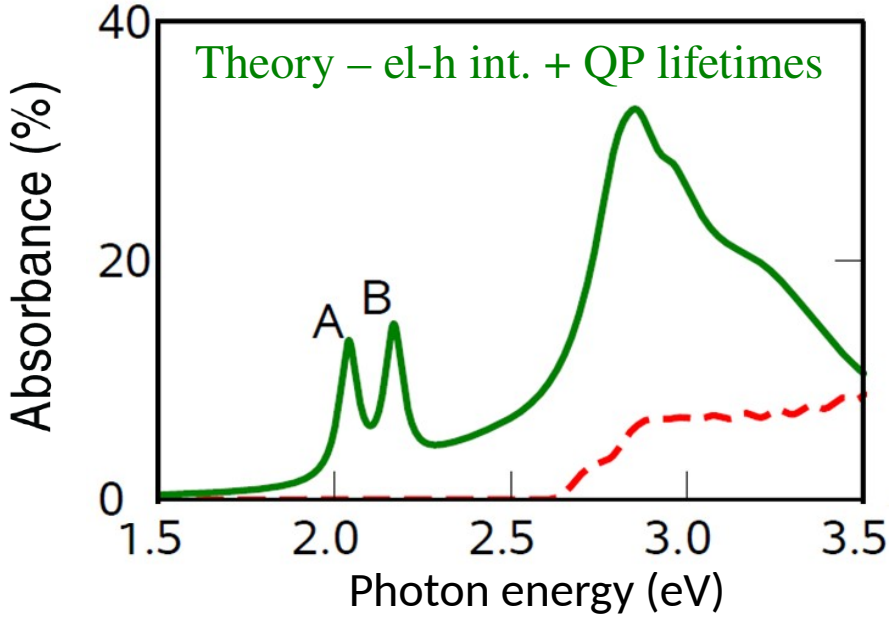




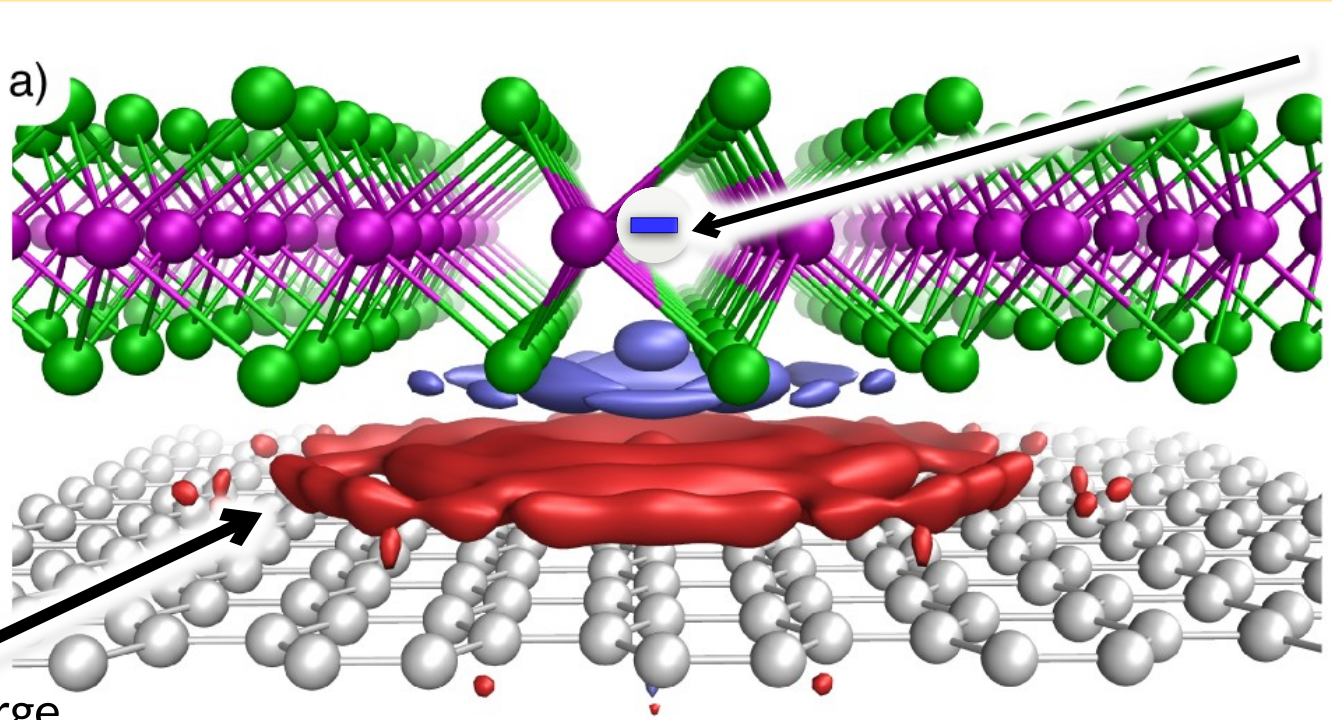


Absorbance per ½ nanometer of material at 2.0 eV :

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



Substrate Screening: Monolayer $MoSe_2$ on bilayer graphene

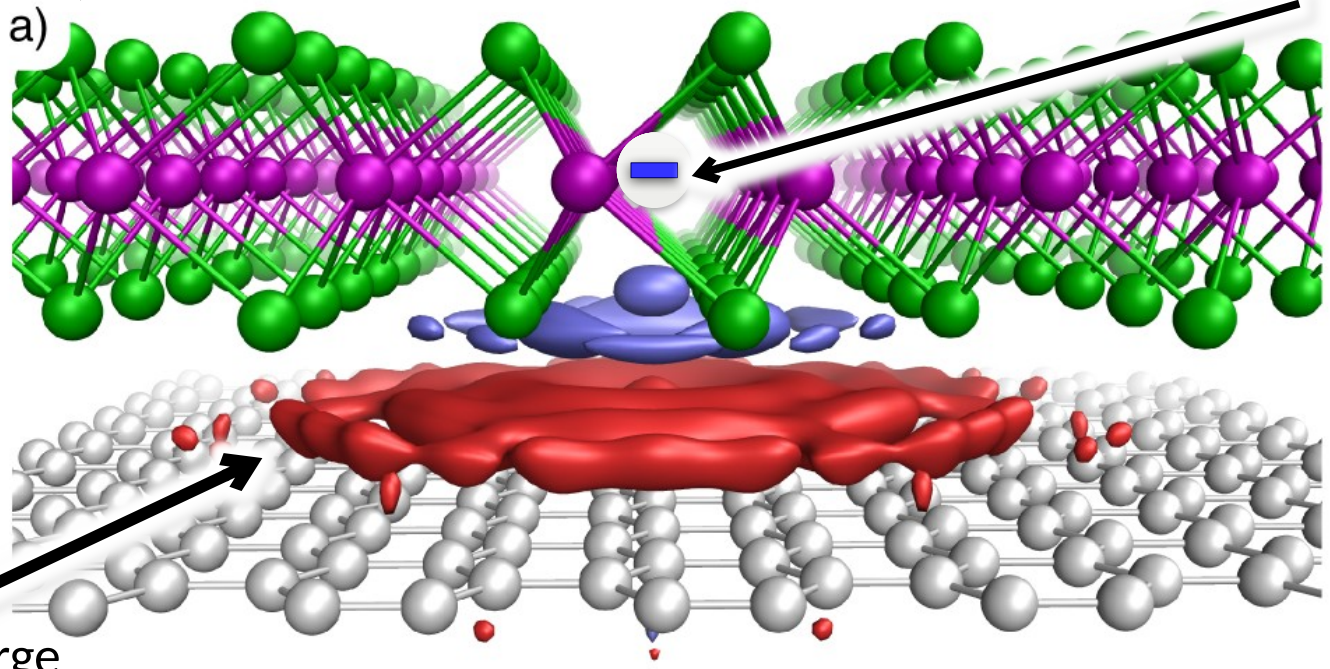


- Screening is nonlocal, frequency dependent
- Incorporate screening of *substrate* by via substrate dielectric matrix $\varepsilon_{Gz,Gz'}(\mathbf{q},\omega)$

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)

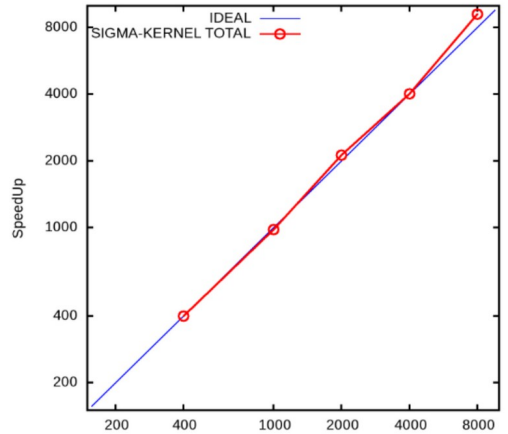
Current BerkeleyGW package - *www.berkeleygw.org*

General excited-state phenomena code that supports:

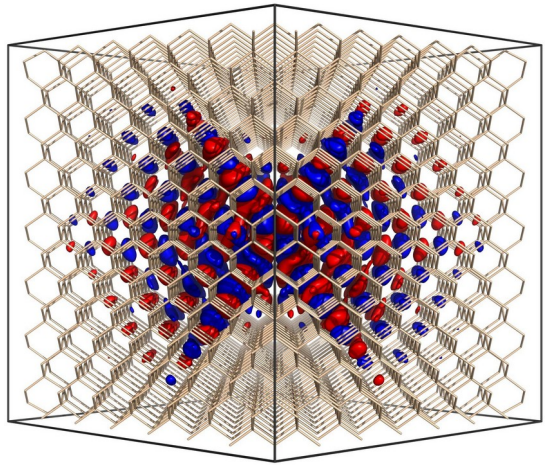
- GW & GW-BSE: 3D, 2D, 1D and molecular systems
- Insulating, metallic and semi-metallic systems
- Interface with a large set of DFT and other mean-field codes: PARATEC, Quantum Espresso, PARSEC, SIESTA, Octopus, ABINIT, RMGDFT, EPW, …
- Massively parallel with MPI, OpenMP and SIMD parallelism
- Linear 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!



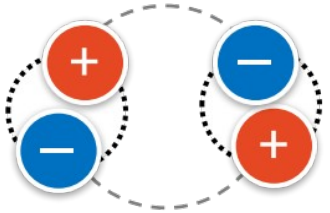
Non-equilibrium
and
beyond 1- & 2-particle excitations

New Phenomena ⟷ New *ab initio* formalisms

Beyond ab initio GW and GW-BSE

Correlated Higher-number-particle Excitations:

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



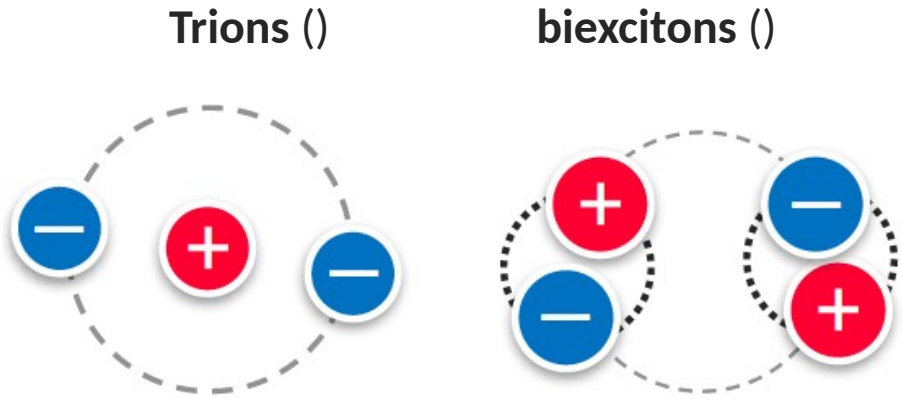
Time-dependent & High-field Phenomena

- 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

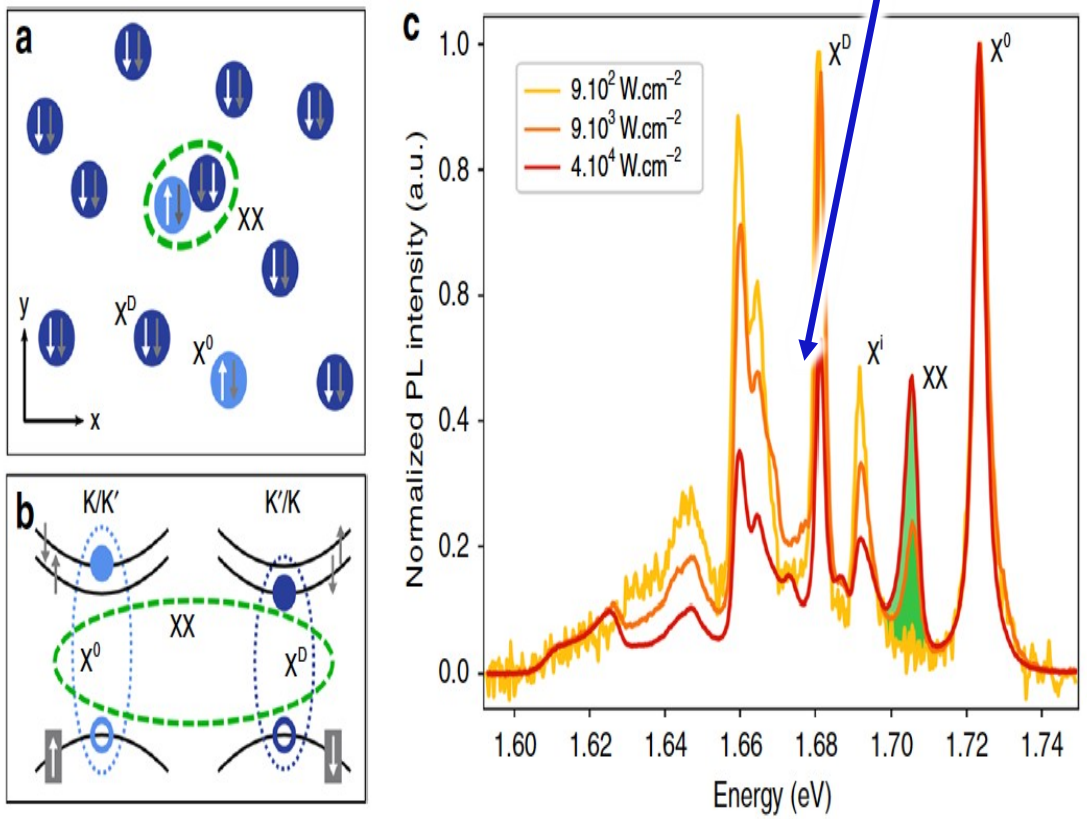
- Multi-particle excitations prominent in atomically thin 1D & 2D systems
- Example: biexcitons on monolayer WSe_2
- Trions & biexcitons - interacting 3- and 4-particle Green's functions



Other fundamental and practical interests:

- Exciton condensates/insulators
- Singlet fission in organic crystals

Experimental Photoluminescence

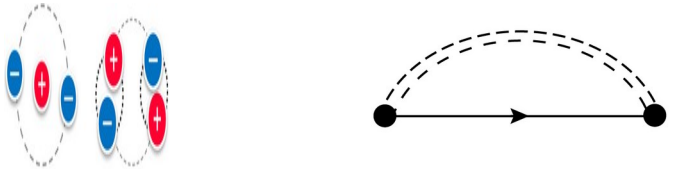


(Monolayer WSe2 encap. w/ hBN)

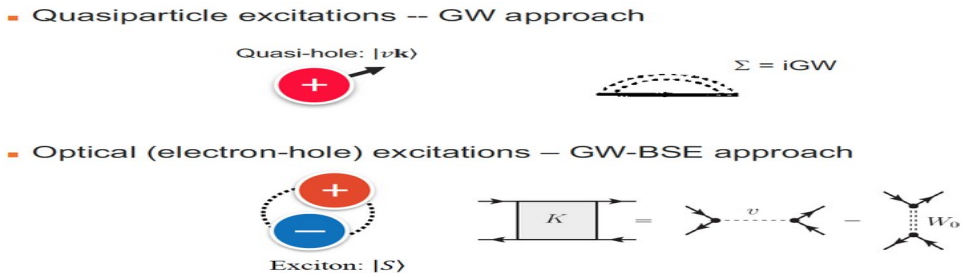
Z. Ye, T. Heinz, et al., Nat. Commun. (2018)

Correlated Multi-particle Excitations

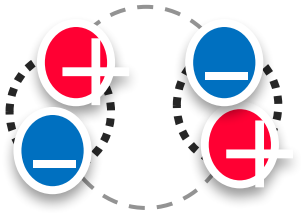
- Quasiparticle excitations -- GW approach (1 diagram)

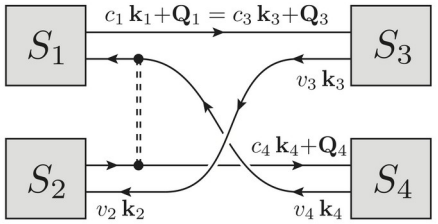


- Optical (electron-hole) excitations – GW-BSE approach (2 diagrams)



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

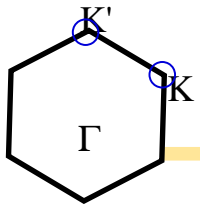


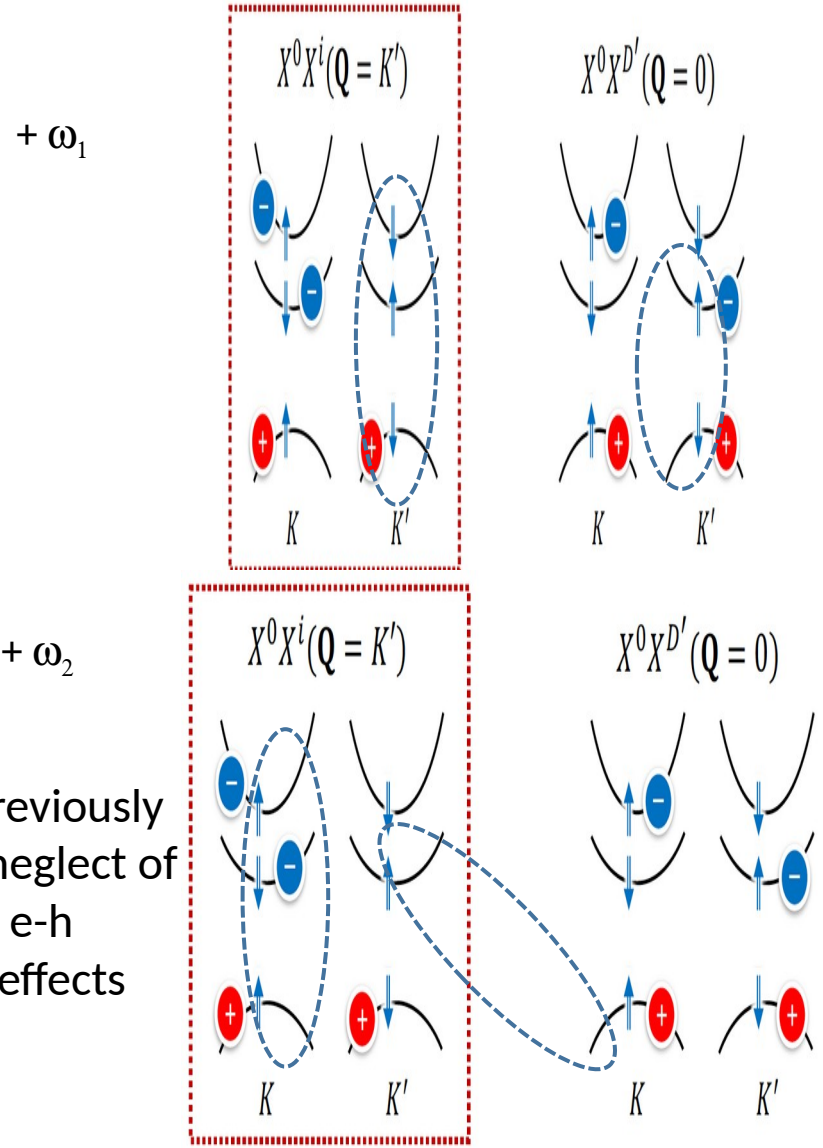


+ 35 other ones

da Jornada, Cepellotti & Louie (2020)

Trions and Biexcitons in Monolayer WSe2: Theory vs. Experiment





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

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

- 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 (2022).

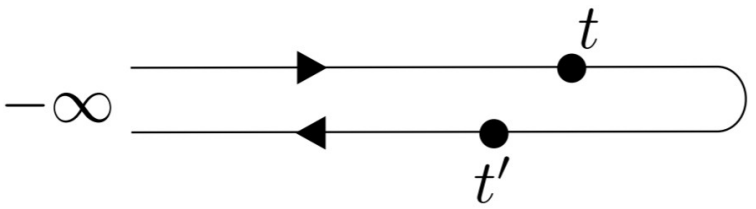
[1] He, Shan, et al, PRL 113, 026803 (2014).
[2] Ye, Heinz, et al, Nat. Commun. 9, 3718 (2018).
[3] Li,, Shi, et al, Nat. Commun. 9, 3719 (2018).
[4] Yong, Wang, et al, Nat. Phys. 14, 1092 (2018).

Time-dependent phenomena and nonlinear optical response: TD-GW

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

1 = (***r*** *t*)
2 = (***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)

TD-aGW Approximation

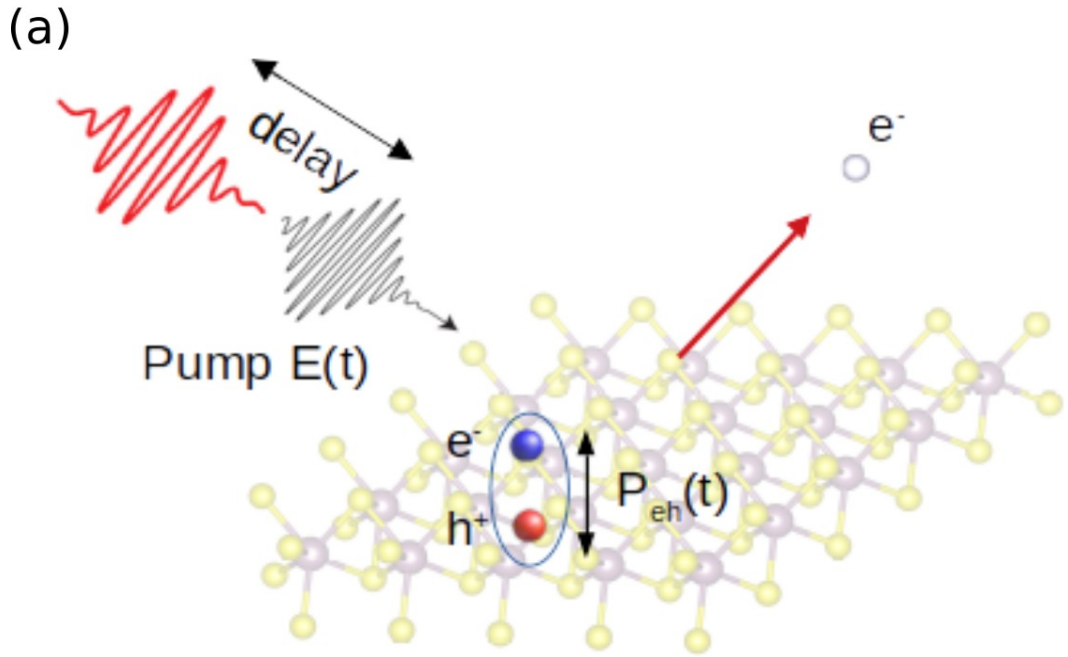
- TD-aGW approach
  - Accurate in weak & moderate field regime
  - Linear response is equivalent to BSE[1]
  - Time propagation ⇒ nonlinear responses and time-resolved phenomena with exciton effects

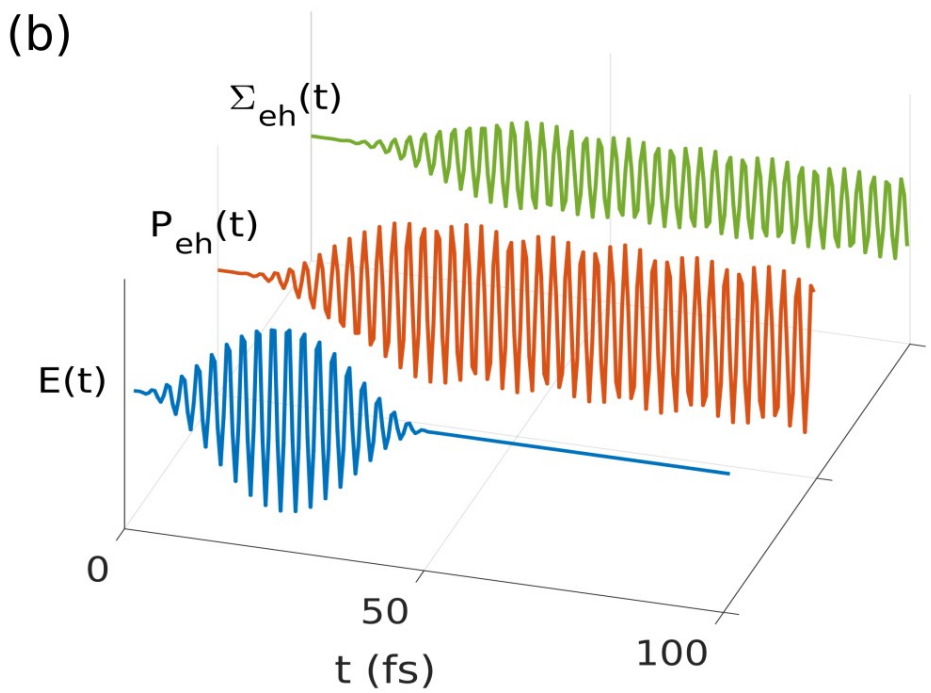
- Can perform propagation with a single time variable[2]!

[1]G. Strinati, Riv. Nuovo Cimento 11, 1 (1988): D. Rocca, D. Lu, and G. Galli, J. Chem. Phys. 133, 164109 (2010)

[2]C. Attaccalite, M. Gruning, A. Marini, PRB 84, 245110 (2011)

Pump field-driven phenomena in tr-ARPES





Photoemission intensity P(ω,t)

$$P(\omega,t) \propto \iint_{t_0}^{t} dt_1 dt_2 e^{i\omega(t_2-t_1)} G(t_1,t_2)$$

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

Optical-Field Pumped Spectral Function: Monolayer GeS

Ab initio time-dependent GW on Keldysh contour

Equilibrium bands

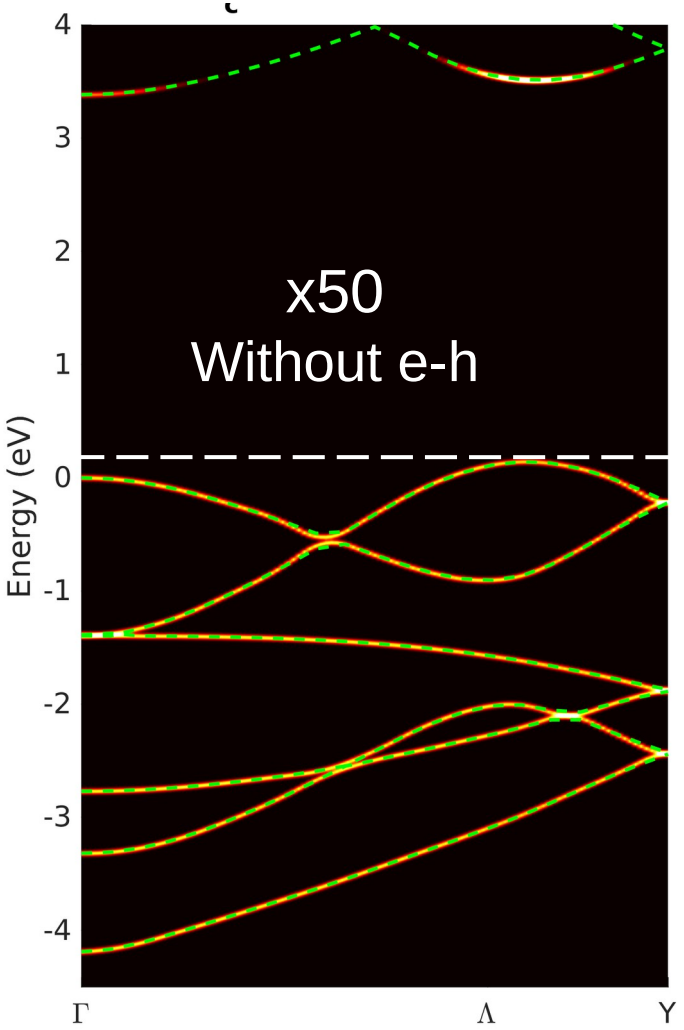
$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vc\mathbf{k}} A^S_{vc\mathbf{k}} \psi^*_{v\mathbf{k}}(\mathbf{r}_h)\psi_{c\mathbf{k}}(\mathbf{r}_e)$$

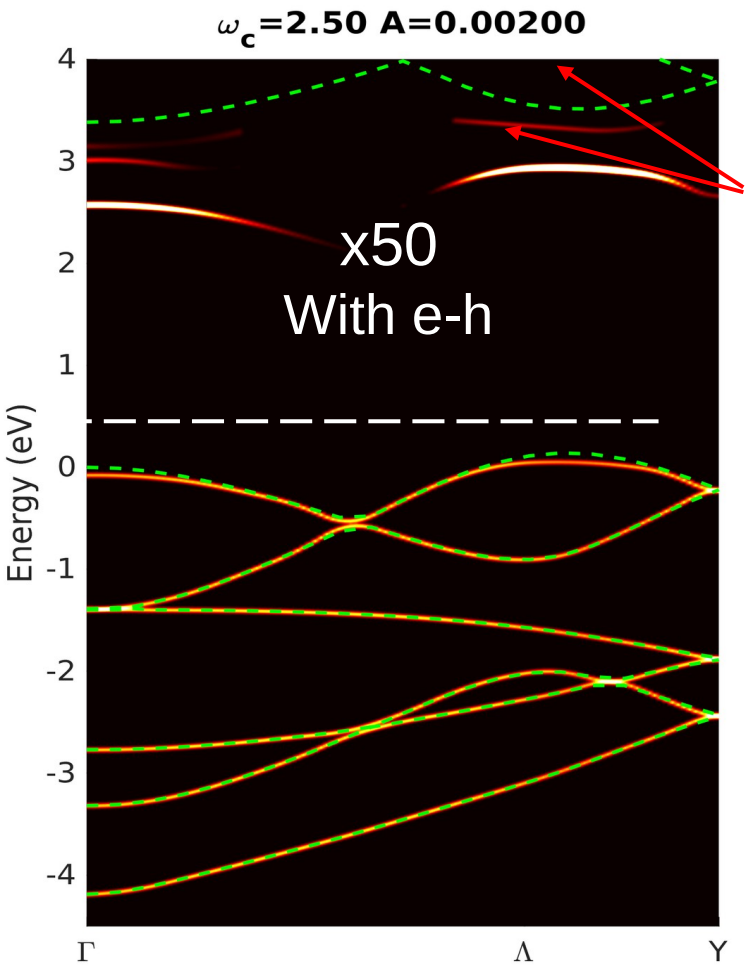
Pump: $\hbar\omega$ = 2.5 eV, τ = 5 fs, 350 μJ/cm^2

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 - a exciton polarization driven exciton−Flouqet effect





excitons

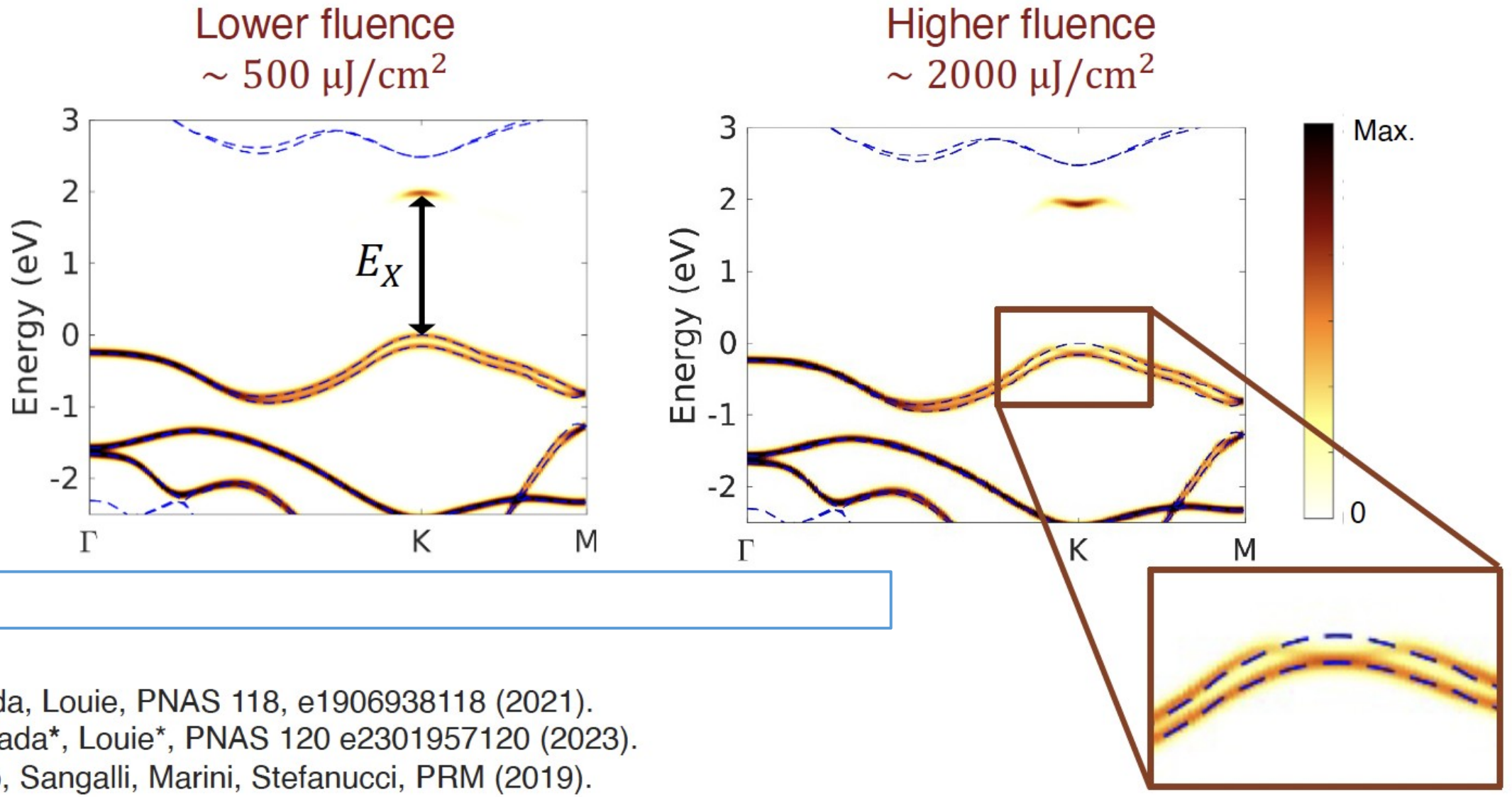
Without e-h interaction

With e-h interaction

Chan, Qiu, da Jornada & Louie, *PNAS* 120, e2301957120 (2023)

Optical-Field Pumped Spectral Function: Monolayer MoS_2

Pump near “A” exciton excitation energy



C effect

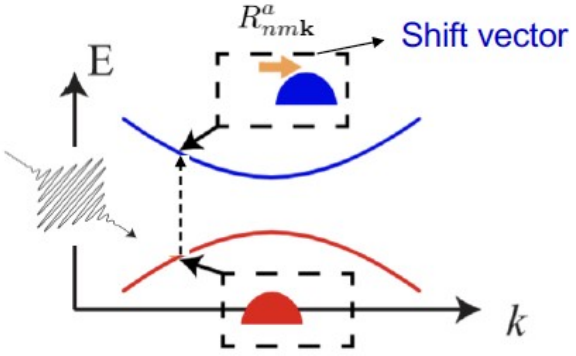
Chan, Qiu, Jornada, Louie, PNAS 118, e1906938118 (2021).
Chan*, Qiu*, Jornada*, Louie*, PNAS 120 e2301957120 (2023).
See also: Perfetto, Sangalli, Marini, Stefanucci, PRM (2019).

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)
- Excitonic effects in 2D semiconductors can enhance shift currents by orders of magnitude[1]

$$(\omega=0) = 2\boldsymbol{\sigma}_{\text{shift}}\,\mathbf{E}(\Omega)\mathbf{E}^*(\Omega)$$

Shift of intracell coordinates from optical transitions

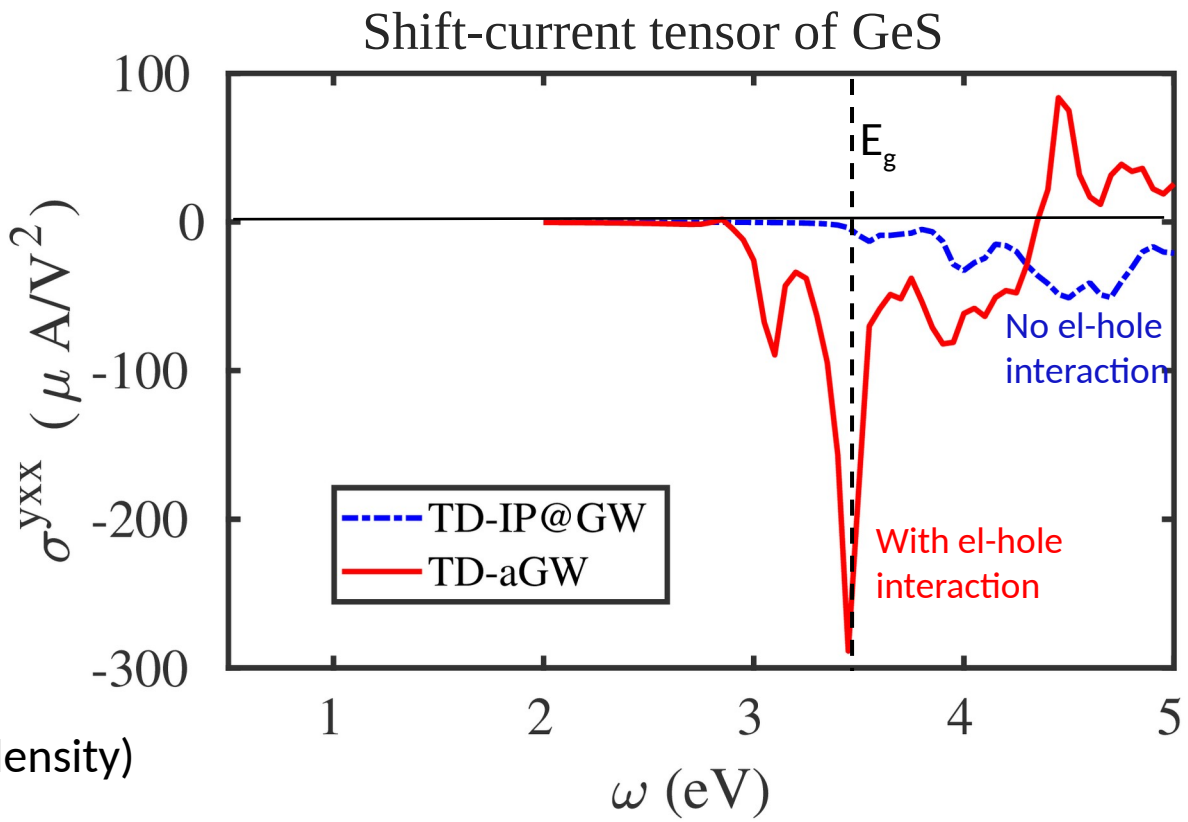


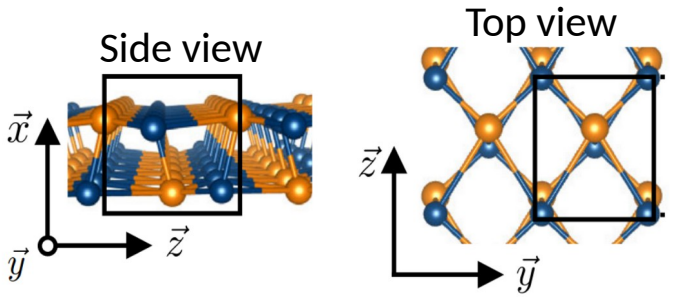
W. Kraut and R. von Baltz, PRB 19, 1548 (1979); B. S. I. Sturman and V.M. Fridkin, Photovoltaic and photorefractive effects in noncentrosymmetric materials (1992)

[1]Chan, Qiu, da Jornada, and Louie, PNAS 118, e1906938118 (2021)

$$R^{a,b}_{\mathbf{k}\,nm} = \left(\partial_{k_a}\phi^b_{\mathbf{k}nm} + A^a_{\mathbf{k}nn} - A^a_{\mathbf{k}mm}\right)$$

TD-aGW Approximation: Shift Currents in Monolayer GeS





$$(0) = 2\,\boldsymbol{\sigma}_{\text{shift}}\,\mathbf{E}(\Omega)\mathbf{E}^*(\Omega)$$

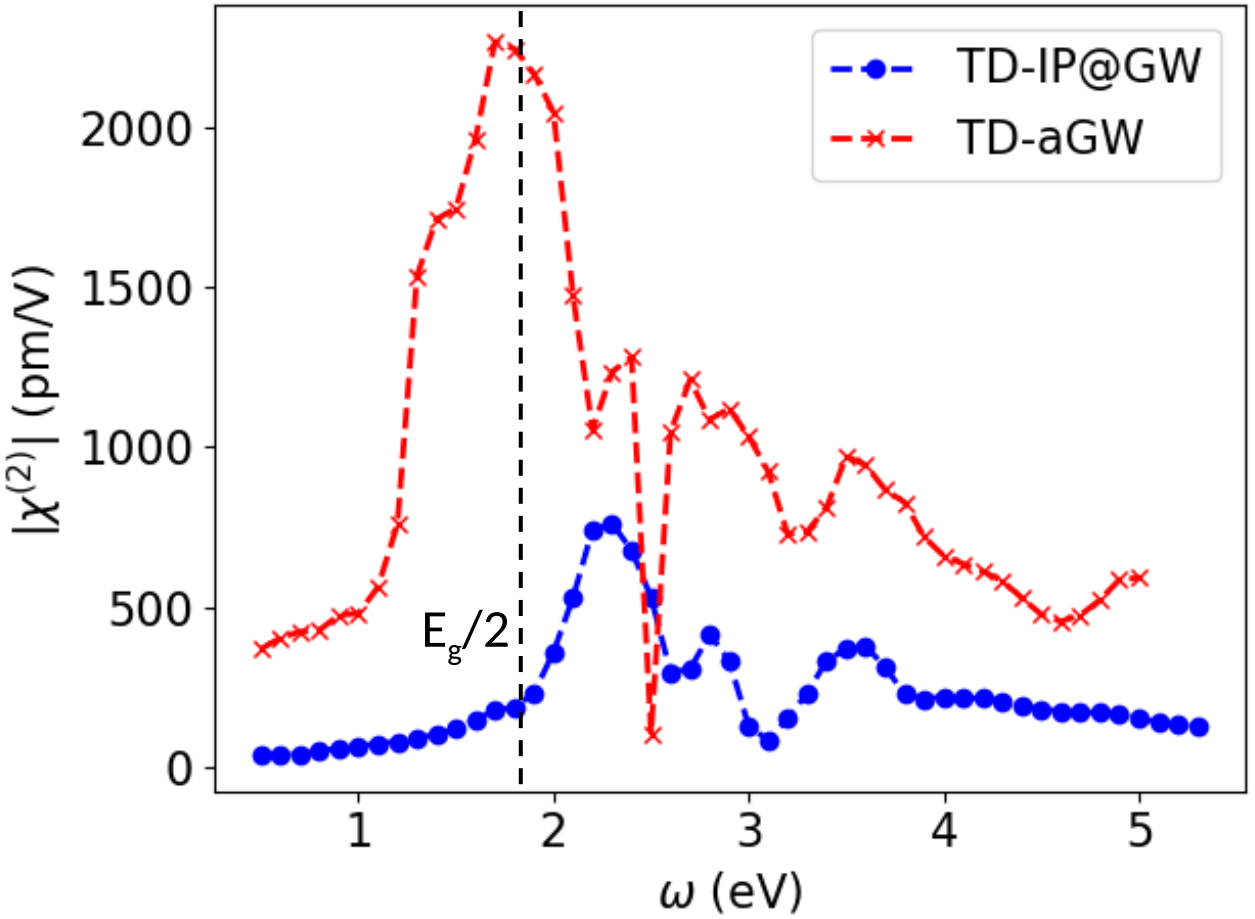
(for 3D current density)

- **Excitons enhance shift currents; effect is *huge – orders of magnitude higher* (also other NLO responses such as 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

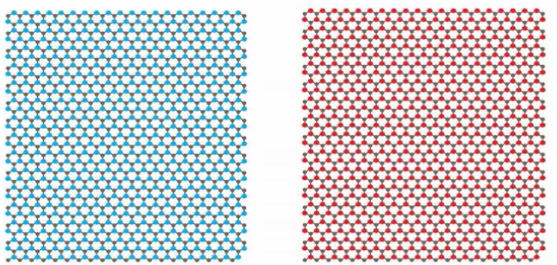
Absolute value of $\chi^{(2)yyy}$



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

Moire Superlattices of Twisted Bilayer 2D Materials

Moiré pattern



Credit:
Kyle Seyler

Twisted bilayer TMDs

Many exciting new physical phenomena

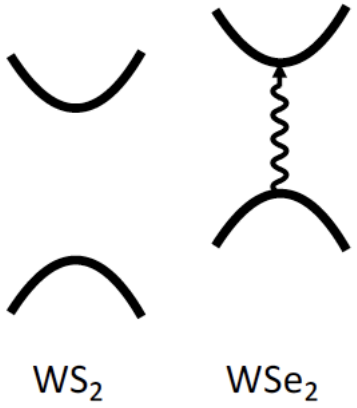
- Flat bands
- Unconventional superconductivity
- Correlated insulating states – Mott insulators, Wigner electron crystals…
- Novel moiré excitons in TMD bilayers

…

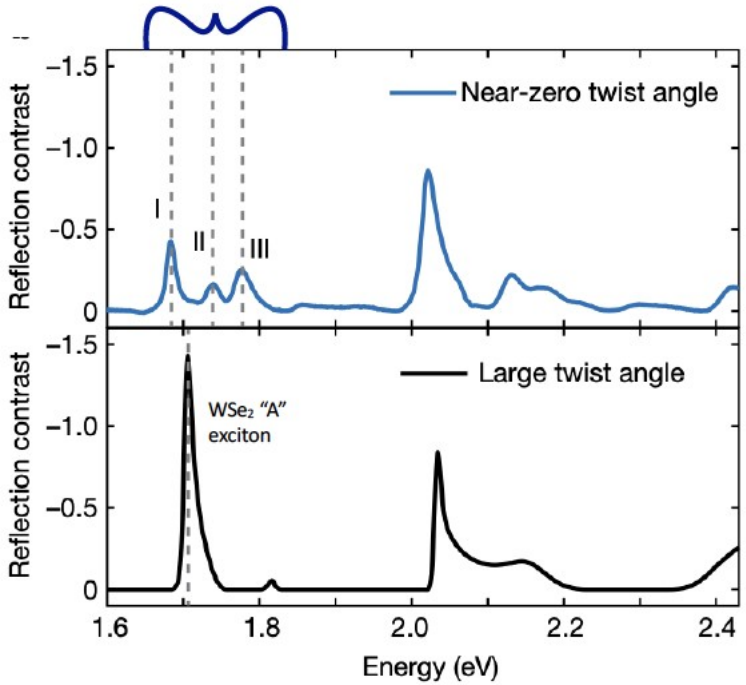
Excitons in twisted bilayer transition metal dichalcogenides (TMD)

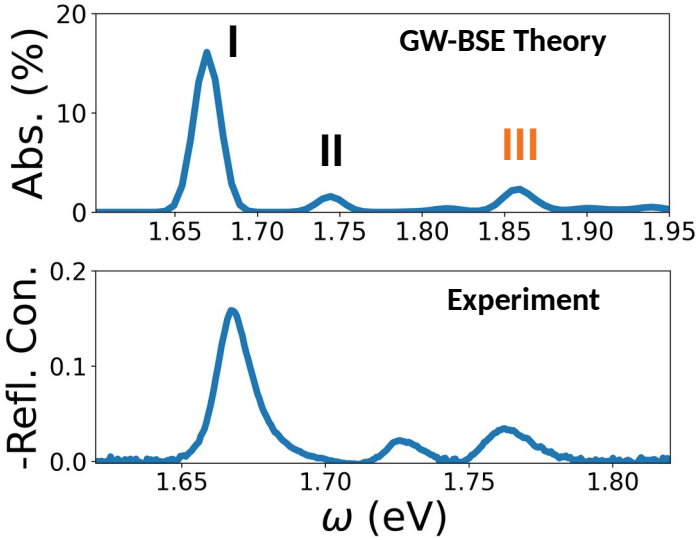
Intralayer moiré excitons in WSe_2/WS_2

Type II band alignment



WSe_2 intralayer excitons

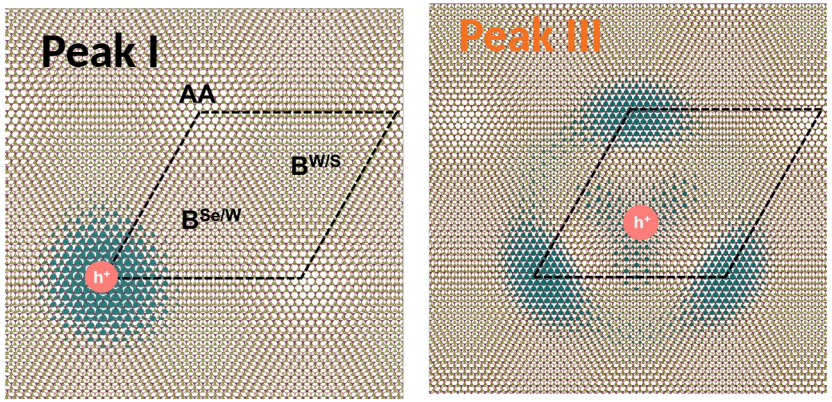




*C. Jin, E. C. Regan, A. Yan,..., S. Tongay, A. Zettl and F. Wang, Nature, **567**, 76–80 (2019) Also, Y. Tang, L. Li, T. Li, ..., A. H. MacDonald, J. Shan and K.F. Mak, Nature 579, 253 (2020)*

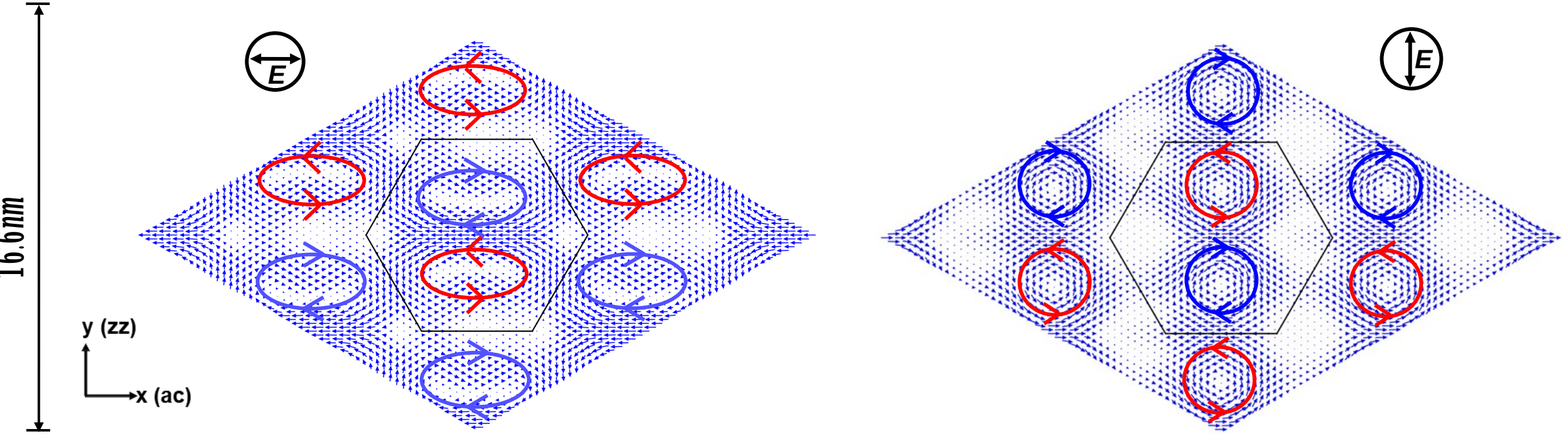
Modulated Wannier exciton

Novel charge-transfer exciton



Naik, Regan, Zhang, ... da Jornada, Wang, and Louie, Nature **609**, 52 (2022)

Current vortex crystals from exciton III with different linear polarizations



Shift current vortex crystal

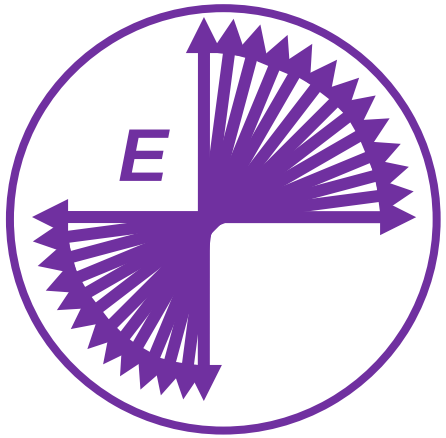
- Two current vortices in each moiré supercell (same magnitude & opposite chirality)
- Different light polarization can control the shift current vortex

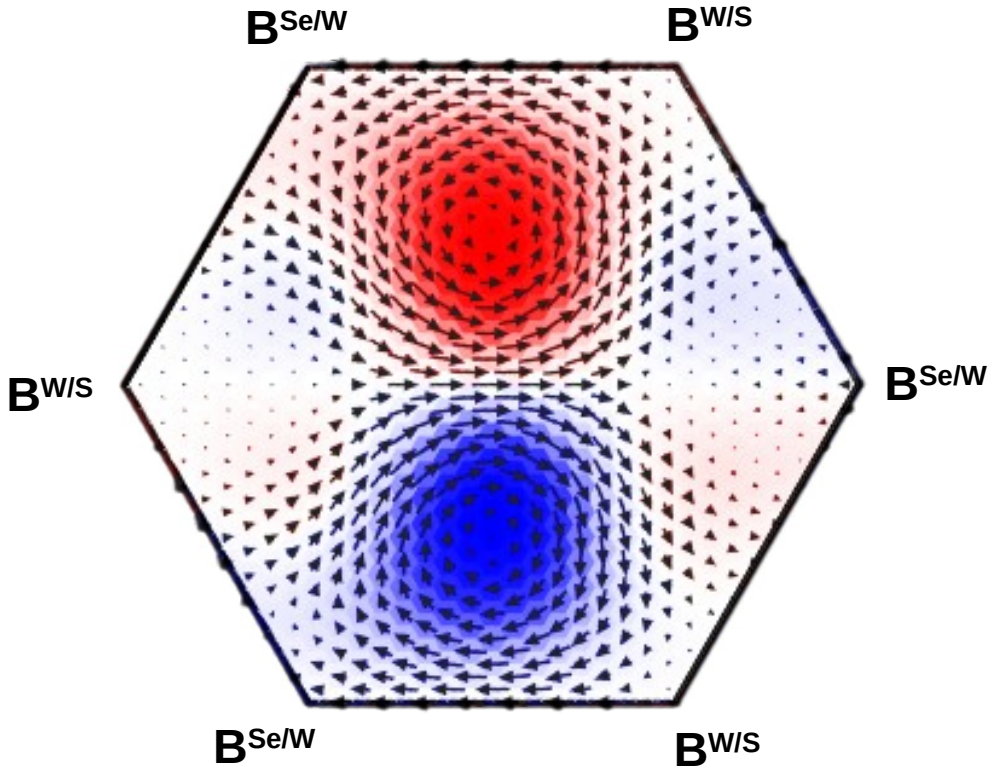
Hu, Naik, Chan, Ruan and Louie, PNAS 120, e2314775120 (2023)

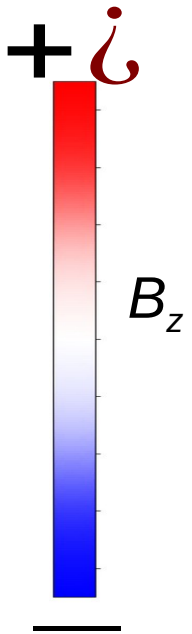
Shift current vortices: Linear polarization direction dependence

$$\boldsymbol{B}(\boldsymbol{r}) = \frac{\mu_0}{4\pi}\int \frac{\boldsymbol{J}(\boldsymbol{r}')\times(\boldsymbol{r}'-\boldsymbol{r})}{(\boldsymbol{r}'-\boldsymbol{r})^3}\,d^2\boldsymbol{r}'$$

Antiparallel out-of-plane magnetic fields



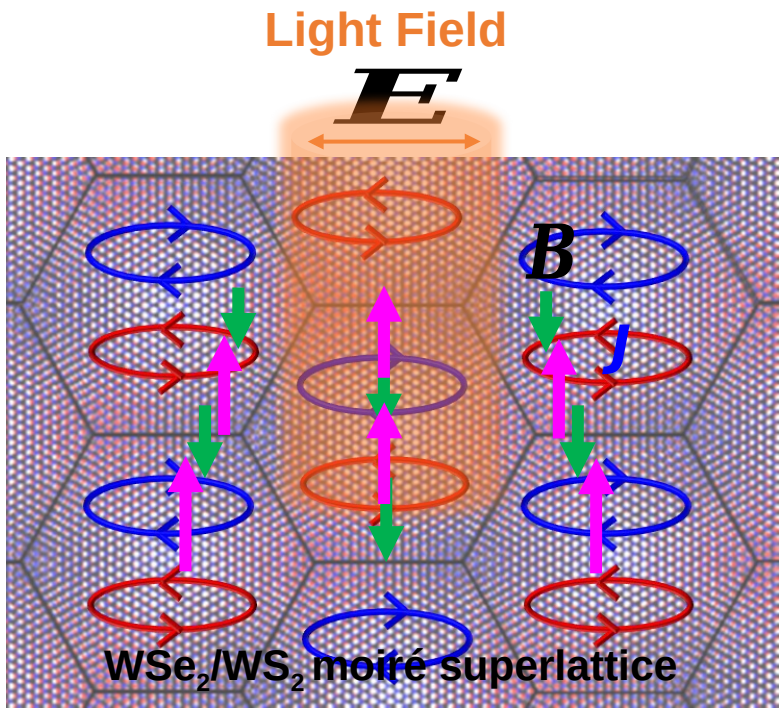




Light polarization direction can tune the shift current vortices continuously (**locations**, **shapes**, **distributions, circulations…**)

Circularly-polarized light illumination ⇨ **Ferrimagnetic vortex crystals**

All-optical control of shift current vortex crystals



- Orbital $\mathbf{J}(\mathbf{r})$ of a 2D material is a vector field on a 2-torus ⛓ net winding numbers of current vortices in a unit cell should be zero (Poincaré–Hopf theorem): vortices of opposite circulation and ferrimagnetism
- Second-order response: $B \propto J \propto E^2 \propto$ light intensity

Expt intensity: I ~

~ hundreds of

~ hundreds of

(Earth's magnetic field: ~)

Incident light
(frequency, intensity, polarization)

All-optical control

Generation/manipulation of current vortices & magnetism
(magnitude, location, shape, chirality)

Hu, Naik, Chan, Ruan and Louie, PNAS 120, e2314775120 (2023)

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)

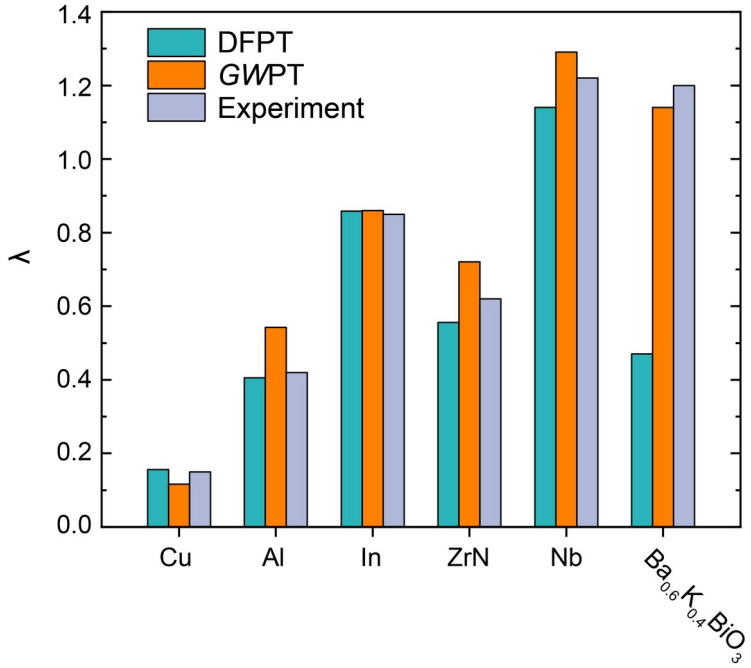
- Standard DFT e-ph matrix elements fail in some materials.
- GW level e-ph matrix elements (GWPT)

$$g^{GW}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{DFT}_{mn\nu}(\mathbf{k},\mathbf{q}) - \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V_{xc} | \psi_{n\mathbf{k}} \rangle + \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} \Sigma | \psi_{n\mathbf{k}} \rangle$$

LDA/GGA single-electron XC

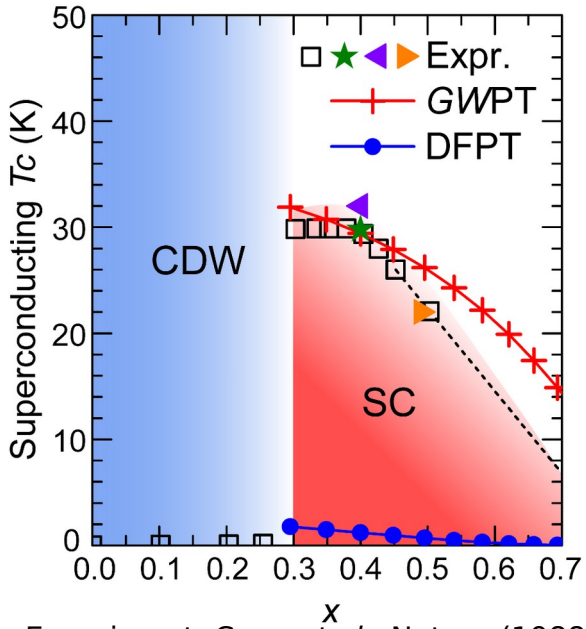
GW many-electron self-energy

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



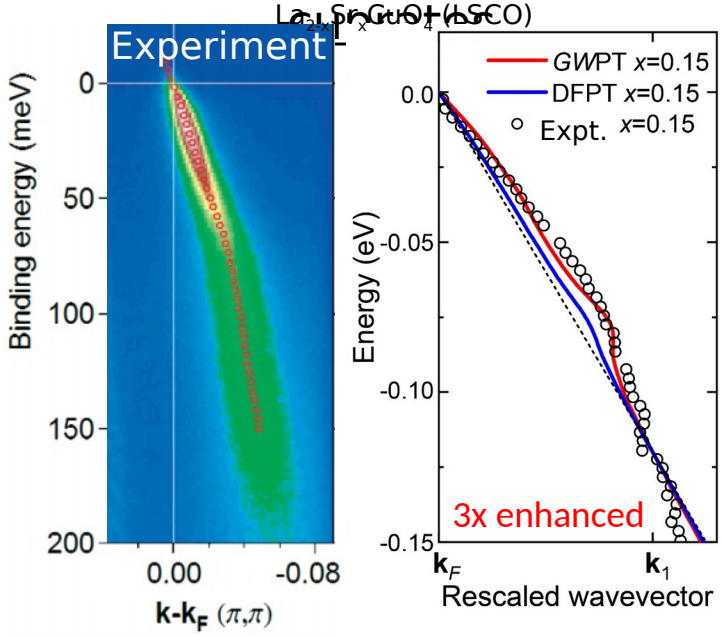
Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)
Li, Wu, Chan, Louie, PRL 126, 146401 (2021)

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 $La_{2-x}Sr_xCuO_4$ (LSCO)



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

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!