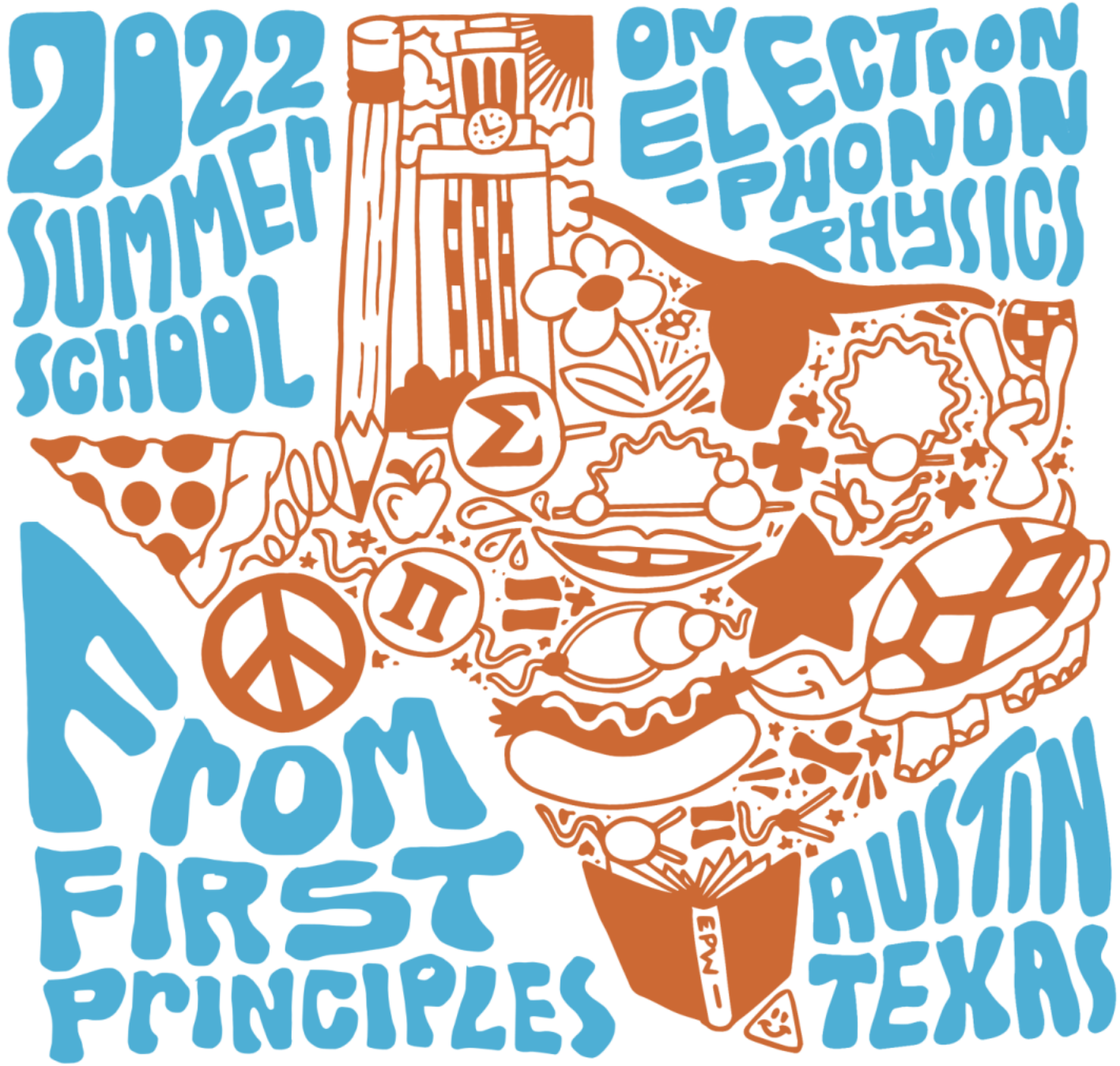
2022 Summer School on Electron-Phonon Physics



From First Principles

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Introduction to GW, GW-Bethe-Salpeter-equation (GW-BSE), and GW perturbation theory (GWPT)

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Materials properties

Ground-state properties

- Total energy
- Structures
- Magnetization
- Vibrations
- …

DFT/DFPT

Excited-state properties (Spectroscopies)

Single-particle excitation

- *N*+1 problem
- Photoemission
- Tunneling
- Band gap
- …

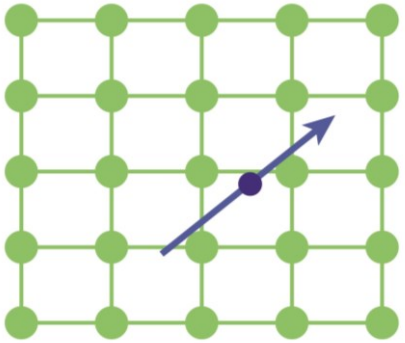
GW

Two-particle excitation

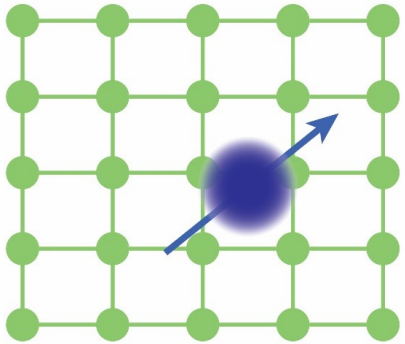
- *N*+2 problem
- Optical responses
- Excitons
- …

GW-BSE

Excited-state phenomena of materials



Bare electron



Dressed electron

⇔ Quasiparticle

Density functional theory (DFT)

- **Ground-state theory**
- Exchange-correlation potential

$$\hat{V}^{\mathrm{xc}} = V^{\mathrm{xc}}(\mathbf{r})$$

- Not the true effective potential seen by a quasiparticle

GW method

- **Excited-state theory**
- Self-energy ⇔ Many-electron correlation

$$\hat{\Sigma}(\mathbf{r}, \mathbf{r}'; \omega) = iGW$$

(*G*: Green's function; *W*: screened Coulomb)

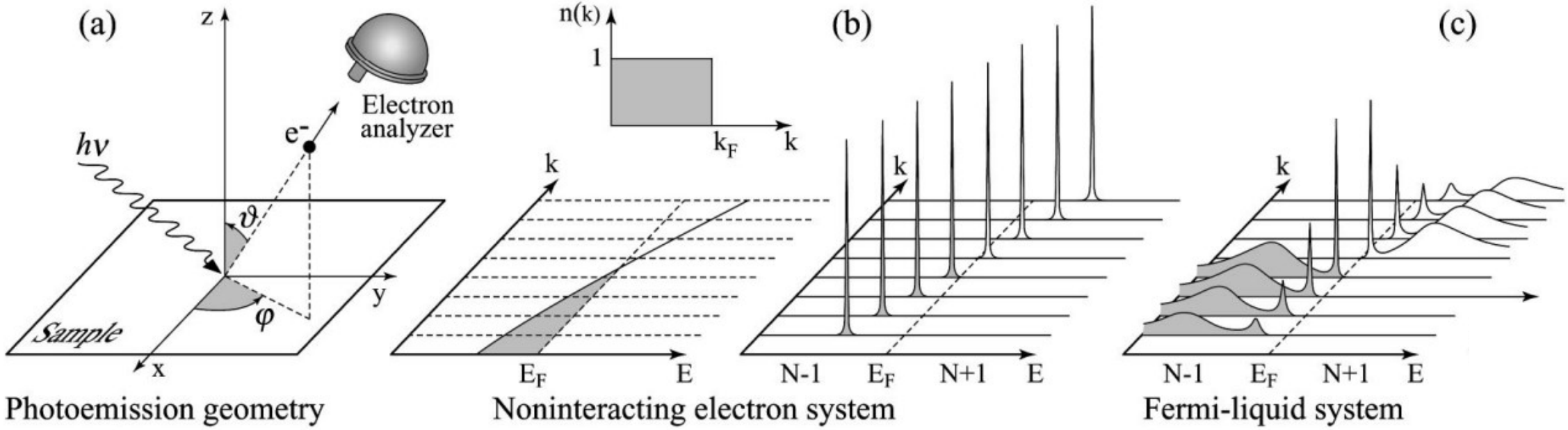
- Non-local, frequency-dependent potential

Spectral function and self-energy effects

cf. Lec. Tue.2.Giustino

Angle-resolve photoemission spectroscopy (ARPES)

Damascelli, Hussain, Shen, RMP **75**, 473 (2003)



- Energy shift
- Peak broadening
- Satellite features

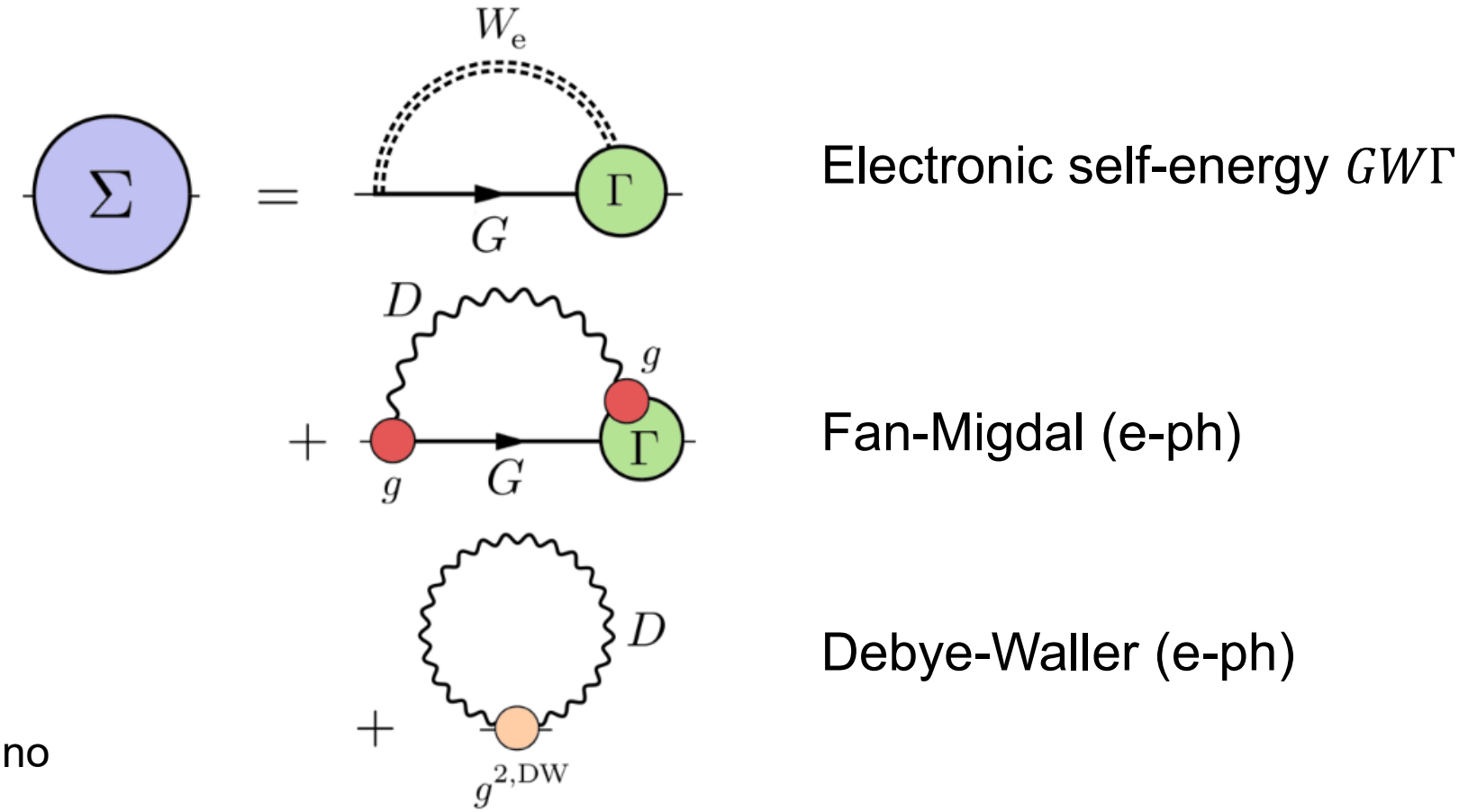
$$E_{n\mathbf{k}}^{\mathrm{QP}} = \varepsilon_{n\mathbf{k}}^{0} + \mathrm{Re}\Sigma_{n\mathbf{k}}(\omega)$$

$$A_{n\mathbf{k}}(\omega) = \frac{1}{\pi} \frac{|\mathrm{Im}\Sigma_{n\mathbf{k}}(\omega)|}{|\omega - \varepsilon_{n\mathbf{k}} - \mathrm{Re}\Sigma_{n\mathbf{k}}(\omega)|^2 + |\mathrm{Im}\Sigma_{n\mathbf{k}}(\omega)|^2}$$

GW approximation to electron-electron self-energy

cf. Lec. Tue.2.Giustino

$$\Sigma = \Sigma^{e-e} + \Sigma^{e-\mathrm{ph}} + \cdots$$



Electronic self-energy $GW\Gamma$

Fan-Migdal (e-ph)

Debye-Waller (e-ph)

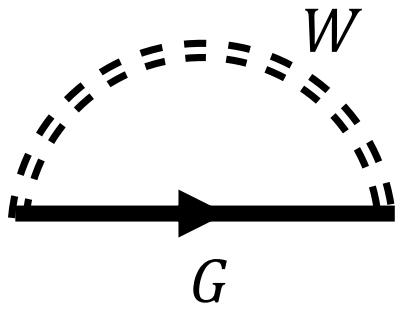
Image from Tue.2.Giustino

Giustino, RMP **89**, 015003 (2017)

GW approximation to electron-electron self-energy

- With $\Gamma = \delta(1,2)\delta(1,3)$, electron self-energy is within the **GW approximation**

$$\Sigma^{e-e} = iGW$$



Hedin, PR **139**, A796 (1965)
Hedin, Lundqvist, Solid State Physics **23**, 1 (1970)

- Dyson's equation (eigenvalue equation)

$$h_0(\mathbf{r})\psi_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r}) + \int \Sigma\left(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}}^{\mathrm{QP}}\right)\psi_{n\mathbf{k}}^{\mathrm{QP}}(\mathbf{r}')d\mathbf{r}' = E_{n\mathbf{k}}^{\mathrm{QP}}\psi_{n\mathbf{k}}^{\mathrm{QP}}$$

$$h_0 = -\nabla^2 + V_{\mathrm{ext}} + V_{\mathrm{H}}$$

- Compare with Kohn-Sham DFT (with standard local functionals)

$$h_0(\mathbf{r})\psi_{n\mathbf{k}}^{\mathrm{DFT}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})\psi_{n\mathbf{k}}^{\mathrm{DFT}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}^{\mathrm{DFT}}\psi_{n\mathbf{k}}^{\mathrm{DFT}}$$

Ab initio GW method

Hybertsen, Louie, PRL **55**, 1418 (1985) & PRB **34**, 5390 (1986)

- Green's function

$$G(\mathbf{r},\mathbf{r}';\omega)=\sum_{n\mathbf{k}}\frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi_{n\mathbf{k}}^{*}(\mathbf{r}')}{\omega-\varepsilon_{n\mathbf{k}}-i\delta_{n\mathbf{k}}}$$

- Screened and bare Coulomb interaction

$$W(\mathbf{r},\mathbf{r}';\omega)=\int\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''$$

$$v(\mathbf{r},\mathbf{r}')=\frac{1}{|\mathbf{r}-\mathbf{r}'|}$$

- Dielectric matrix from random-phase approximation (RPA) polarizability

$$\varepsilon(\mathbf{r},\mathbf{r}'';\omega)=1-vP^{\mathrm{RPA}}$$

$$P^{\mathrm{RPA}}=-iGG$$

Ab initio GW method

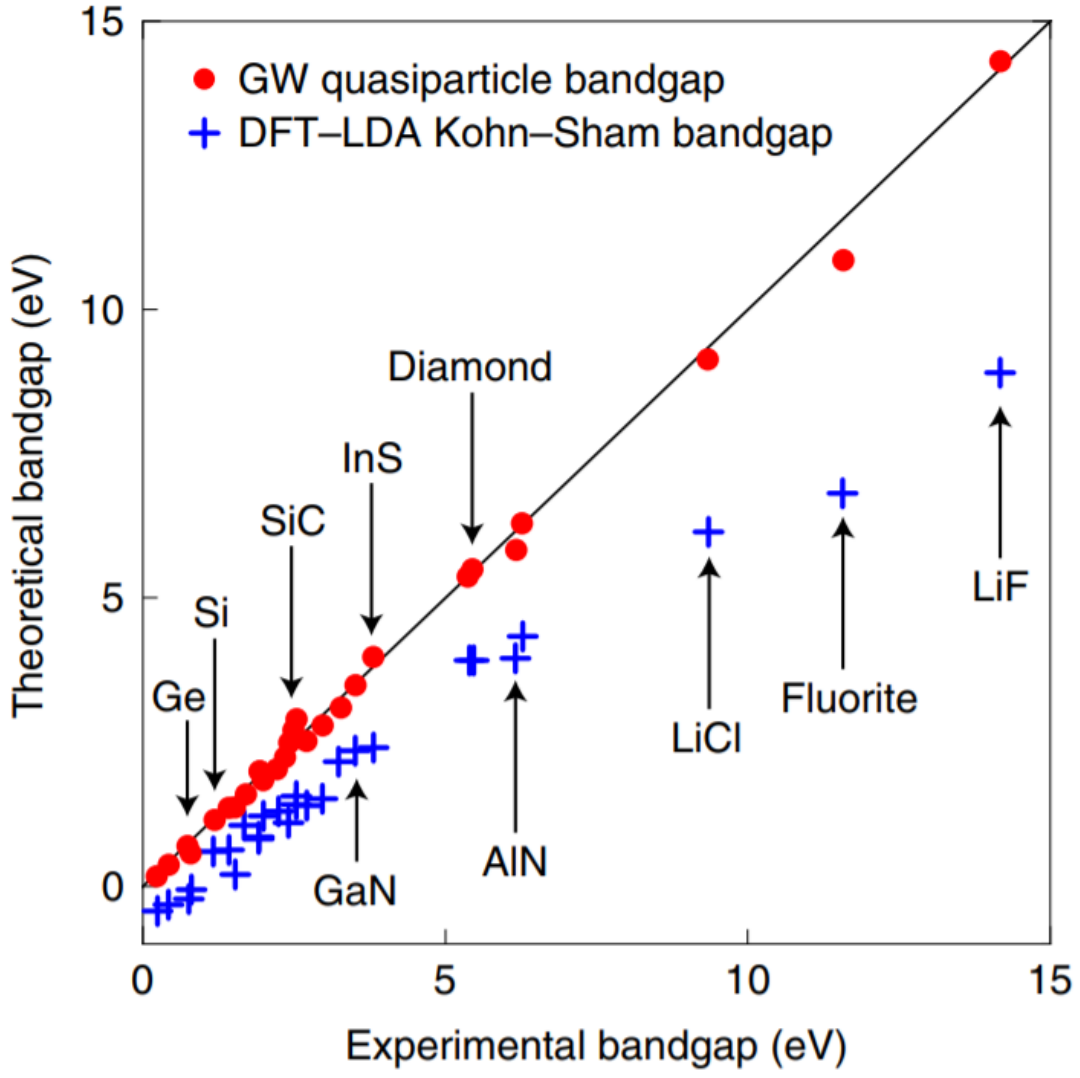
Hybertsen, Louie, PRL **55**, 1418 (1985)
& PRB **34**, 5390 (1986)

- Commonly, GW self-energy is constructed with DFT starting points (eigenvalues and wavefunctions)
- GW self-energy matrix elements are computed as a many-body correction to the DFT eigenvalues

$$E_{n\mathbf{k}}^{GW} = \varepsilon_{n\mathbf{k}}^{\mathrm{DFT}} + \langle \psi_{n\mathbf{k}} | \Sigma\left(E_{n\mathbf{k}}^{GW}\right) - V_{\mathrm{xc}} | \psi_{n\mathbf{k}} \rangle$$

✓ Sum over bands: in principle to full Hilbert space, in practice hundreds to thousands for convergence

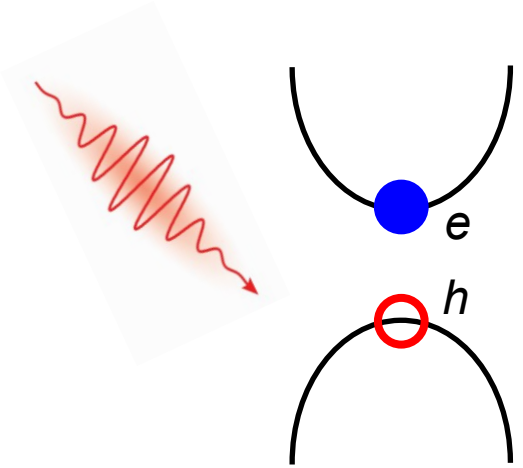
GW quasiparticle band gaps



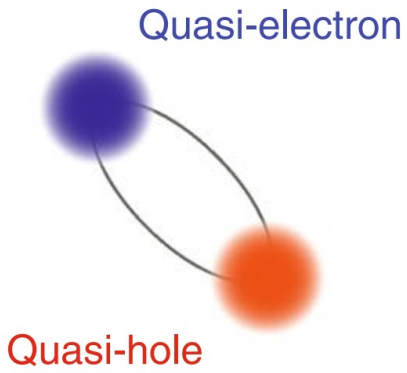
Louie, Chan, Jornada, Li, and Qiu, Nature Materials **20**, 728 (2021), Perspective article

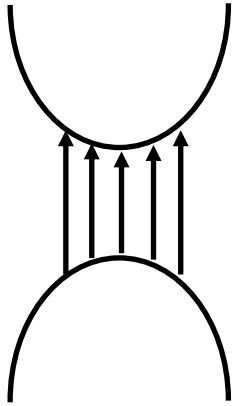
GW-Bethe-Salpeter-equation (GW-BSE) approach

- Optical absorption processes involve two excited-state quasiparticles



- Quasi-electron and quasi-hole can bind via Coulomb interaction and forma a new excitation: Exciton





GW-Bethe-Salpeter-equation (GW-BSE) approach

- The **Bethe-Salpeter equation** for each exciton state *S*

$$\left(E_{c\mathbf{k}}^{\mathrm{QP}} - E_{v\mathbf{k}}^{\mathrm{QP}}\right) A_{vc\mathbf{k}}^{S} + \sum_{v'c'\mathbf{k}} \langle vc\mathbf{k}|K^{e-h}|v'c'\mathbf{k}\rangle A_{v'c'\mathbf{k}}^{S} = \Omega^{S} A_{vc\mathbf{k}}^{S}$$

- Ω^S is the excitation energy, and $A_{vc\mathbf{k}}^{S}$ is exciton wavefunction (in quasiparticle basis)

- Exciton wavefunction in real space $\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vc\mathbf{k}} A_{vc\mathbf{k}}^{S}\, \psi_{c\mathbf{k}}(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)$

- The GW-BSE kernel

$$K^{e-h} = \frac{\delta(V_H + \Sigma^{\mathrm{GW}})}{\delta G} = v - W$$

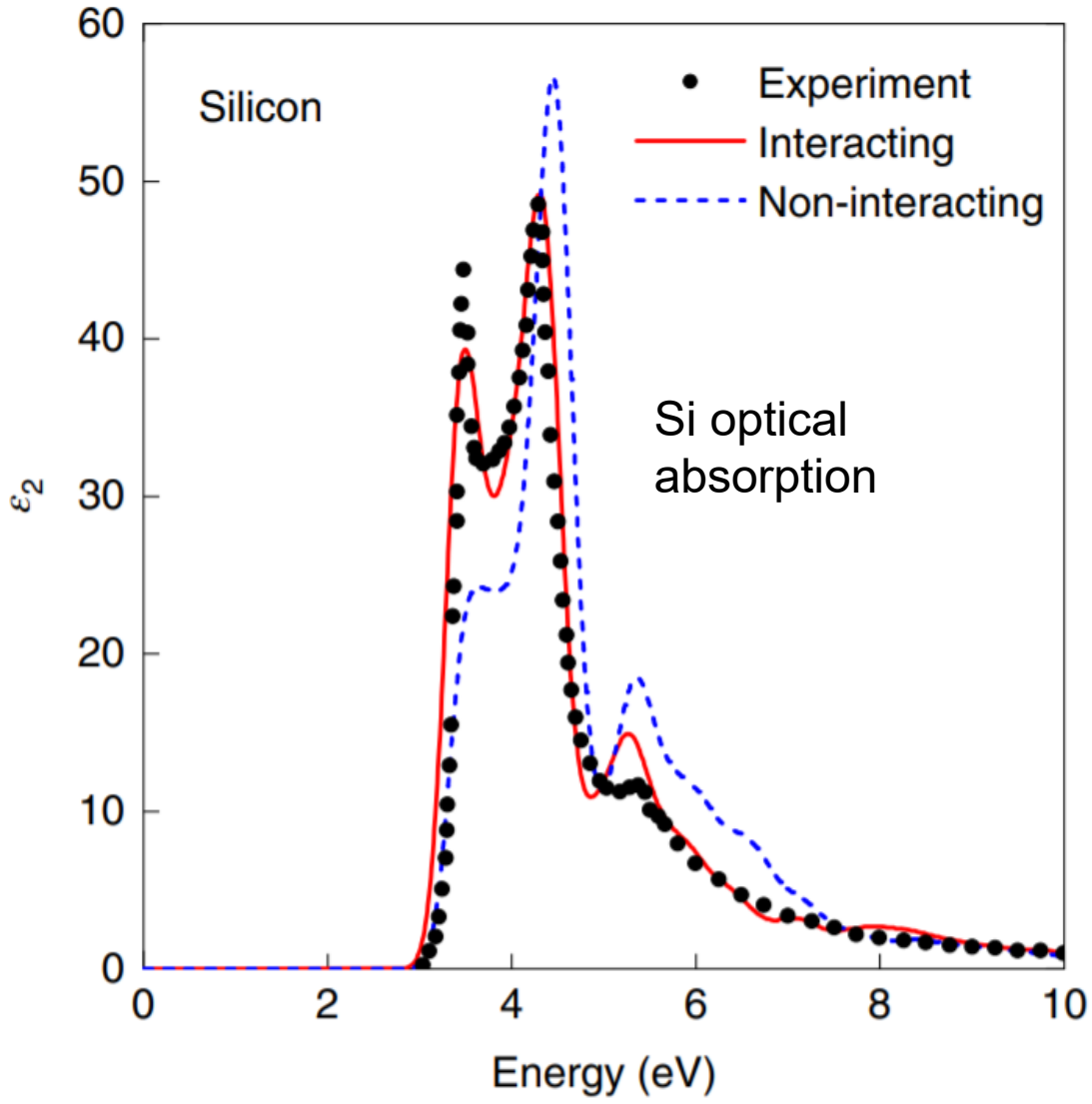
Rohlfing, Louie, PRL **81**, 2312 (1998)
Onida, Reining, Rubio, RMP **74**, 601 (2002)

GW-Bethe-Salpeter-equation (GW-BSE) approach

- Imaginary part of the dielectric function (optical absorption)

$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S |\mathbf{e} \cdot \langle 0|\mathbf{v}|S\rangle|^2 \delta(\omega - \Omega^S)$$

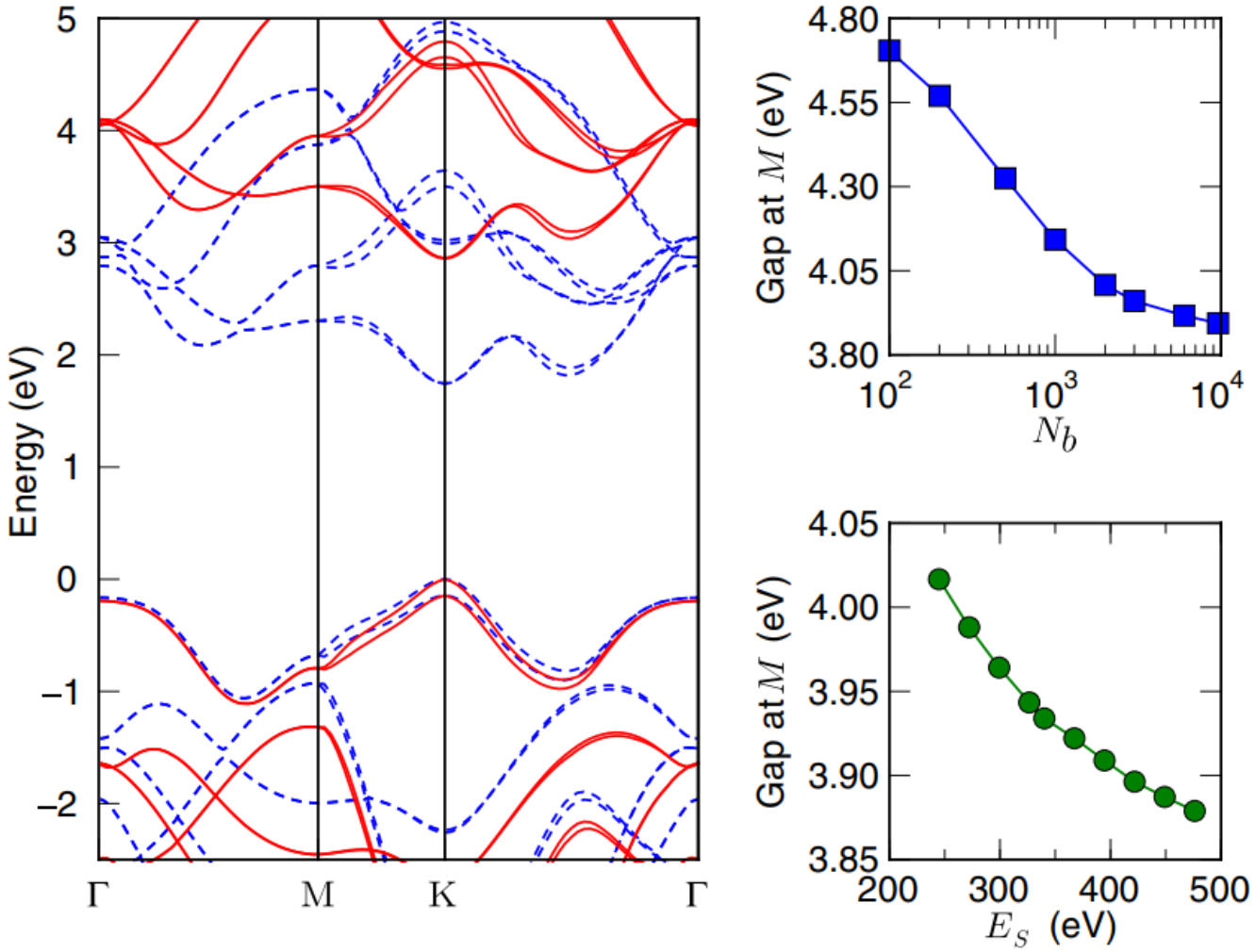
$\mathbf{e}$: photon polarization
$\mathbf{v}$: velocity operator



Louie, Chan, Jornada, Li, and Qiu, Nature Materials **20**, 728 (2021), Perspective article

Example: 2D transition-metal dichalcogenides MoS_2

- Monolayer MoS_2: Direct band-gap semiconductor



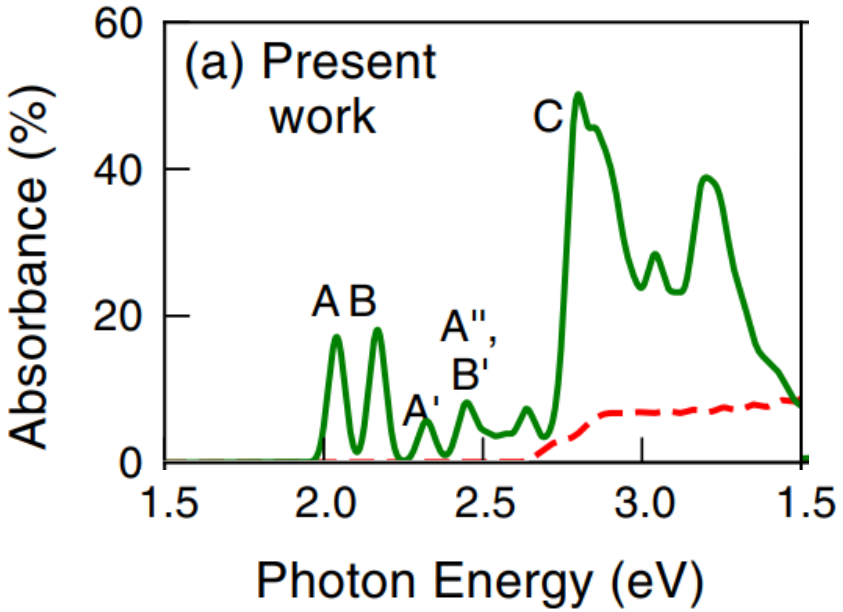
N_b: Number of bands

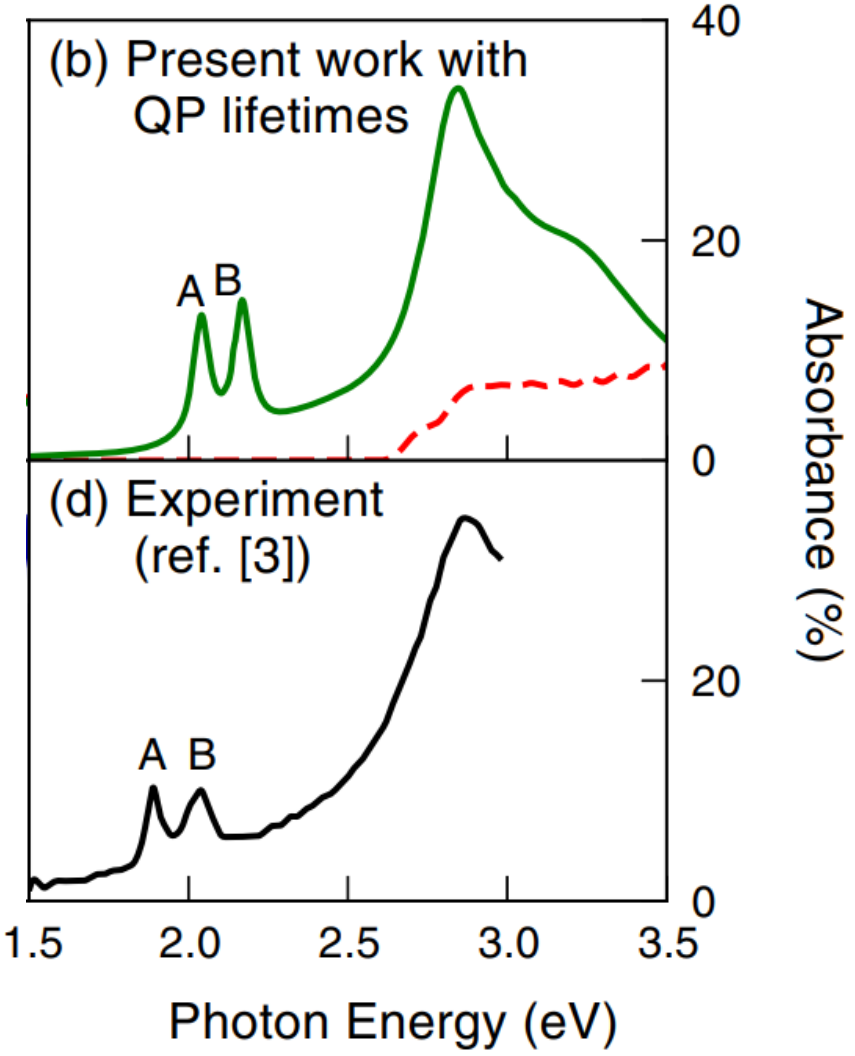
E_S: Energy cutoff for dielectric matrix

Convergence is an important issue in GW calculations

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

Example: 2D transition-metal dichalcogenides MoS_2



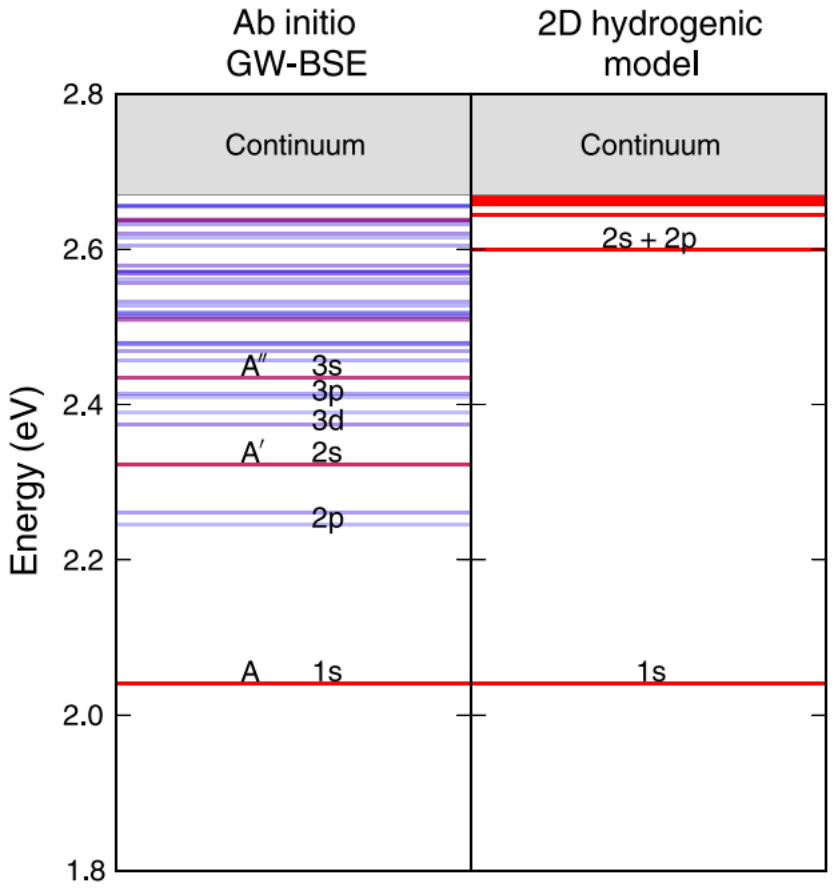


- Tightly bound excitons in monolayer MoS_2
- Strong absorbance ~ 20% at exciton excitations
- *e*-ph interaction introduces QP lifetimes

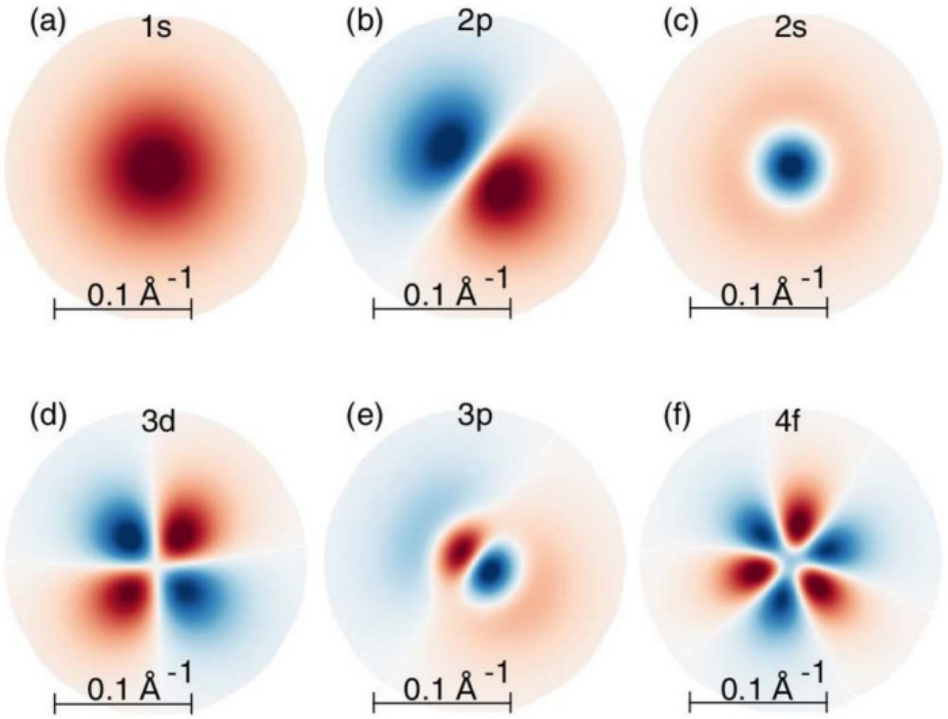
Theory: Qiu, Jornada, Louie, PRL **111**, 216805 (2013)
Expt: Mak, Lee, Hone, Shan, Heinz, PRL **105**, 136805 (2010)

Example: 2D transition-metal dichalcogenides MoS_2

Exciton energy levels



Exciton wavefunctions in **k**-space



- Rich exciton structures in 2D TMD materials

Qiu, Jornada, Louie, PRB **93**, 235435 (2016)

Self-consistency in GW calculations

Eigenvalue self-consistency GW

- Notation: G_nW_m where n and m label iteration steps
- **Mostly used: one-shot G_0W_0**
- Self-consistency in W worsens results
  - Increasing band gaps reduces screening
  - RPA-W with DFT energies has error cancellation: vaguely speaking, mimicking excitonic effects
- **Commonly seen: G_nW_0 or GW_0**

$$G(\mathbf{r},\mathbf{r}';\omega) = \sum_{n\mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')}{\omega - E^{\mathrm{QP}}_{n\mathbf{k}} - i\delta_{n\mathbf{k}}}$$

$$\psi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) \approx \psi^{\mathrm{DFT}}_{n\mathbf{k}}(\mathbf{r})$$

Eigenvector self-consistency GW

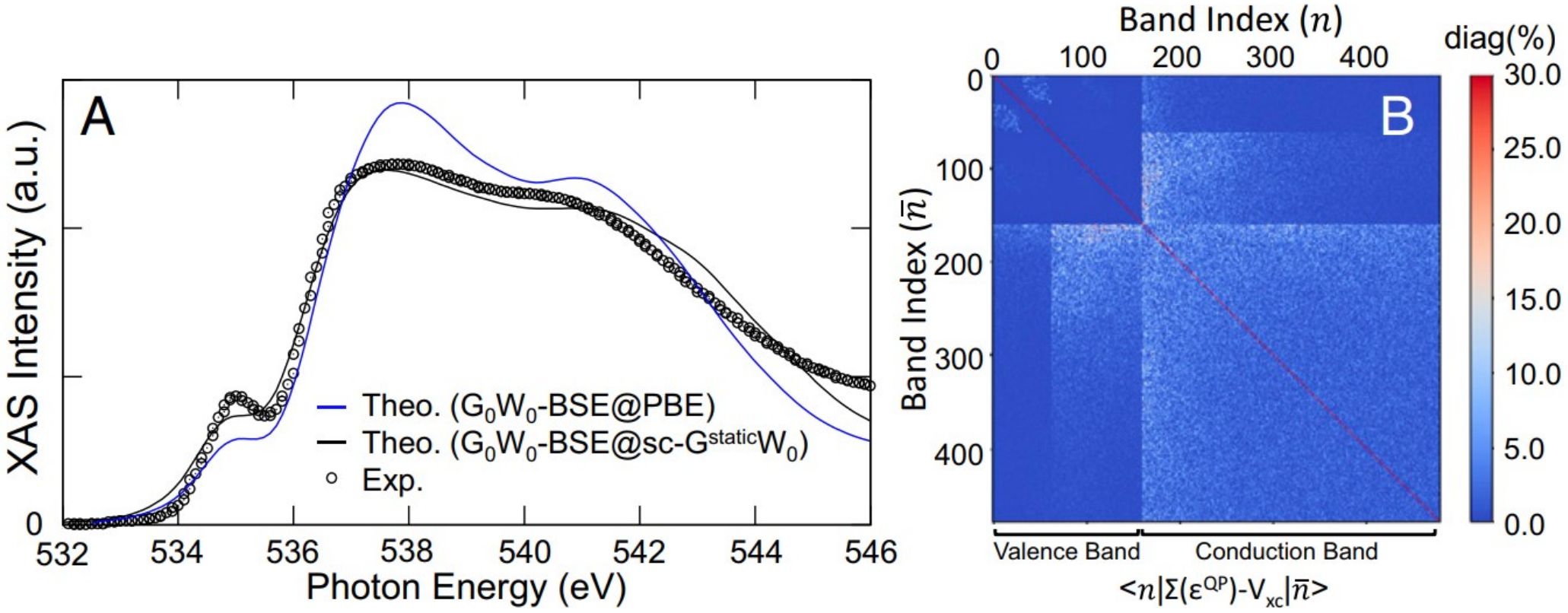
$$\psi^{\mathrm{QP}}_{n\mathbf{k}}(\mathbf{r}) \neq \psi^{\mathrm{DFT}}_{n\mathbf{k}}(\mathbf{r})$$

- Compute off-diagonal GW matrix elements $\langle\psi_{m\mathbf{k}}|\Sigma - \mathrm{V}^{\mathrm{xc}}|\psi_{n\mathbf{k}}\rangle$
- Diagonalization gives GW-corrected QP wavefunctions

See also: Quasiparticle self-consistent GW, van Schilfgaarde, Kotani, Faleev, PRL **96**, 226402 (2006)

Self-consistency in GW calculations

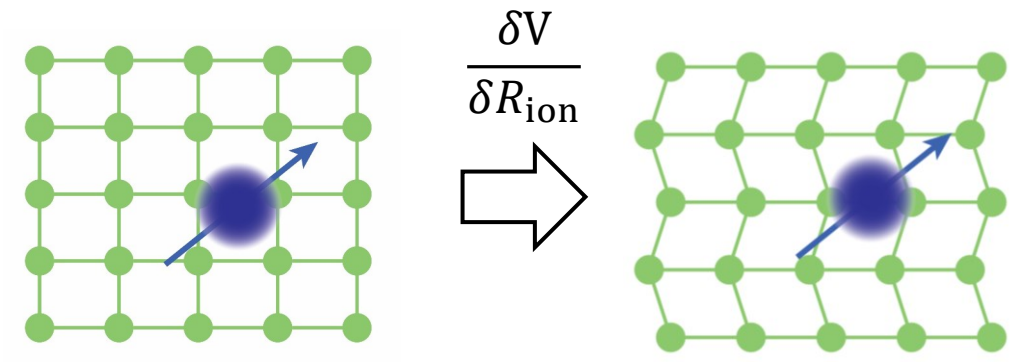
GW-BSE calculation of X-ray absorption spectra of liquid water



- GW-corrected quasiparticle wavefunction improves BSE absorption spectra

Tang, Li, Zhang, Louie, Car, Qiu, Wu, PNAS **119**, e2201258119 (2022)

Electron-phonon coupling from lattice vibrations



Potential (seen by a quasiparticle) change induced by ion displacements

Density-functional perturbation theory (DFPT)

- Very powerful in computing e-ph properties
- Inadequate for many-electron correlations
- Not true potential seen by quasiparticles

cf. Lec. Mon.2.Giannozzi

Lec. Tue.2.Giustino

GW perturbation theory (GWPT)

- Linear-response (to phonon perturbations) theory within GW approximation
- Compute *e*-ph matrix elements at the GW level
- Captures many-electron correlation effects in the e-ph coupling

Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)

GW perturbation theory (GWPT)

- Electron-phonon coupling

Electron-phonon interaction includes $\frac{\delta\Sigma}{\delta R_{\mathrm{ion}}}$

- **Electron-phonon matrix element**: ***building blocks*** to all microscopic electron-phonon theories

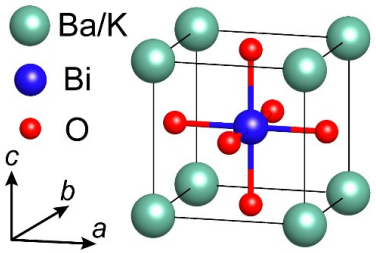
$$g^{GW}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathrm{DFT}}_{mn\nu}(\mathbf{k},\mathbf{q}) - \underbrace{\langle\psi_{m\mathbf{k}+\mathbf{q}}|\Delta_{\mathbf{q}\nu}V^{\mathrm{xc}}|\psi_{n\mathbf{k}}\rangle}_{\text{DFT: single-electron exchange-correlation}} + \underbrace{\langle\psi_{m\mathbf{k}+\mathbf{q}}|\Delta_{\mathbf{q}\nu}\Sigma|\psi_{n\mathbf{k}}\rangle}_{\text{GW: many-electron self-energy}}$$

- DFPT starting point to generate: g^{DFT}, $\Delta_{\mathbf{q}\nu}V^{\mathrm{xc}}$, and $\Delta_{\mathbf{q}\nu}\psi_{n\mathbf{k}}$ (*for both valence and conduction bands*)

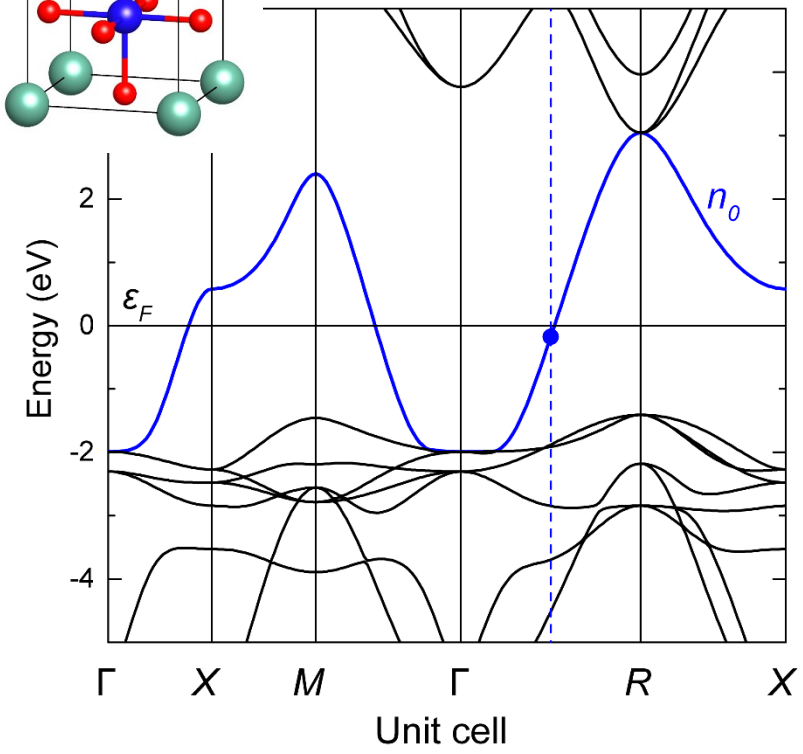
Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)

Correlation-enhanced electron-phonon coupling and superconductivity

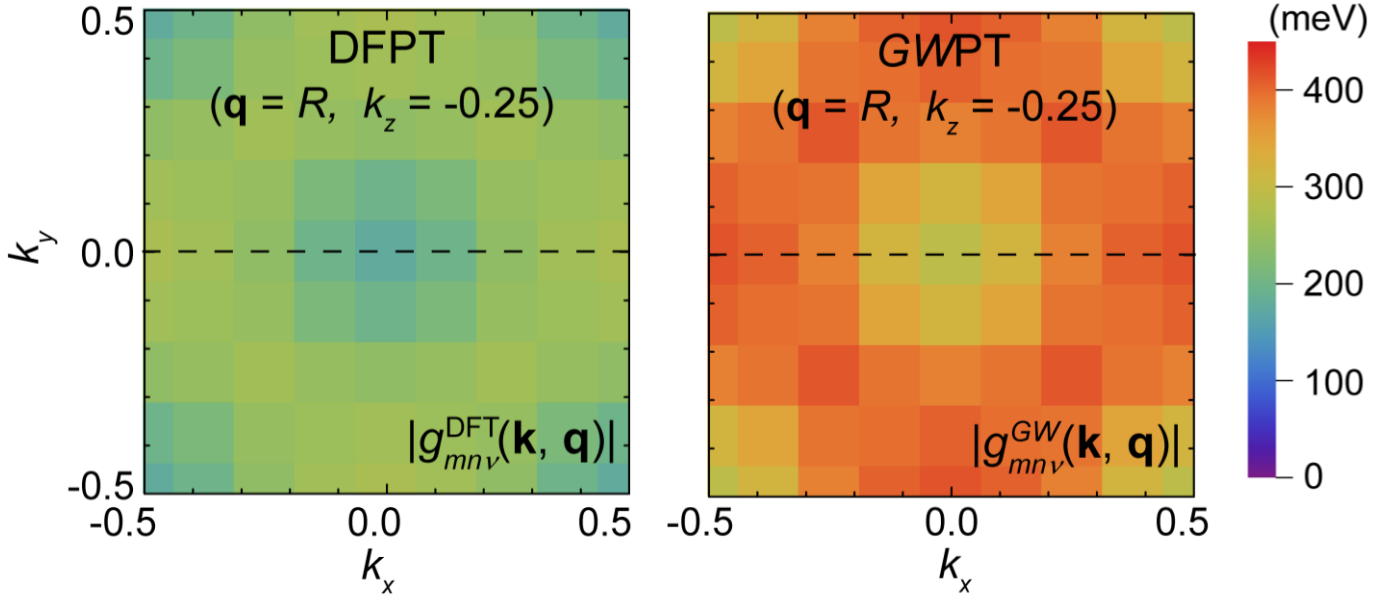
$Ba_{1-x}K_xBiO_3$: experimental T_c = 32 K at x = 0.4



Band structure



Distribution of e-ph matrix elements |g|

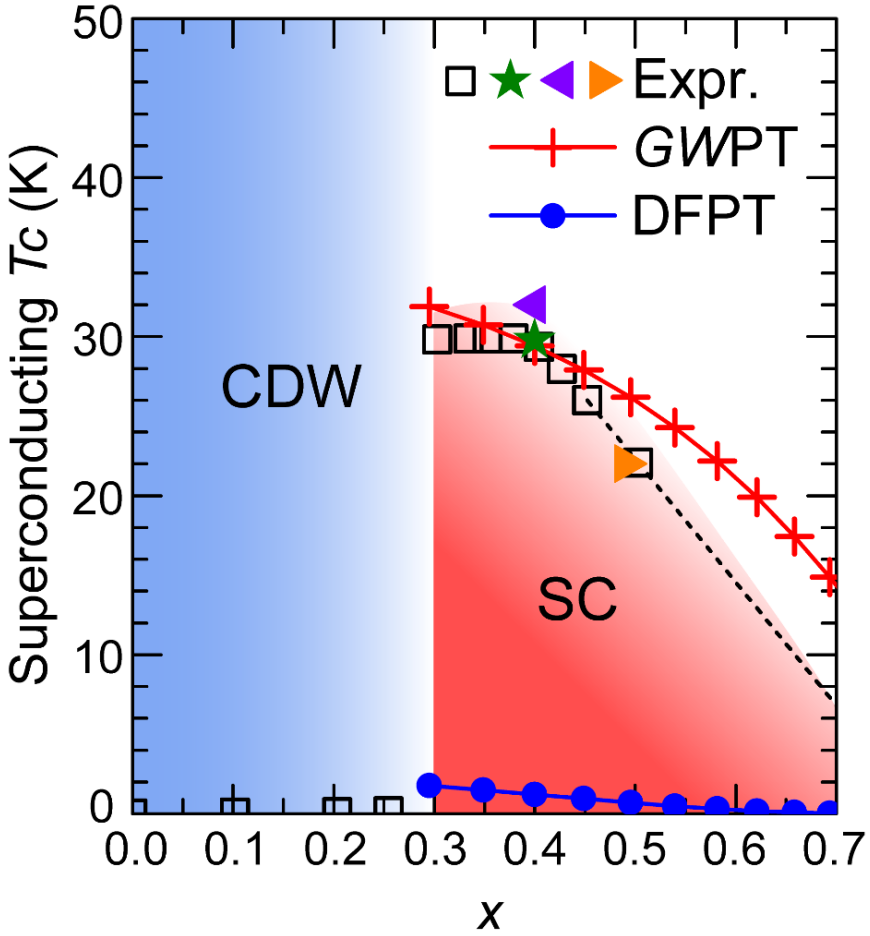


- Strong GW renormalization in *g*
- Non-uniform renormalization in BZ

Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)

Correlation-enhanced electron-phonon coupling and superconductivity

$Ba_{1-x}K_xBiO_3$: experimental T_c = 32 K at x = 0.4

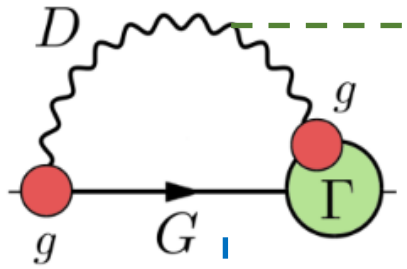


McMillan–Allen-Dynes formula to estimate superconducting T_c with $\mu^* = 0.16$

Li, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)

GW-level electron-phonon phenomena with EPW + BerkeleyGW

Fan-Migdal self-energy



e-ph matrix elements

g^{DFT} vs. g^{GW}

Electron propagator *G*

$\varepsilon^{\mathrm{DFT}}$ vs. E^{GW}

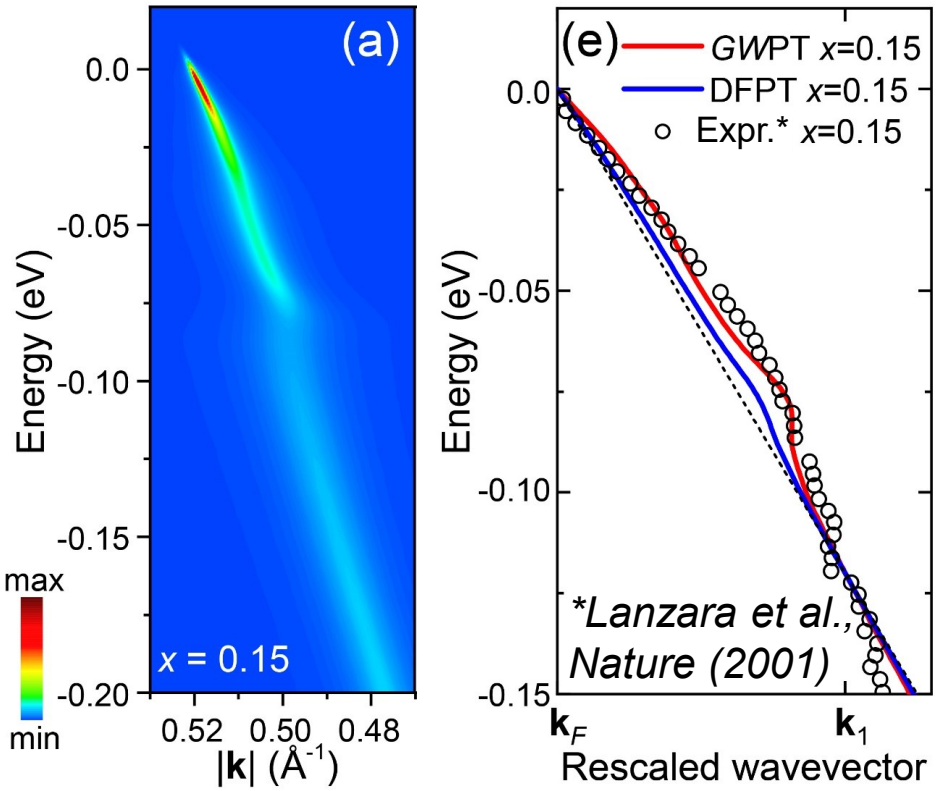
Phonon propagator *D*

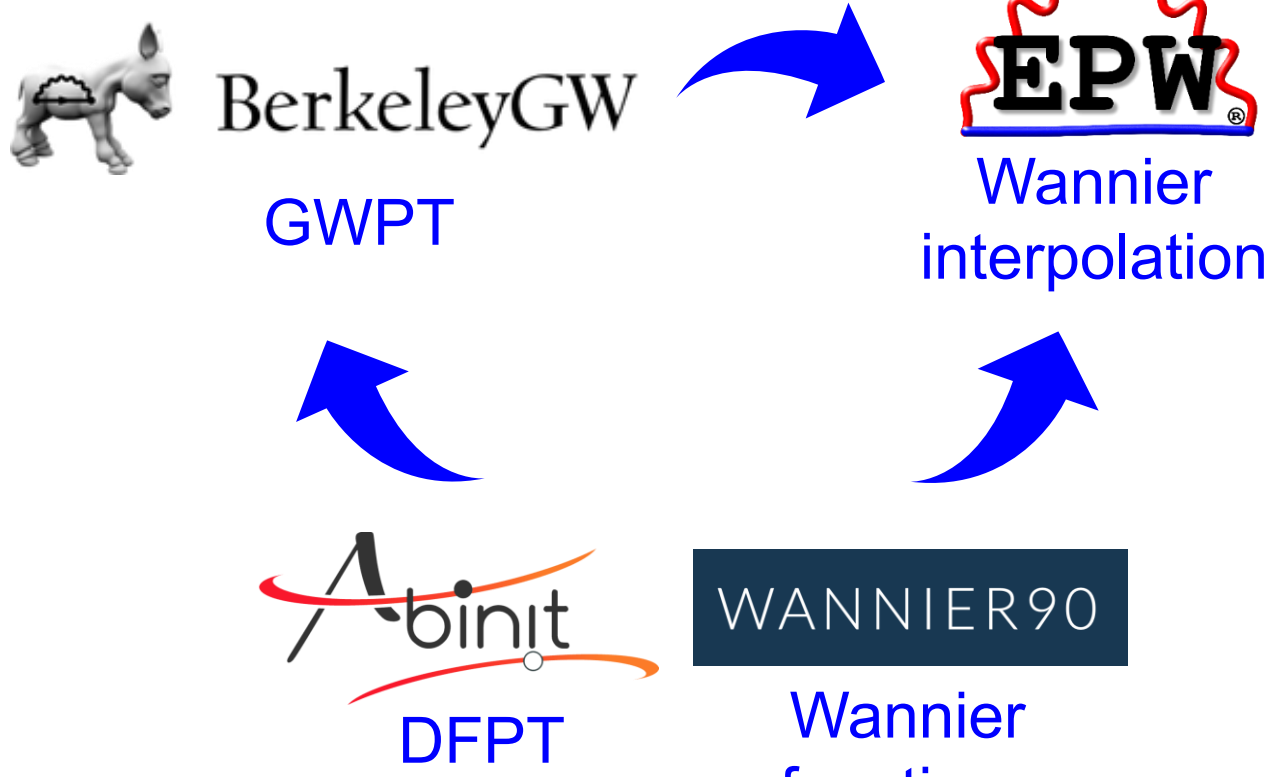
DFPT phonon is based on the ground-state total energy ⇔ Generally very accurate

GW-level electron-phonon phenomena with EPW + BerkeleyGW

Photoemission kink in $La_{2-x}Sr_xCuO_4$

Theory GWPT **Comparison**





Li, Wu, Chan, Louie, PRL **126**, 146401 (2021)

See also: Giustino, Cohen, Louie, Nature **452**, 975 (2008)

Heid *et al.*, PRL **100**, 137001 (2008)

BerkeleyGW tutorial at the Electron-Phonon School 2022

BerkeleyGW developer group leader

BerkeleyGW

berkeleygw.org

Prof. Steven G. Louie

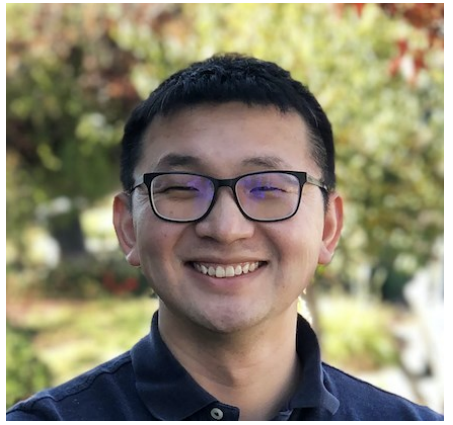
UCB/LBNL

Dr. Jack R. Deslippe

LBNL

Dr. Mauro Del Ben

LBNL



Dr. Zhenglu Li

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