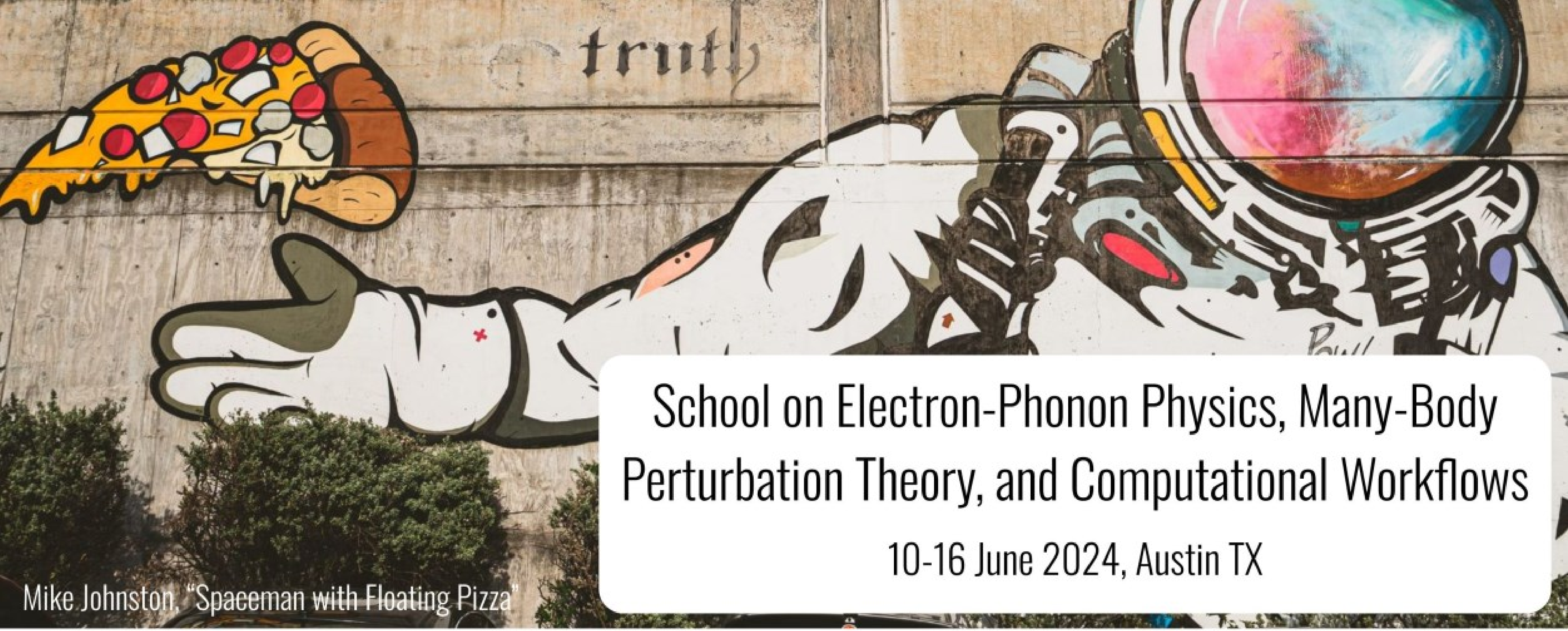

Mike Johnston, “Spaceman with Floating Pizza”

School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

10-16 June 2024, Austin TX

U.S. DEPARTMENT OF ENERGY

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Lecture Fri.3

Electron-phonon coupling from GW perturbation theory

Zhenglu Li

Mork Family Department of Chemical Engineering and Materials Science

University of Southern California

USC University of Southern California

USC Viterbi School of Engineering

Electron-phonon coupling from lattice vibrations

❖ **Electron-phonon coupling**

- Phonon-mediated superconductivity
- Electrical and thermal transport
- Temperature-dependent and indirect optical absorption
- Charge-density wave
- Hot carrier dynamics in materials
- …

Transistors

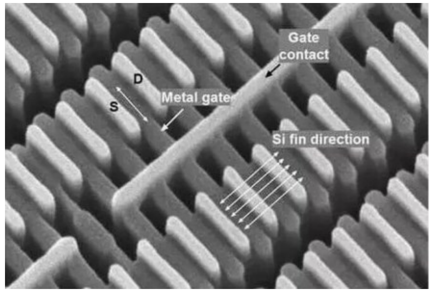
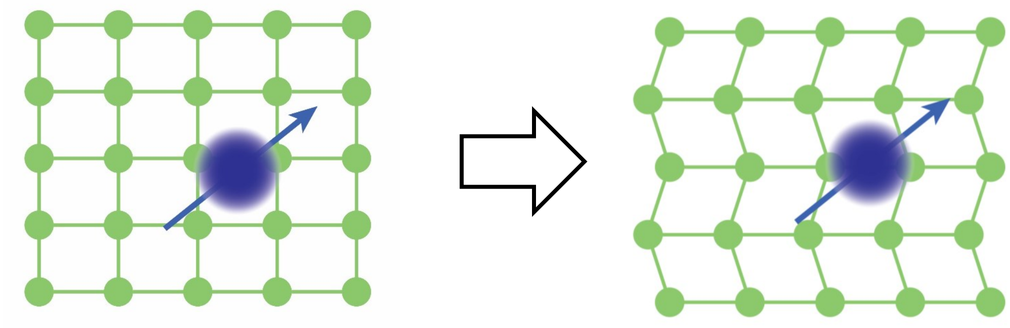


Image: Wikipedia

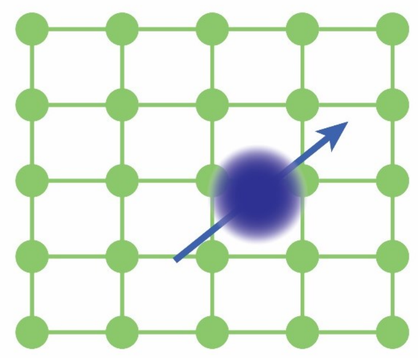
Solar cell

Image: science.org



Electronic structure methods: DFT vs. GW

→ Lec. Thu.1 Louie

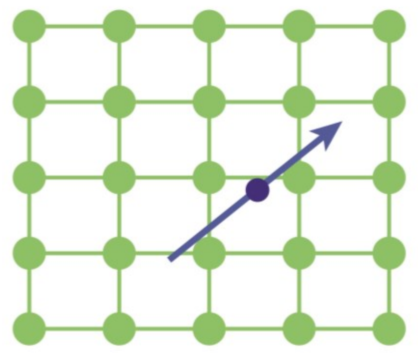


Quasiparticle

GW method

- **Excited-state theory**
- Manybody self-energy

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

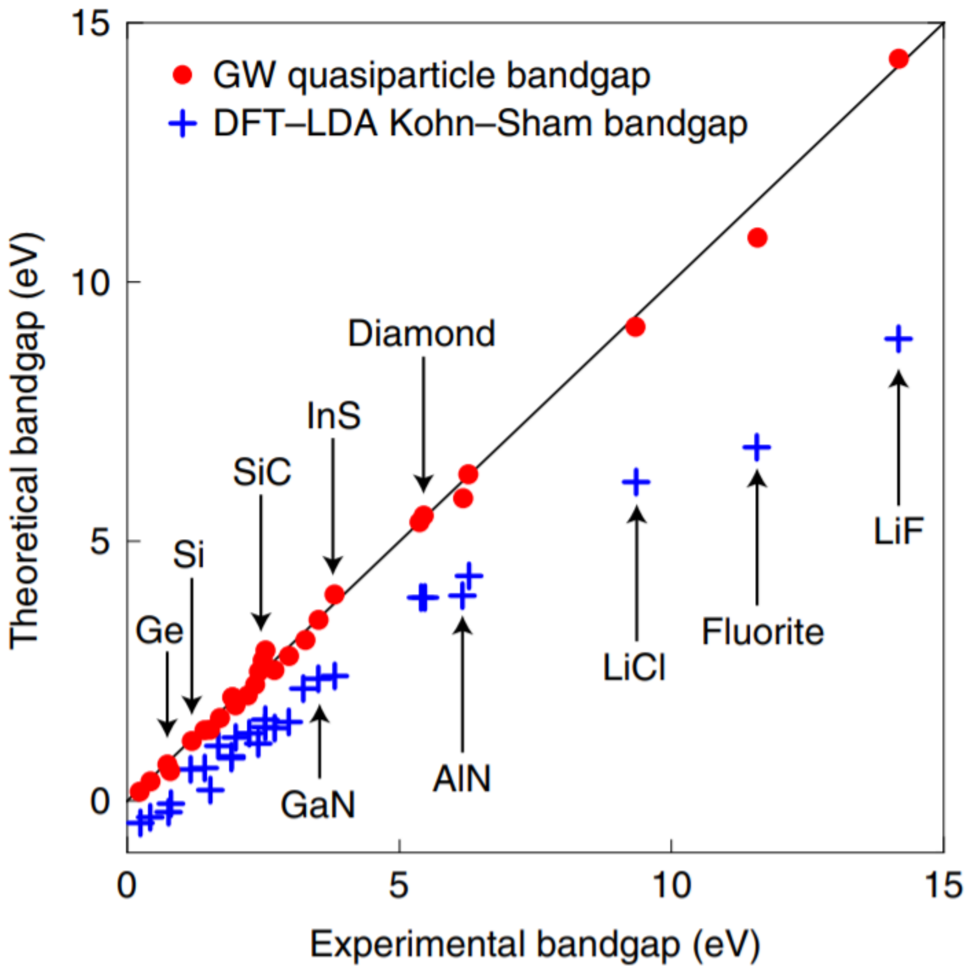


Bare electron

Density functional theory (DFT)

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

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



Hybertsen and Louie, Phys. Rev. Lett. ***55****, 1418 (1985)*
Hybertsen and Louie, Phys. Rev. B ***34****, 5390 (1986)*
Hedin, Phys. Rev. ***139****, A796 (1965)*
Onida, Reining, Rubio, Rev. Mod. Phys. ***74****, 601 (2002)*
Louie, Chan, Jornada, ZL, and Qiu, Nature Materials ***20****, 728 (2021)*

Are there self-energy effects in electron-phonon coupling?

Straightforward approach: Frozen-phonon technique

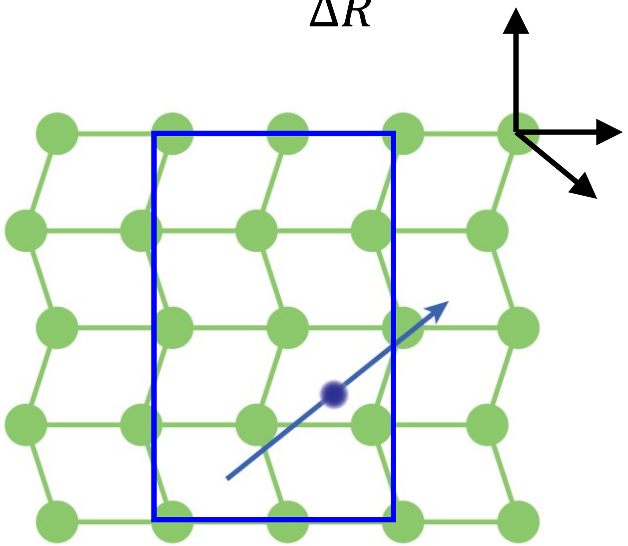
→ Lec. Mon.1 Giustino

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{n\mathbf{k}}(\mathbf{r};\{\mathbf{R}_i\}) + V(\mathbf{r};\{\mathbf{R}_i\})\psi_{n\mathbf{k}}(\mathbf{r};\{\mathbf{R}_i\}) = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r};\{\mathbf{R}_i\})$$

$$\mathbf{R}_i \to \mathbf{R}_i + \Delta\mathbf{R}_i$$

<u>Frozen-phonon (finite-difference)</u>

$$\partial V \approx \frac{V(R+\Delta R) - V(R)}{\Delta R}$$

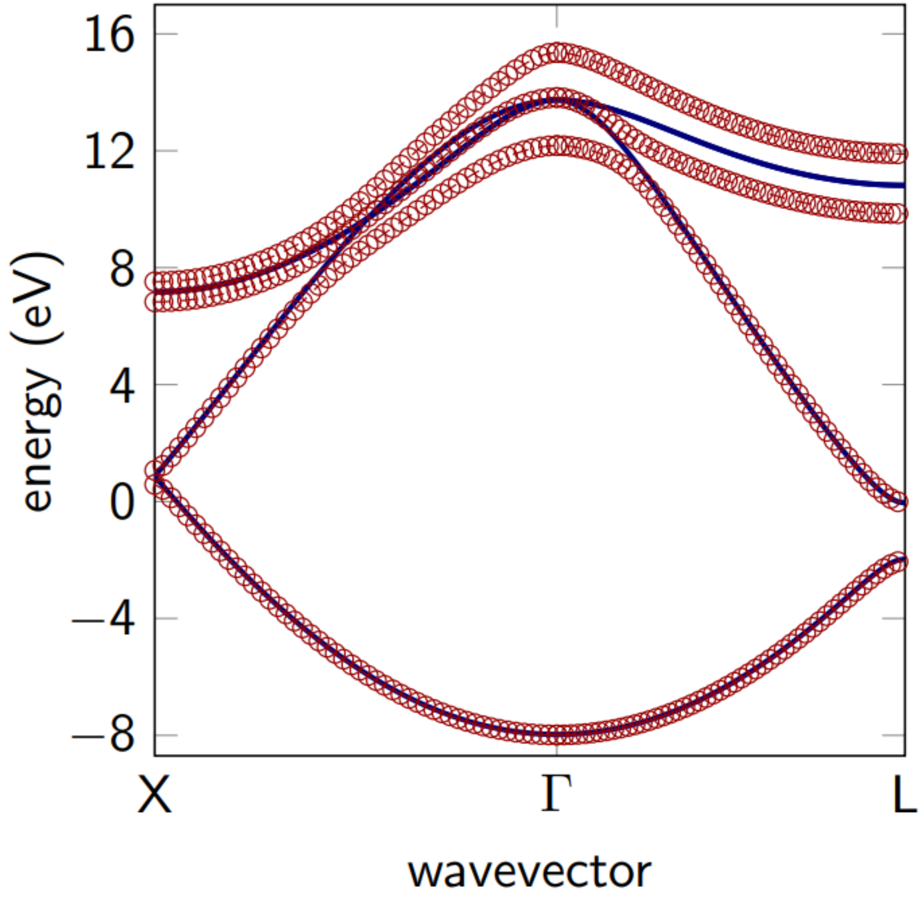


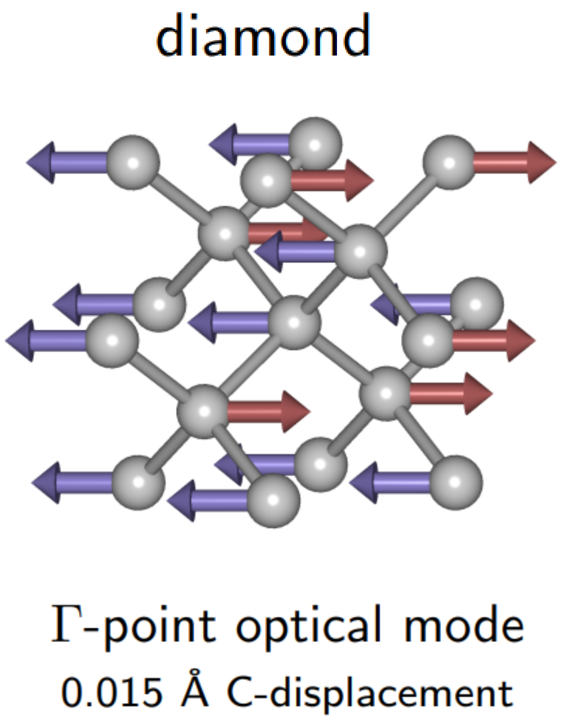
Any electronic structure methods:

- DFT-LDA, DFT-GGA
- Hybrid functional
- Koopmans functional → Lec. Mon.3 Marzari
- GW
- Dynamical mean-field theory (DMFT)
- …

Frozen-phonon technique

Zone-center phonon ⇔ Primitive unit cell → Lec. Mon.1 Giustino

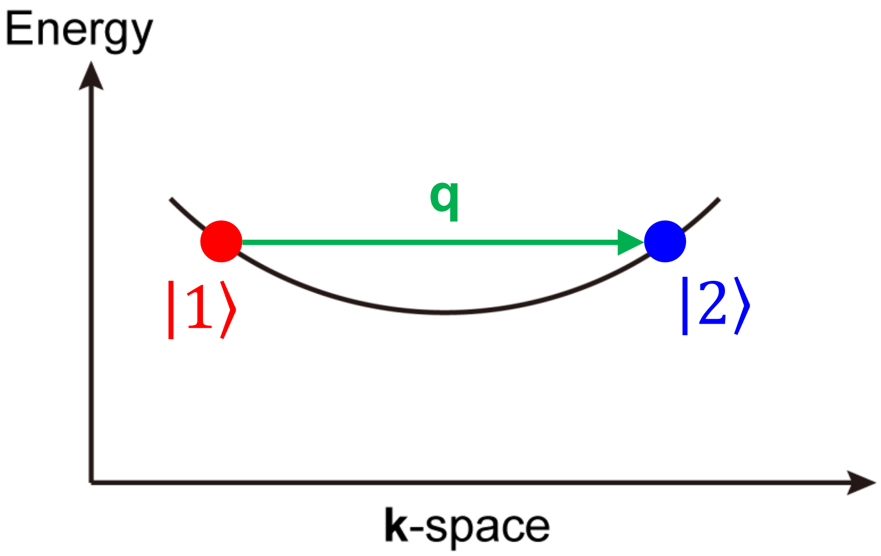




Images from Lec. Mon.1 Giustino

Frozen-phonon technique

Finite-momentum phonon



Supercell with displacements

$$H = H_0 + \Delta V$$

$$\begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix} = \begin{pmatrix} \varepsilon_1 & \Delta V_{12} \\ \Delta V_{12}^* & \varepsilon_2 \end{pmatrix}$$

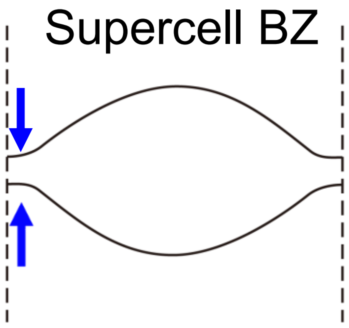
Diagonalization:

$$E_\pm = \frac{\varepsilon_1 + \varepsilon_2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|\Delta V_{12}|^2}}{2}$$

- In a **special case** of $\varepsilon_1 = \varepsilon_2$

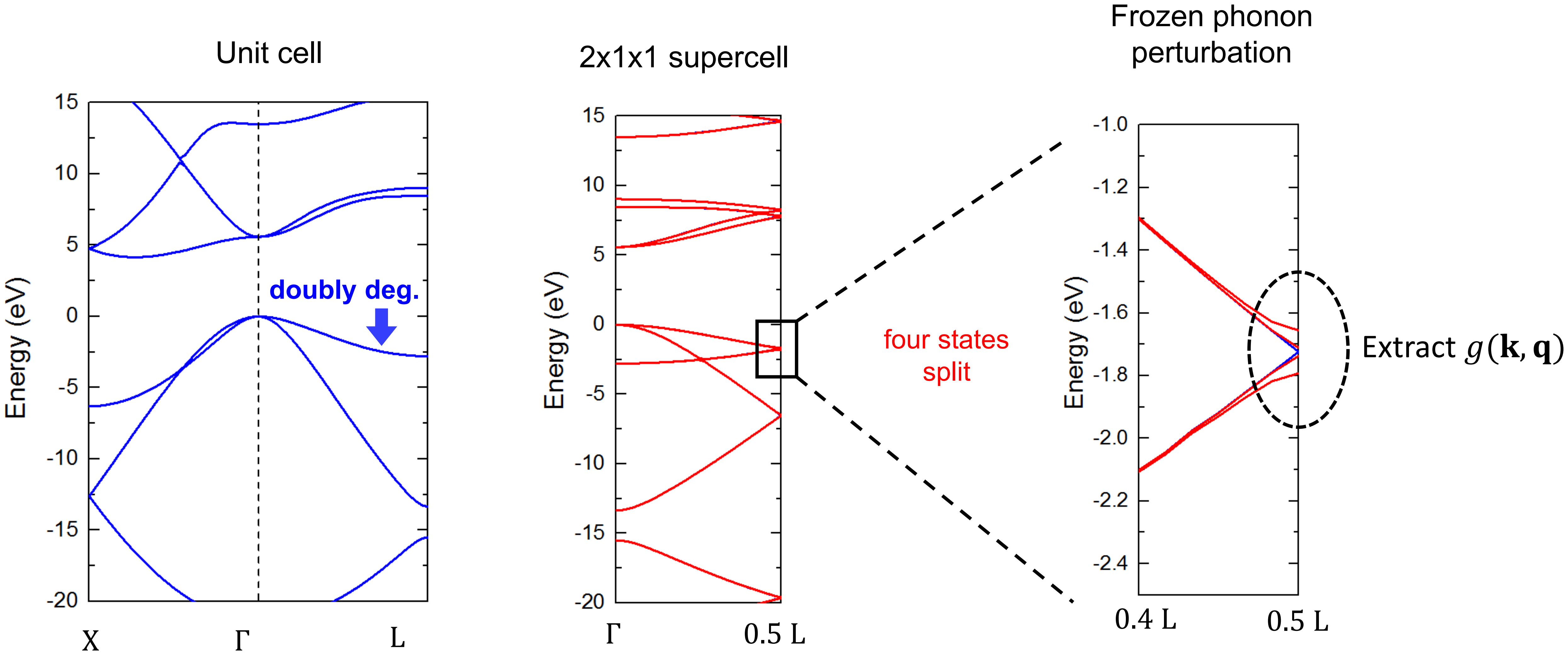
$$E_\pm = \varepsilon_1 \pm |\Delta V_{12}|$$

$$\Delta V_{12} = g_{12} * \Delta x$$



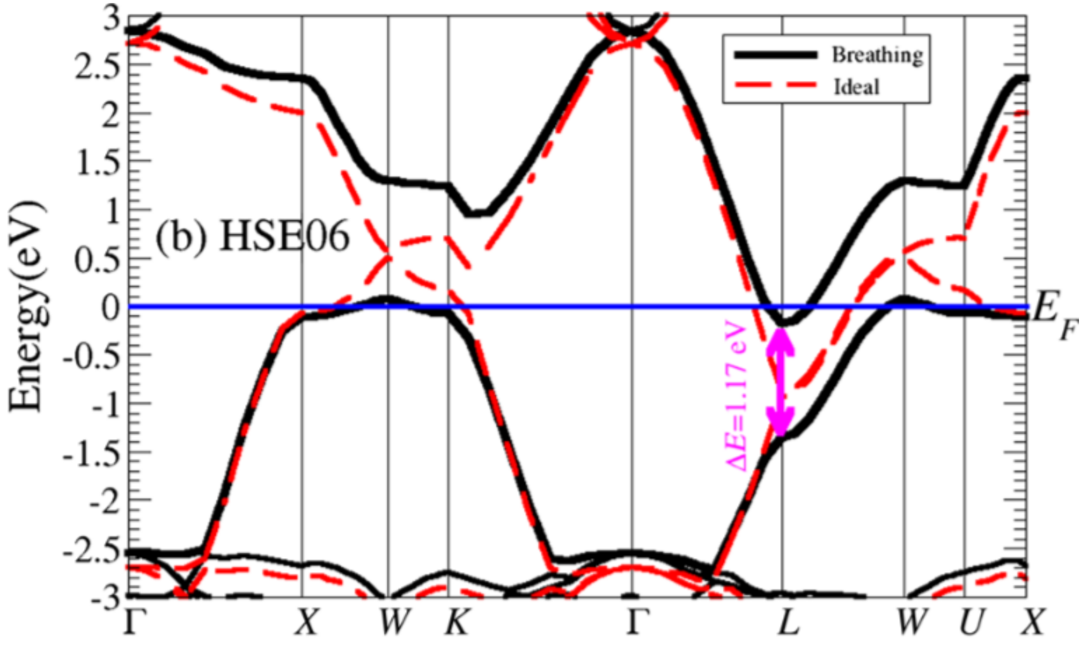
Frozen-phonon technique

- Diamond: L = (0.5, 0.0, 0.0)



Self-energy effects in electron-phonon coupling from frozen phonons

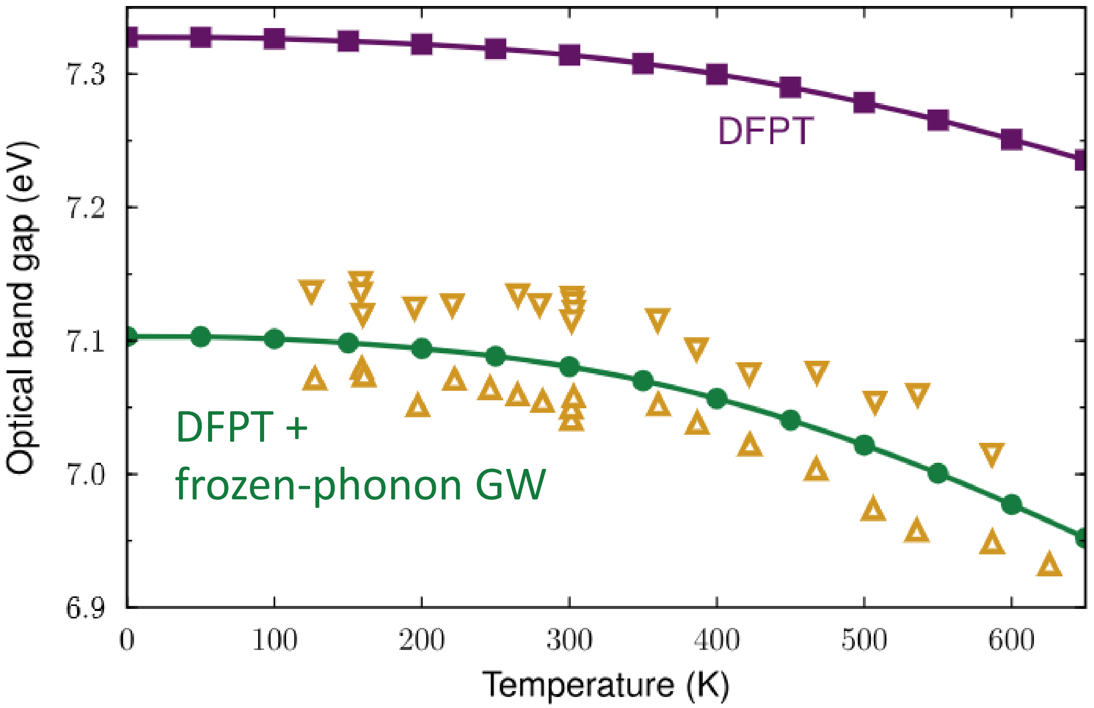
$Ba_{1-x}K_xBiO_3$



Compounds	Mode	λ(LDA)	λ (HSE)	T_c(LDA)	T_c (HSE)	T_c (experiment)
$BaBiO_3$	O breathing at R	0.33	1.0	0.6	31	32.0 [1]

Z. P. Yin, A. Kutepov, G. Kotliar, Phys. Rev. X **3**,021011 (2013)

Diamond



G. Antonius, S. Poncé, P. Boulanger, M. Côté, X. Gonze, Phys. Rev. Lett. **112**, 215501 (2014)

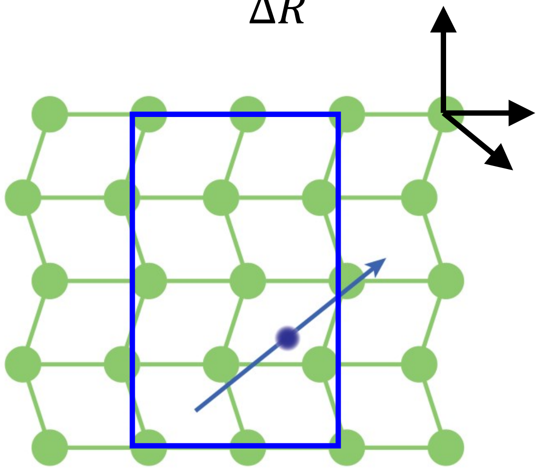
See also:

M. Lazzeri, *et al.*, Phys.Rev. B **78**, 081406(R) (2008); A. Grüneis, *et al.*, Phys. Rev. B **80**, 085423 (2009); C. Faber, *et al.*, Phys. Rev. B **84**, 155104 (2011); C. Faber, *et al.*, Phys. Rev. B **91**,155109 (2015); B. Monserrat, Phys. Rev. B **93**, 100301(R) (2016) …

Frozen-phonon technique *vs.* Linear-response approach

Frozen-phonon (finite-difference)

$$\partial V \approx \frac{V(R+\Delta R) - V(R)}{\Delta R}$$



Supercell

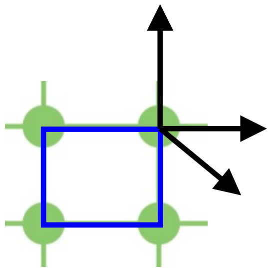
→ Lec. Fri.1 Zacharias

- Easy implementation for any electronic structure methods
- Extract both harmonic and non-harmonic effects
- Thermal configuration sampling

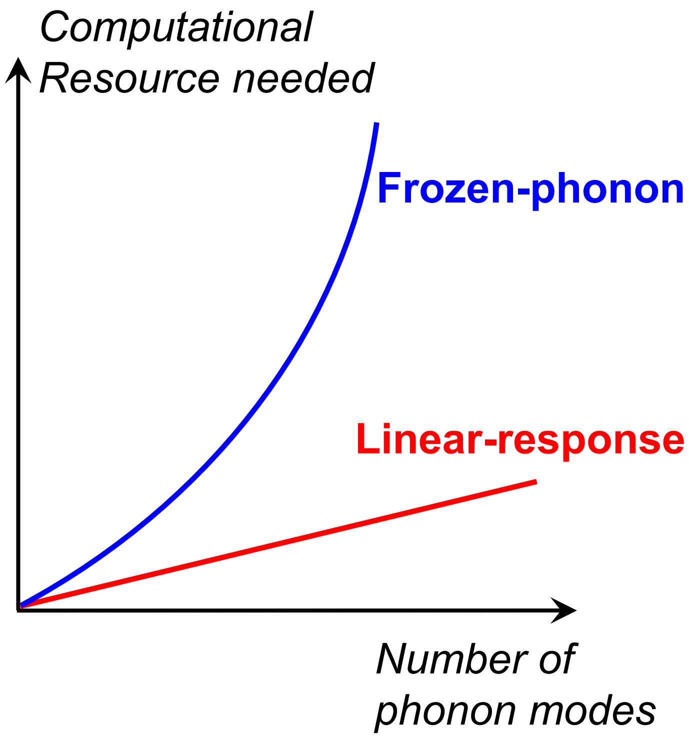
Zacharias, Giustino, Phys. Rev. B **94**, 075125 (2016)
Monserrat, J. Phys. Condens. Matter **30**, 083001 (2018)

Linear-response (differential)

$$\partial_{\mathbf{q}} = \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \frac{\partial}{\partial R}$$



Unit cell



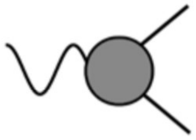
→ Lec. Mon.2 Giannozzi

- Direct formulation of linear-response theories
- Linear O(N) scaling in # of phonon modes
- Direct construction of perturbative quantities
- **Density-functional perturbation theory (DFPT)**

Baroni, Giannozzi, and Testa, Phys. Rev. Lett. **58**, 1861 (1987)

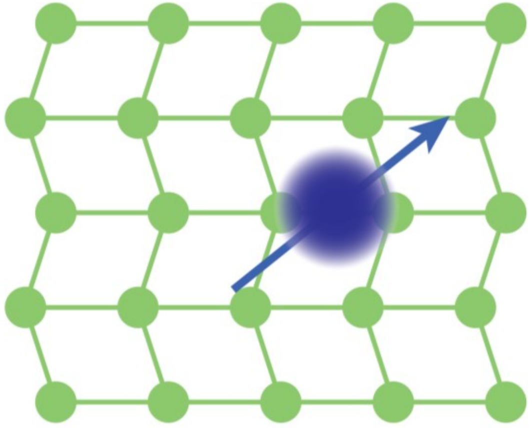
Electron-phonon coupling from first principles

Electron-phonon matrix elements can be **efficiently** and **directly** evaluated by linear-response methods

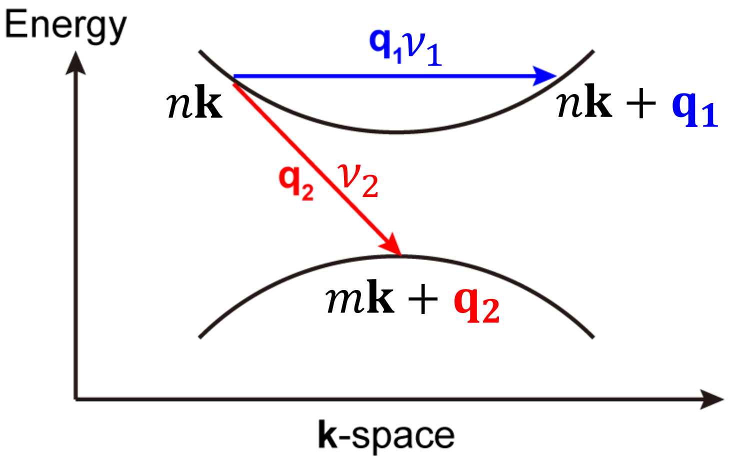


***<u>Electron-phonon matrix element</u>*:** $g_{mn\nu}(\mathbf{k},\mathbf{q})$ scattering amplitude

- **Building blocks** of microscopic *e*-ph theories



$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle$$



k: electron wavevector
n: electron band index

q: phonon wavevector
ν: phonon branch

Giustino, Electron-phonon interactions from first principles, Rev. Mod. Phys. **89**, 015003 (2017)

GW perturbation theory (GWPT)

❖ Electron-phonon coupling from a linear-response formulation within the GW approximation

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

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

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

DFT: single-electron exchange-correlation

GW: many-electron self-energy

m, n: electron band index
ν: phonon band index
$\mathbf{k}, \mathbf{q}$: wave vectors

GWPT enables **systematic**, **efficient**, and **accurate** electron-phonon computation

ZL, Antonius, Wu, da Jornada, Louie, Phys. Rev. Lett. **122**, 186402 (2019)

GW perturbation theory (GWPT)

ZL, Antonius, Wu, da Jornada, Louie, Phys. Rev. Lett. **122**, 186402 (2019)

- We work in crystal coordinates (ABINIT convention), a: lattice vectors $\Delta_{\mathbf{q}\kappa a} = \sum_{l}^{N_l} e^{i\mathbf{q}\cdot\mathbf{R}_l} \frac{\partial}{\partial \tau_{\kappa a l}}$

- First-order change in wavefunctions

$$\Delta_{\mathbf{q}\kappa a}\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{m} \frac{\langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\kappa a} V^{\mathrm{KS}} | \psi_{n\mathbf{k}} \rangle}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}} \psi_{m\mathbf{k}+\mathbf{q}}(\mathbf{r})$$

- First-order change in Green's functions (gauge consistency between $\psi_{n\mathbf{k}}(\mathbf{r})$ and $\Delta_{\mathbf{q}\kappa a}\psi_{n\mathbf{k}}(\mathbf{r})$)

$$\Delta_{\mathbf{q}\kappa a} G(\mathbf{r}, \mathbf{r}'; \varepsilon) = \sum_{n\mathbf{k}} \frac{\Delta_{\mathbf{q}\kappa a}\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}') + \psi_{n\mathbf{k}}(\mathbf{r})\left[\Delta_{-\mathbf{q}\kappa a}\psi_{n\mathbf{k}}(\mathbf{r}')\right]^*}{\varepsilon - \varepsilon_{n\mathbf{k}} - i\delta_{n\mathbf{k}}}$$

- First-order change in GW self-energy and its matrix elements

$$\Delta_{\mathbf{q}\kappa a}\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon) = i \int \frac{d\varepsilon'}{2\pi} e^{-i\delta\varepsilon'} \Delta_{\mathbf{q}\kappa a} G(\mathbf{r}, \mathbf{r}'; \varepsilon - \varepsilon') W(\mathbf{r}, \mathbf{r}', \varepsilon'),$$

$$g^{\Sigma}_{mn\kappa a}(\mathbf{k}, \mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\kappa a} \Sigma | \psi_{n\mathbf{k}} \rangle$$

- Constant screening approximation $\partial_{\mathbf{q}\nu} W = 0$, equivalent to well-justified approximation $\delta W / \delta G \approx 0$ in *GW*-BSE

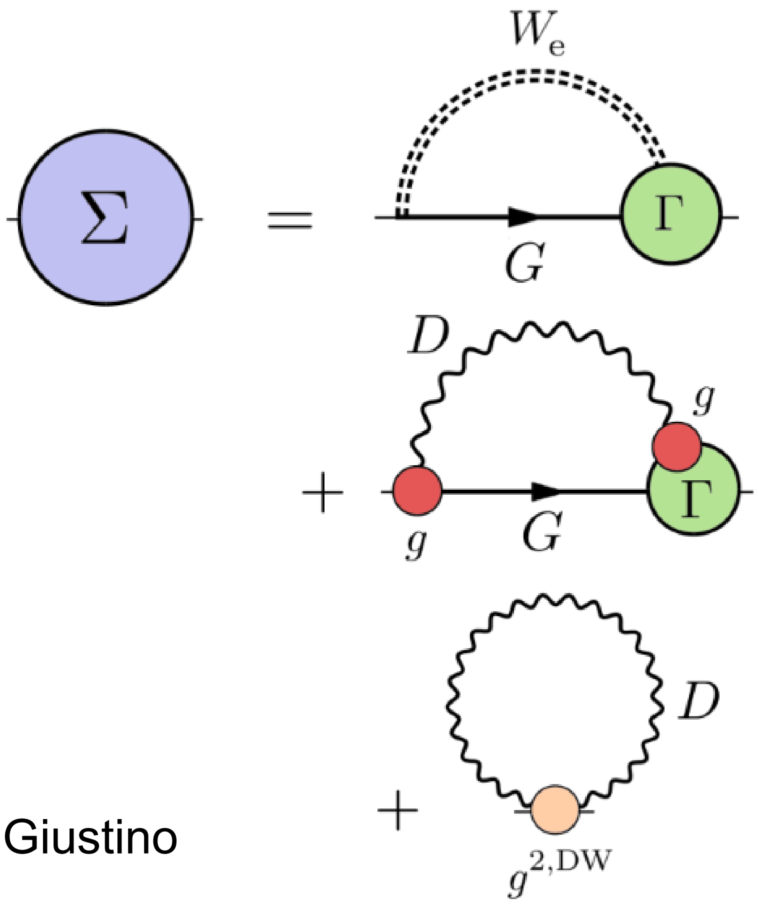
Faber *et al.*, Phys. Rev. B **91**, 155109 (2015)

Electron self-energy from many-body perturbation theory

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

→ Lec. Mon.1.Giustino

→ Lec. Thu.1.Louie



Electronic self-energy $GW\Gamma$

Fan-Migdal (e-ph)

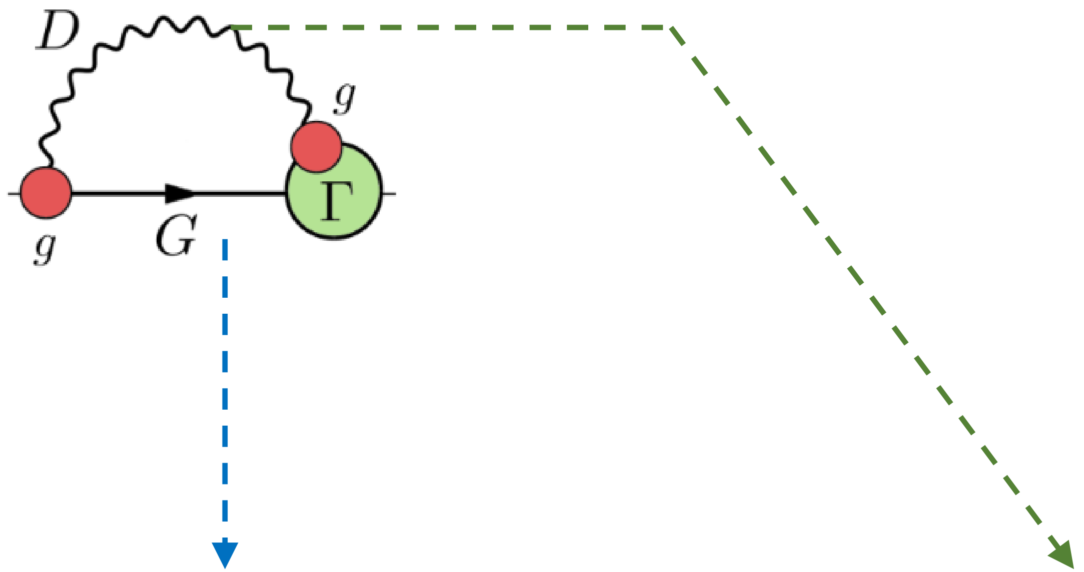
Debye-Waller (e-ph)

Images from Lec. Mon.1.Giustino

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

GW-level electron-phonon phenomena with EPW + BerkeleyGW

Fan-Migdal self-energy



e-ph matrix elements

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

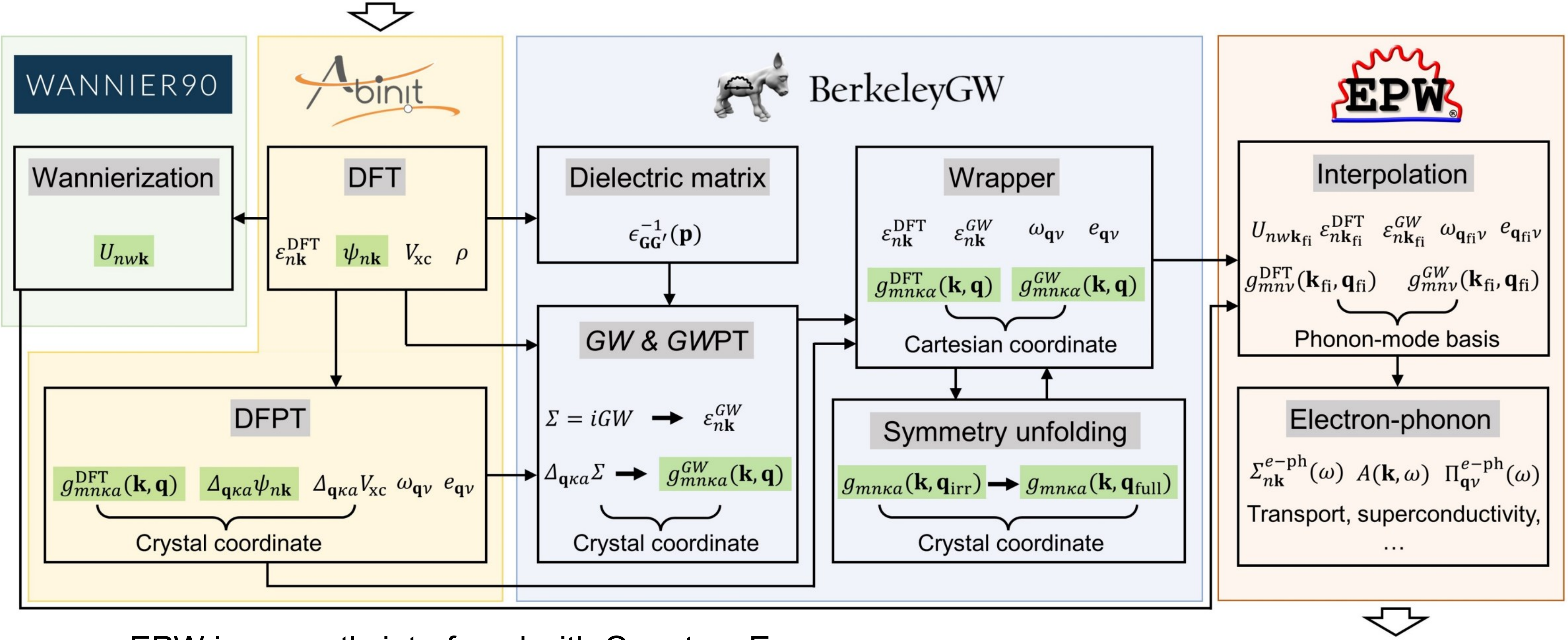
Electron propagator *G*

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

Phonon propagator *D*

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

Practical workflow combining BerkeleyGW, ABINIT, and EPW

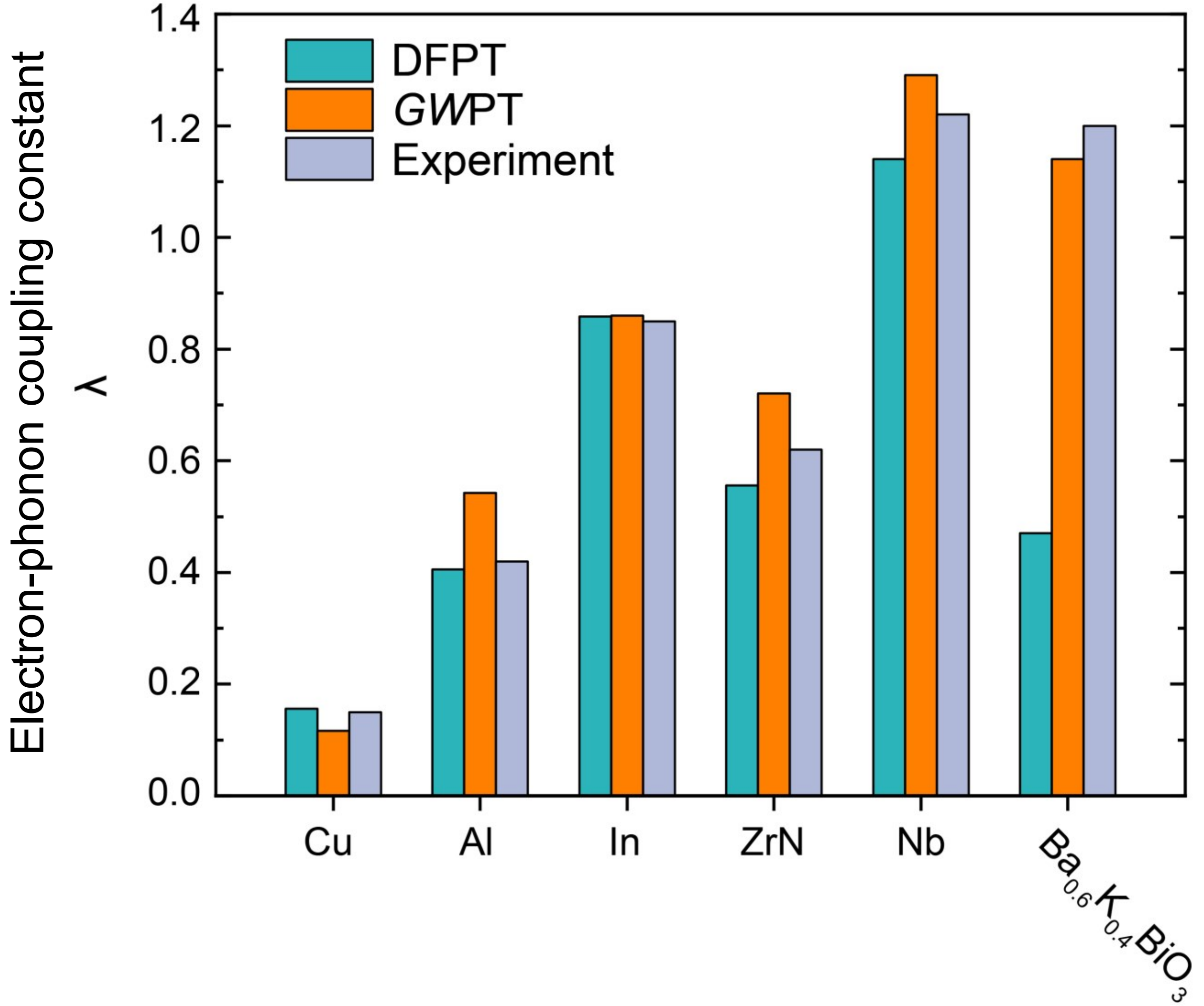


- EPW is currently interfaced with Quantum Espresso
- This workflow enables BerkeleyGW-EPW & ABINIT-EPW interfaces
- Green boxes highlight gauge-consistent quantities fixed to a unique set of $\{\psi_{n\mathbf{k}}\}$ in DFT
  - Construction of 0th- and 1st-order self-energy operators
  - Wannierization

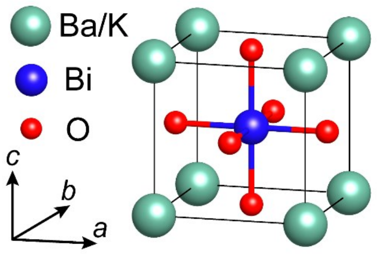
ZL, Antonius, Chan, Louie, Comput. Phys. Commun. **295**, 109003 (2024)

GWPT validation set

GWPT shows predictive power in a wide range of materials (sp-band, d-band, elemental, compound, oxide)

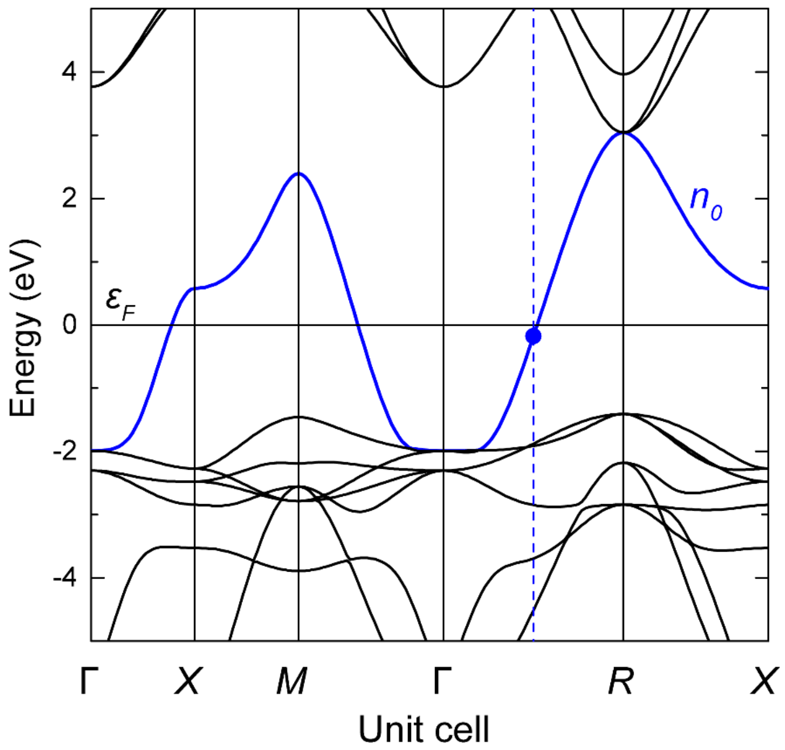


Superconductor $Ba_{1-x}K_xBiO_3$

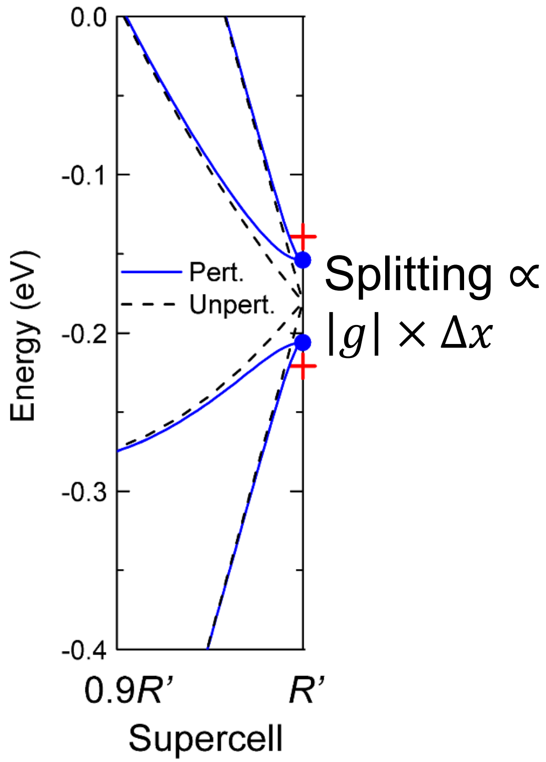


$Ba_{1-x}K_xBiO_3$: experimental T_c = 32 K at x = 0.4

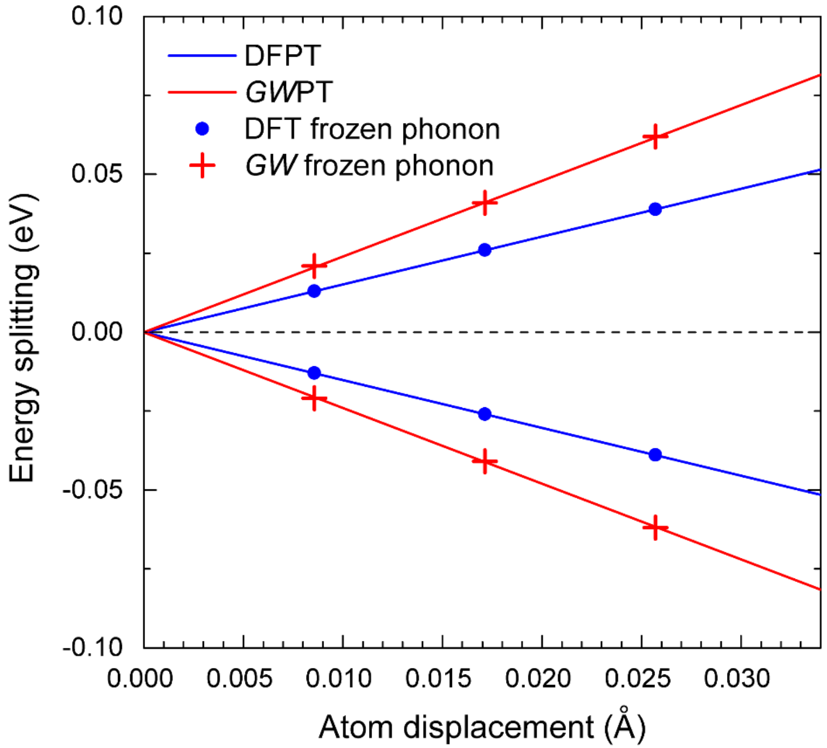
Band structure



Band structure of supercell



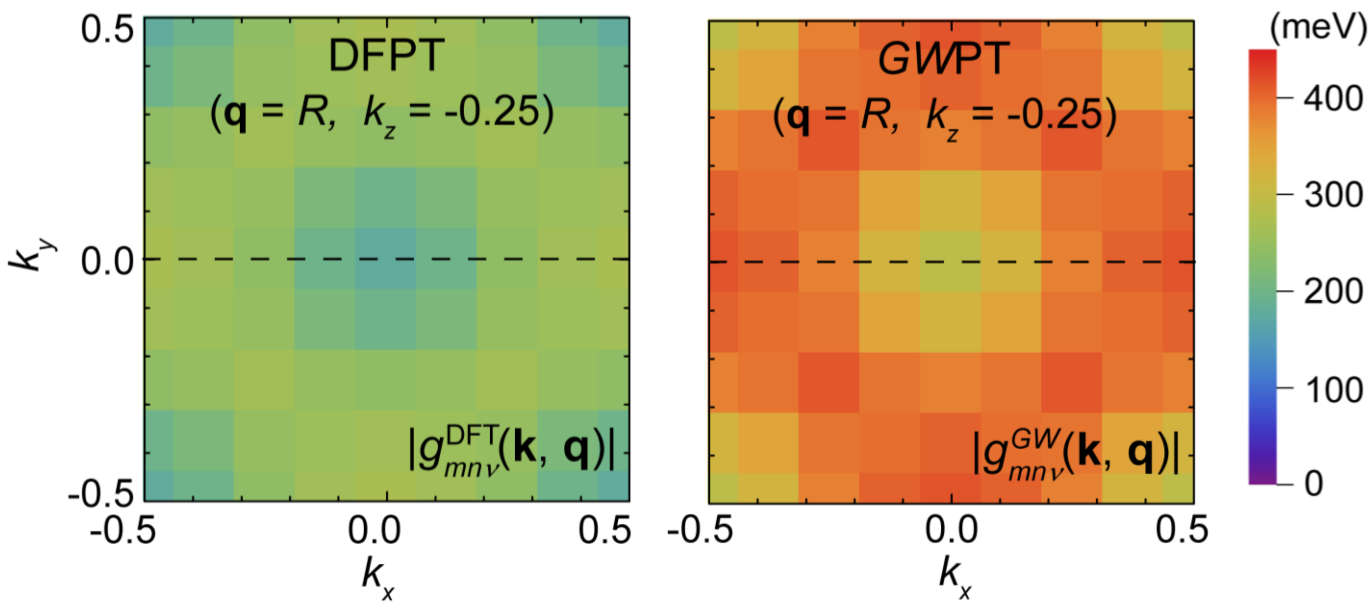
Linear response *vs.* frozen phonon



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

Access to matrix elements in full BZ with unit-cell calculations

Distribution of e-ph matrix elements $|g|$



8x8x8 phonon **q**-grid

8x8x8 electron **k**-grid

(2560 atoms for frozen-phonon GW)

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

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

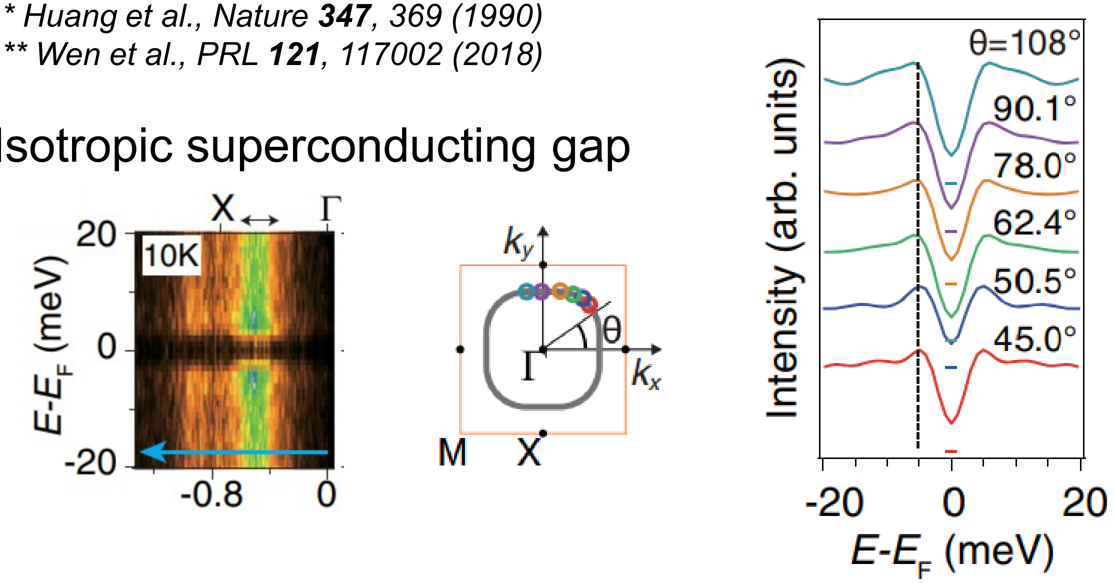
Correlation-enhanced superconductivity in $Ba_{1-x}K_xBiO_3$

❖ Electron-phonon coupling strength λ

BKBO	DFPT	GWPT	Experiment
λ	0.47	1.14	1.2* (x = 0.4) 1.3** (x = 0.49)

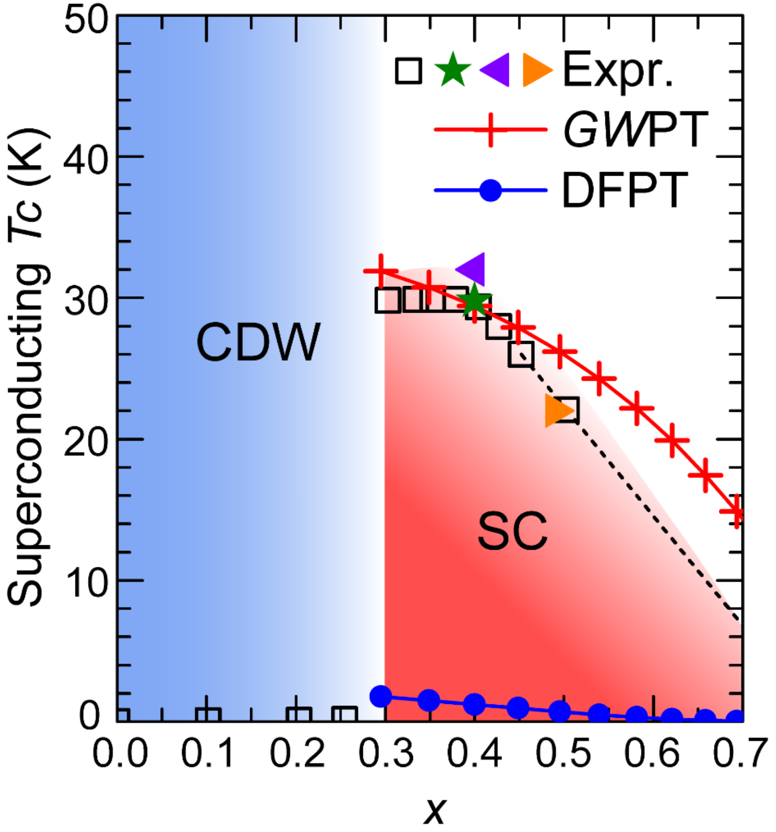
** Huang et al., Nature* ***347****, 369 (1990)*
*** Wen et al., PRL* ***121****, 117002 (2018)*

❖ Isotropic superconducting gap



❖ McMillan–Allen-Dynes formula to estimate superconducting T_c

$$T_c \sim e^{-1/\lambda}$$



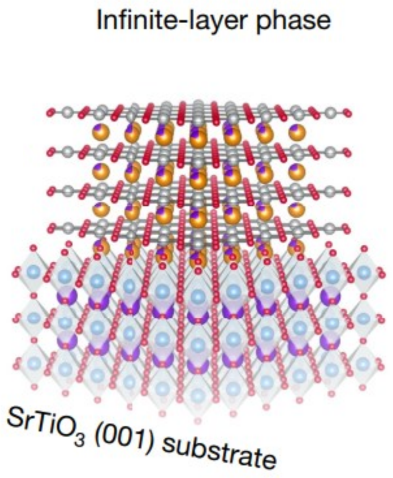
ZL, Antonius, Wu, da Jornada, Louie, PRL **122**, 186402 (2019)

Many-electron correlations greatly enhance phonon-mediated T_c!

Discovery of superconductivity in infinite-layer nickelates

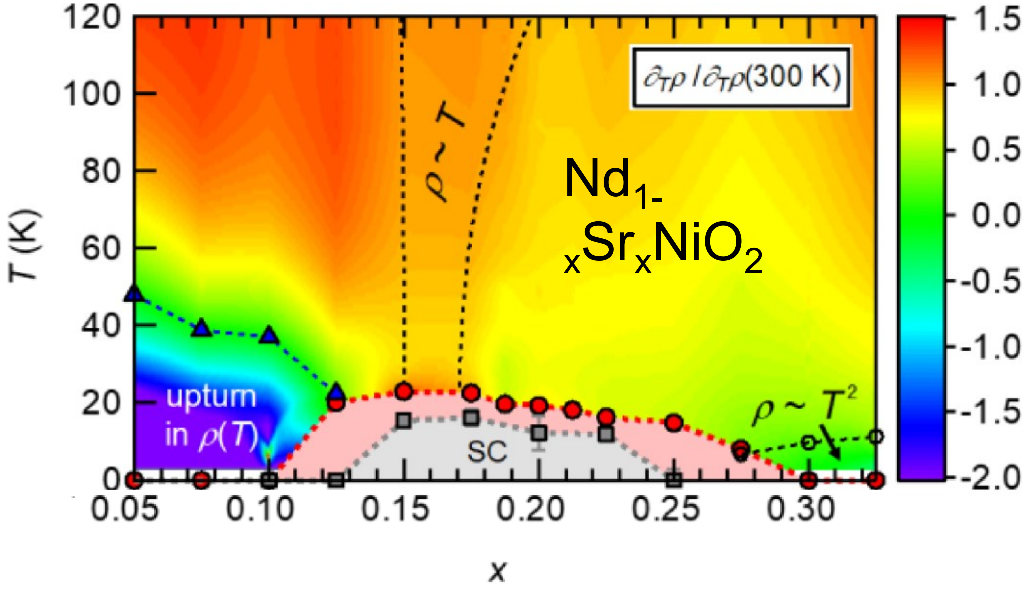
- In 2019, superconductivity was observed in infinite-layer nickelate $Nd_{0.8}Sr_{0.2}NiO_2$ thin films
- Nickelates are thought of as being analogs of unconventional high-T_c cuprate superconductors
- DFT electron-phonon coupling predicted a $T_c < 1$ K

DFT: Nomura *et al.*, PRB **100**, 205138 (2019)



$Nd_{0.8}Sr_{0.2}NiO_2$
(112 phase)

Phase diagram, max. T_c ~ 20 K



- Higher T_c and larger dome in cleaner samples

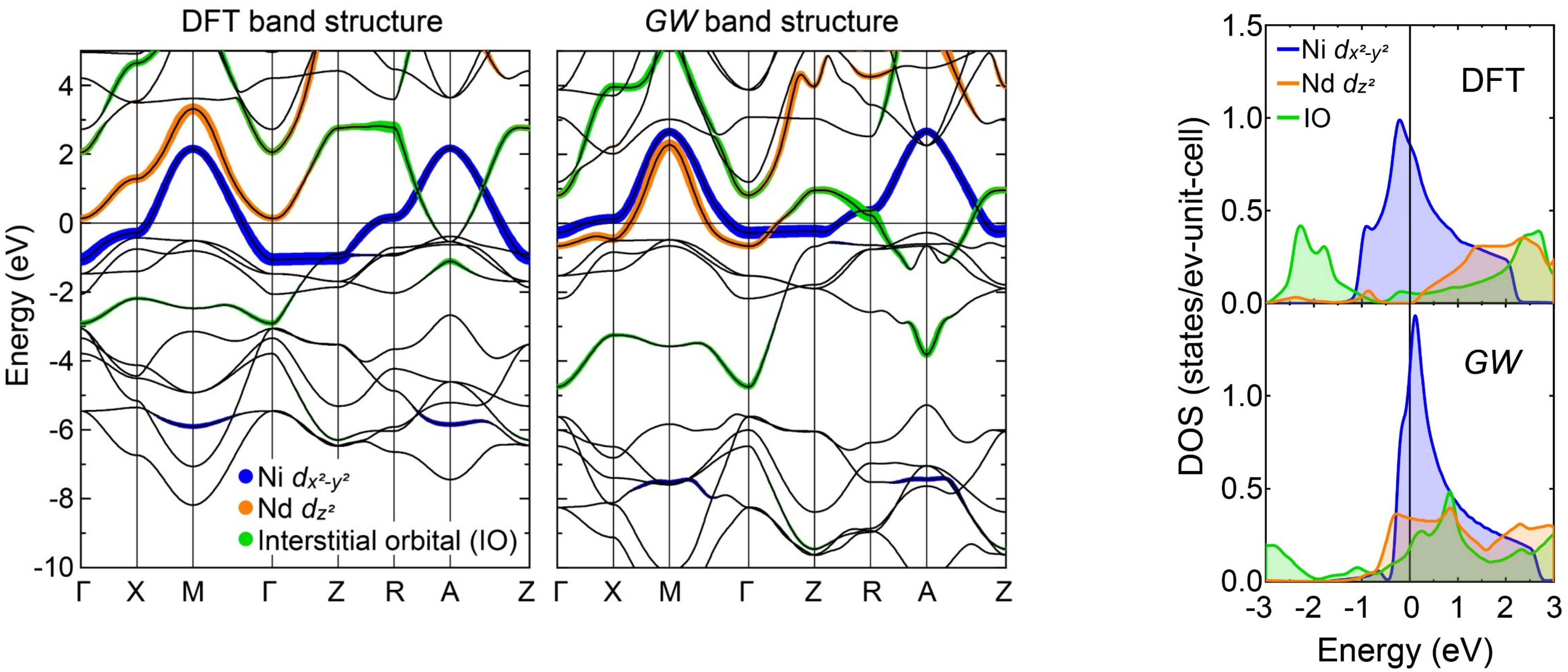
Discovery: Li *et al.*, Nature **572**, 624 (2019)

Doping dependence: Li *et al.*, Phys. Rev. Lett. **125**, 027001 (2020)
Zeng *et al.*, Phys. Rev. Lett. **125**, 147003 (2020)

Lee *et al.*, Nature **619**, 288 (2023)

DFT vs. *GW* band structures

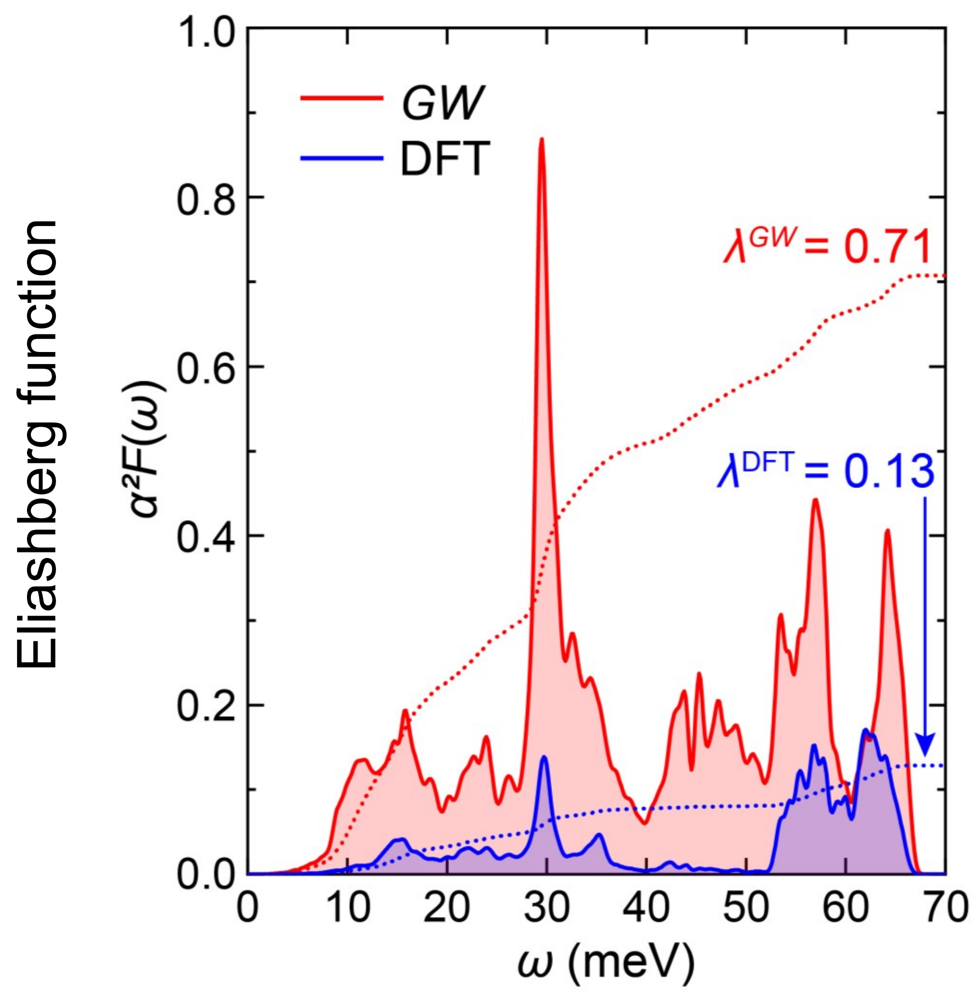
$Nd_{1-x}Sr_xNiO_2$ (x = 0.2)



- *GW* self-energy effects significantly enhance the DOS of Nd-IO at E_F
- Within systematic uncertainty (e.g. self-consistency), feature is robust across doping phase diagram

ZL and Louie, arXiv:2210.12819 (2022)

DFT vs. *GW* Electron-phonon coupling



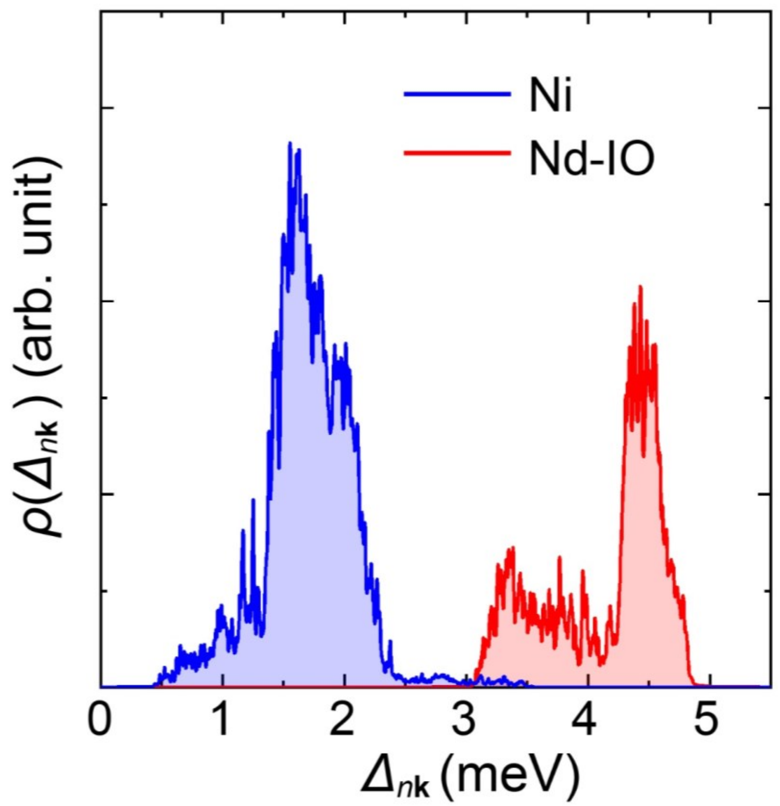
Phonon-frequency dependent coupling strength

- ***Factor of 5.5 enhancement in total coupling λ!***
- Two major *GW* self-energy effects:
  - ❖ Introduce significant Nd-IO DOS to E_F ⇔ *Enhance λ by a factor of* ***3.7*** (DFT vs. GW bands, fixing DFT e-ph matrix)
  - ❖ Renormalize *e*-ph matrix elements ⇔ *Enhance λ by a factor of* ***1.5*** (DFT vs. GW e-ph matrix, fixing GW bands)

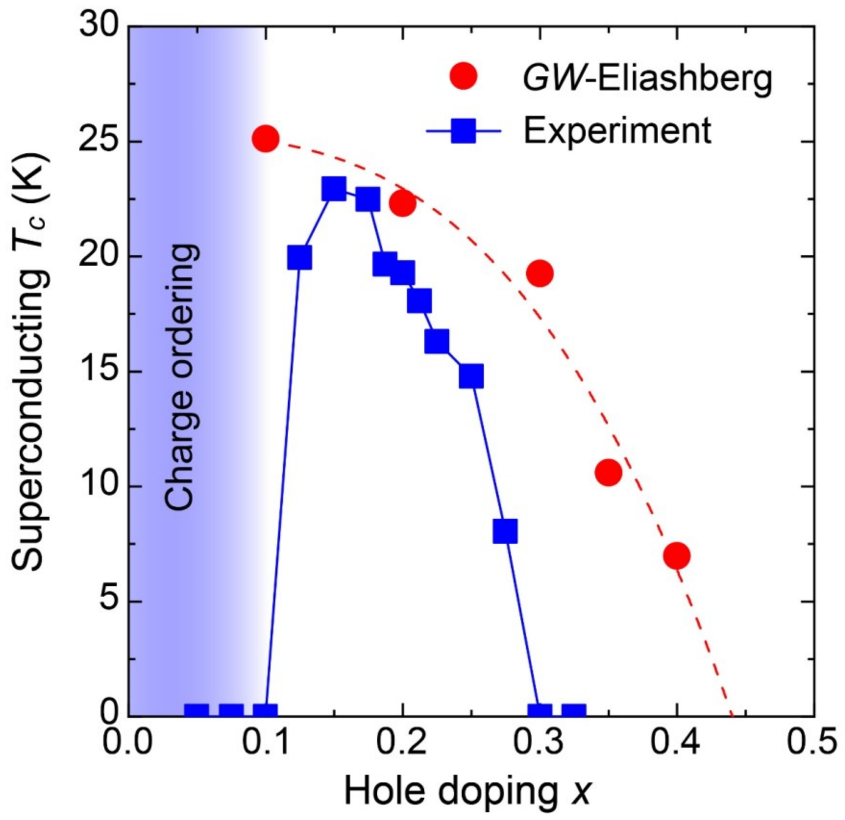
ZL and Louie, arXiv:2210.12819 (2022)

Superconducting properties

_GW_-Eliashberg solutions



Doping dependence



Ab initio prediction
⇔ A _possible_ phonon-mediated two-gap _s_-wave superconductivity

Experimental data: Lee *et al.*, Nature **619**, 288 (2023)

ZL and Louie, arXiv:2210.12819 (2022)

Dispersion kinks from angle-resolved photoemission spectra

Angle-resolved photoemission spectroscopy (ARPES)

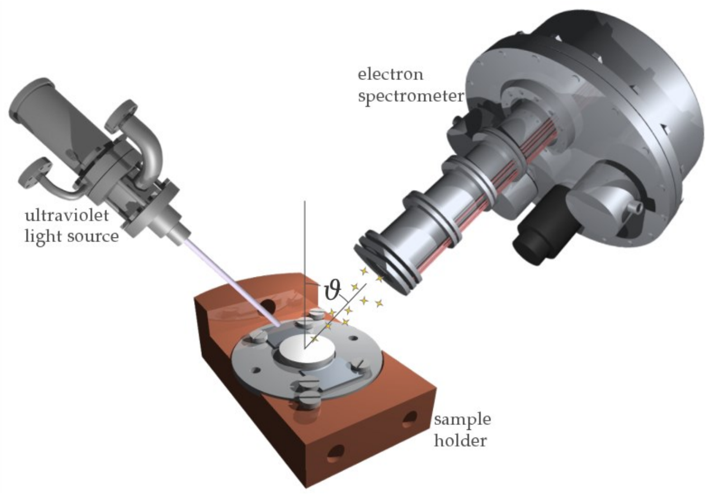


Image: Wikipedia

Copper-oxide superconductors

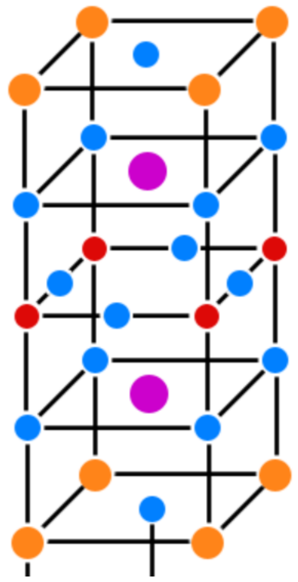
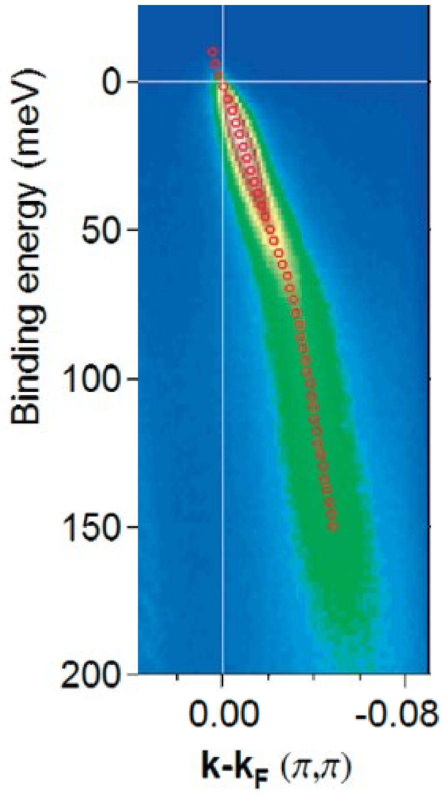


Image: Wikipedia

Ubiquitous 70-meV kinks in dispersion relations



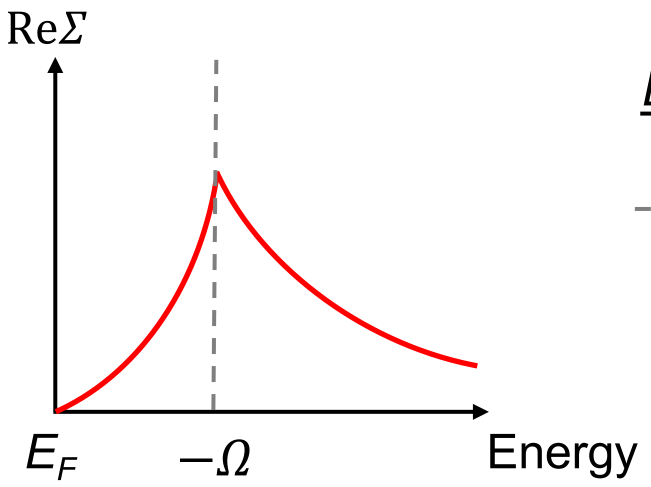
Is electron-phonon coupling the origin of the photoemission kink?

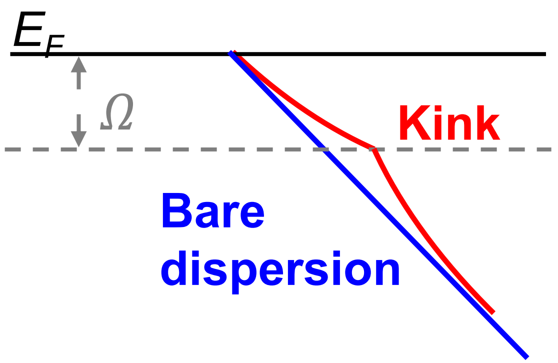
*Lanzara, et al., Nature **412**, 510 (2001)*
*Koralek et al., Phys. Rev. Lett. **96**, 017005 (2006)*

Electron-phonon self-energy

- ❖ **Electron-phonon self-energy** $\Sigma^{e-\mathrm{ph}}$
- ○ Simple model: single phonon frequency Ω

→ Lec. Tue.2 Giustino





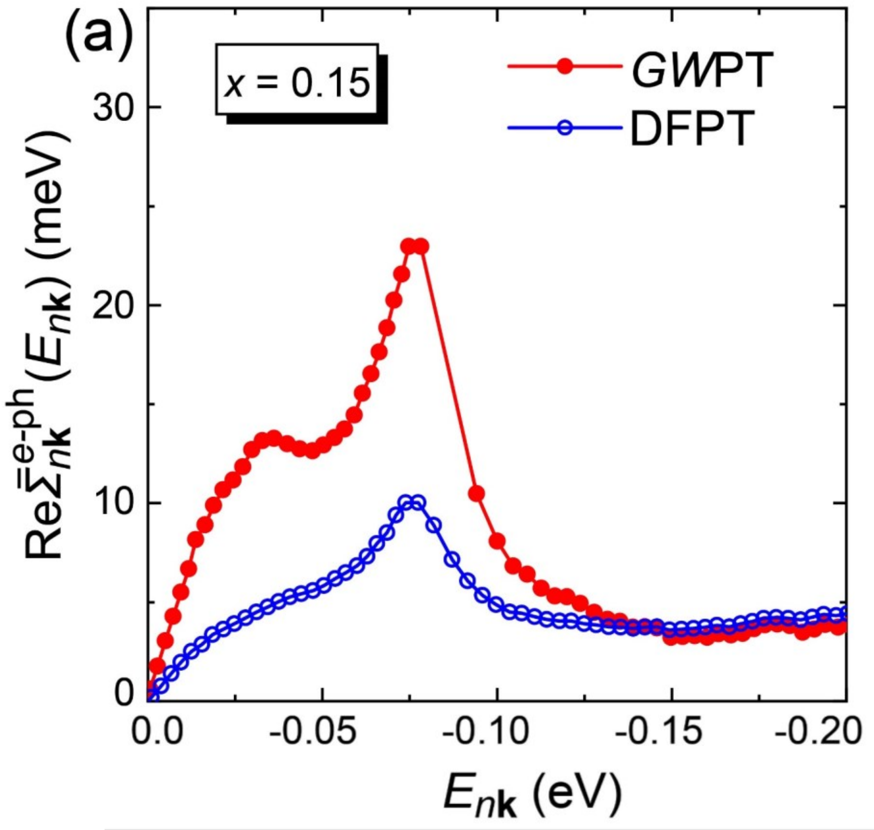
ZL, Wu, Chan, Louie, PRL **126**, 146401 (2021)

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

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

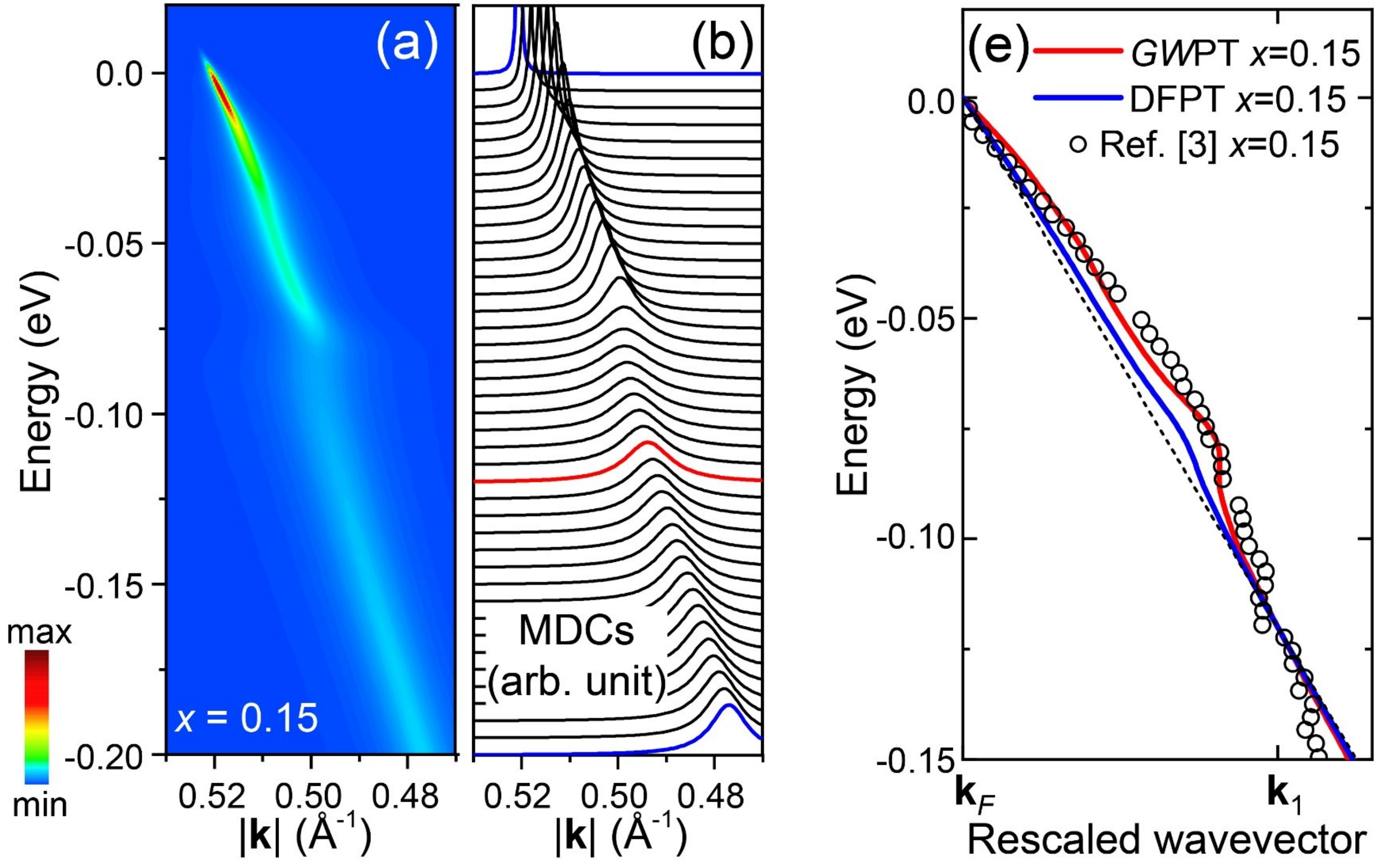
❖ **First-principles calculations**

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



Spectral function analysis

- Fit momentum distribution curves (MDCs) to extract dispersions



❖ **GWPT** electron-phonon coupling ***explains*** kink in cuprates

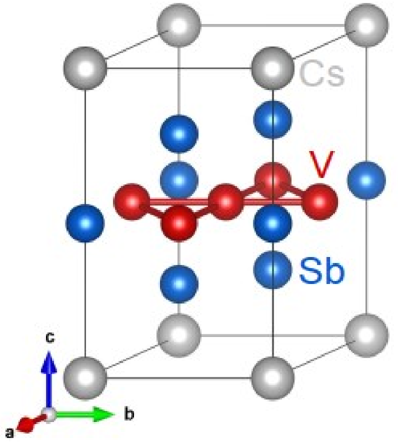
- *Dispersion*
- *Linewidth*
- *Temperature dependence*
- *Doping dependence*

Correlation-enhanced electron-phonon coupling induces kinks in cuprates

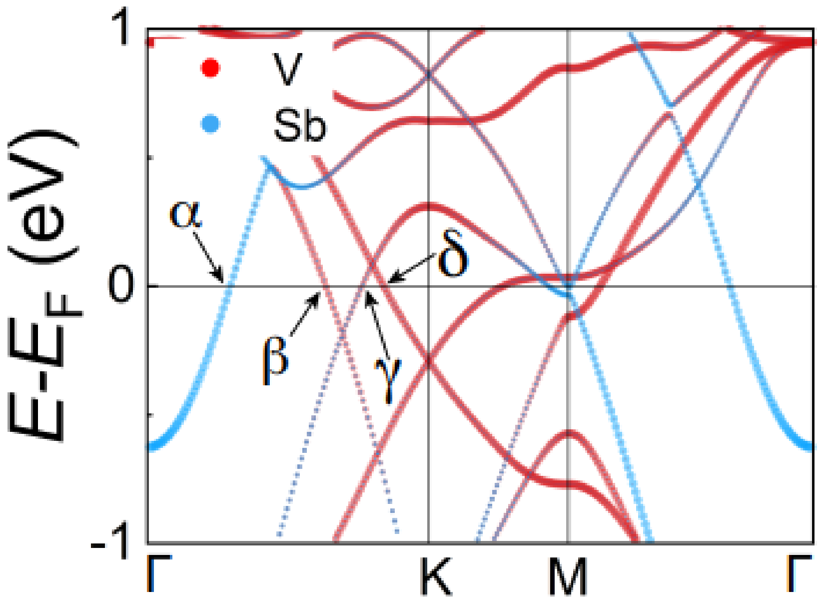
ZL, Wu, Chan, Louie, Phys. Rev. Lett. **126**, 146401 (2021)

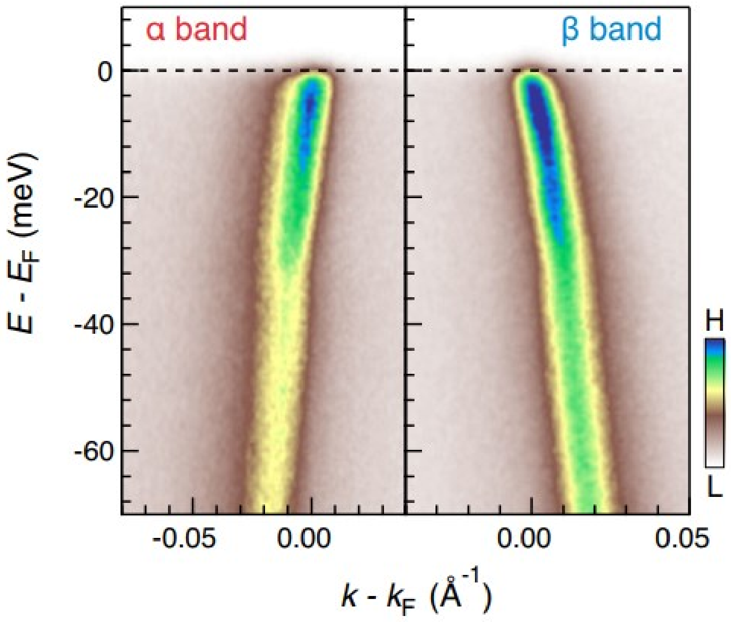
Expt. data from: Lanzara, Shen *et al.* Nature (2001)

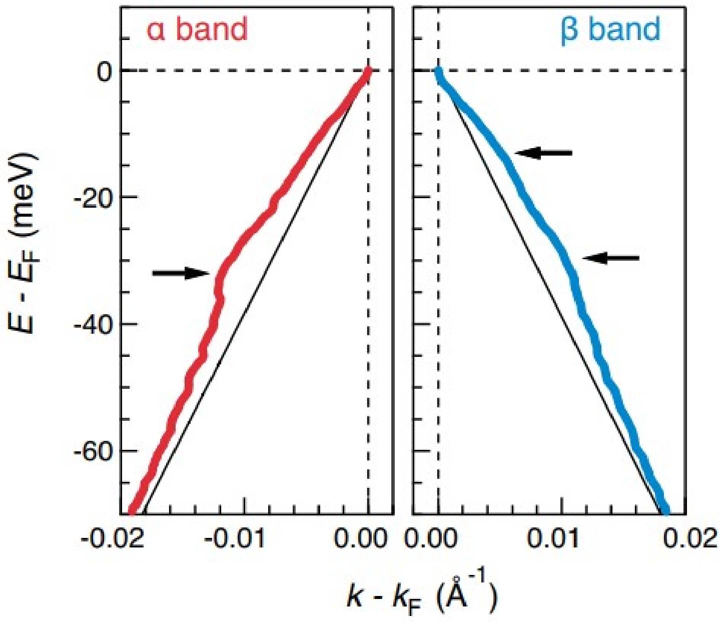
Kagome superconductor CsV_3Sb_5



- Kagome metals AV_3Sb_5 (A = K, Rb, Cs) host superconductivity, charge-density wave, and topological states
- Different kink profiles in two bands



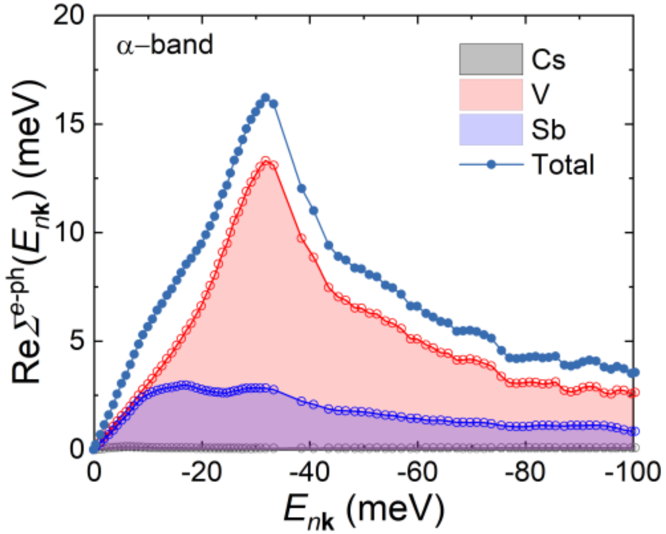




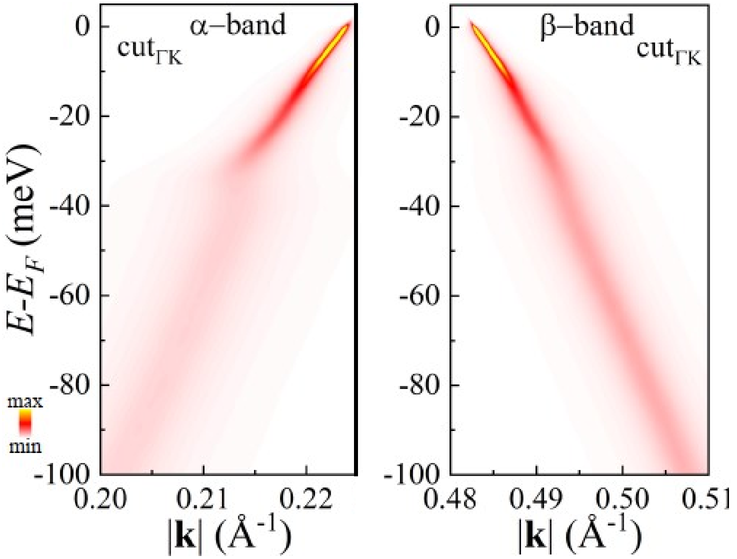
Zhong et al., Nature Commun. **14**, 1945 (2023)
Zhong et al., Nature **617**, 488 (2023).

Multimodal photoemission kinks from phonons

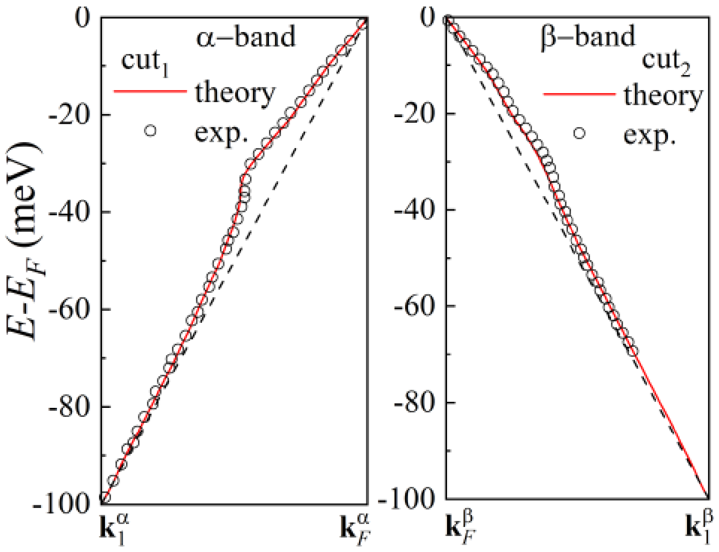
- Vibration decomposition

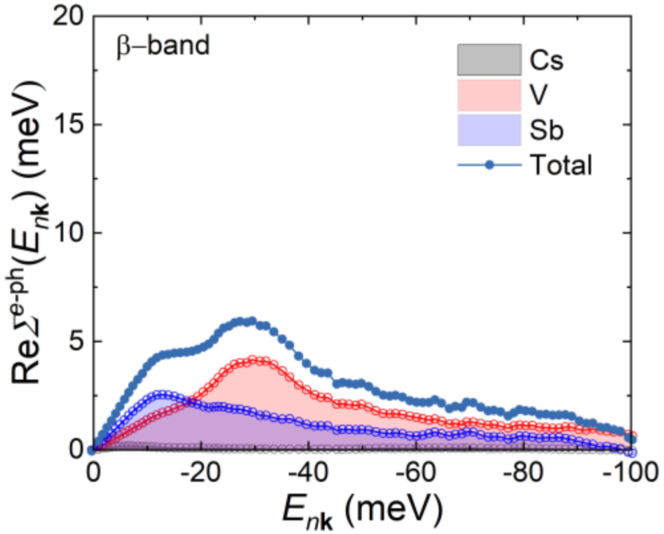


- Theoretical spectral functions



- Theory *vs.* experiment



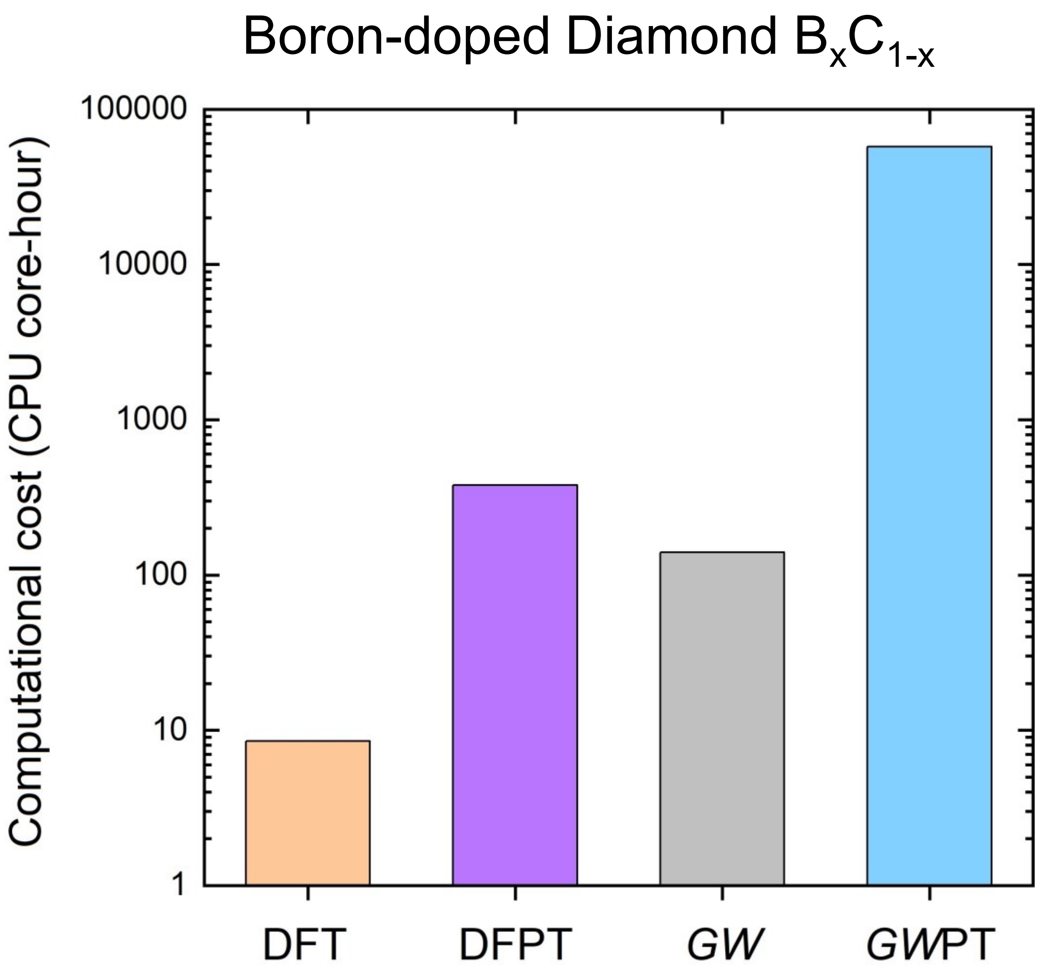


- Theory shows multimodal kinks and different behaviors in α and β bands

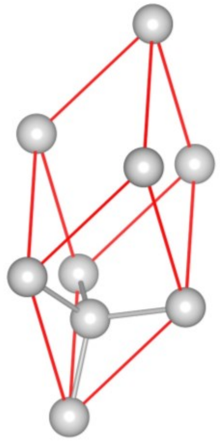
Experiment: Zhong et al., Nature Commun. **14**, 1945 (2023)

Jing-Yang You, Mauro Del Ben, ZL, submitted (2024)

Computational cost of GWPT



Running on Frontera at TACC



Two-atom unit-cell calculations

➢ $N_{\mathrm{mode}} = 3 \times N_{\mathrm{atom}} \times N_{\mathbf{q}}$

Computational cost

- $t_{GW} \sim t_{DFPT}$
- $t_{DFPT} / t_{DFT} \sim 10^1 - 10^2$
- **$t_{GWPT} / t_{GW} \sim 10^2 - 10^3$**

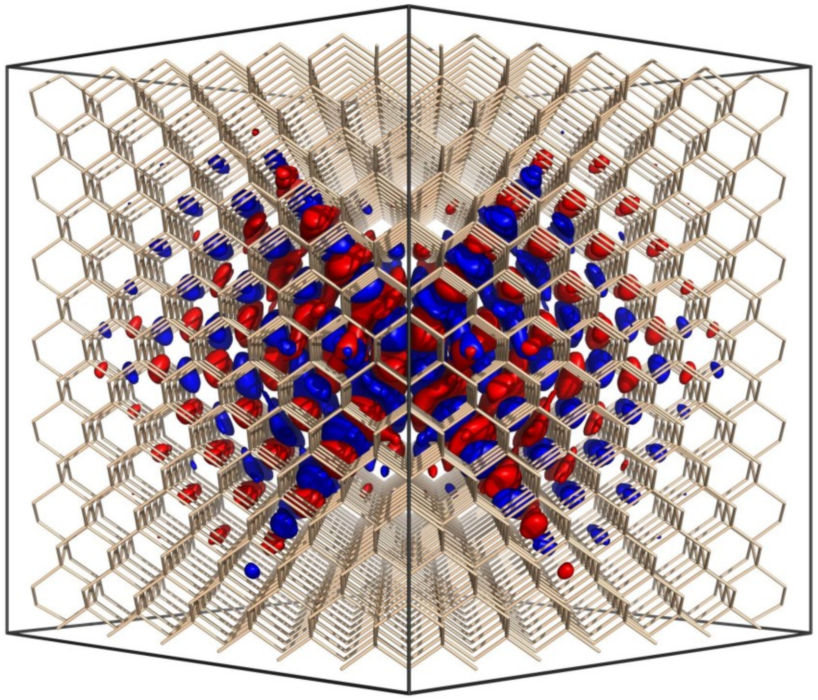
ZL, Antonius, Chan, Louie, Comput. Phys. Commun. **295**, 109003 (2024)

Highly scalable BerkeleyGW package

BerkeleyGW

→ Lec. Thu.5 Deslippe

→ Lec. Thu.6 DelBen



Large-scale GW calculations

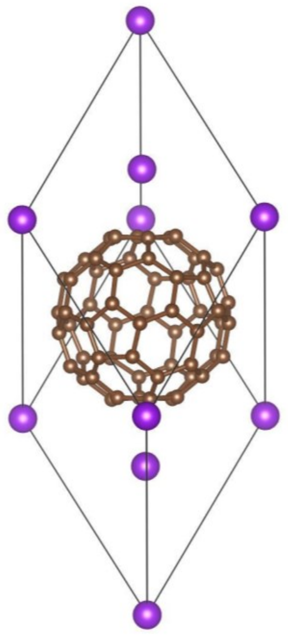
- 10,968 electrons (2,742 atoms)
- 27,648 GPUs, full scale on Summit
- 105.9 PFLOP/s
- 52.7% of theoretical peak of Summit
- Time-to-solution 10 minutes

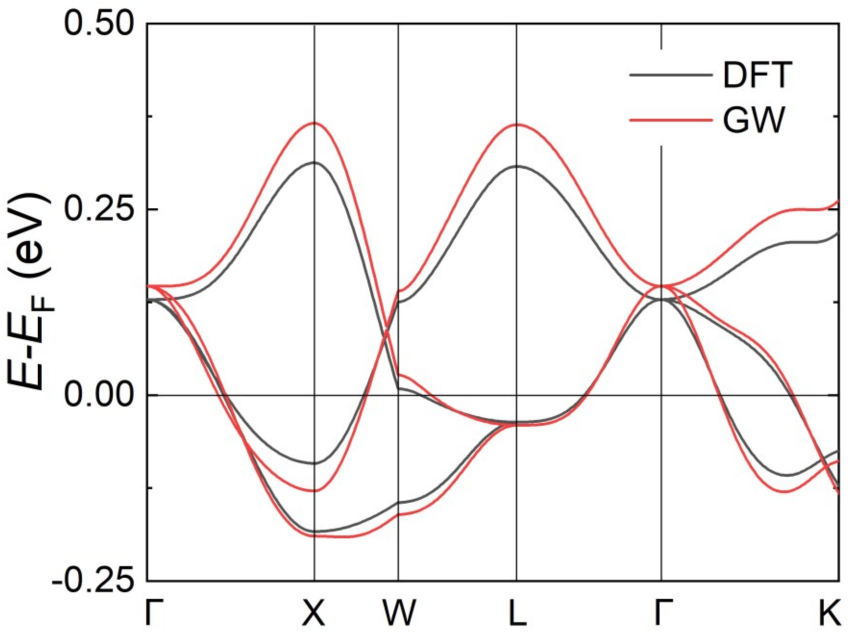
- Continuing efforts in porting to new HPC
- Cross-architecture implementation

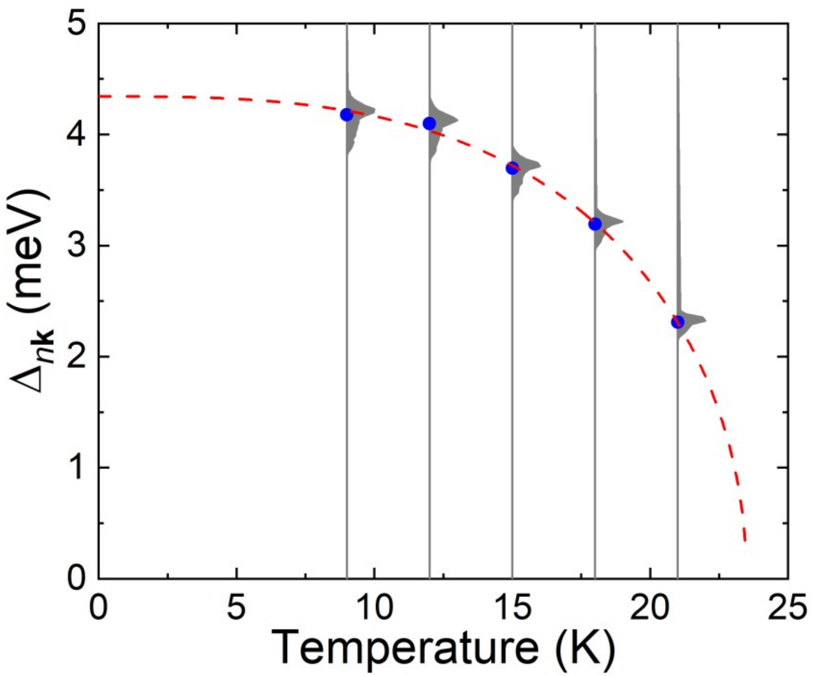
Del Ben, Yang, ZL, Jornada, Louie, and Deslippe, *SC20* **1**, 36 (2020)

Large-scale GWPT calculation of K_3C_{60}

BerkeleyGW EPW







You, Del Ben, Louie, Li *et al.*, (2024)

- 63-atom GWPT calculations [Jing-Yang You (*USC*)] w/ GPUs
- BerkeleyGW interfaces to latest EPW version
  [Nick Pant (*UT Austin*) & Chih-En (Andy) Hsu (*USC*)]
- Full-bandwidth Migdal-Eliashberg theory

  ⟶ Lec. Wed.2 Margine

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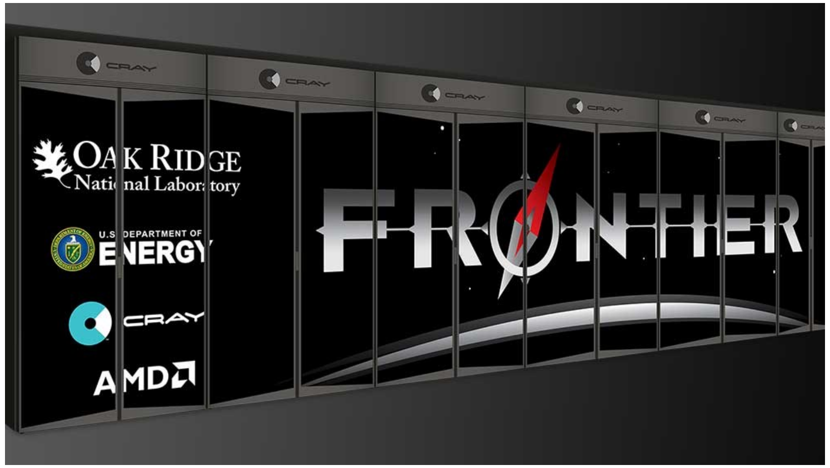

Advanced functionalities enabled by interoperable software packages

BerkeleyGW

- Many-body quasiparticle excitations
- Electron-phonon interactions with GW self-energy effects ⇔ GWPT
- …

EPW

- Transport
- Superconductivity
- Phonon-assisted optics
- Polarons
- …

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10th BerkeleyGW Tutorial Workshop
and
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Location: Oakland, CA, USA

Workshop Time: August 12 – 14, 2024, Pacific Standard Time

Conference Time: August 15 – 16, 2024, Pacific Standard Time

Registration is OPEN!

https://workshop.berkeleygw.org/