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

June 5-9 2023

Lecture Fri.2

GW perturbation theory for electron-phonon coupling: Theory, practical workflow, and applications

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

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

The Nobel Prize in Physics 1972

Photo from the Nobel Foundation archive.
John Bardeen
Prize share: 1/3

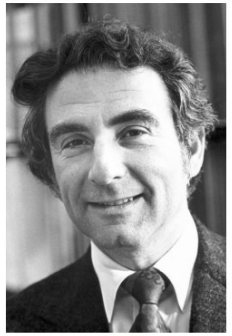


Photo from the Nobel Foundation archive.
Leon Neil Cooper
Prize share: 1/3

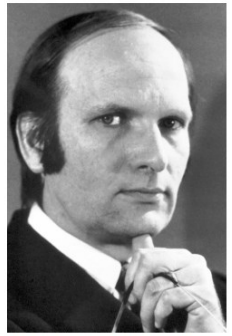
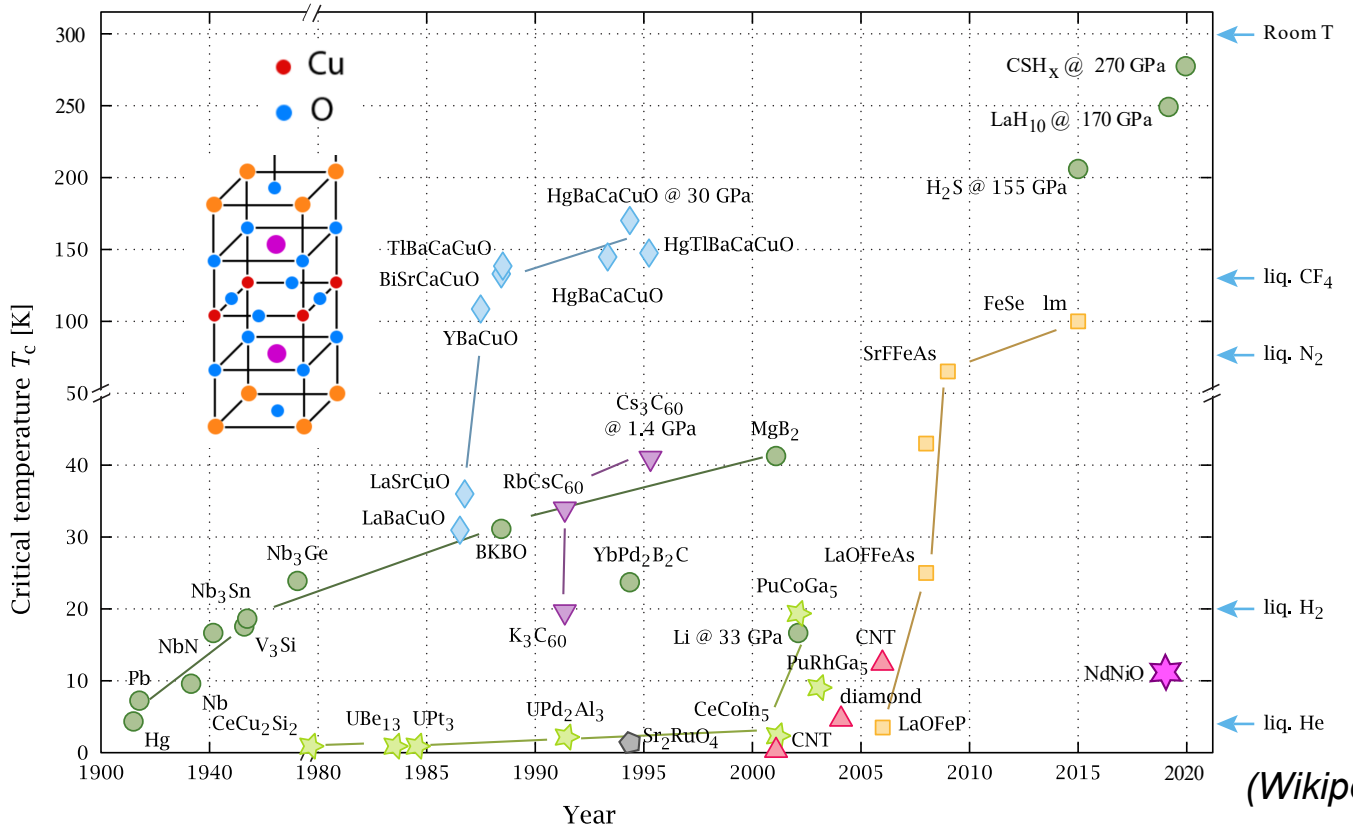


Photo from the Nobel Foundation archive.
John Robert Schrieffer
Prize share: 1/3

- **Bardeen-Cooper-Schrieffer theory for superconductivity**
- Electrical and thermal transport
- Optical spectra
- Charge-density wave
- Carrier dynamics in materials
- …

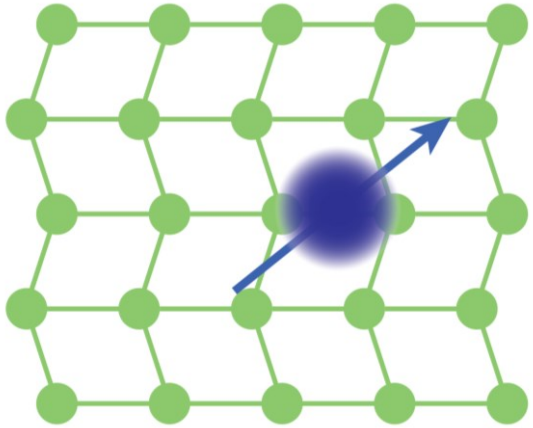


(*Wikipedia*)

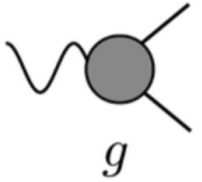
Need predictive first-principles computational methods

Electron-phonon coupling from first principles

Electrons are Bloch states propagating in solids; they can be scattered by phonons

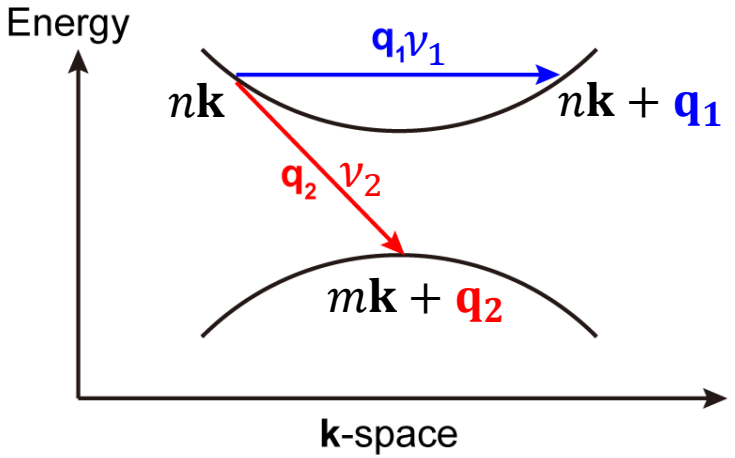


Electron-phonon matrix element: $g_{mn\nu}(\mathbf{k},\mathbf{q})$ scattering amplitude



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

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

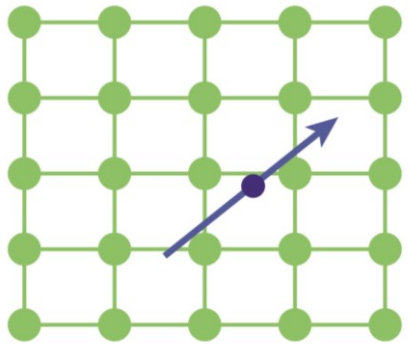


k: electron wavevector
n: electron band index

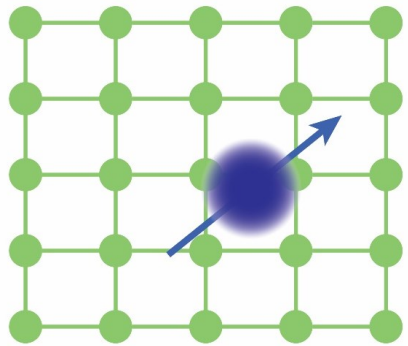
q: phonon wavevector
ν: phonon branch

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

DFT vs. Many-body perturbation theory



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 effects

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

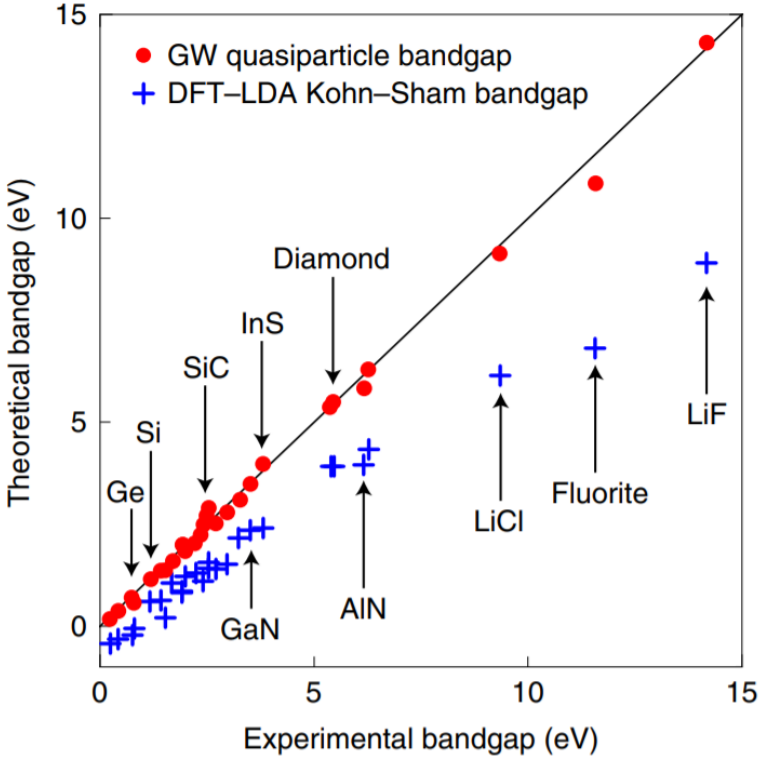
(*G*: Green's function; *W*: screened Coulomb)

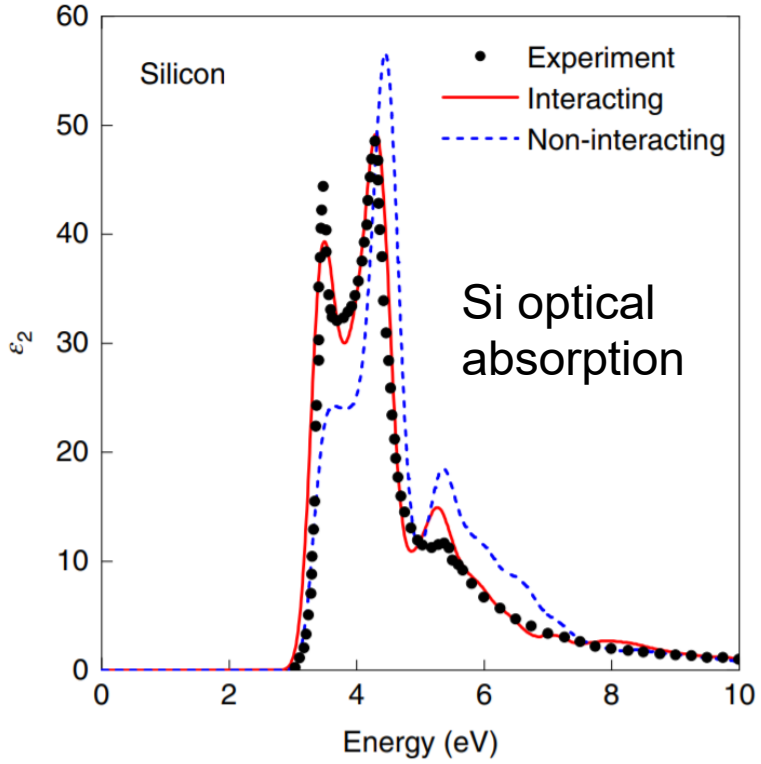
- Non-local, frequency-dependent potential

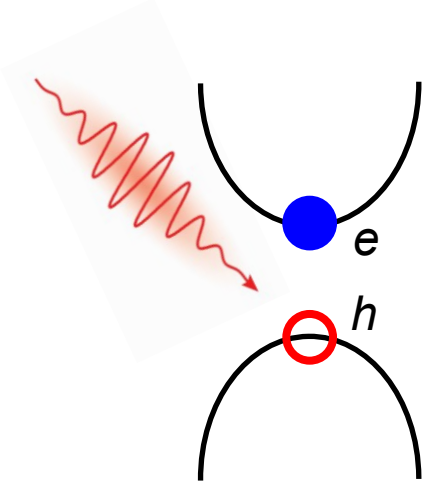
First-principles GW and GW-Bethe-Salpeter-equation approaches

$\Sigma = iGW$

Electron-hole kernel includes $\frac{\delta\Sigma}{\delta G}$







GW plus Bethe-Salpeter equation (GW-BSE)

First-principles GW, GW-BSE methods ⇔
Standard *ab initio* quasiparticle property and optical excitation methodologies

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, Topics in Computational Materials Science 96–142 (1998)
Louie, Chan, Jornada, Li, and Qiu, Nature Materials ***20****, 728 (2021), Invited Perspective*

GW perturbation theory (GWPT)

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

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

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

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

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

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

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

GW perturbation theory (GWPT)

Li, 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

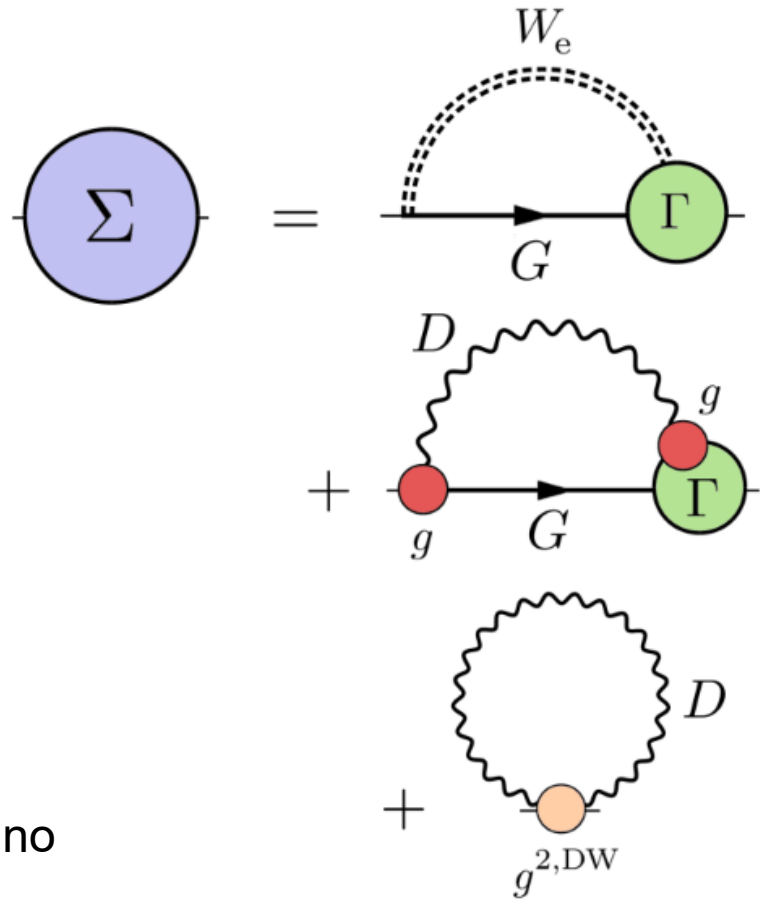
  Faber *et al.*, Phys. Rev. B **91**, 155109 (2015)

Electron self-energy from many-body perturbation theory

cf. Lec. Mon.1.Giustino

cf. Lec. Thu.1.Louie

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



Electronic self-energy $GW\Gamma$

Fan-Migdal (e-ph)

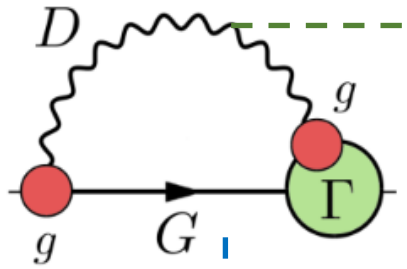
Debye-Waller (e-ph)

Image from 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}

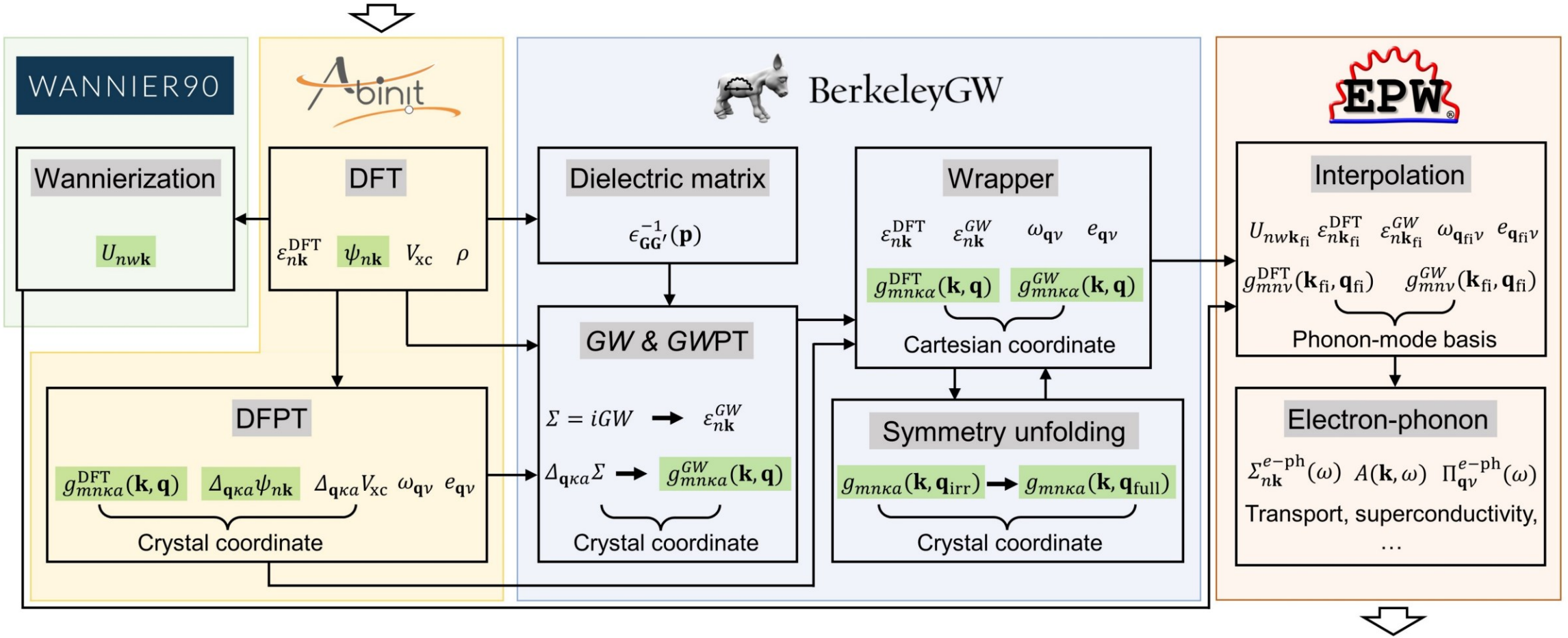
Electron propagator *G*

$\varepsilon^{\mathrm{DFT}}$ 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

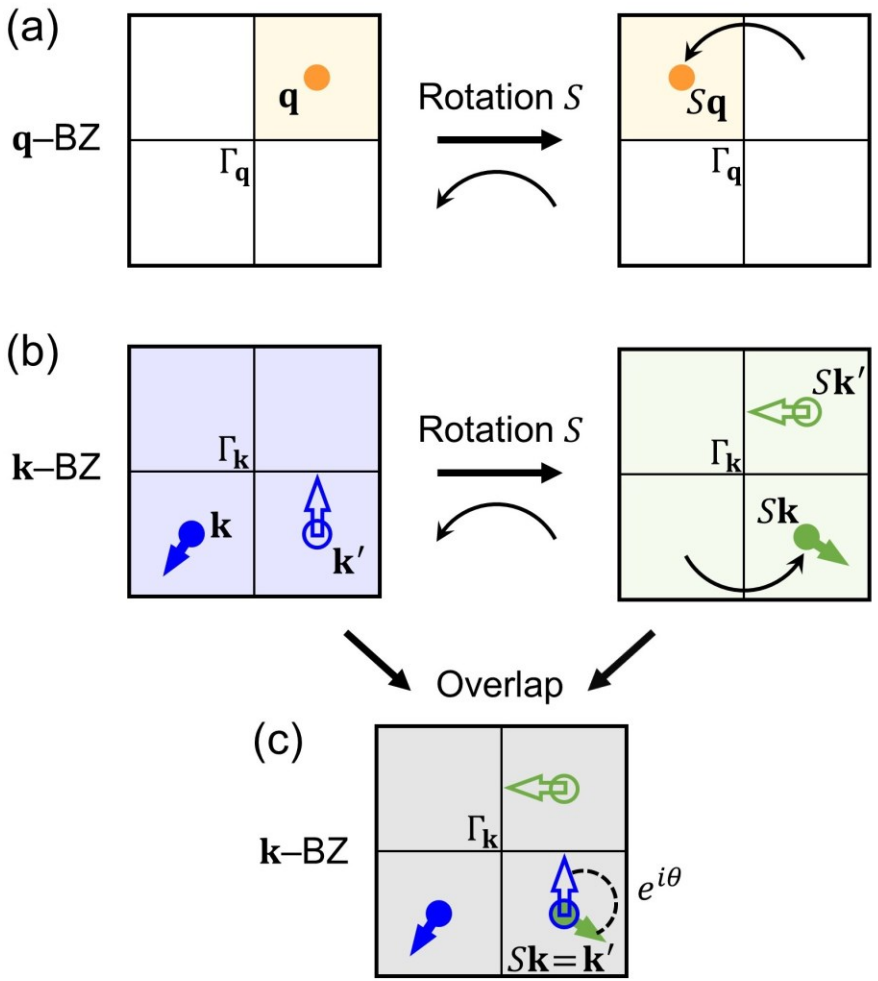


- EPW is currently interfaced with Quantum Espresso
- This workflow enables BerkeleyGW-EPW & ABINIT-EPW interfaces
- Green boxes highlight gauge-consistent quantities fixed to a unique set of $\{\psi_{n\mathbf{k}}\}$ in DFT
  - Construction of 0th- and 1st-order self-energy operators
  - Wannierization

Li, Antonius, Chan, Louie, to be submitted

Symmetry unfolding with gauge recovering

Wannierization requires the gauge to be consistent with the unique set of $\{\psi_{n\mathbf{k}}\}$



- Symmetry operation $\{S|\mathbf{v}\}\mathbf{r} = S\mathbf{r} + \mathbf{v}$
- Symmetry-rotated wavefunction

$$\tilde{u}_{nS\mathbf{k}}(\mathbf{r}) = e^{-iS\mathbf{k}\cdot\mathbf{v}} u_{n\mathbf{k}}(S^{-1}\mathbf{r} - S^{-1}\mathbf{v})$$

- Find the gauge difference

$$D^{\mathbf{k}}_{mn} = \langle \tilde{u}_{mS\mathbf{k}} | u_{n\mathbf{k}'} \rangle$$

- Recover the gauge of *e*-ph matrix elements

$$g_{mnK\alpha}(\mathbf{k}, S\mathbf{q}) = e^{i\mathbf{q}\cdot\boldsymbol{\tau}_\kappa - iS\mathbf{q}\cdot\boldsymbol{\tau}_K + iS\mathbf{q}\cdot\mathbf{v}} \sum_{m'n'} \left(D^{\mathbf{k}+S\mathbf{q}}_{m'm}\right)^* D^{\mathbf{k}}_{n'n} \sum_{\beta} S_{\alpha\beta} g_{m'n'\kappa\beta}(S^{-1}, \mathbf{kq})$$

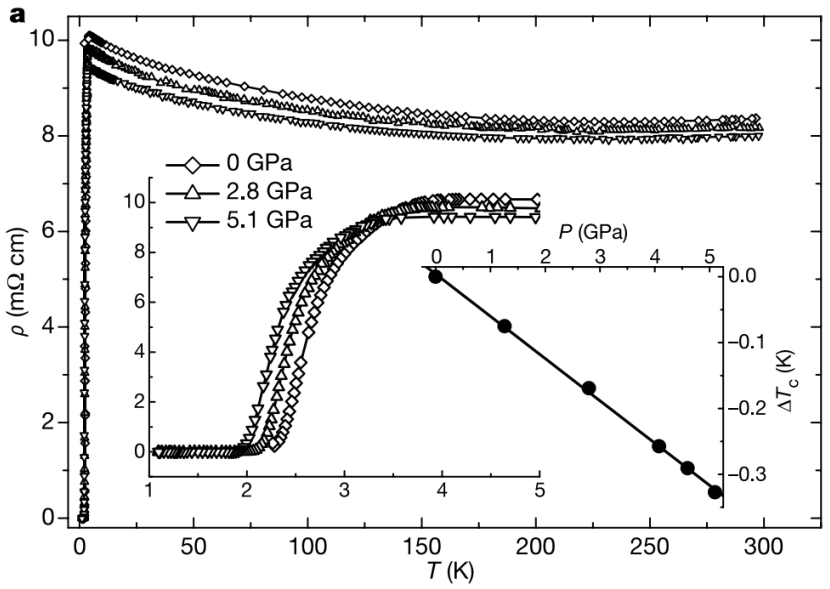
Li, Antonius, Chan, Louie, to be submitted

A similar treatment in latest EPW: H. Lee et al. arXiv:2302.08085

Example: Boron-doped Diamond B_xC_{1-x}

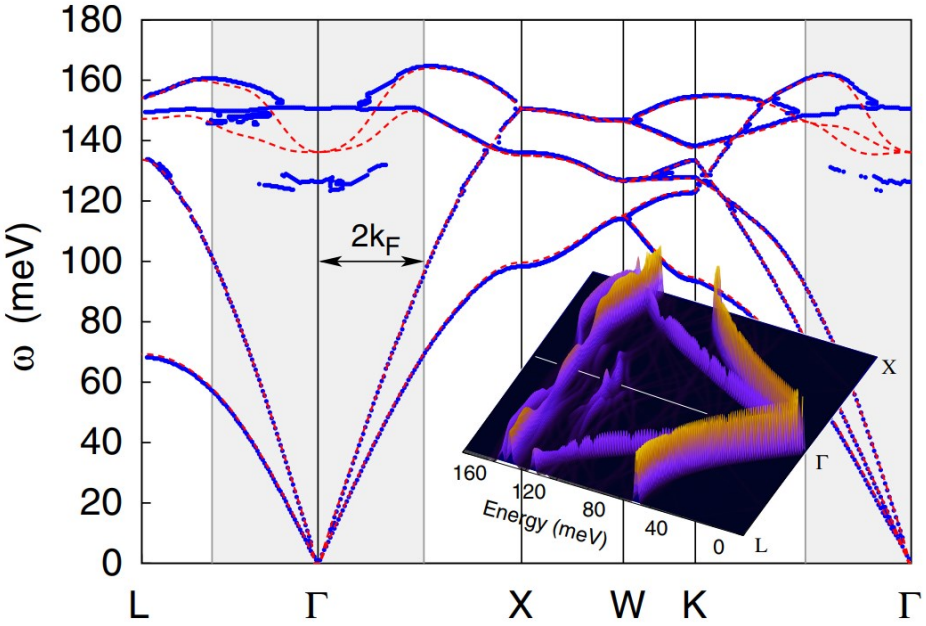
Superconductivity in B-doped diamond

$T_c \sim 4$ K



*Ekimov et al., Nature **428**, 542 (2004)*

Boron-dopant phonon modes enhance e-ph coupling



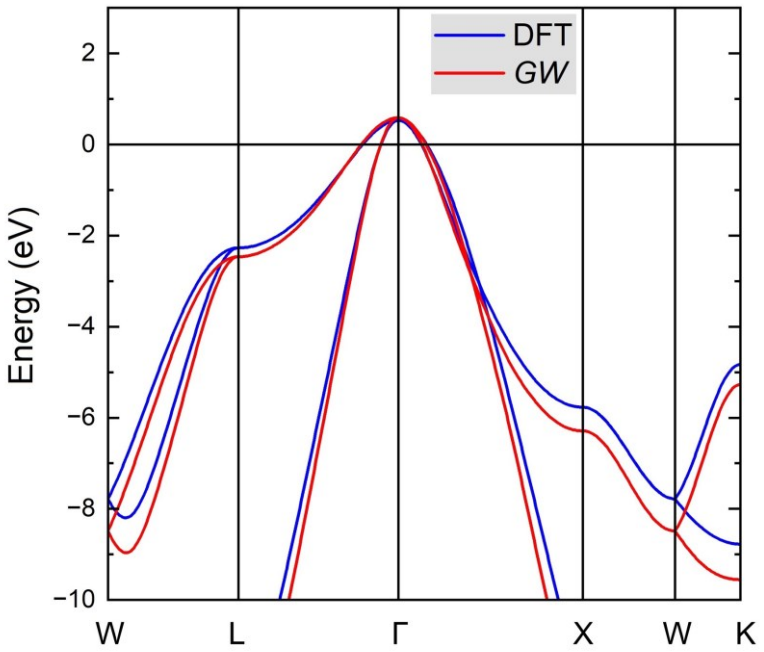
Virtual-crystal approximation: $\lambda_{\mathrm{VC}} = 0.237$

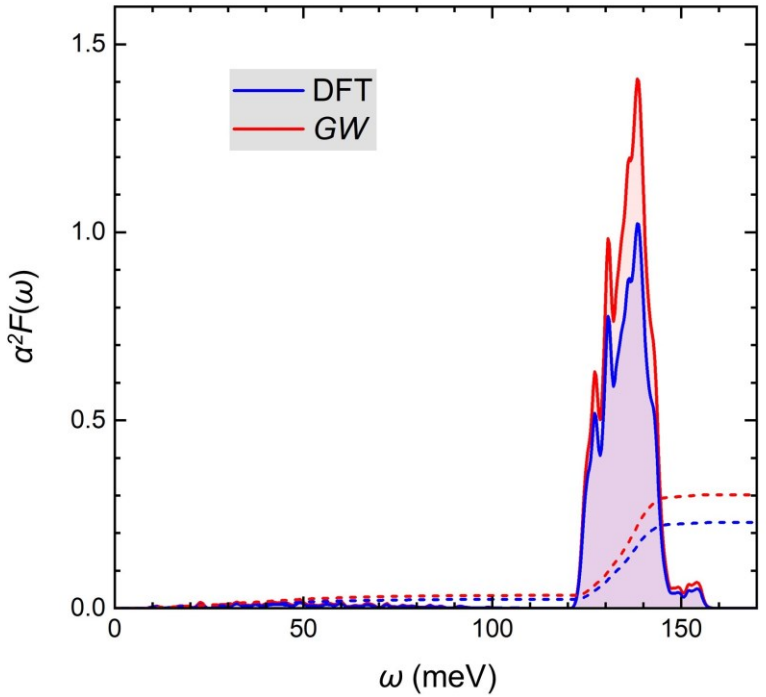
Supercell with B dopants: $\lambda_{\mathrm{SC}} = 0.336$

*Giustino, Yates, Souza, Cohen, Louie, PRL **98**, 047005 (2007)*

Example: Boron-doped Diamond B_xC_{1-x}

ABINIT-BerkeleyGW-EPW





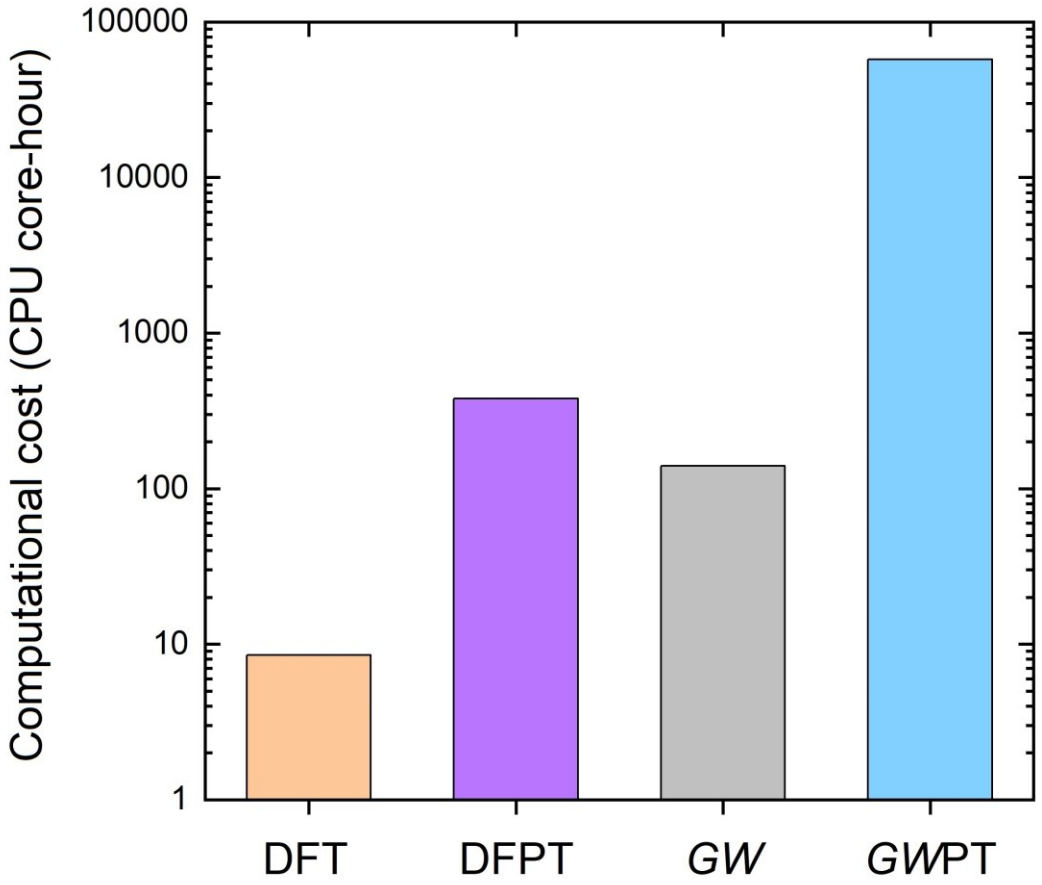
- Virtual crystal approximation
- GW self-energy effects enhance the *e*-ph coupling strength
- Mainly from renormalization in *e*-ph matrix elements

	λ	ω_{log} (K)	T_c (K)		
			(μ^* = 0.05)	(μ^* = 0.08)	(μ^* = 0.1)
DFT + DFPT	0.228	1360.6	0.65	0.099	0.015
GW + GWPT	0.302	1348.7	4.2	1.6	0.69

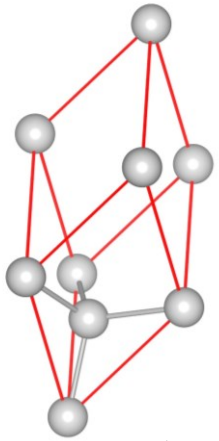
Li, Antonius, Chan, Louie, to be submitted

Example: Boron-doped Diamond B_xC_{1-x}

Two-atom unit-cell calculations



Running on Frontera at TACC



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

- GWPT computes off-diagonal elements (GW typically only need diagonal elements)

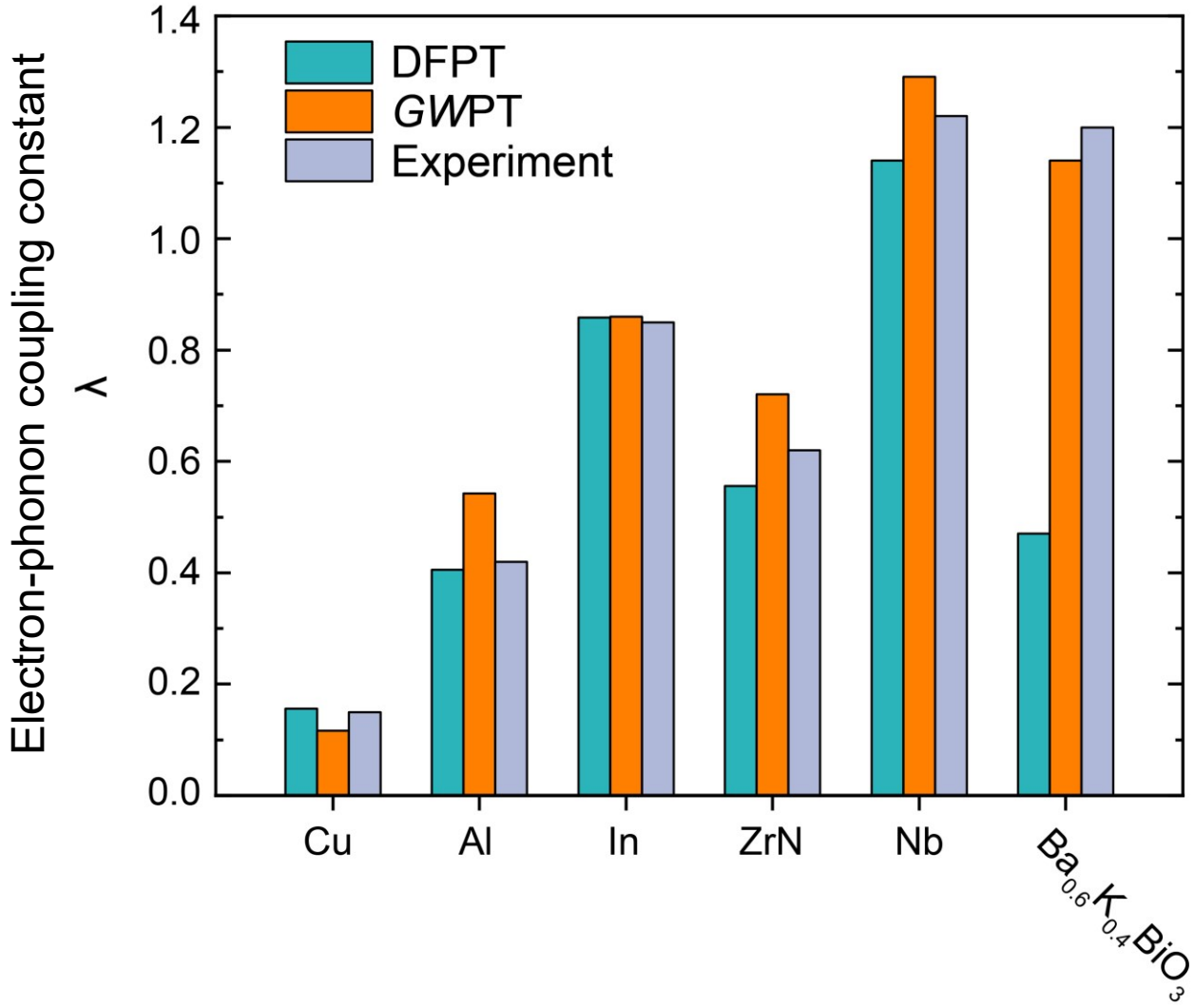
Computational cost

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

Li, Antonius, Chan, Louie, to be submitted

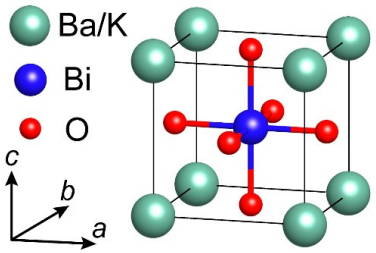
GWPT validation set

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

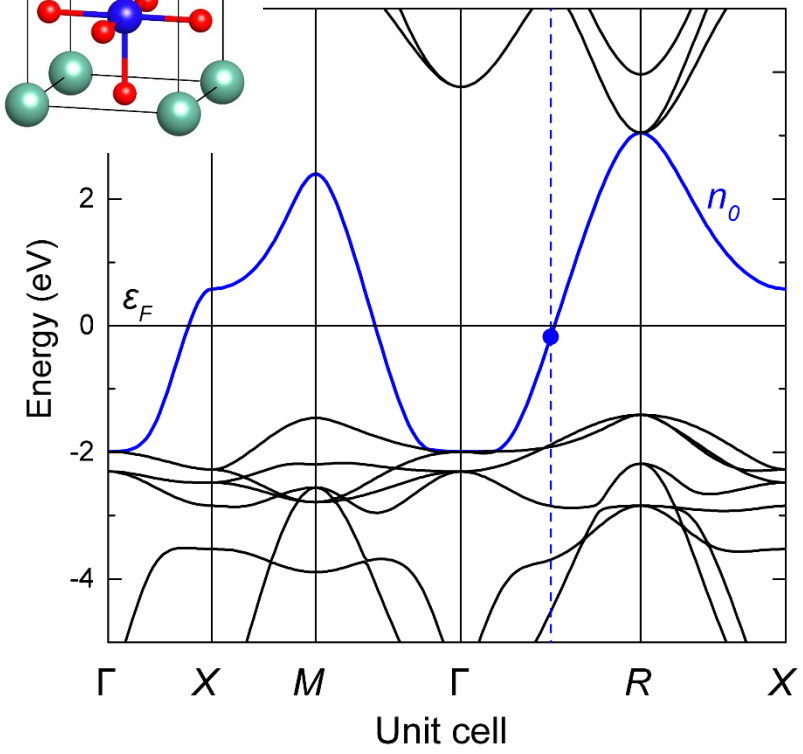


Correlation-enhanced electron-phonon coupling and superconductivity

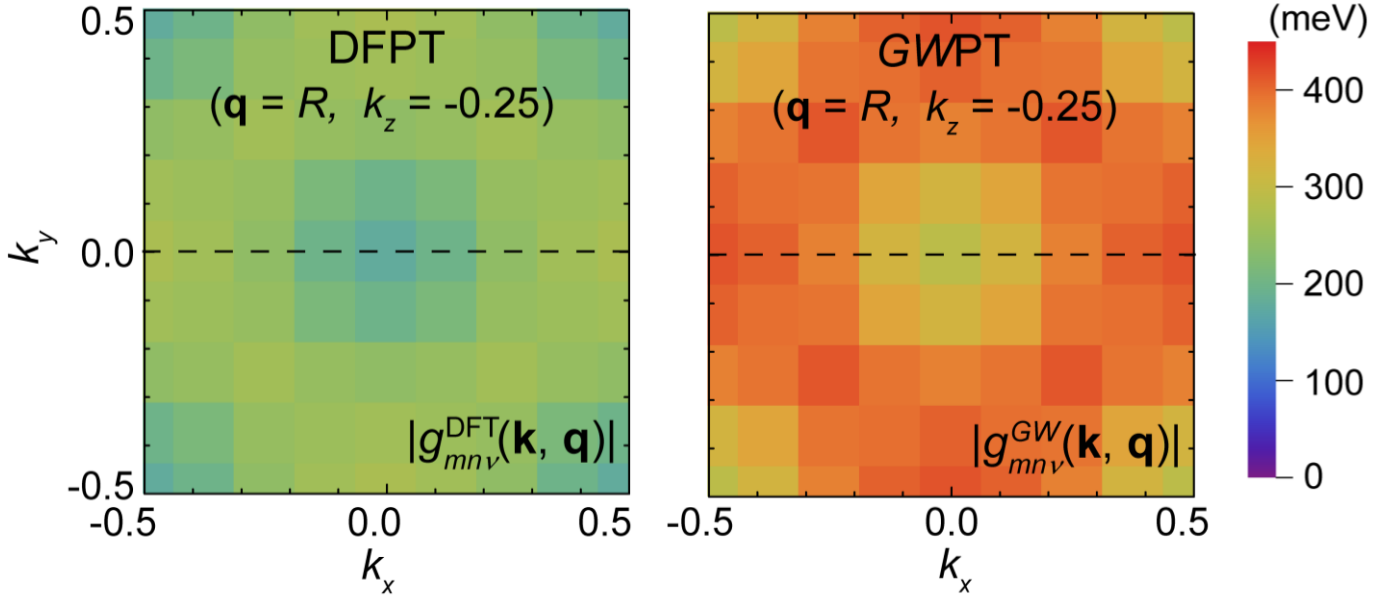
$Ba_{1-x}K_xBiO_3$: experimental T_c = 32 K at x = 0.4



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)

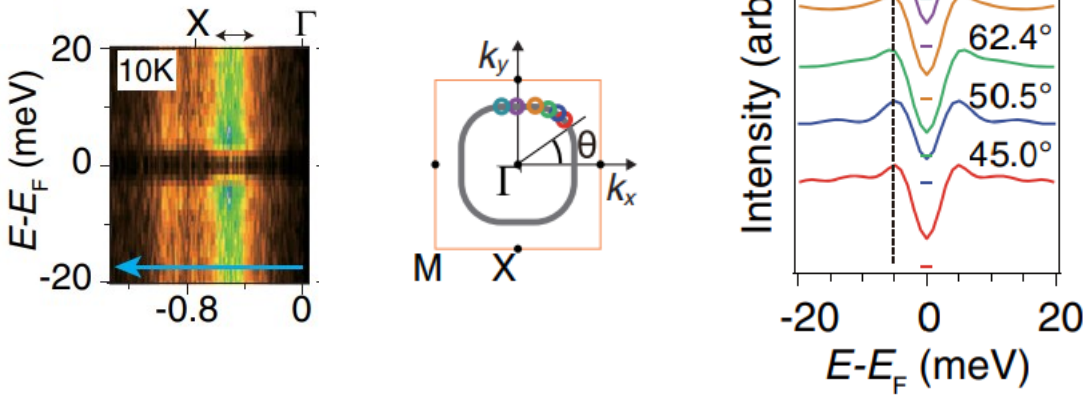
Correlation-enhanced superconductivity in $Ba_{1-x}K_xBiO_3$

❖ 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)*

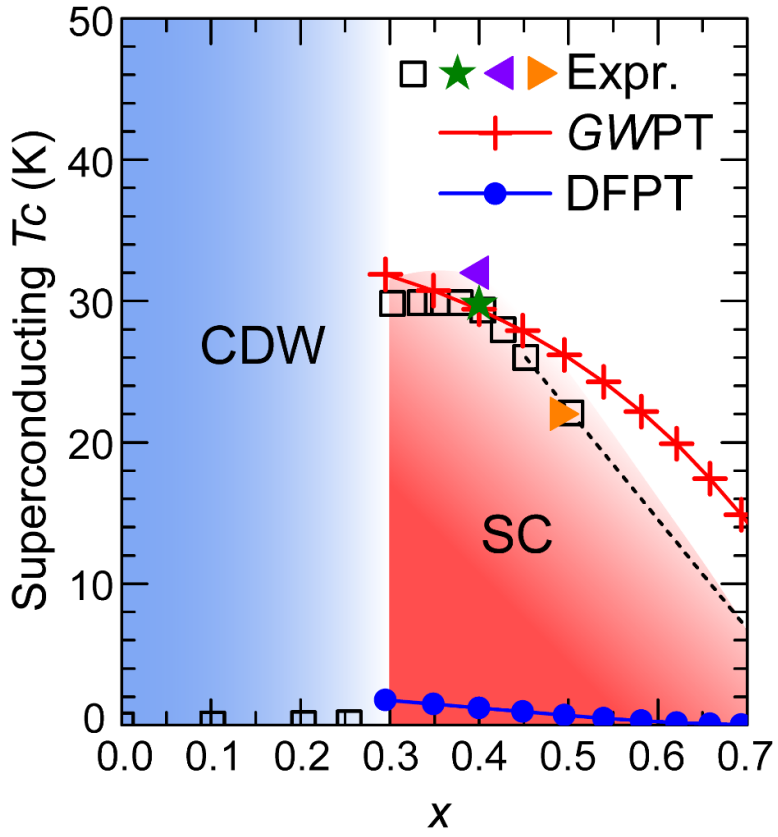
❖ Isotropic superconducting gap



Many-electron correlations greatly enhance phonon-mediated T_c!

❖ McMillan–Allen-Dynes formula to estimate superconducting T_c

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



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

Photoemission kinks in cuprate superconductors

Copper-oxide superconductors

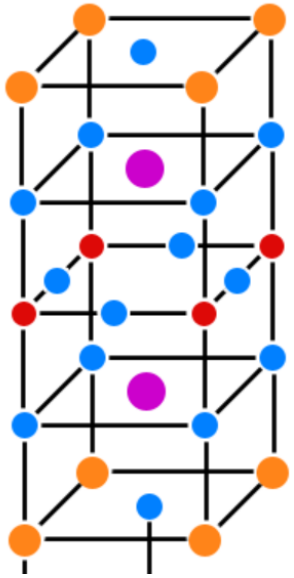
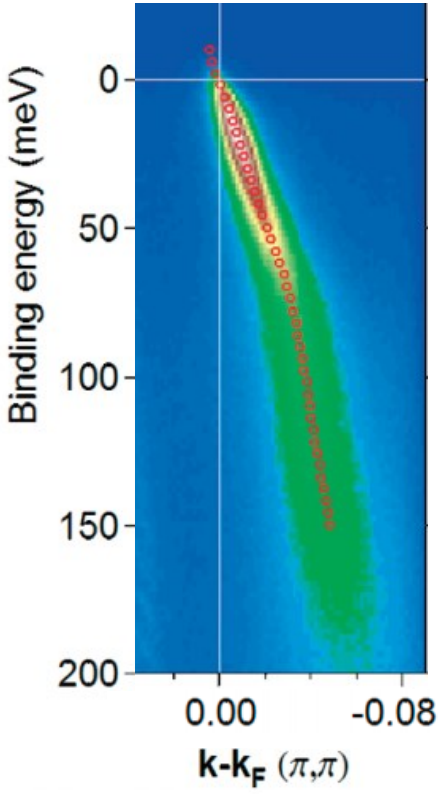


Image: Wikipedia

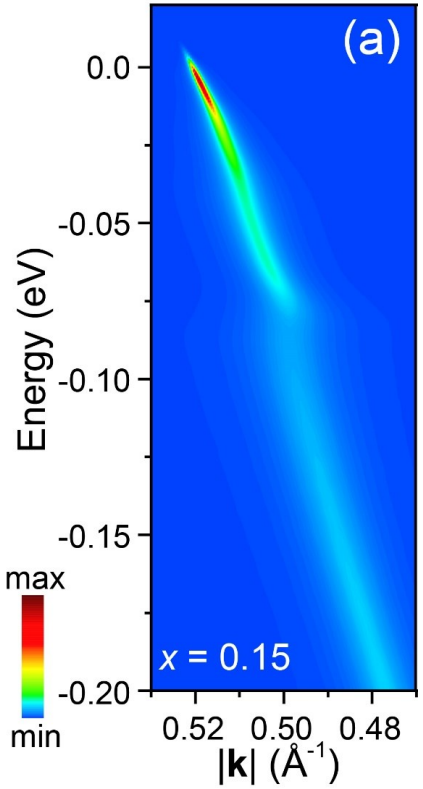
Ubiquitous 70-meV kinks in dispersion relations



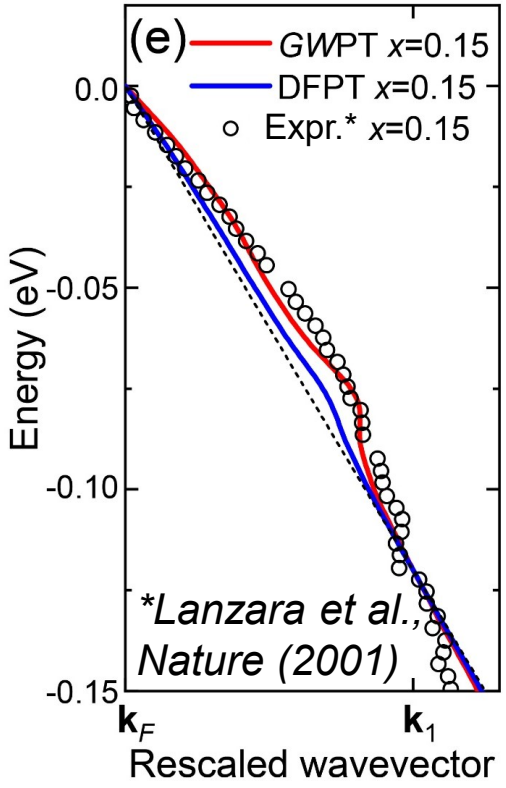
*Lanzara, et al., Nature **412**, 510 (2001)*
*Koralek et al., Phys. Rev. Lett. **96**, 017005 (2006)*

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

Theory GWPT



Comparison

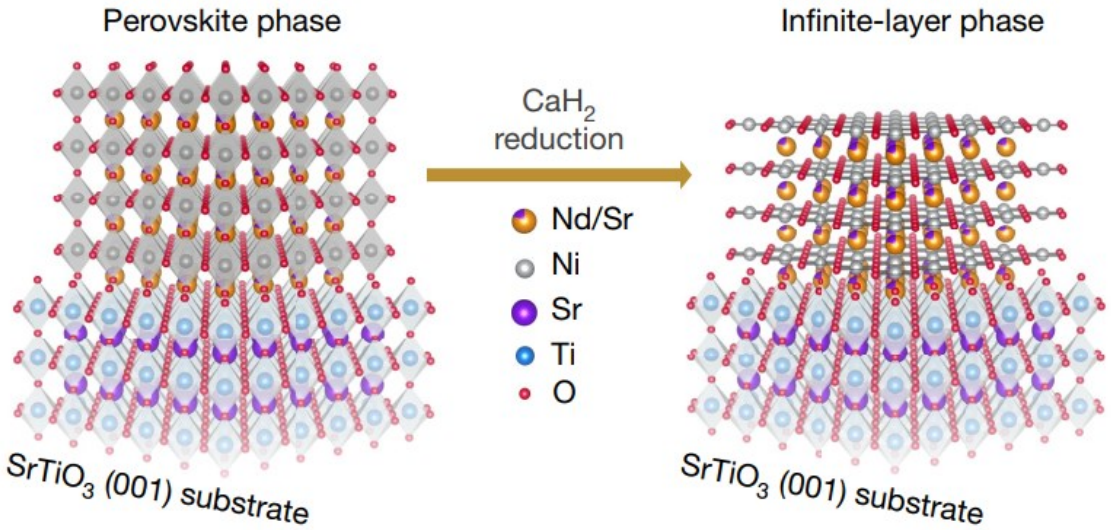


Li, Wu, Chan, Louie, PRL **126**, 146401 (2021)

See also: Giustino, Cohen, Louie, Nature **452**, 975 (2008)
Heid *et al.*, PRL **100**, 137001 (2008)

Discovery of superconductivity in infinite-layer nickelates

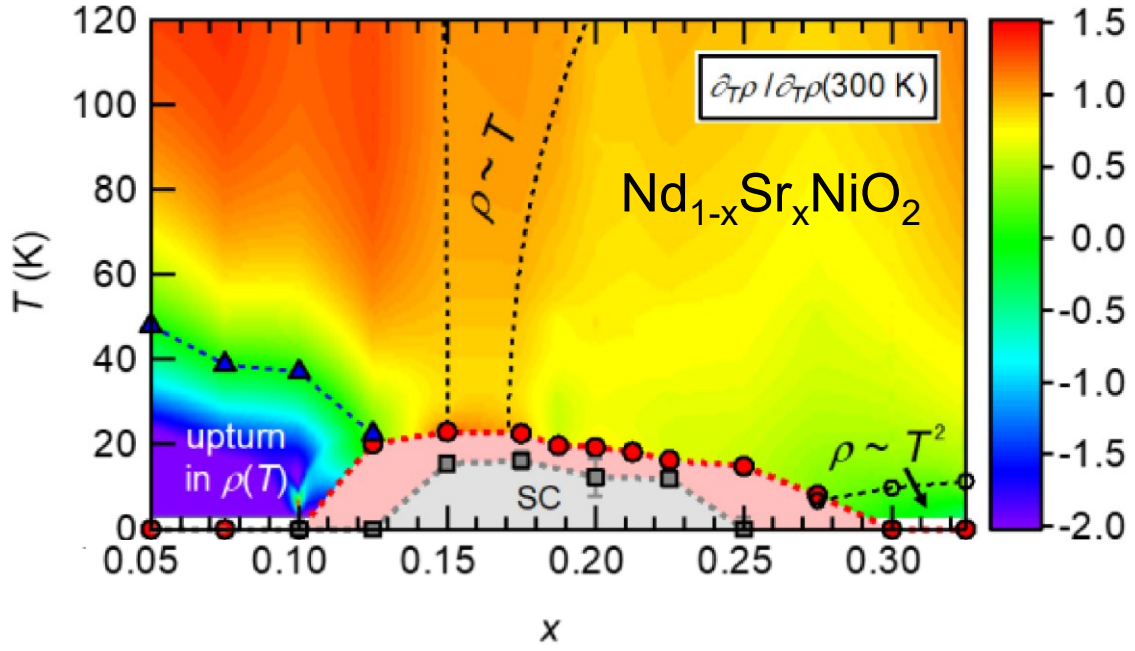
- Nickelates are thought of as being analogs of unconventional high-T_c cuprate superconductors
- In 2019, superconductivity was observed in infinite-layer nickelate $Nd_{0.8}Sr_{0.2}NiO_2$ thin films



$Nd_{0.8}Sr_{0.2}NiO_3$
(113 phase)

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

Phase diagram, max. T_c ~ 20 K



- Higher T_c and larger dome in cleaner samples

Lee *et al.*, arXiv:2203.02580 (2022)

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)

Small electron-phonon coupling from DFT calculations

*In terms of the **mechanism for superconductivity** in nickelates*

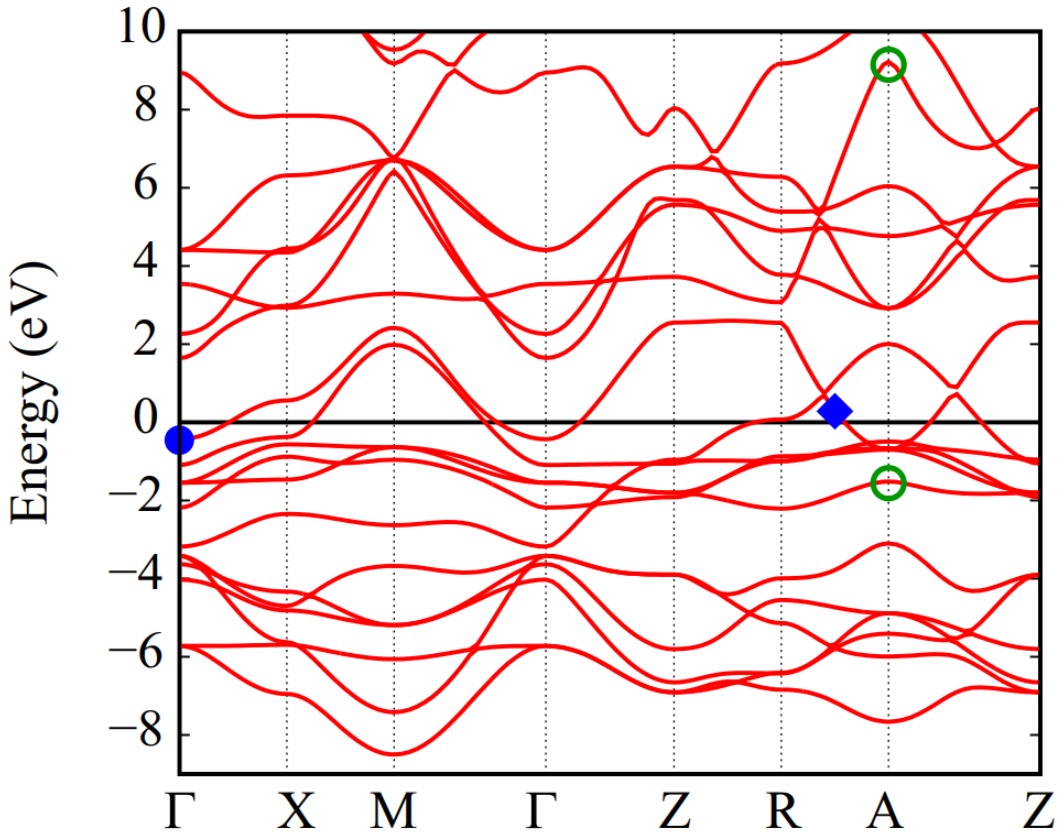
- Natural and prevailing thought: ***Unconventional*** – nickelates are cuprates analog
- ***Conventional mechanism*** – electron-phonon coupling – is **weak** from DFT calculations

$NdNiO_2$

λ	ω_{ln} (K)	T_c (K)
0.22	283	0.00

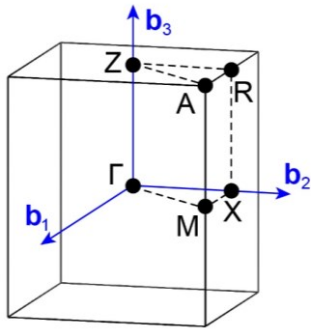
- DFT $\lambda \sim 0.2$, $T_c \sim 0$ K
- Multiple bands near E_F

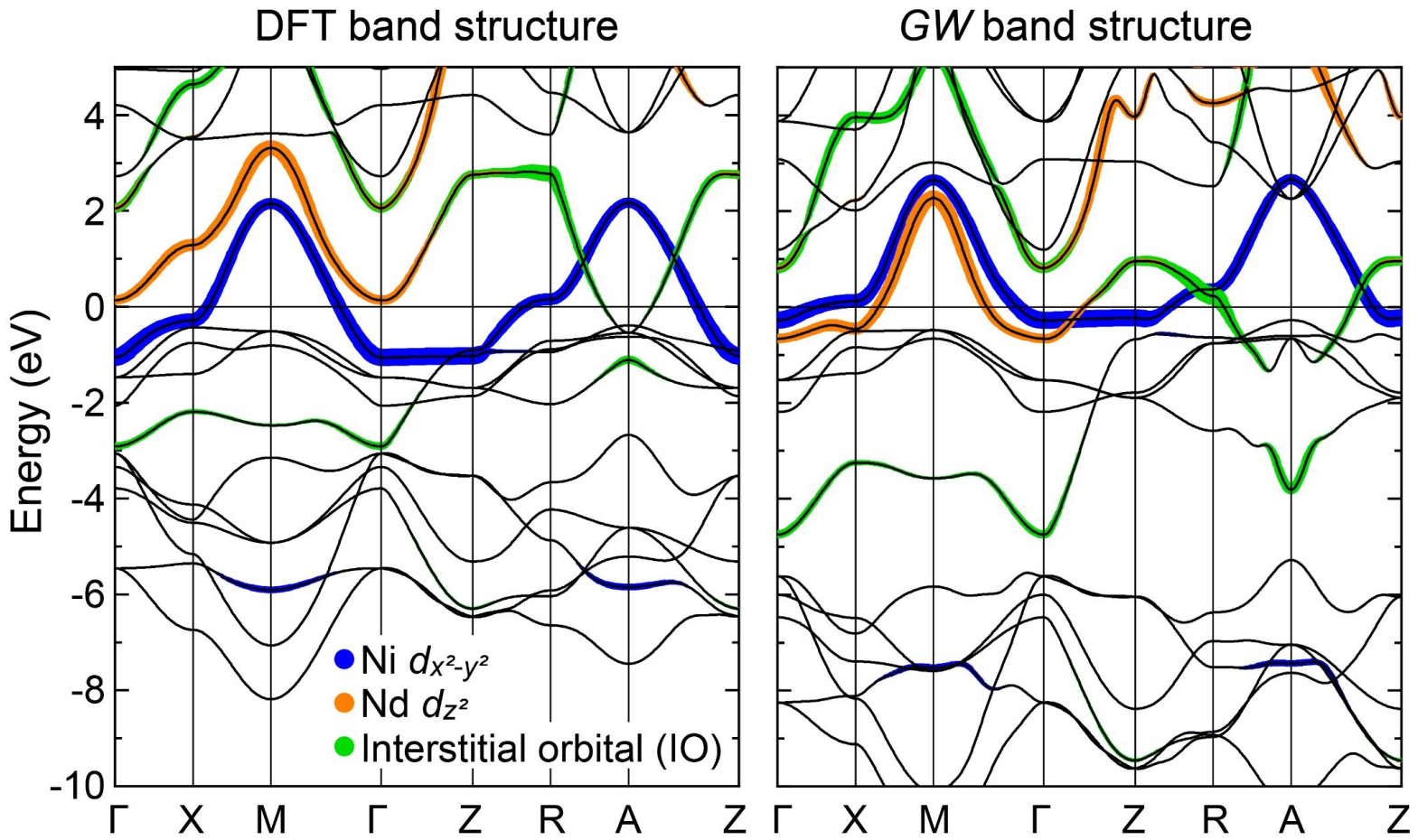
Nomura *et al.*, Phys. Rev. B **100**, 205138 (2019)



DFT vs. *GW* band structures

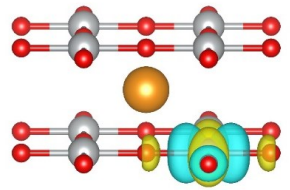
$Nd_{0.8}Sr_{0.2}NiO_2$



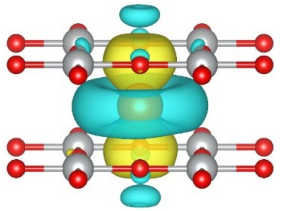


Wannier basis orbitals

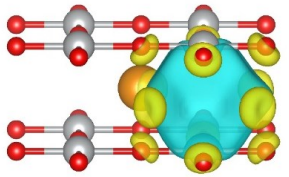
Ni $d_{x^2-y^2}$



Nd d_{z^2}



Interstitial orbital (IO)

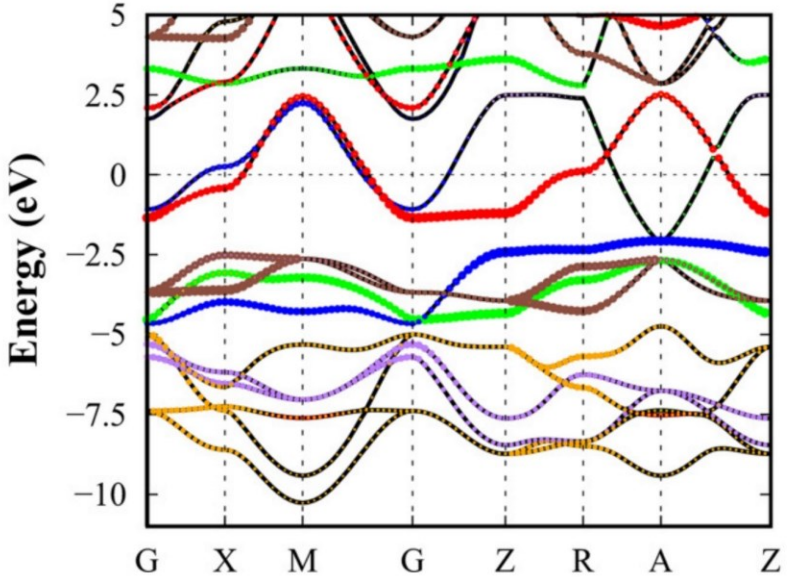


- *GW* self-energy effects significantly renormalize the band structure
- In particular, near E_F, band order swaps within $k_z = 0$ plane

Li and Louie, arXiv:2210.12819 (2022)

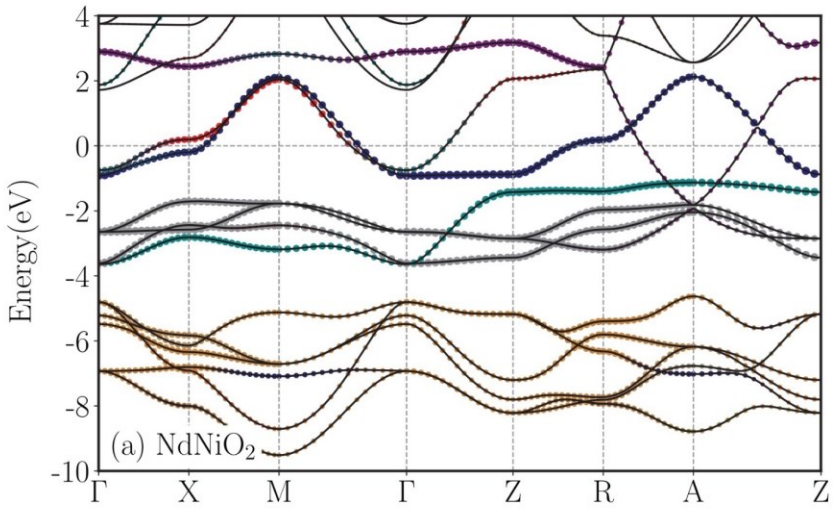
Other ab initio results from advanced methods

HSE06 hybrid functional



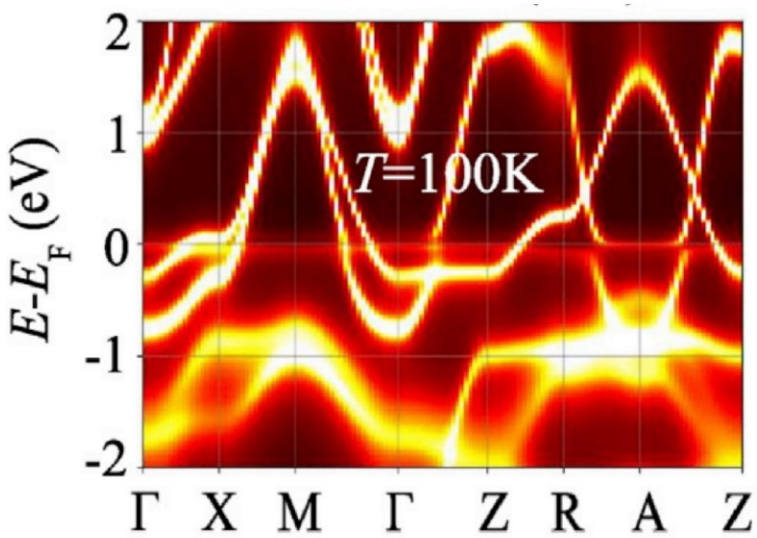
Phys. Rev. Res. **2**, 013214 (2020)

mBJ meta-GGA



Europhys. Lett. **135**, 67001 (2021)

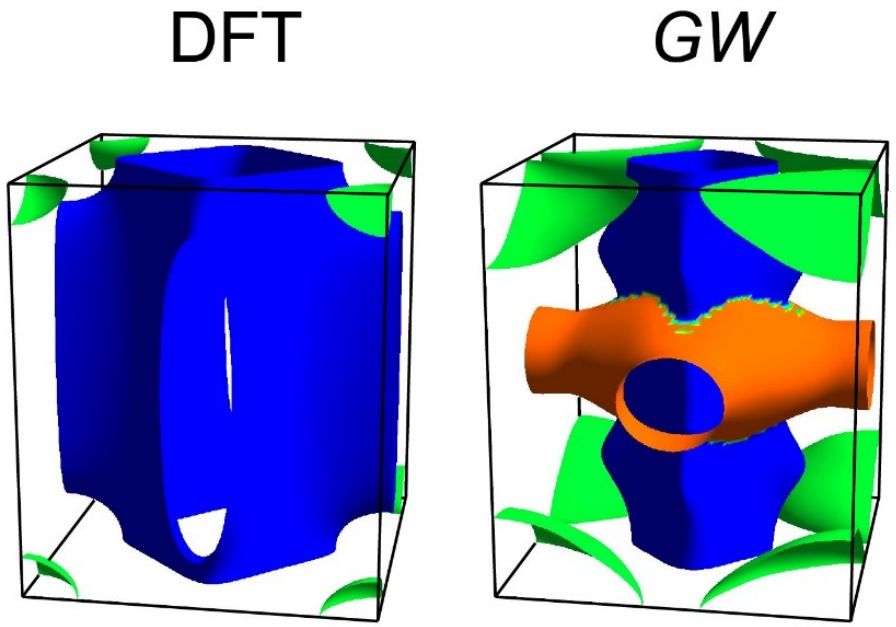
GW+DMFT

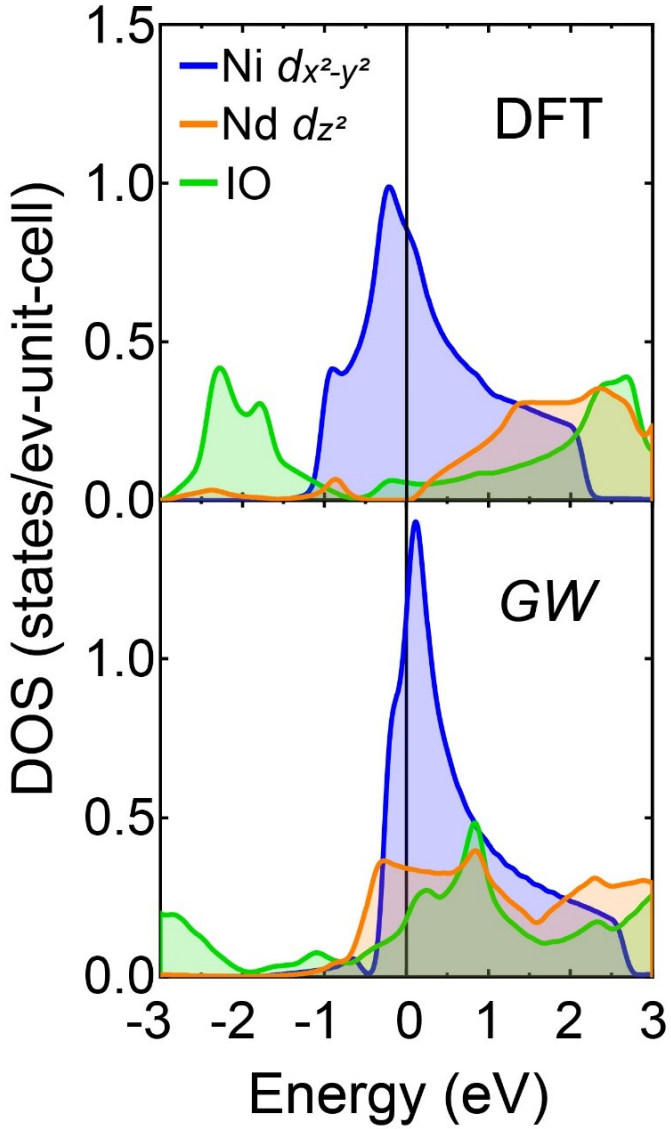


Cell Reports Physical Science **4**, 101325 (2023)

- Advanced DFT functionals and GW+DMFT show similar band renormalization trend by better capturing correlation effects

DFT vs. *GW* Fermi surfaces



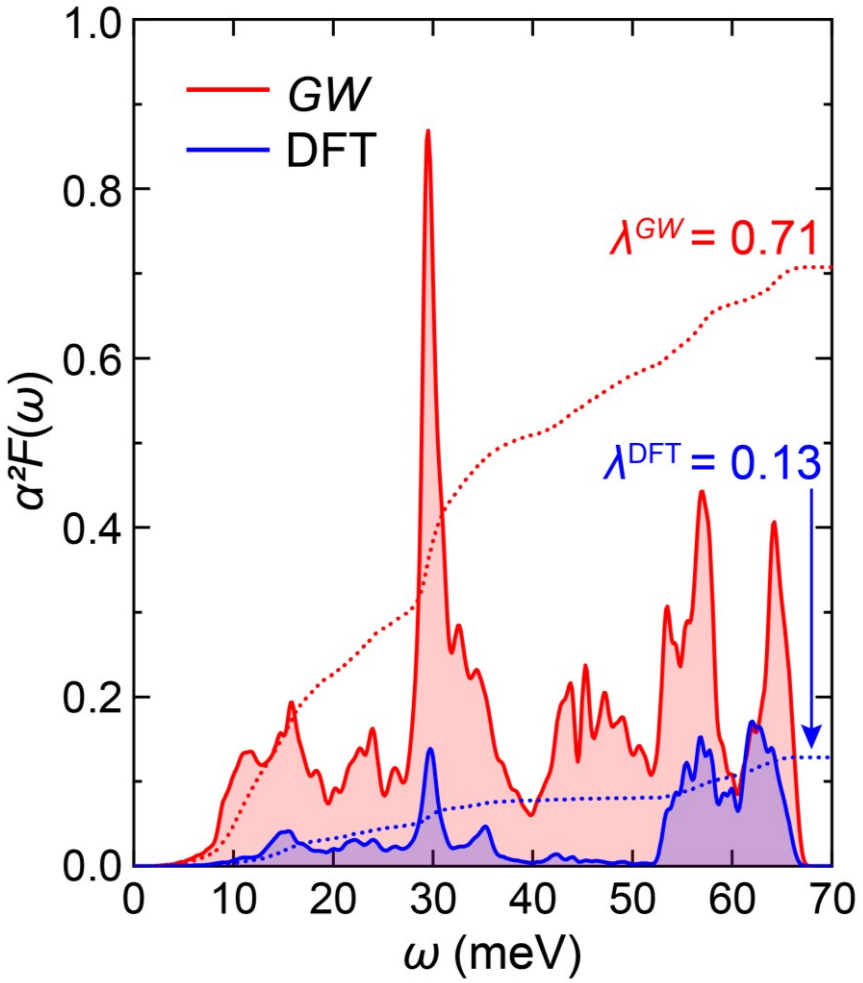


- Extra **Nd FS sheet** and enlarged **IO FS sheet** in *GW* results
- Shrinking **Ni FS sheet**
- While Ni states dominate at E_F in DFT, ***GW* calculations** show a comparable presence of **Nd-IO** states

Li and Louie, arXiv:2210.12819 (2022)

DFT vs. *GW* Electron-phonon coupling

$$\alpha^2F(\omega) = \frac{1}{N_F}\sum_{mn\nu\mathbf{kq}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \delta(\varepsilon_{n\mathbf{k}} - E_\mathrm{F}) \times \delta\left(\varepsilon_{m\mathbf{k+q}} - E_\mathrm{F}\right)\delta\left(\hbar\omega - \hbar\omega_{\mathbf{q}\nu}\right)$$



Running integral $\lambda^{<}(\omega) = 2\int_0^{\omega} \frac{\alpha^2F(\omega')}{\omega'} \mathrm{d}\omega'$

- Eliashberg function α^2F gives phonon-frequency dependent coupling strength

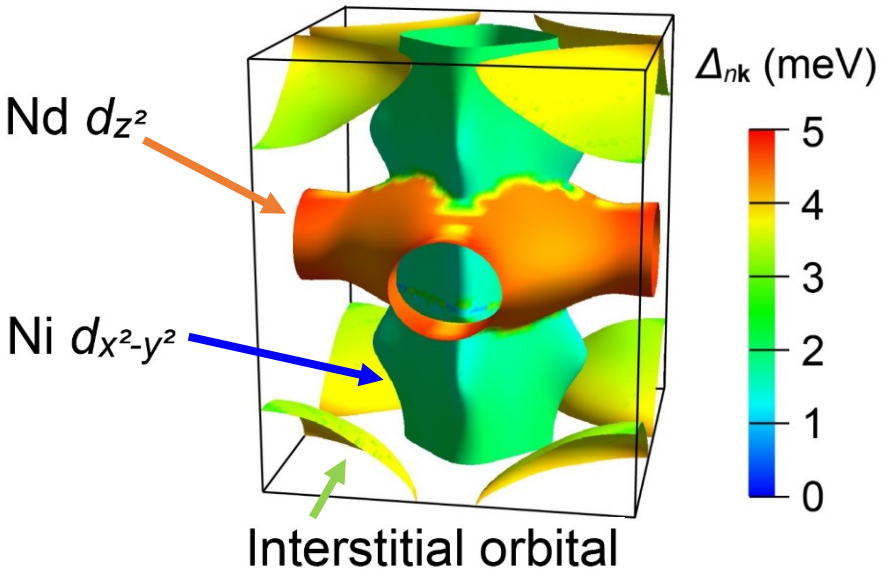
- ***Factor of 5.5 enhancement in total coupling λ!***

- Two major *GW* self-energy effects:
  - ❖ Introduce significant Nd-IO characters 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)

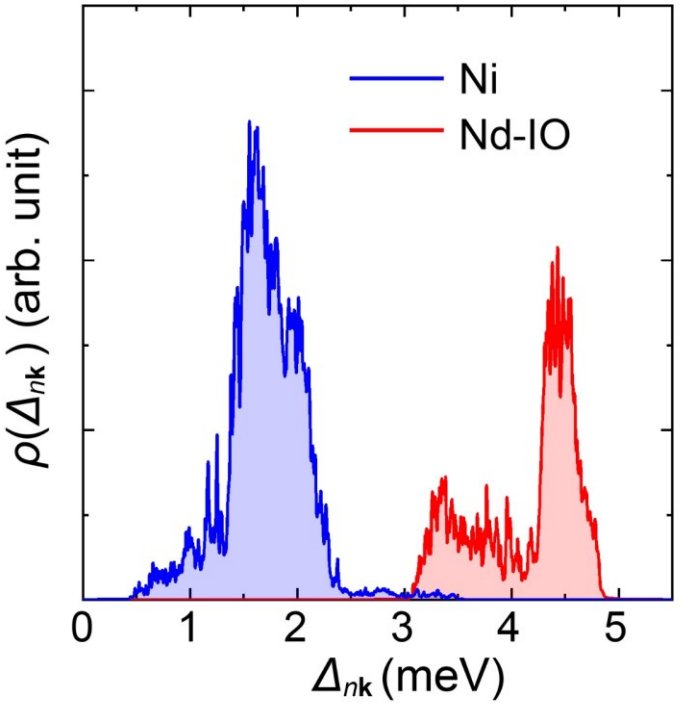
Two-gap superconductivity from *ab initio GW*-Eliashberg calculations

- Anisotropic Eliashberg theory for superconductivity at the *GW* level (BerkeleyGW + EPW)

FS with SC gaps



SC gap distribution near E_F



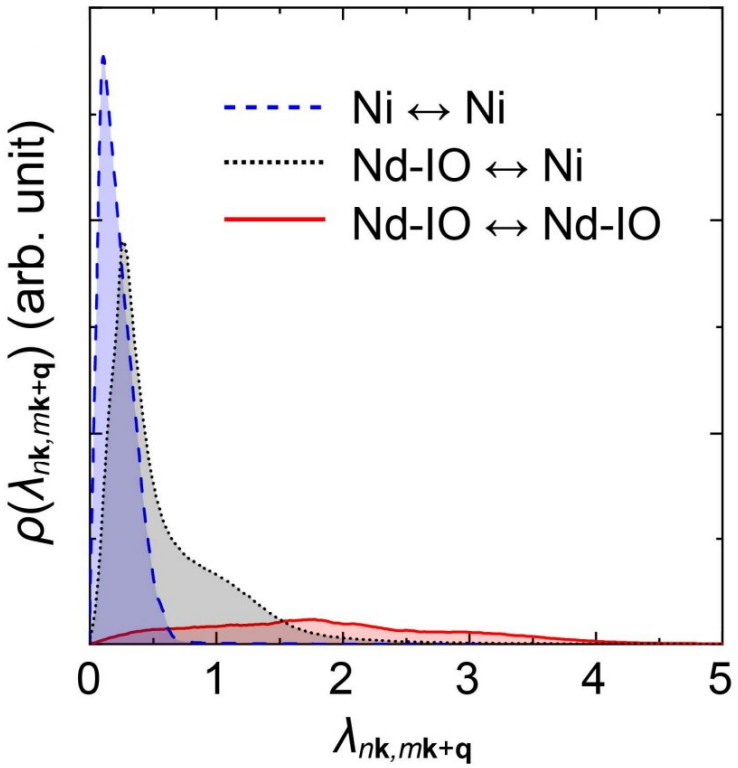
- Distinctive **bimodal distribution**
- Large gap on Nd-IO band, small gap on Ni band

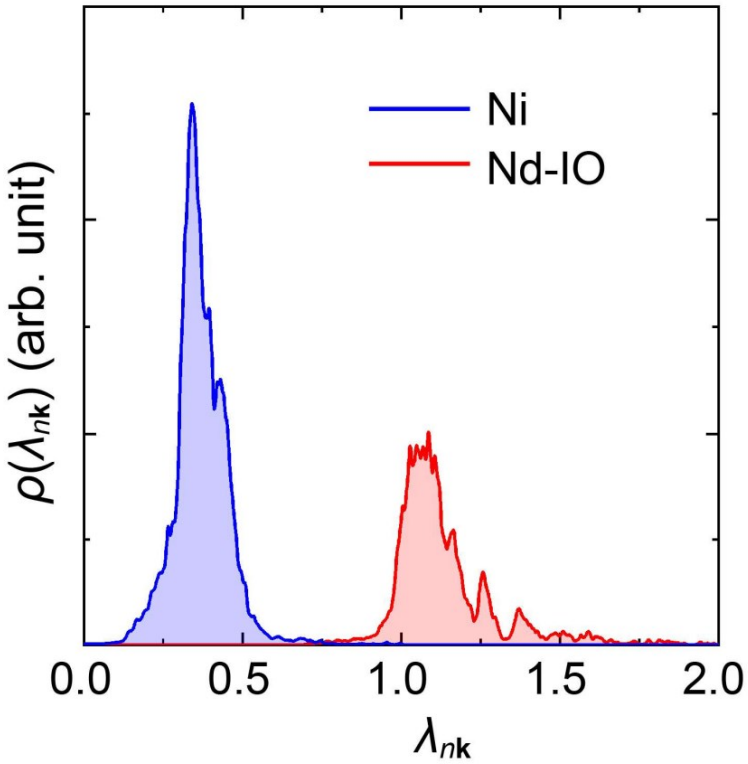
- Full **k**-dependence is important
- Nd-IO characters dominate, not Ni

(T_c is insensitive to effective Coulomb repulsion μ^* in physical range, here we take $\mu^* = 0.05$)

Two-gap superconductivity from *ab initio GW*-Eliashberg calculations

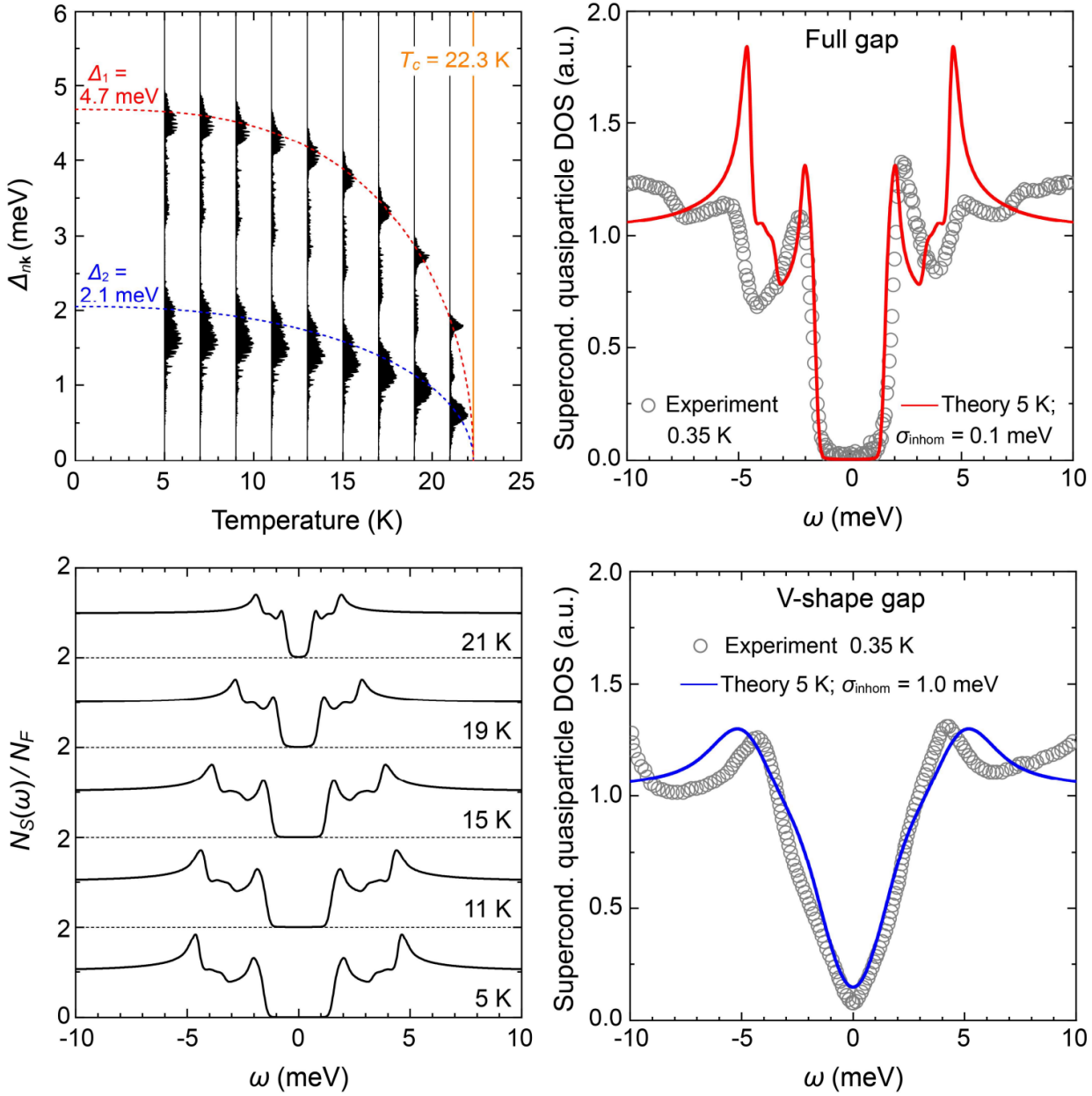
- Distinctive state-pair-resolved coupling $\lambda_{n\mathbf{k},m\mathbf{k+q}}$
- Bimodal state-resolved coupling $\lambda_{n\mathbf{k}}$





Li and Louie, arXiv:2210.12819 (2022)

Temperature-dependent superconducting gaps



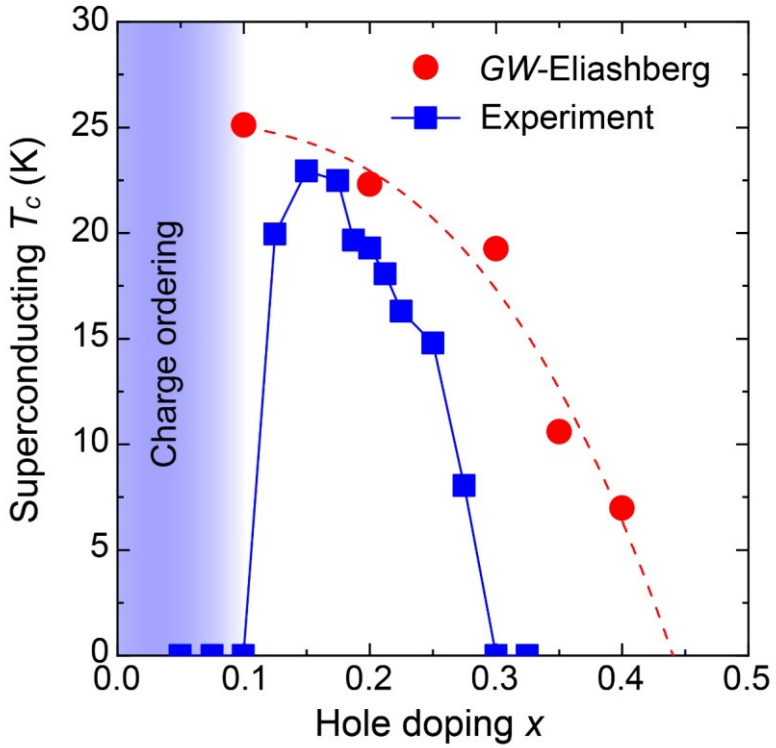
- T_c = 22.3 K (μ^* = 0.05)
- Introduce a simple **broadening parameter** σ_{inhom} in SC-qDOS to account for sample inhomogeneity
- Explain the different experimental tunneling profiles with a straightforward broadening parameter

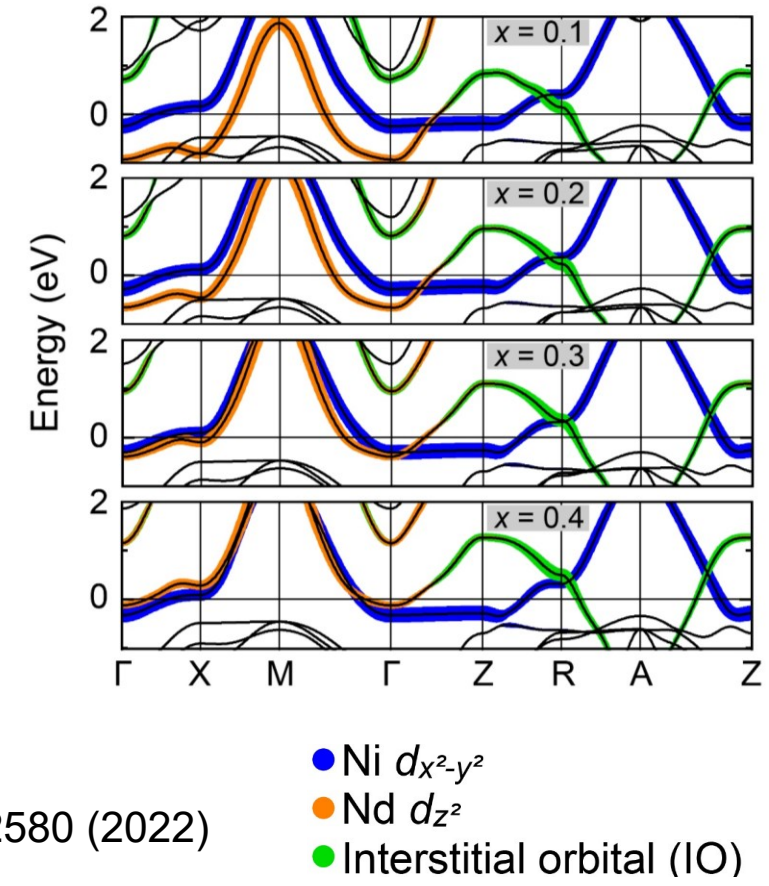
Experimental data: Gu *et al.*, Nature Commun. **11**, 6027 (2020)

Li and Louie, arXiv:2210.12819 (2022)

Superconducting phase diagram

- Full band structure effects included (*e*-ph matrix elements from $x = 0.2$)
- Non-rigid-band doping behavior explains the dome shape on overdoped side





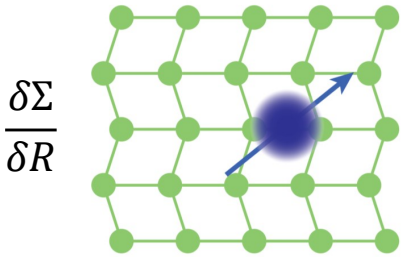
Ab initio GW results reveal and predict a phonon-mediated two-gap *s*-wave superconductivity in infinite-layer nickelates

Experimental data: Lee *et al.*, arXiv:2203.02580 (2022)

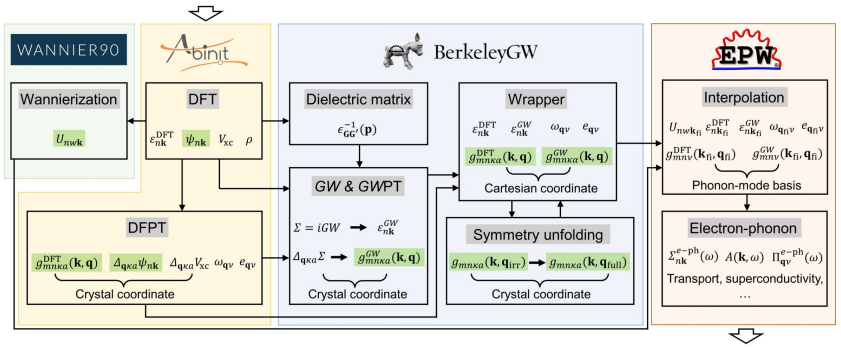
Li and Louie, arXiv:2210.12819 (2022)

Conclusions

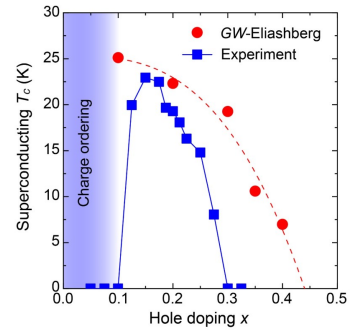
- GWPT method for electron-phonon coupling with correlation effects included



- Practical workflow combining ABINIT-BerkeleyGW-EPW



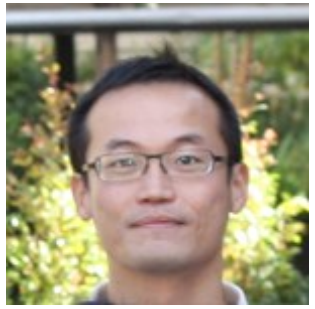
- Self-energy effects can largely renormalize electron-phonon coupling in certain materials



Acknowledgment

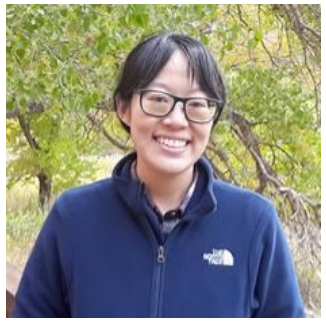
Steven G. Louie
UC Berkeley
LBNL

Gabriel Antonius
Université du Québec
à Trois-Rivières



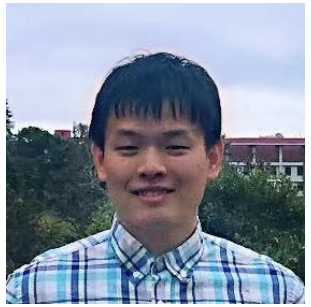
Yang-Hao Chan
Academia Sinica

Felipe H. da Jornada
Stanford



Diana Y. Qiu
Yale

Mauro Del Ben
LBNL



Meng Wu
Schrödinger, Inc.

Funding agencies and computation resources

U.S. DEPARTMENT OF ENERGY | Office of Science

NSF

C2SEPEM

BERKELEY LAB

USC University of Southern California

NERSC

TACC

OAK RIDGE National Laboratory | LEADERSHIP COMPUTING FACILITY