Deep Learning Electron-Phonon Couplings Beyond Mean-Field Level

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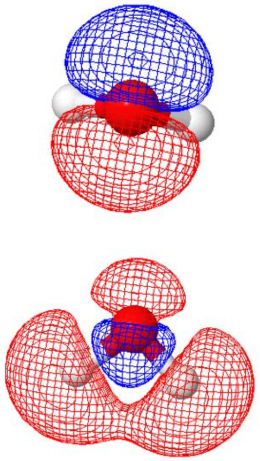
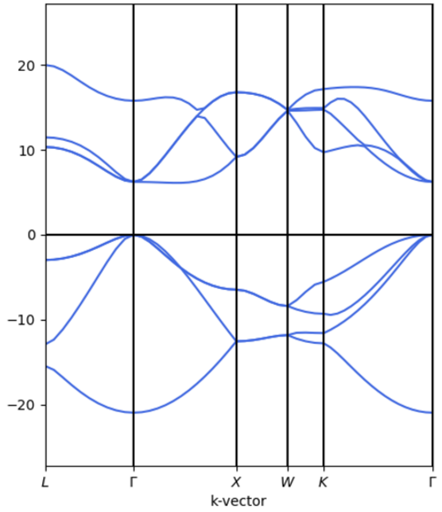
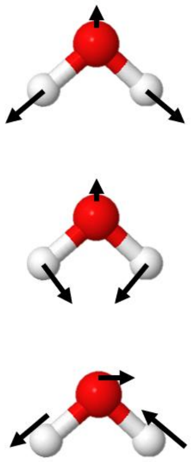
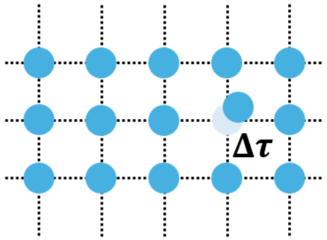
Electron-phonon / vibronic coupling

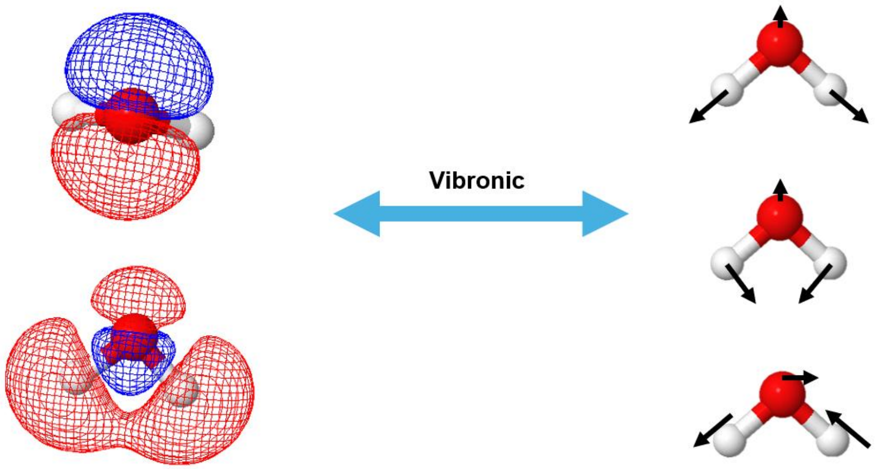


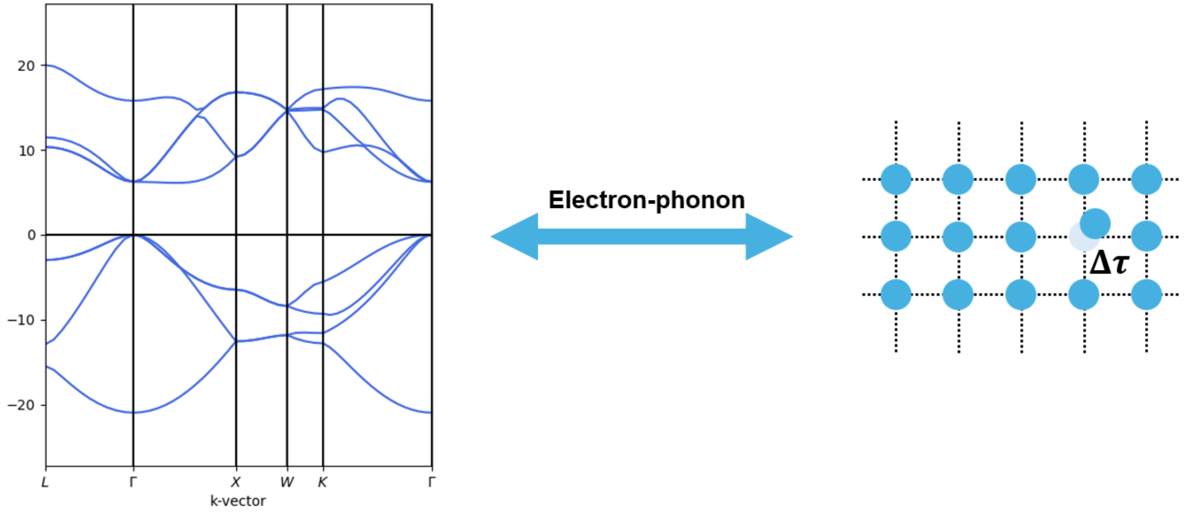






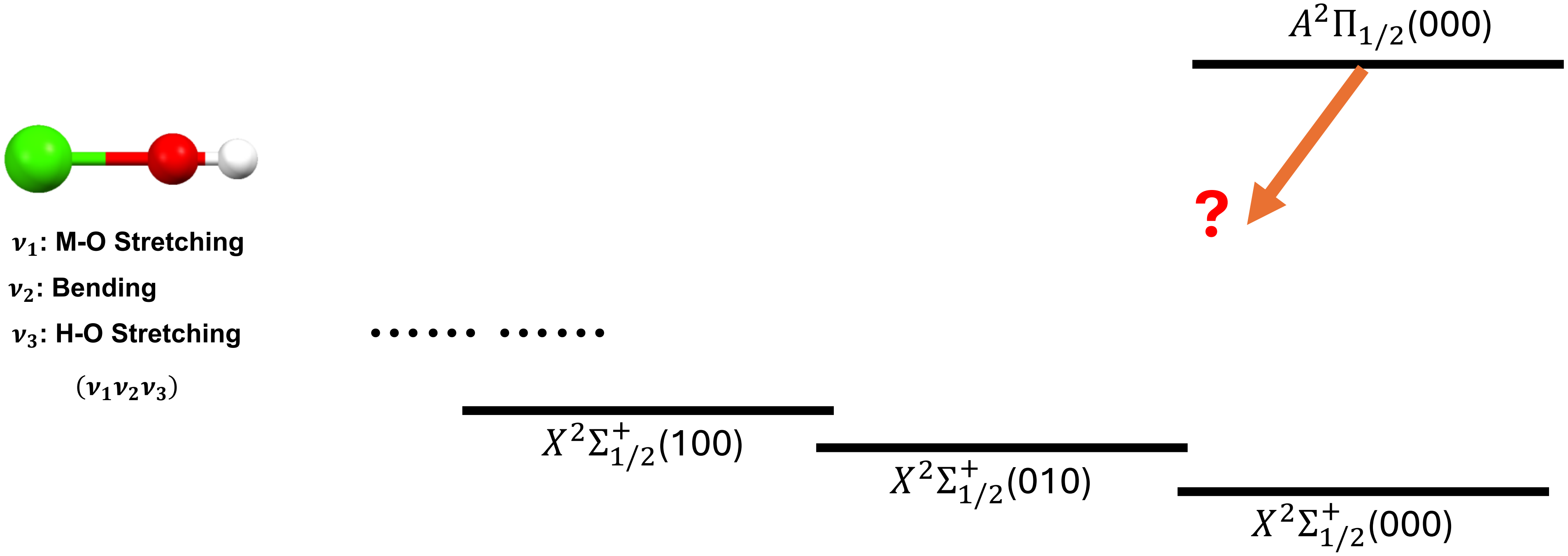
Electron-phonon / vibronic coupling





Why electron-phonon coupling?

- Application in laser cooling of CaOH



ν_1: M-O Stretching

ν_2: Bending

ν_3: H-O Stretching

$(\nu_1\nu_2\nu_3)$

C Zhang, et al, J. Chem. Phys. 155, 091101 (2021)

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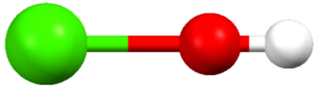

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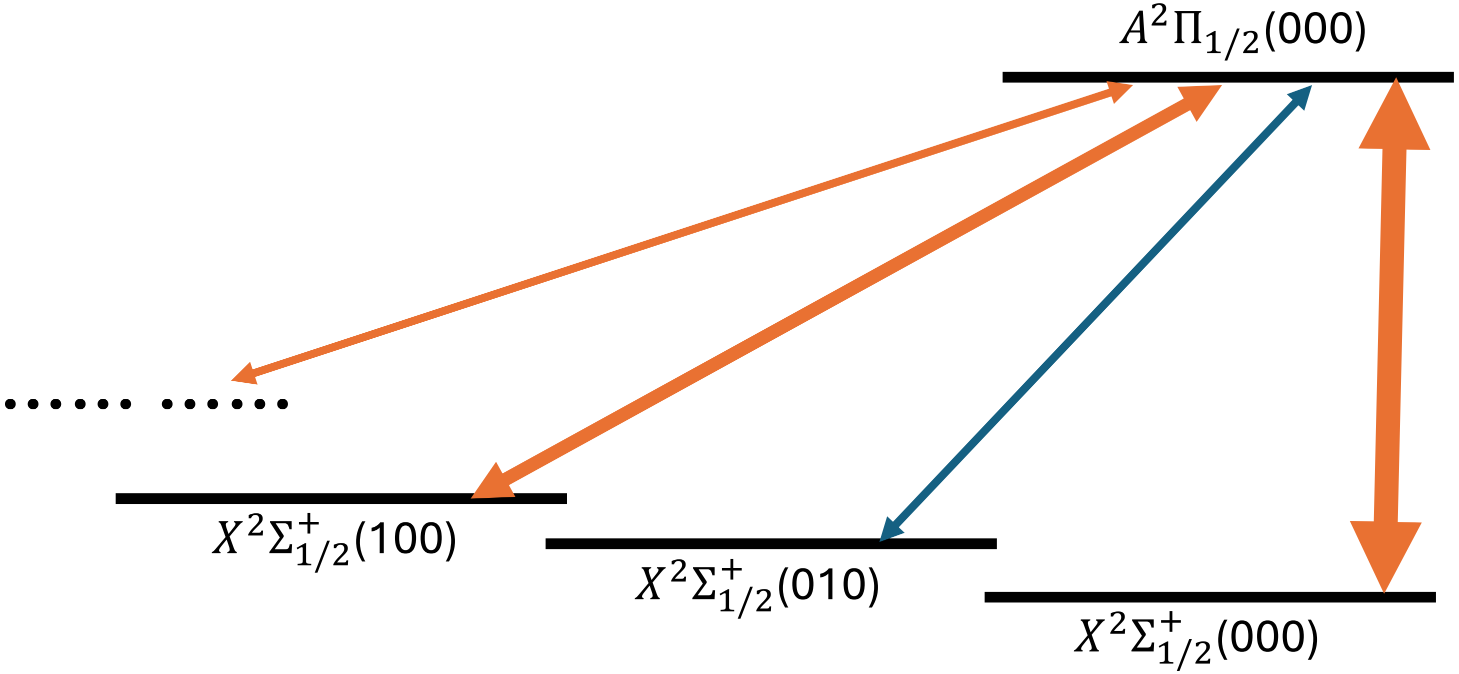

C Zhang, et al, J. Chem. Phys. 155, 091101 (2021)

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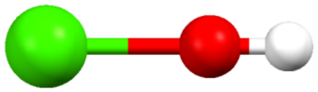

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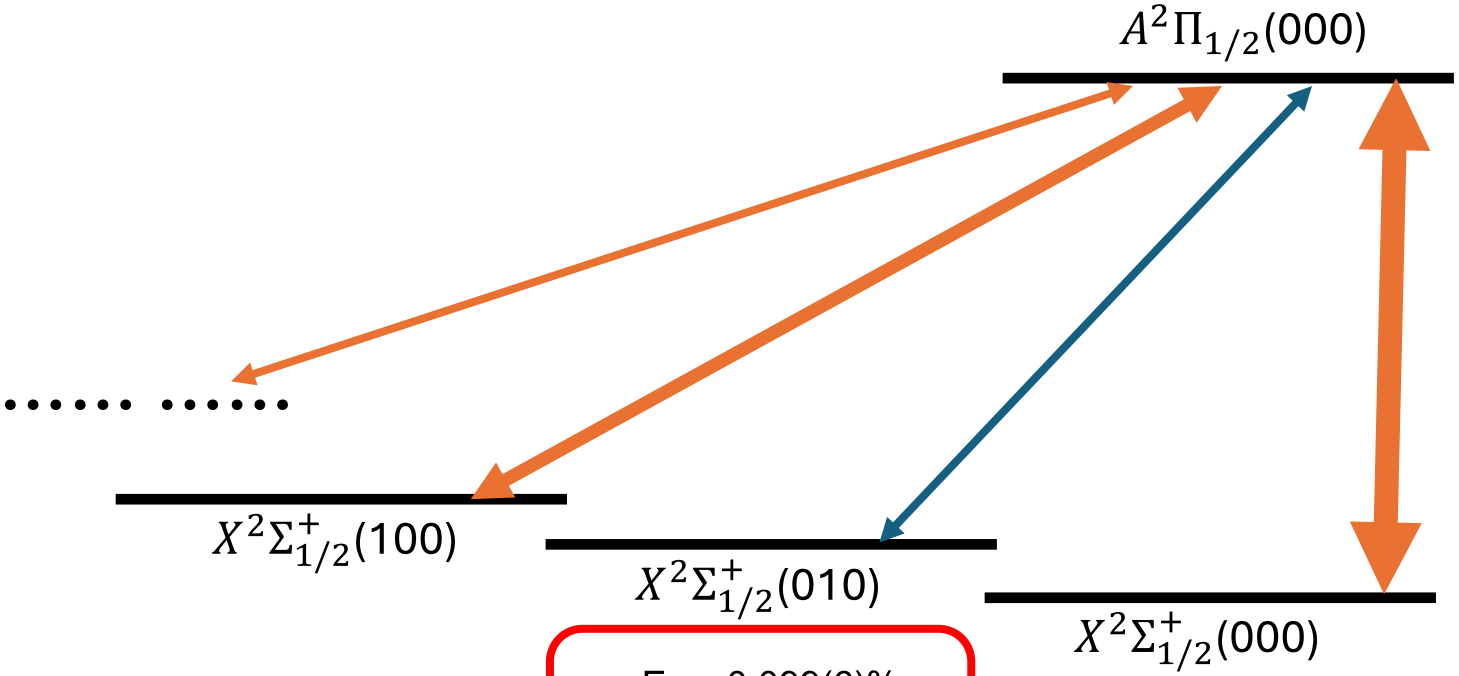


$A^2\Pi_{1/2}(000)$

…… ……

$X^2\Sigma^+_{1/2}(100)$

$X^2\Sigma^+_{1/2}(010)$

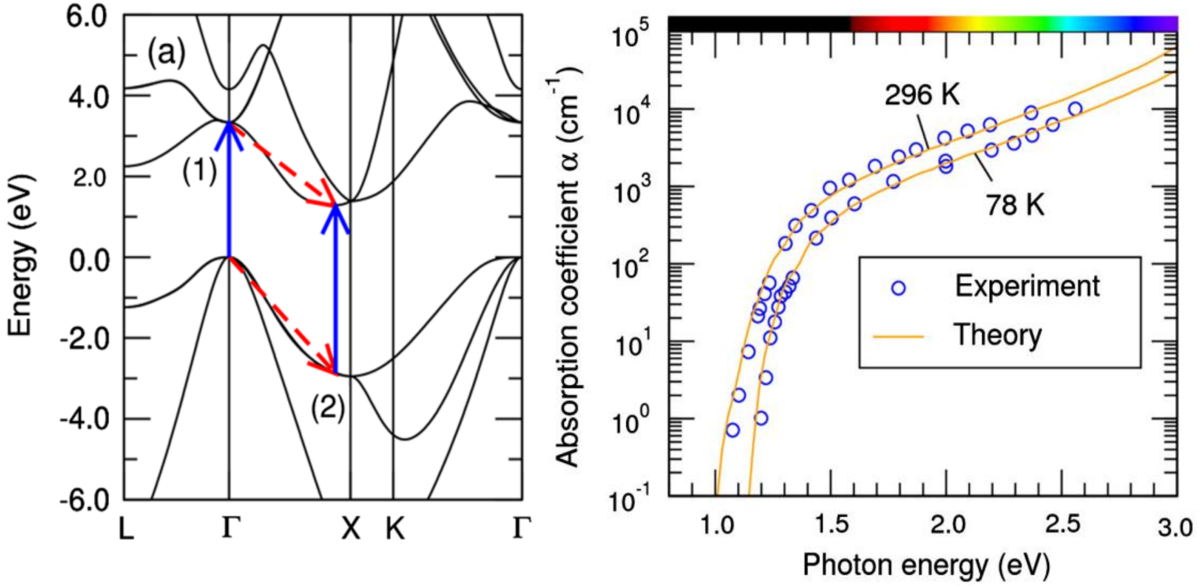
$X^2\Sigma^+_{1/2}(000)$

Exp. 0.099(6)%
Calc. 0.063%
w/o vibronic 0.0%

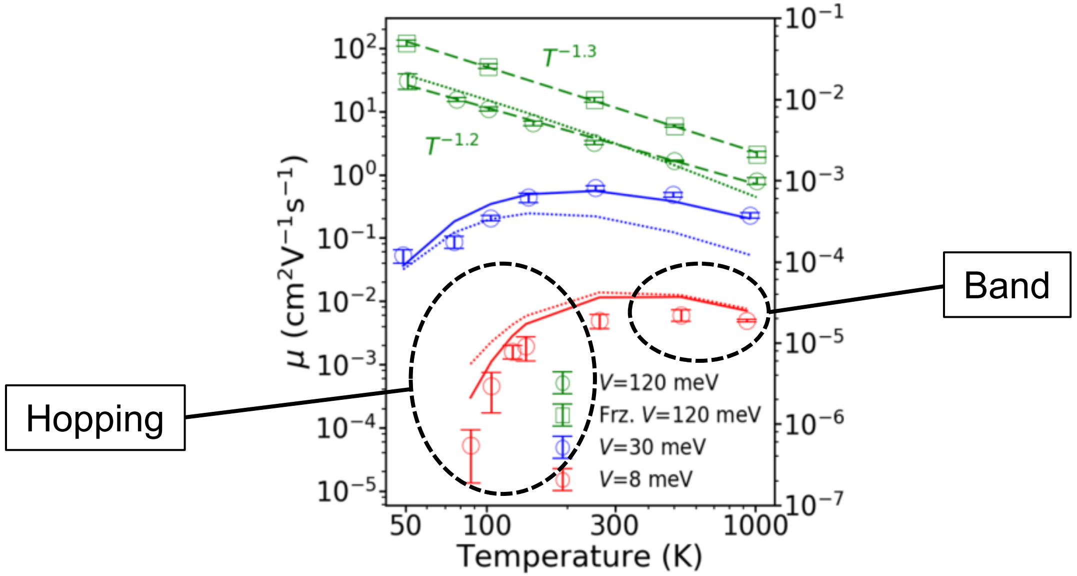
C Zhang, et al, J. Chem. Phys. 155, 091101 (2021)

Why electron-phonon coupling?

Phonon-assisted optical transition in silicon



Charge transportation



Hopping

Band

J Noffsinger, et al, Phys. Rev. Lett. 108, 167402 (2012)
S Giannini, A Carof, J Blumberger, J. Phys. Chem. Lett. 9, 3116 (2018)

How to calculate electron-phonon couplings

- Molecular wave function: direct-product basis $|\Psi_i(r,R_0)\chi_m(R)\rangle$

$$H(r,R) = H_{elec}(r,R_0) + H_{nuc}^{(2)}(R) + V_{e-ph}^{(1+2)}(r,R)$$

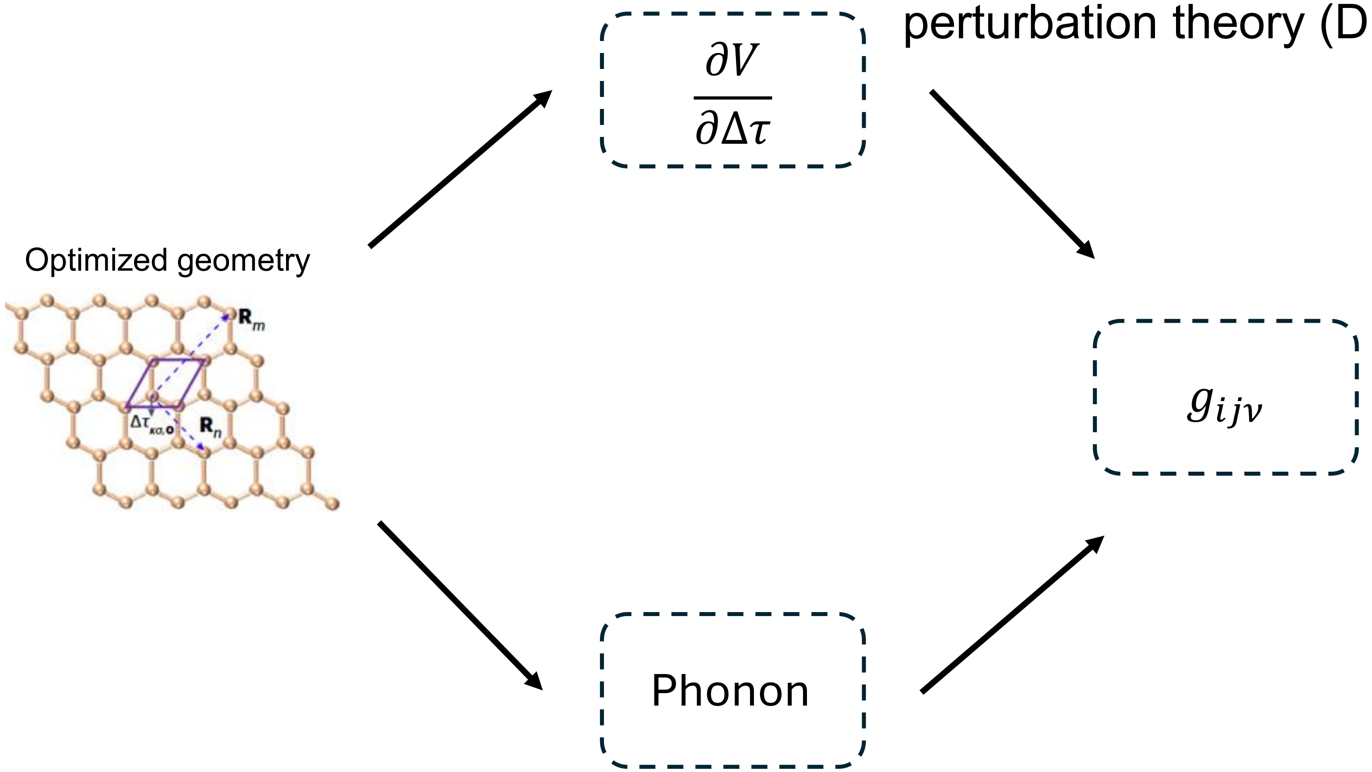
$$= H_{elec}(r,R_0) + \sum_{\nu} \hbar\omega_{\nu}\left(b_{\nu}^{\dagger}b_{\nu} + 1/2\right)$$

$$+ \sum_{ij\nu} g_{ij\nu}^{(1)}\left(b_{\nu}^{\dagger} + b_{\nu}\right) + \sum_{ij\nu\nu'} g_{ij\nu\nu'}^{(2)}\left(b_{\nu}^{\dagger} + b_{\nu}\right)\left(b_{\nu'}^{\dagger} + b_{\nu'}\right)$$

$$g_{ij\nu}^{(1)} \equiv \left\langle \Psi_i(r,R_0) \middle| \left(\frac{\partial H_{elec}}{\partial R_{\nu}}\right)_0 \middle| \Psi_j(r,R_0) \right\rangle$$

$$g_{ij\nu\nu'}^{(2)} \equiv \left\langle \Psi_i(r,R_0) \middle| \left(\frac{\partial^2 H_{elec}}{\partial R_{\nu'}\partial R_{\nu}}\right)_0 \middle| \Psi_j(r,R_0) \right\rangle$$

DFT electron-phonon couplings workflow



Optimized geometry

$$\frac{\partial V}{\partial \Delta\tau}$$

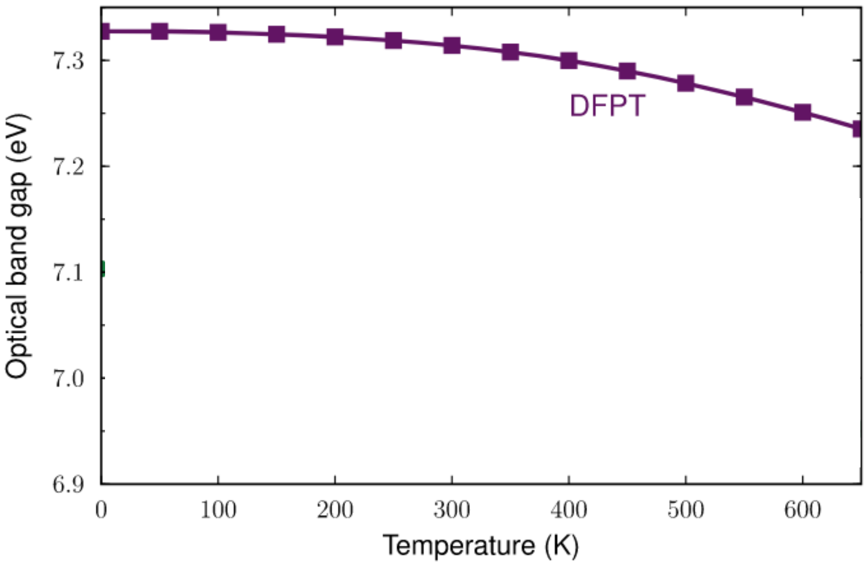
Density functional perturbation theory (DFPT)

Phonon

$g_{ij\nu}$

DFT code validation

Diamond band gap renormalization



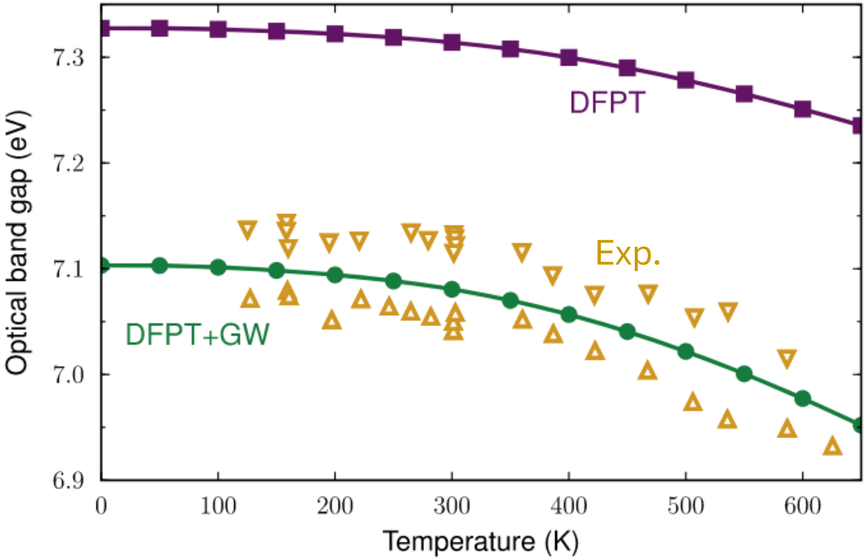
$$\Delta E_{n,k} = \sum_{\nu} \int \frac{dq}{\Omega_{BZ}} \left(2n_{q\nu} + 1\right) \left[\sum_{m} \frac{|g_{mn\nu}(k,q)|^2}{\varepsilon_{n,k} - \varepsilon_{m,k+q}} + g^{DW}_{nn\nu\nu}(k,q,-q) \right]$$

Basis	Zero-point renormalization (ZPR, in meV)
Planewave [1]	-437
Gaussian [2]	-407
Gaussian [This work]	-446

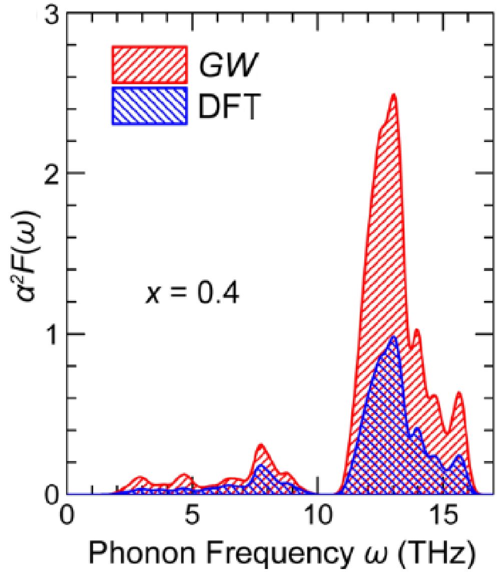
[1] G Antonius, et al, Phys. Rev. Lett. 112, 215501 (2014)
[2] G Mann, M Rohlfing, T Deilmann, Phys. Rev. B. 110, 075145 (2024)

Is DFT enough for all systems?

Diamond band gap renormalization



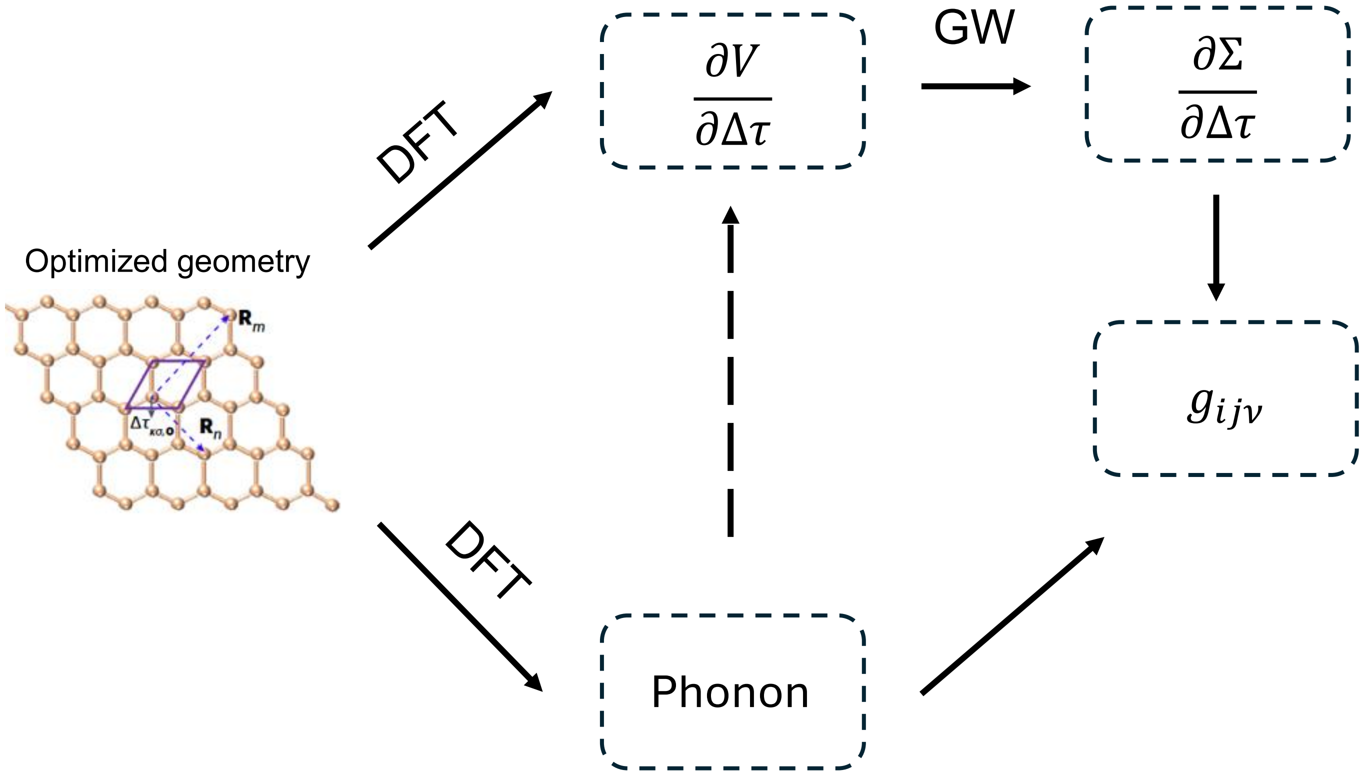
Superconductivity



	λ	$T_c(K)$
DFT	0.47	0.6 – 6
GW	1.14	29 – 45
Exp.	-	30 – 32

G Antonius, et al, Phys. Rev. Lett. 112, 215501 (2014)
Z Li, et al, Phys. Rev. Lett. 122, 186402 (2019)

Workflow is the same for quasi-particle picture



Optimized geometry

DFT

$$\frac{\partial V}{\partial \Delta\tau}$$

GW

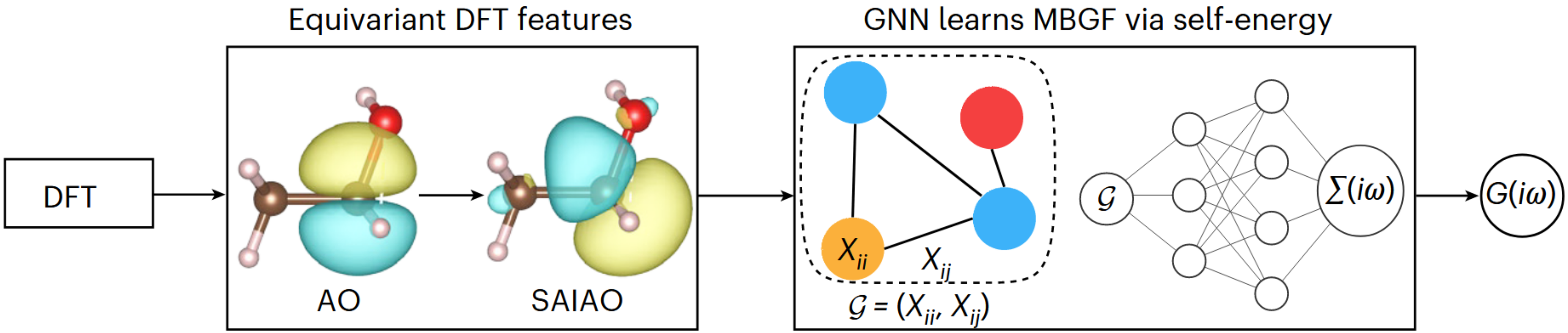
$$\frac{\partial \Sigma}{\partial \Delta\tau}$$

$$g_{ij\nu}$$

DFT

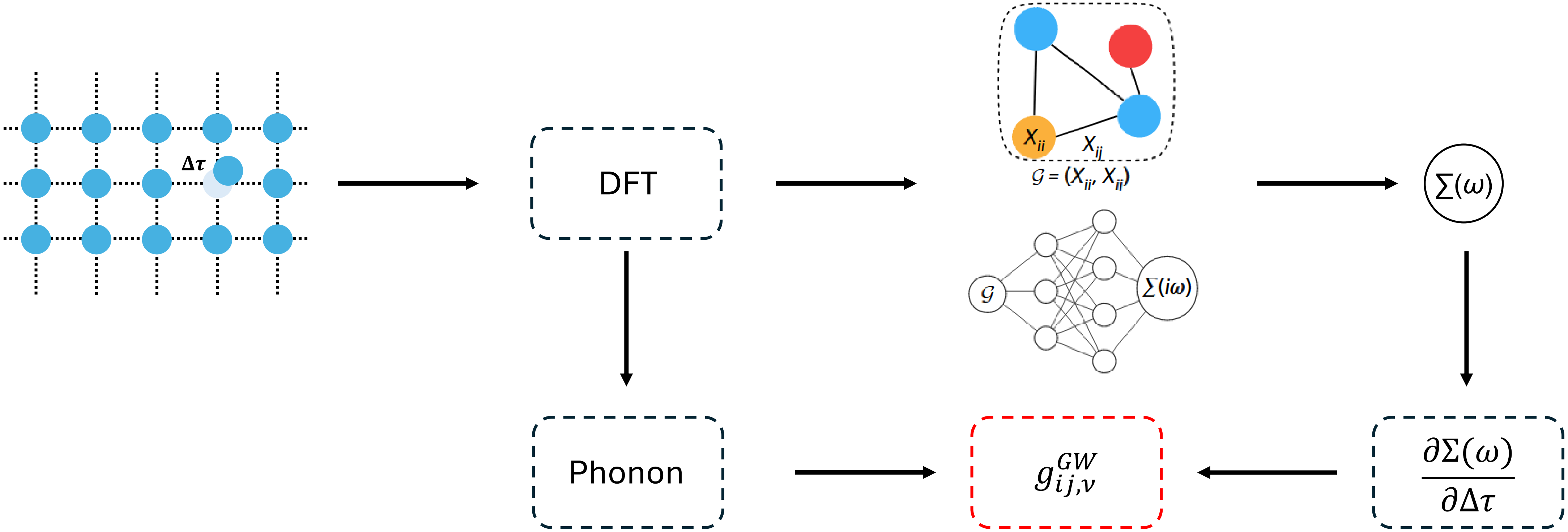
Phonon

Accurate machine learning Green’s function



C. Venturella, et al, J. Chem. Theory Comput. 20, 143 (2024)
C. Venturella, J. Li, T. Zhu, Nat. Comput. Sci. 5, 502 (2025)

Machine learning workflow



DFT

$\Sigma(\omega)$

Phonon

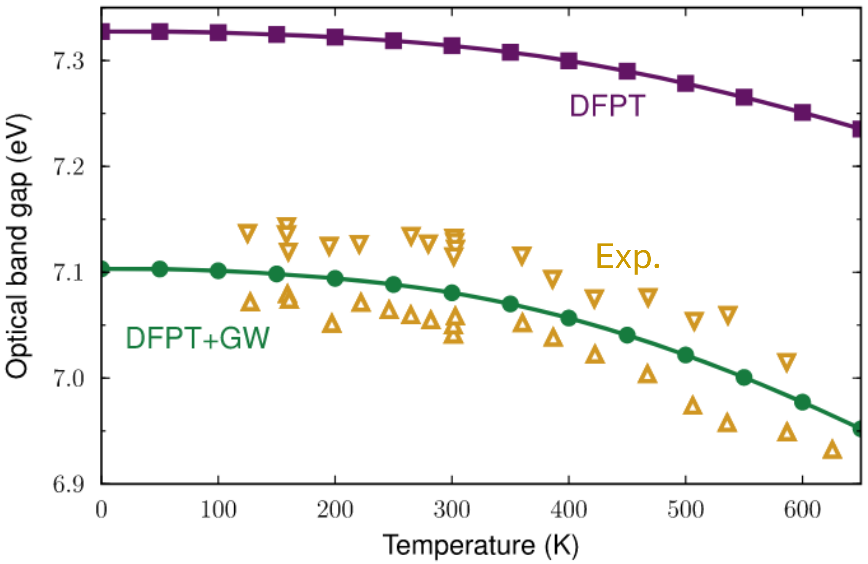
$g_{ij,\nu}^{GW}$

$\frac{\partial \Sigma(\omega)}{\partial \Delta\tau}$

C. Zhang, in preparation

Preliminary results: band gap correction

Diamond band gap renormalization



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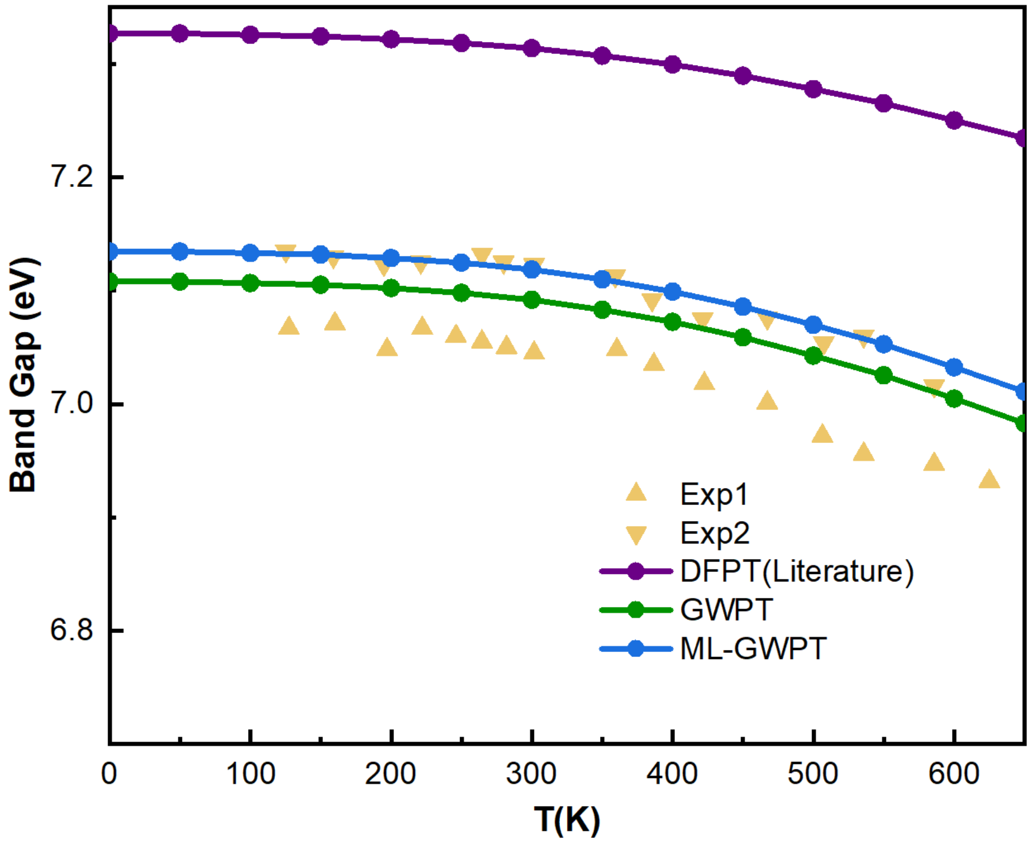
ZPR (meV)	Ref.	ML
$2 \times 2 \times 2$	-1272	-1281
$3 \times 3 \times 3$	-1079	-1052
$4 \times 4 \times 4$	-953	-1021

G Antonius, et al, Phys. Rev. Lett. 112, 215501 (2014)
C. Zhang, in preparation

Preliminary results: temperature dependence



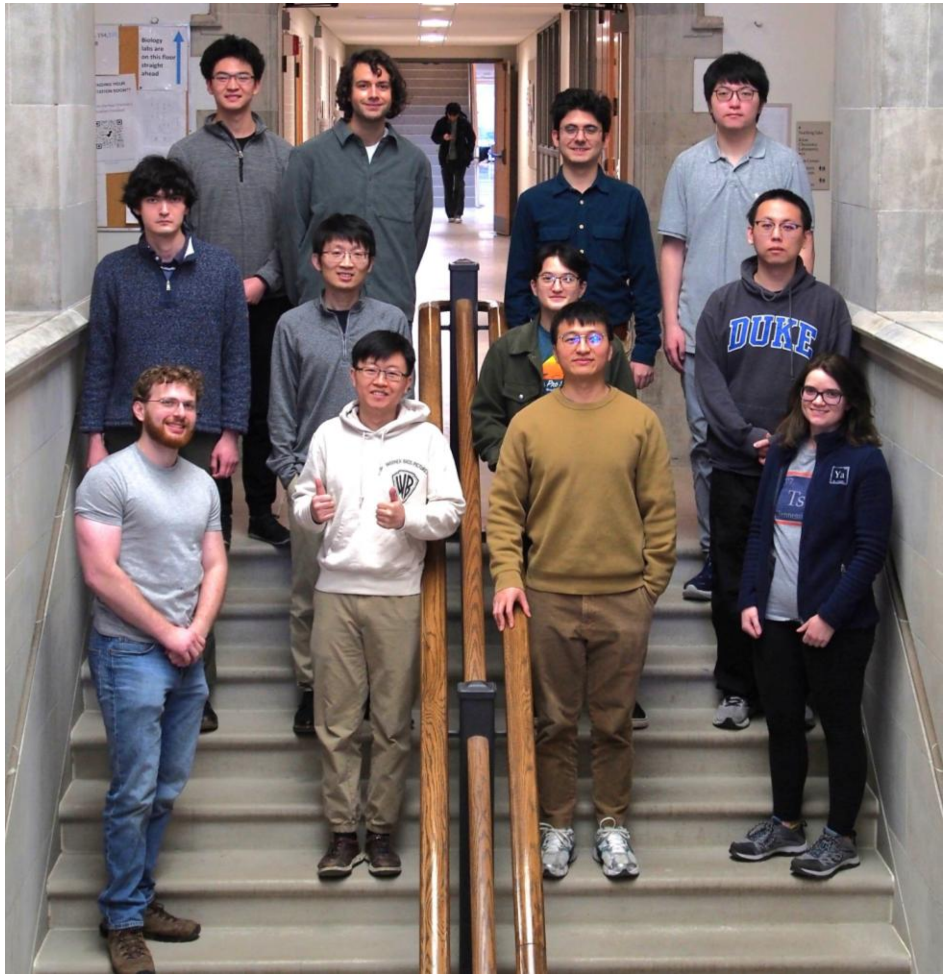
G Antonius, et al, Phys. Rev. Lett. 112, 215501 (2014)
C. Zhang, in preparation

Summary

- What we have:
  - We implemented finite difference e-ph couplings in PySCF for DFT and GW.
  - Machine learning Green's function workflow was extended to GW e-ph couplings.

- More work to be done:
  - More physical observables from e-ph couplings
  - Better k-points extrapolation

Acknowledgment



Zhu Lab

Dr. Junjie Yang