Special displacement method for the calculation of materials' properties at finite temperatures

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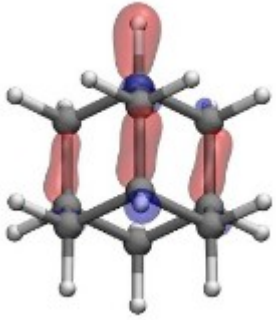
Cyprus University of Technology

THE CYPRUS INSTITUTE
RESEARCH·TECHNOLOGY·INNOVATION

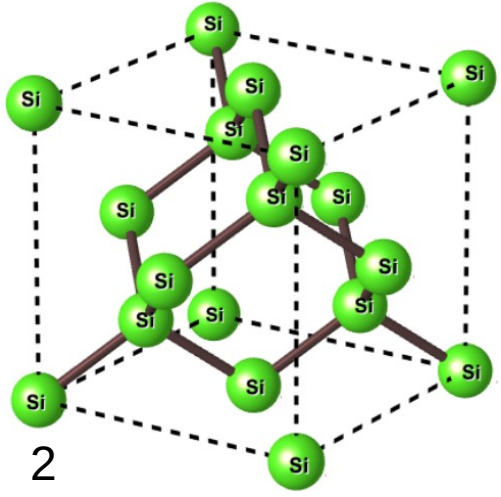
EURO CaSToRC - HPC National Competence Centre Seminar

Computational materials modeling from first principles

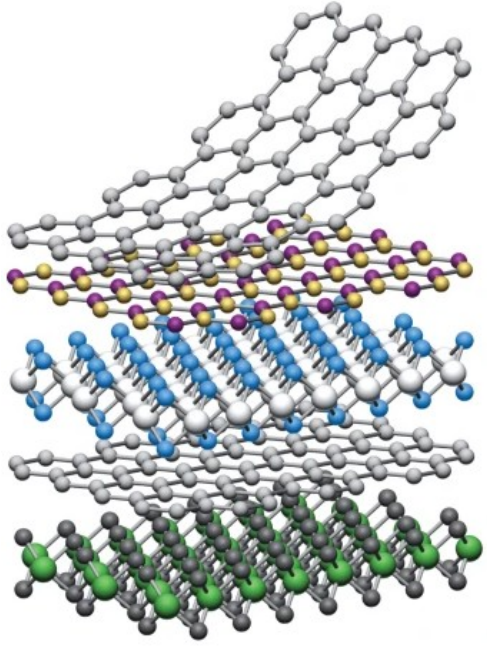
Molecules



Crystals



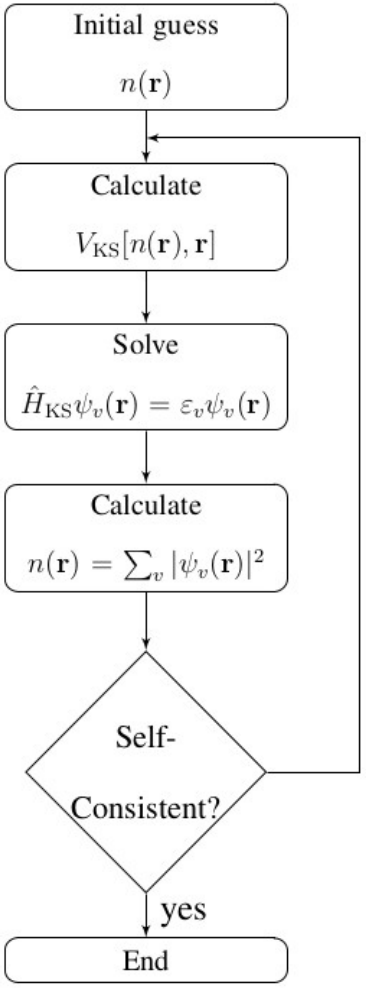
Surfaces
Interfaces
Heterostructures

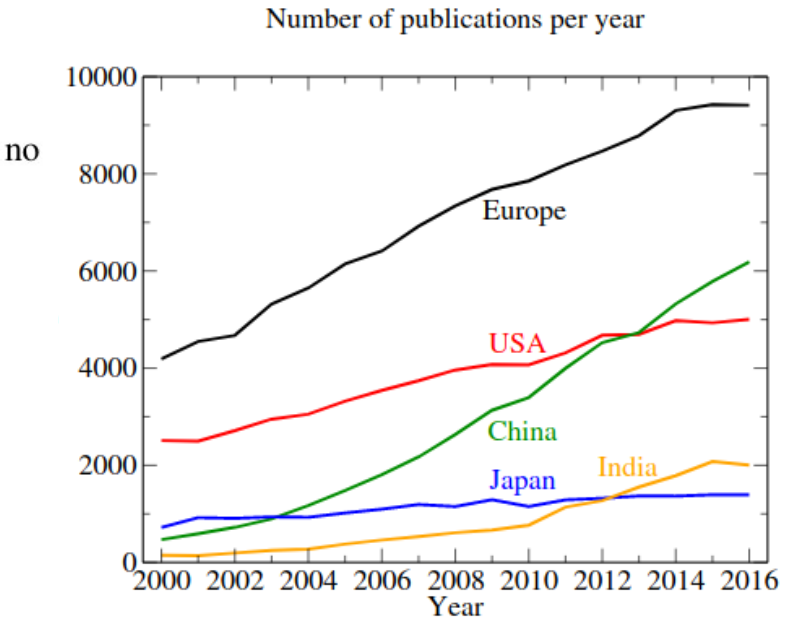


- ***Materials modeling*** is the use of mathematical models to describe materials properties.
- ***First-principles*** refers to a bottom-up strategy that relies on Quantum Mechanics and is empirical free.
- ***Computational*** requires high-performance computing (HPC) and highly-parallel codes for solving the Schrödinger equation.

Density functional Theory (DFT)

- **DFT** is the state-of-the-art tool used as a starting point to study the properties of many-body systems from functionals that depend on the electron density $\mathbf{n(r)}$.
- The premise of DFT is to start from an initial guess of $\mathbf{n(r)}$ and solve iteratively the Kohn-Sham equations (variant of the Schrödinger equation for electrons).
- Requires parallel computations that depend on many planewave coefficients $\mathbf{G}$ (or orbital basis functions) and electron $\mathbf{k}$ states. The cost scales with the number of atoms.

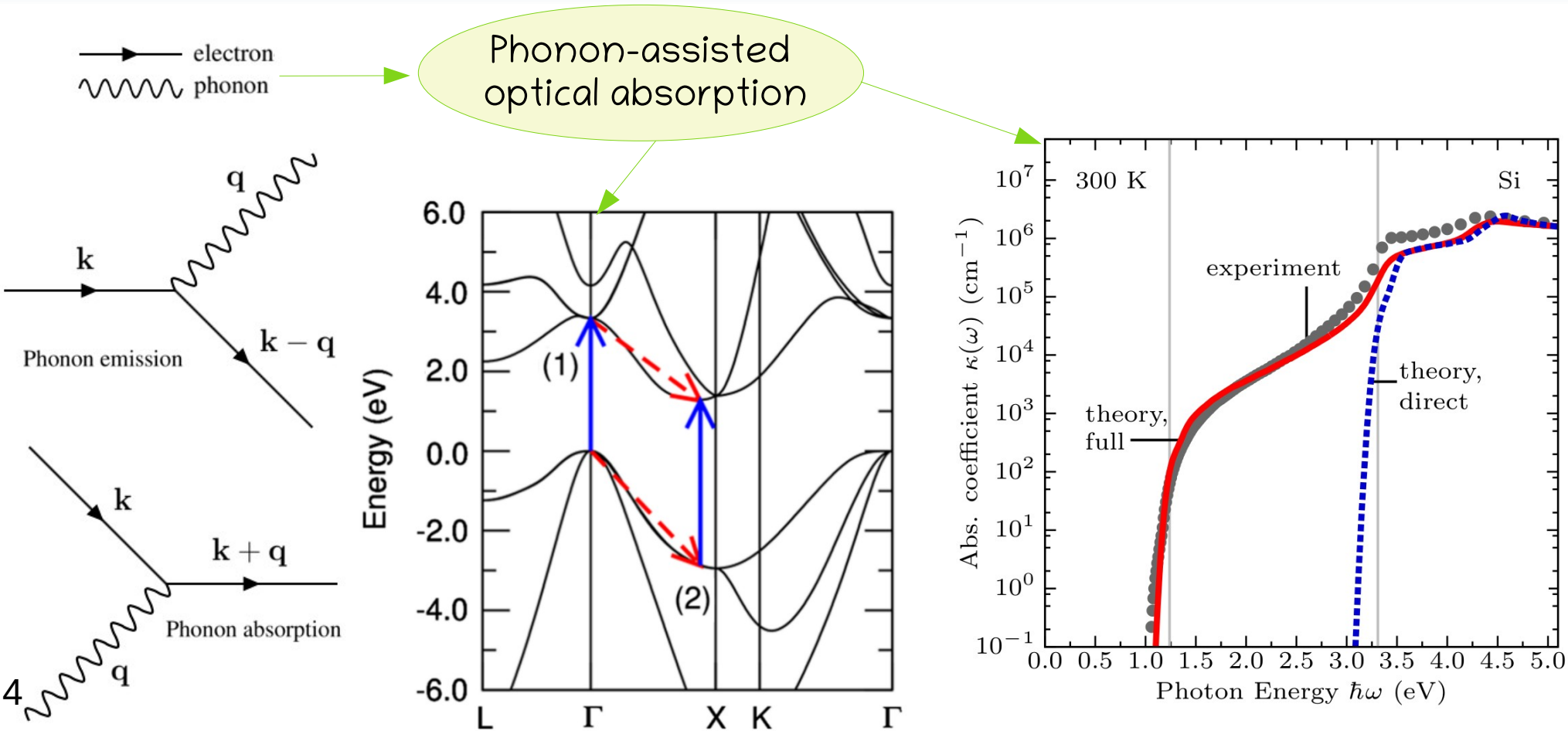




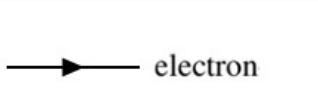
"Statistical Data about Density Functional Calculations"
Mavropoulos P. and Dederichs P.

Cypriot Universities have to invest more on HPC and DFT

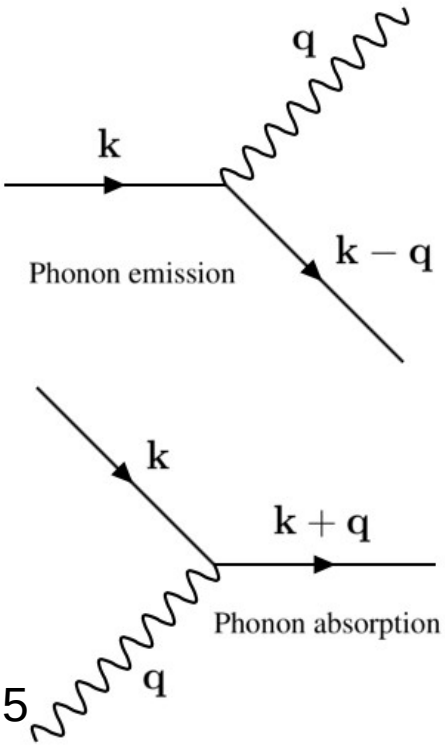
Beyond DFT: Electron-phonon interactions for quantum nuclear and temperature effects I

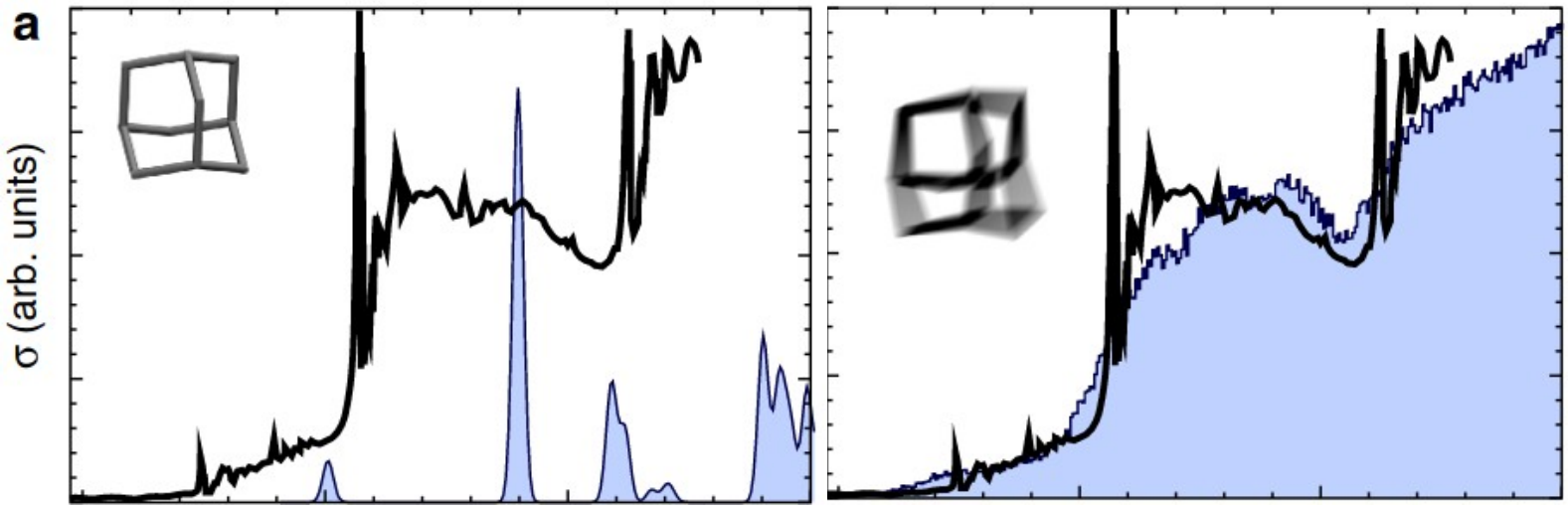


Beyond DFT: Electron-phonon interactions for quantum nuclear and temperature effects II



Phonon-assisted optical absorption

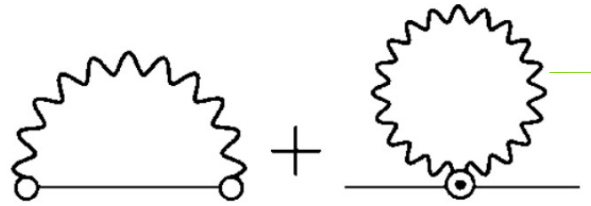




Quantum nuclear dynamics in the photophysics of **diamondoids**

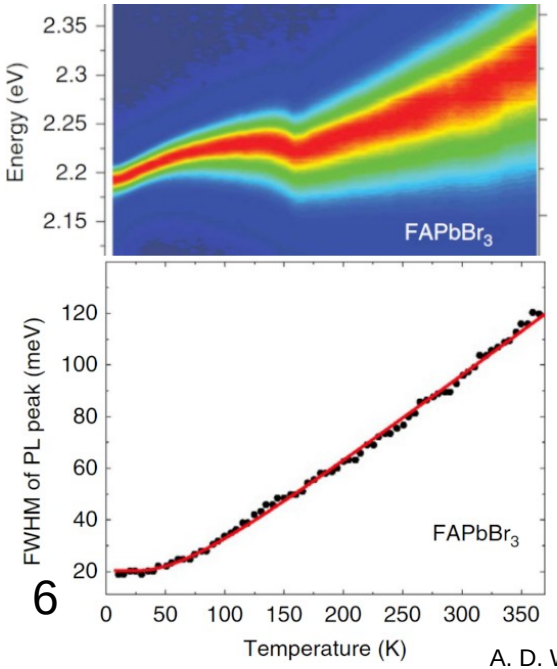
C. E. Patrick and F. Giustino, Nature Commun., **4**, 2006, (2013)

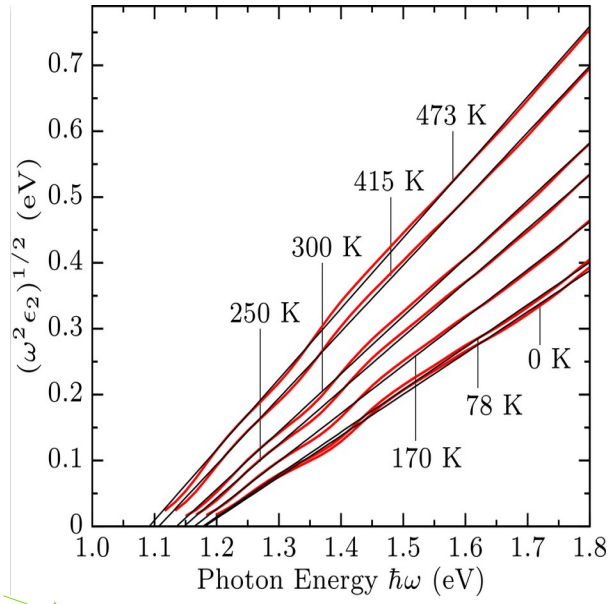
Electron-phonon interaction: Quantum nuclear and temperature effects III

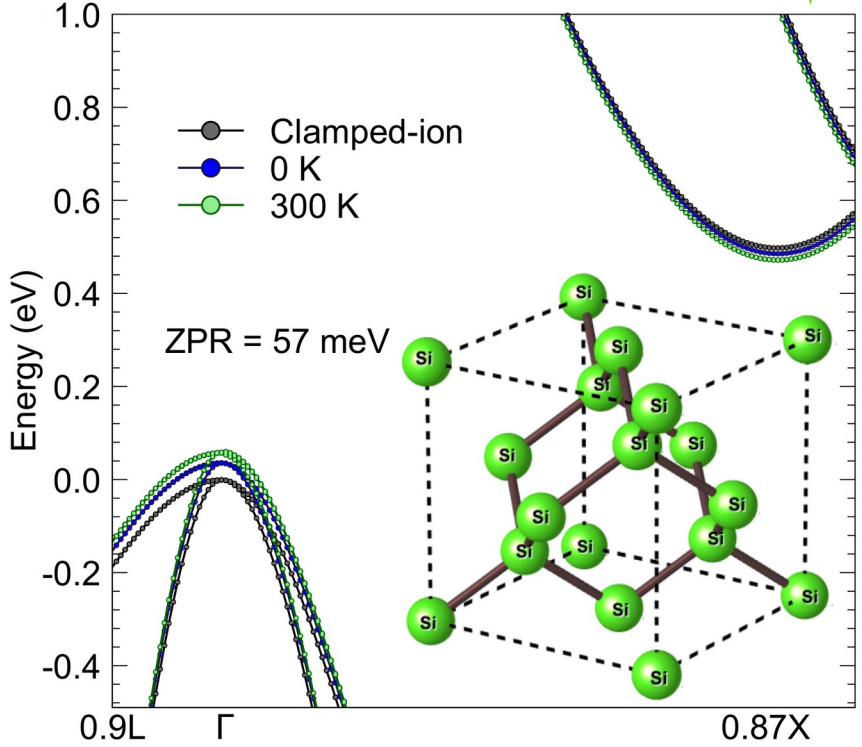
$$\Delta E_{n\mathbf{k}} =$$  $$+$$

SE DW

Energy level renormalization / T-dependent absorption onset

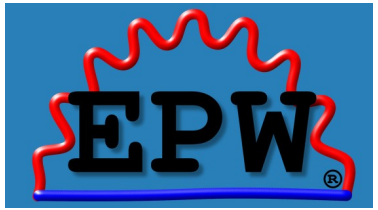






A. D. Wright, C. Verdi et al., Nat. Commun. **7**, 11755 (2016)

Electron-phonon coupling (EPC) from first principles: Some code developments



- Electron-phonon coupling strengths (λ)
- Superconducting properties
- Electron and phonons self energies
- Electron and phonon line-widths, -times
- T-dependent carrier lifetimes, mobilities

- T-dependent transport properties
- Superconducting properties
- T-dependent band structures within Allen-Heine theory: DW and SE terms

EPC: Linear response
Unitcell calculations

Harmonic Approximation

ZG-package

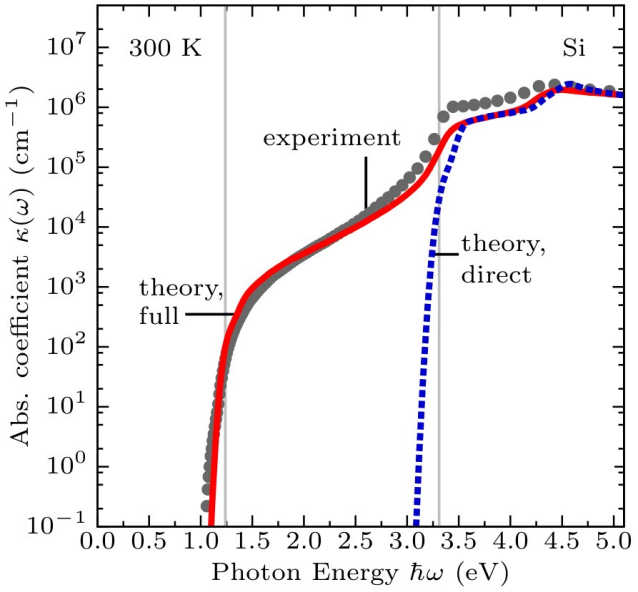
- Any T-dependent property that can be described by the *Fermi-Golden rule*
- Already implemented in VASP [1]
- New version in QE/EPW soon

EPC: Non-perturbative
Supercell calculations

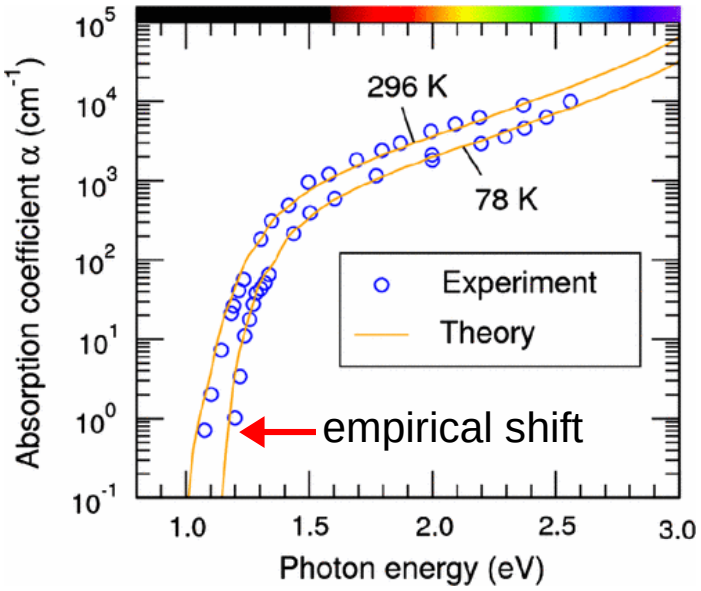
[1] https://www.vasp.at/wiki/index.php/Electron-phonon_interactions_from_Monte-Carlo_sampling

Nonperturbative approaches Vs perturbative (linear response) approaches

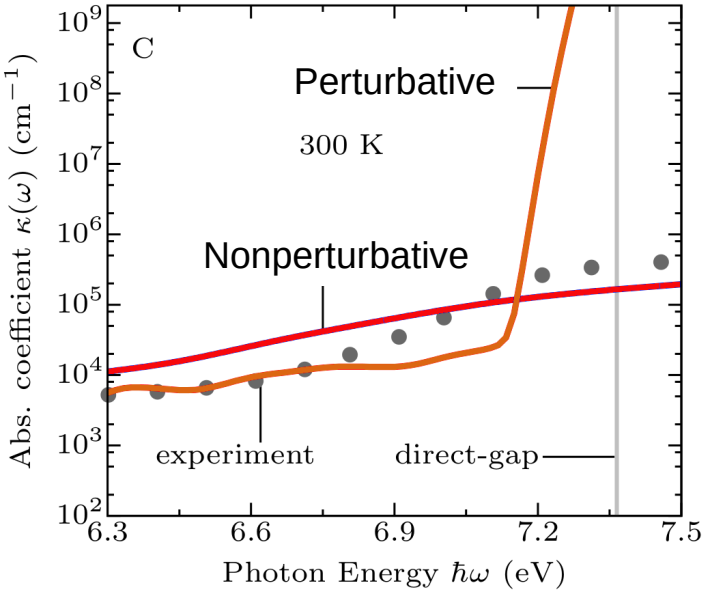
Nonperturbative (ZG)



Perturbative (EPW)



Differences



[1] M. Zacharias and F. Giustino, Phys. Rev. Res. 2, 013357 (2020). [2] J. Noffsinger, E. Kioupakis, et al., Phys. Rev. Lett. 108, 167402, (2012).

- ZG gives the full spectrum → all terms in perturbation theory ✓
- ZG accounts for the T-dependent band structure ✓
- ZG requires supercells → EPW elegance of unitcell calculations ✗
- ZG misses non-adiabatic terms ✗

EPC using the special displacement method (SDM) and the ZG configuration

SDM: Gives the set of atomic displacements (ZG displacements) that best incorporate the effect of electron-phonon coupling in *ab-initio* calculations

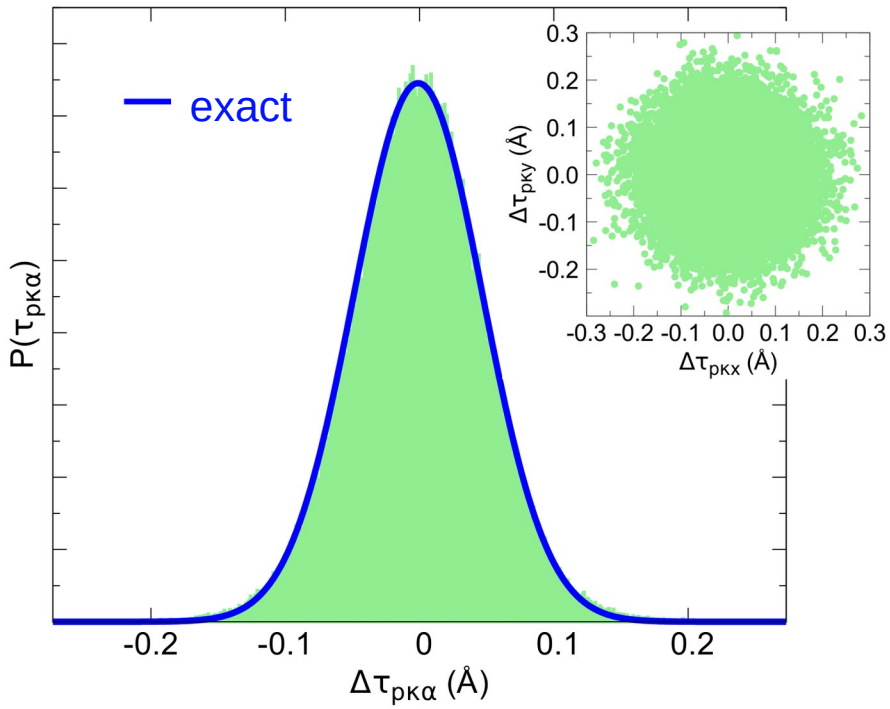
$$\Delta\boldsymbol{\tau}_{p\kappa} = \sum_{\mathbf{q}\in\mathcal{B},\nu} S_{\mathbf{q}\nu} \left[\frac{\hbar}{2N_p M_\kappa \omega_{\mathbf{q}\nu}} (2n_{\mathbf{q}\nu,T} + 1) \right]^{\frac{1}{2}} \times 2\,\mathrm{Re}[e^{i\mathbf{q}\cdot\mathbf{R}_p}\mathbf{e}_{\kappa,\nu}(\mathbf{q})]$$

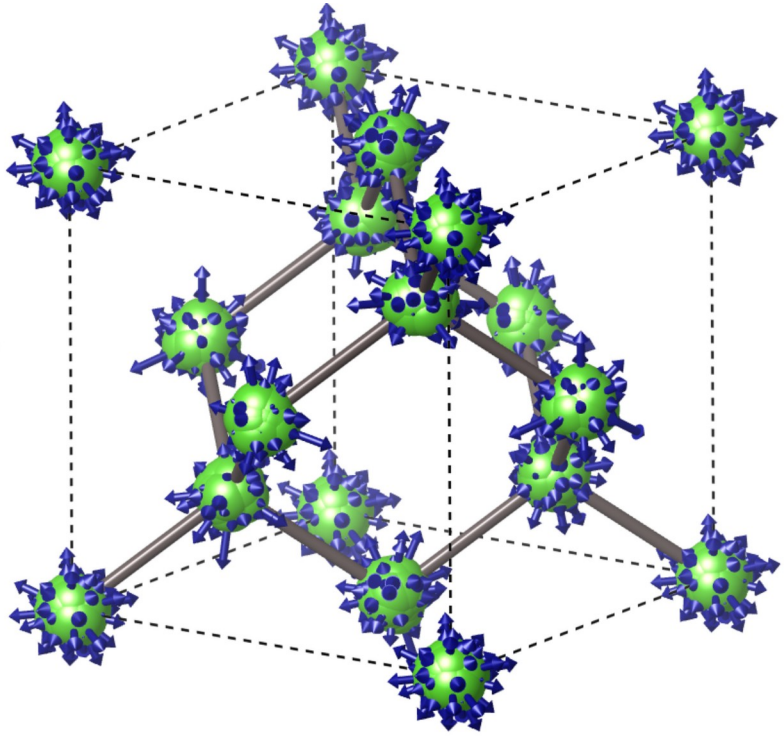
Special set of signs allocated by the code so that nonperturbative error is minimized

M. Zacharias and F. Giustino, Phys. Rev. B 94, 075125 (2016) and Phys. Rev. Res. 2, 013357 (2020).

EPC using the special displacement method (SDM) and the ZG configuration. **Physical meaning (I):**

SDM: Gives the set of atomic displacements (ZG displacements) that best incorporate the effect of electron-phonon coupling in *ab-initio* calculations





M. Zacharias and F. Giustino, Phys. Rev. B 94, 075125 (2016) and Phys. Rev. Res. 2, 013357 (2020).

EPC using the special displacement method (SDM) and the ZG configuration. **Physical meaning (ii):**

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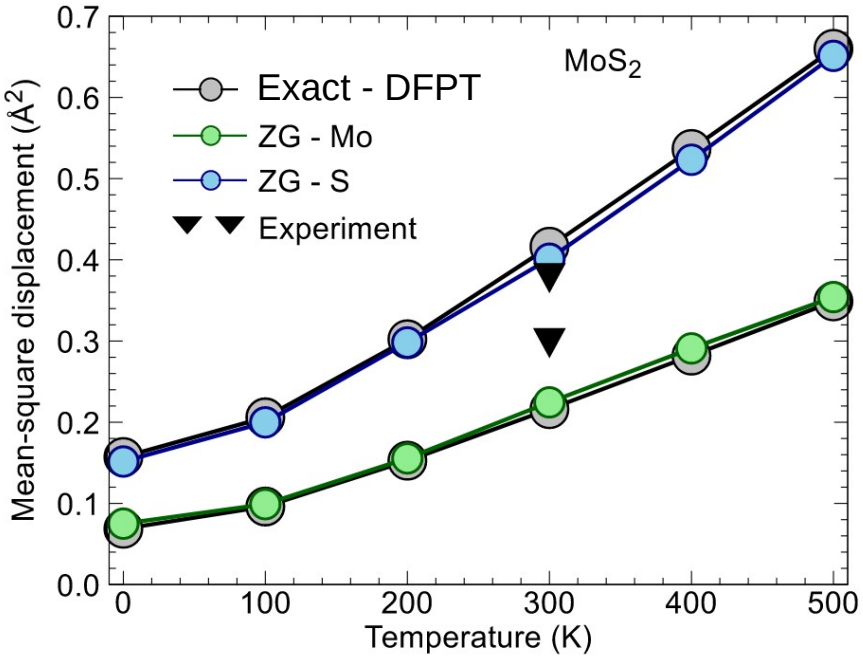
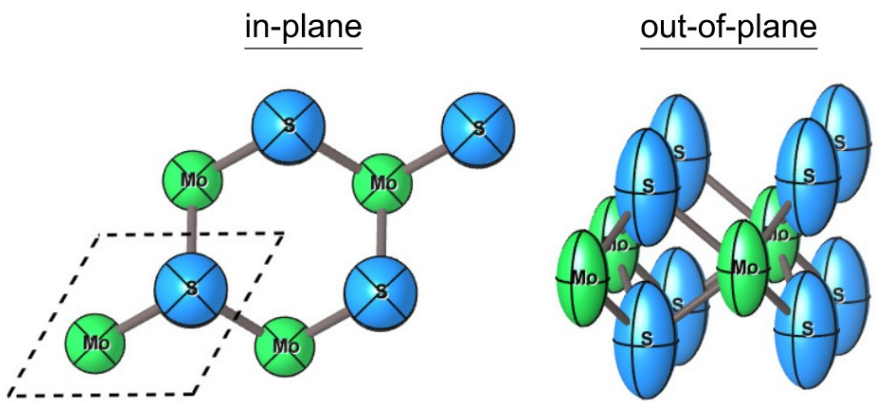




Thermal Ellipsoids of MoS_2

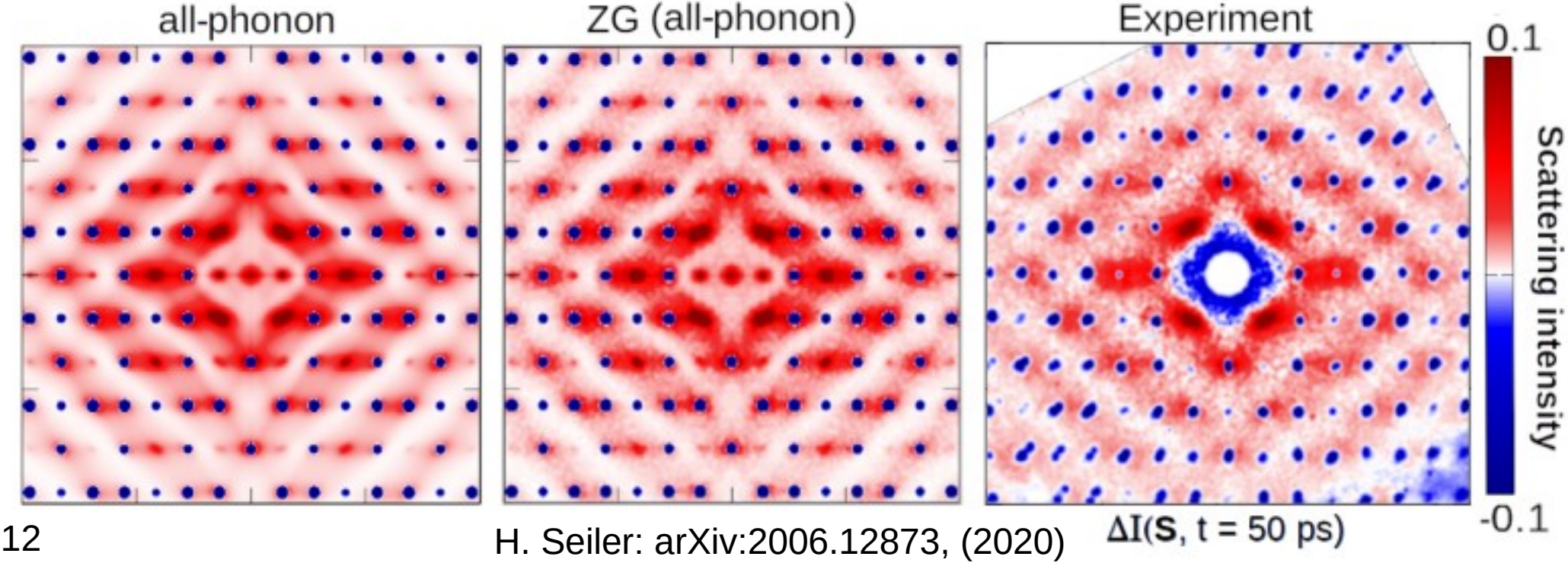
M. Zacharias and F. Giustino, Phys. Rev. B 94, 075125 (2016) and Phys. Rev. Res. 2, 013357 (2020).

Gives also exact phonon properties. **Physical meaning (iii):**

Scattering structure factor map of black phosphorus:

(1) $$I(\mathbf{S},T) = I^{\{\tau^{\mathrm{ZG}}\}}(\mathbf{S}) = \sum_{pp'}\sum_{\kappa\kappa'} f_\kappa(\mathbf{S}) f^*_{\kappa'}(\mathbf{S}) e^{i\mathbf{S}\cdot[\mathbf{R}_p-\mathbf{R}_{p'}+\mathbf{R}_\kappa-\mathbf{R}_{\kappa'}+\Delta\boldsymbol{\tau}^{\mathrm{ZG}}_{p\kappa}-\Delta\boldsymbol{\tau}^{\mathrm{ZG}}_{p'\kappa'}]}$$

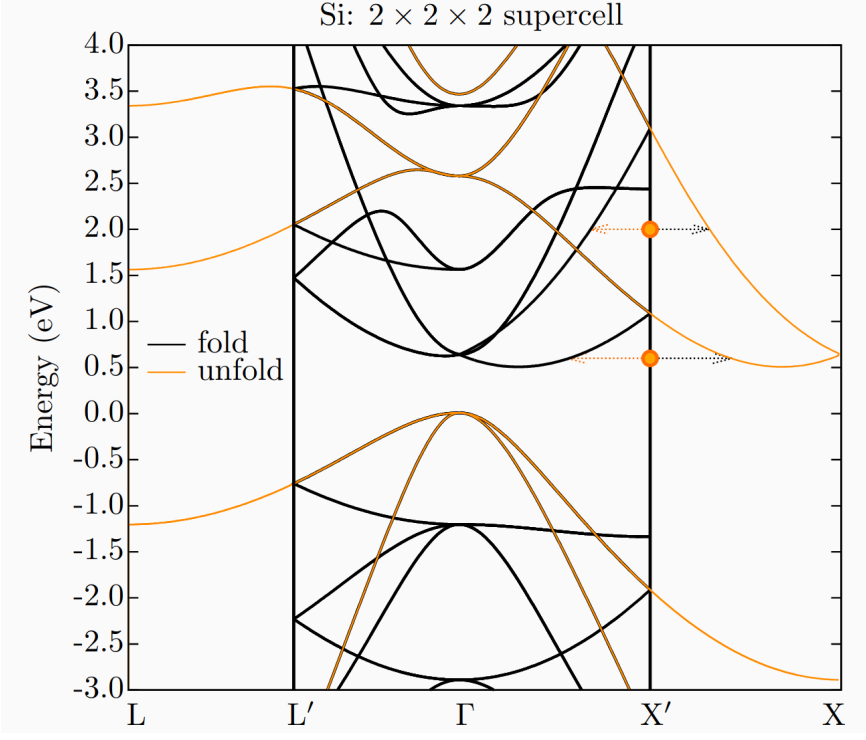
(2) $$I_1(\mathbf{S},T) = N_p \sum_{\kappa\kappa'} f_\kappa(\mathbf{S}) f^*_{\kappa'}(\mathbf{S}) \frac{e^{-W_{\kappa,T}(\mathbf{S})} e^{-W_{\kappa',T}(\mathbf{S})}}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\nu\alpha\alpha'} S_\alpha S_{\alpha'} \mathrm{Re}\left[e^{\nu}_{\kappa\alpha}(\mathbf{S}) e^{\nu *}_{\kappa'\alpha'}(\mathbf{S})\right] \cos\left[\mathbf{S}\cdot(\mathbf{R}_\kappa - \mathbf{R}_{\kappa'})\right] u^2_{\mathbf{S}\nu}(T),$$



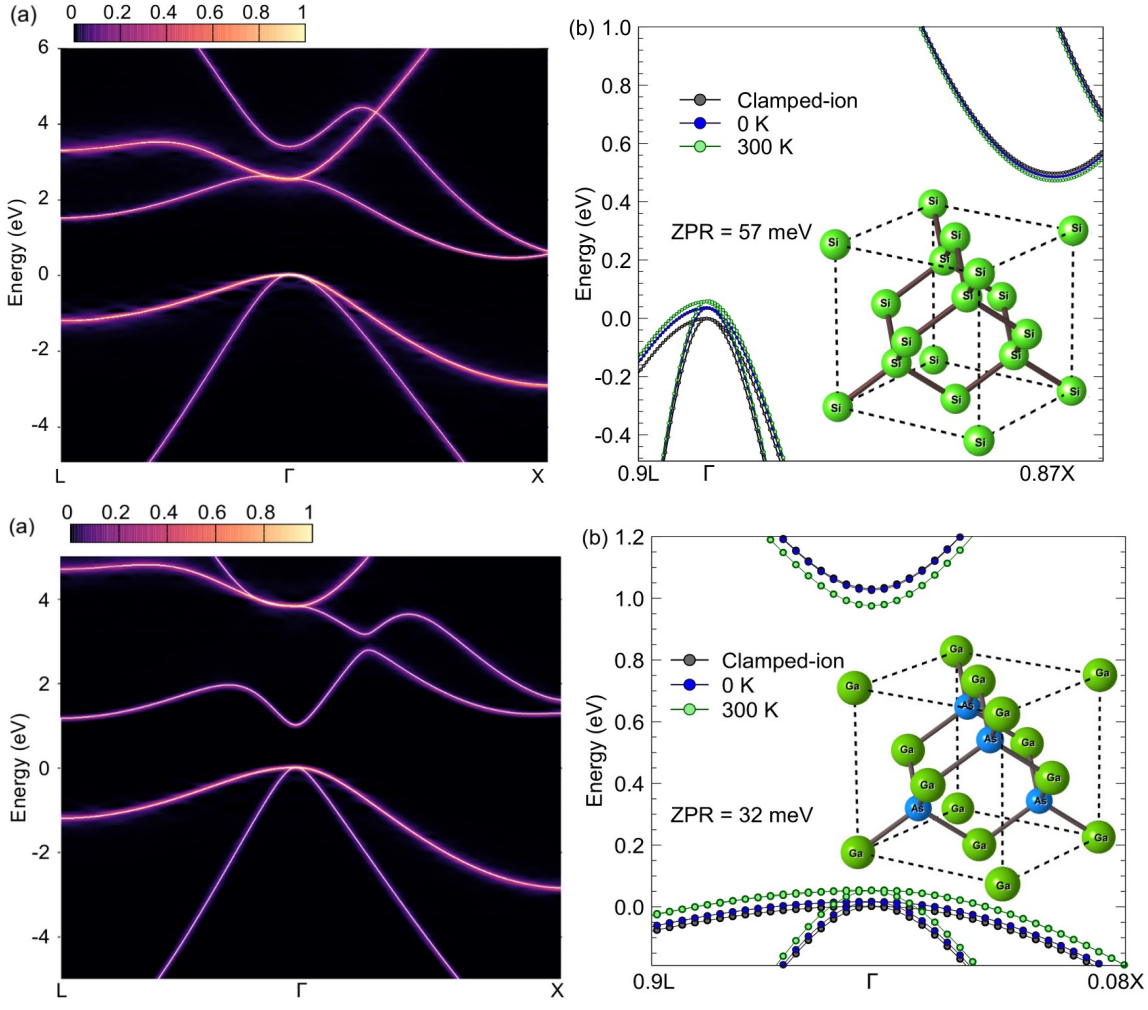
H. Seiler: arXiv:2006.12873, (2020)

Some applications of SDM (i)

Full temperature-dependent
band structures using the
band structure unfolding technique



M. Zacharias and F. Giustino, Phys. Rev. Res. 2, 013357 (2020).



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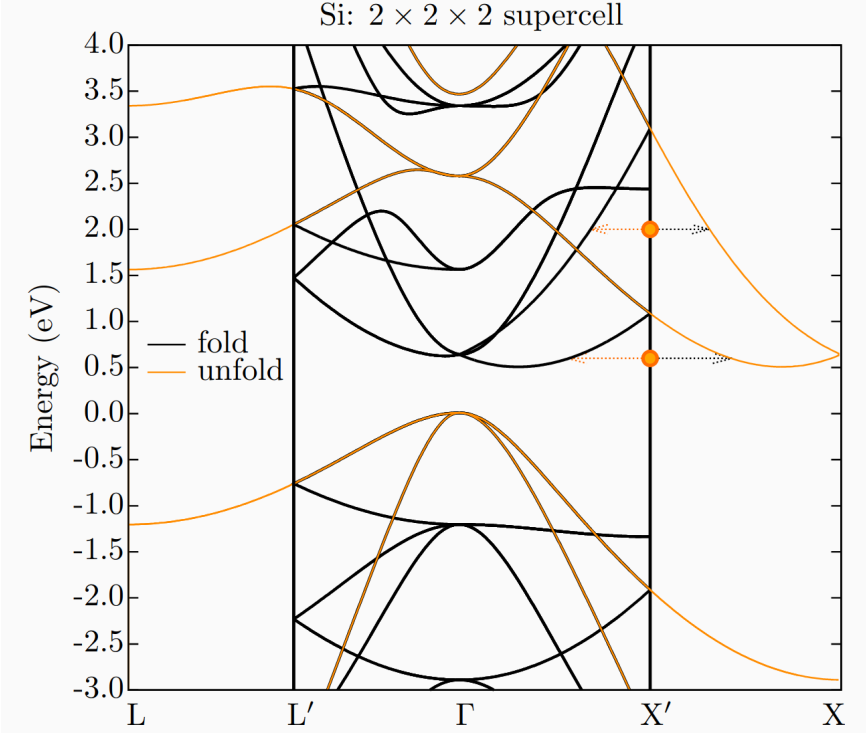
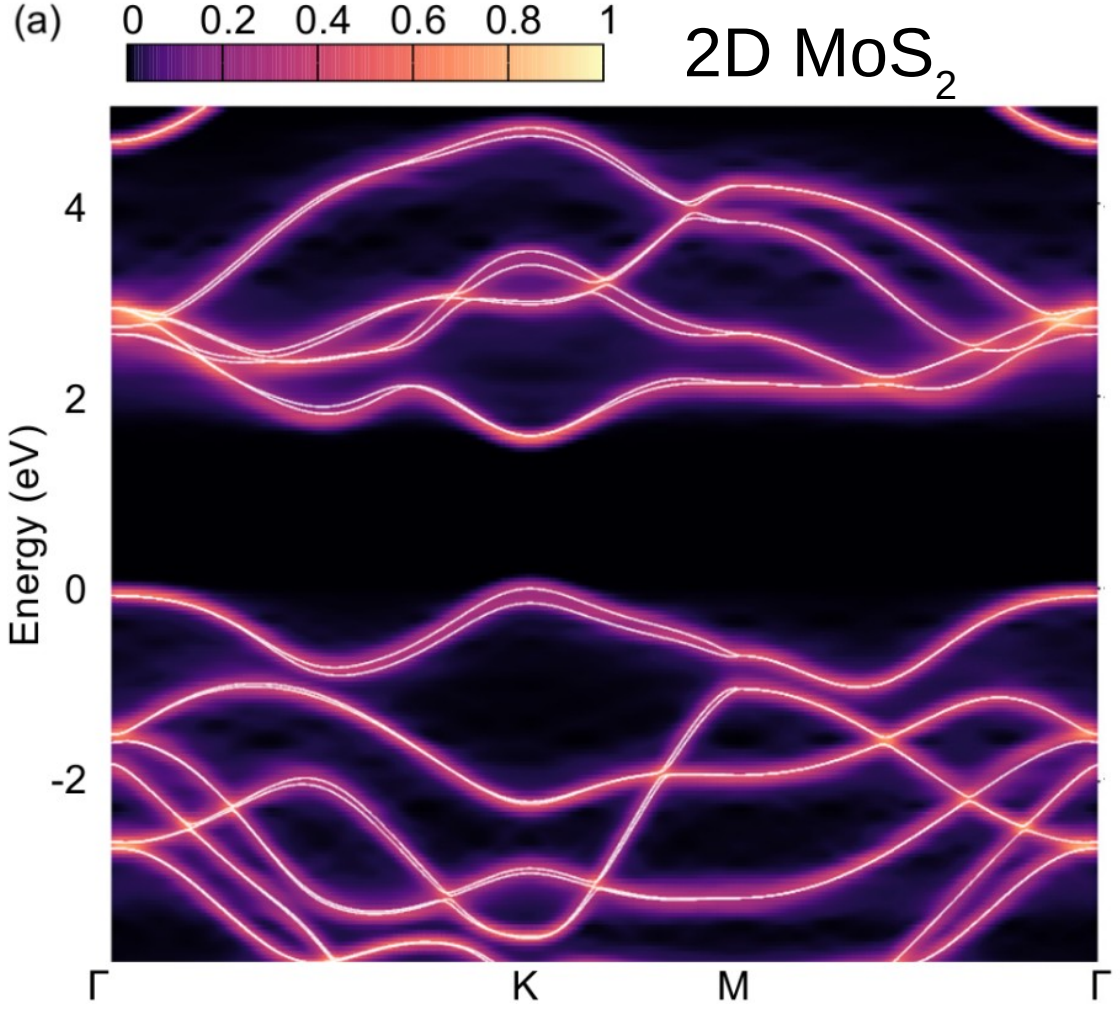
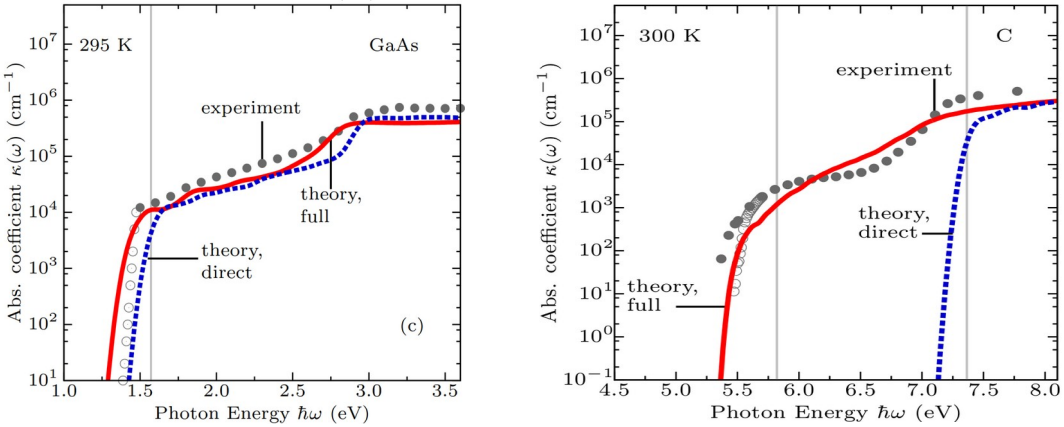


M. Zacharias and F. Giustino, Phys. Rev. Res. 2, 013357 (2020).

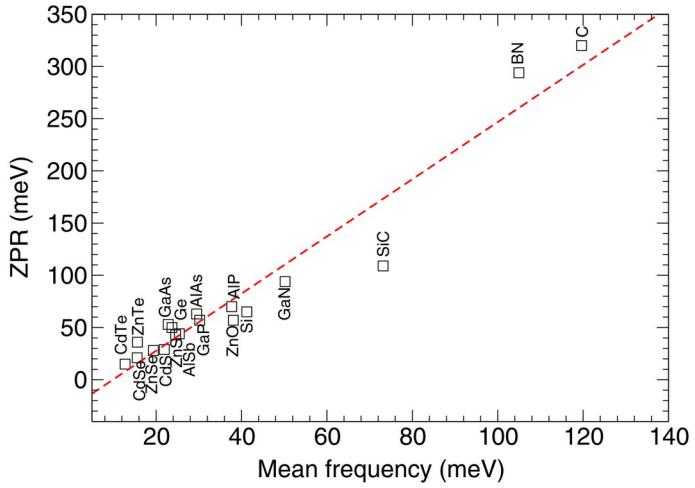


Some applications of SDM (ii)

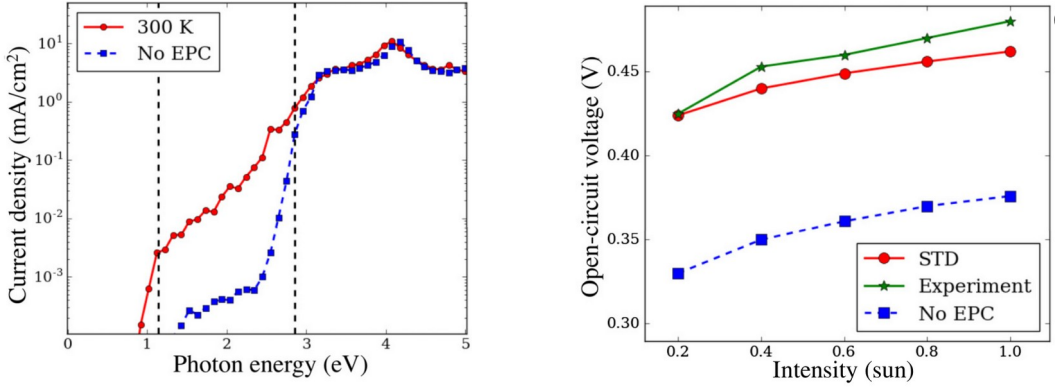
T-dependent optical absorption of GaAs and C [1]



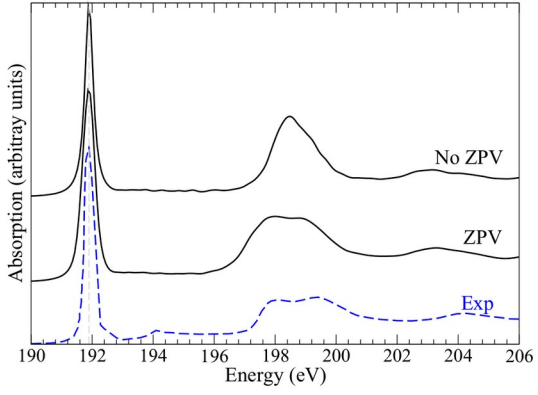
Zero-point renormalization with GW [2]



Phonon-Assisted Photocurrent in Large Solar-Cell Devices [3]



Exciton-phonon coupling in hexagonal BN [4]



[1] M. Zacharias and F. Giustino, Phys. Rev. B 94, 075125 (2016)
[2] F. Karsai, M. Engel, G. Kresse, E. Flage-Larsen, New J. Phys. 20 123008 (2018).
[3] M. Palsgaard, T. Markussen, T. Gunst, M. Brandbyge, K. Stokbro, Phys. Rev. Appl. 10, 014026 (2018).
[4] F. Karsai, M. Humer, E. Flage-Larsen, P. Blaha, G. Kresse, Phys. Rev. B 98, 235205 (2018).

Input file

```
&input
    asr='crystal', amass(1)=95.94, amass(2) = 32.06,
    flfrc='mos2.882.fc',  q_in_cryst_coord = .true. , q_in_band_form = .true.
    dimx = 8, dimy=8, dimz = 8, atm_zg(1) = 'Mo', atm_zg(2) = 'S',
    synch =.true., T= 300, error_thresh = 0.05, incl_qA = .false.
/
       260
  0.000000  0.000000  0.000000 1
  0.000000  0.000000  0.125000 1
  0.000000  0.000000  0.250000 1
  0.000000  0.000000  0.375000 1
  0.000000  0.000000  0.500000 1
```

q-list, commensurate to supercell, points in sets A and B

Output files

- ZG_configuration_*xxx*.dat
- ZG_velocities_*xxx*.dat
- equil_pos_*xxx*.dat

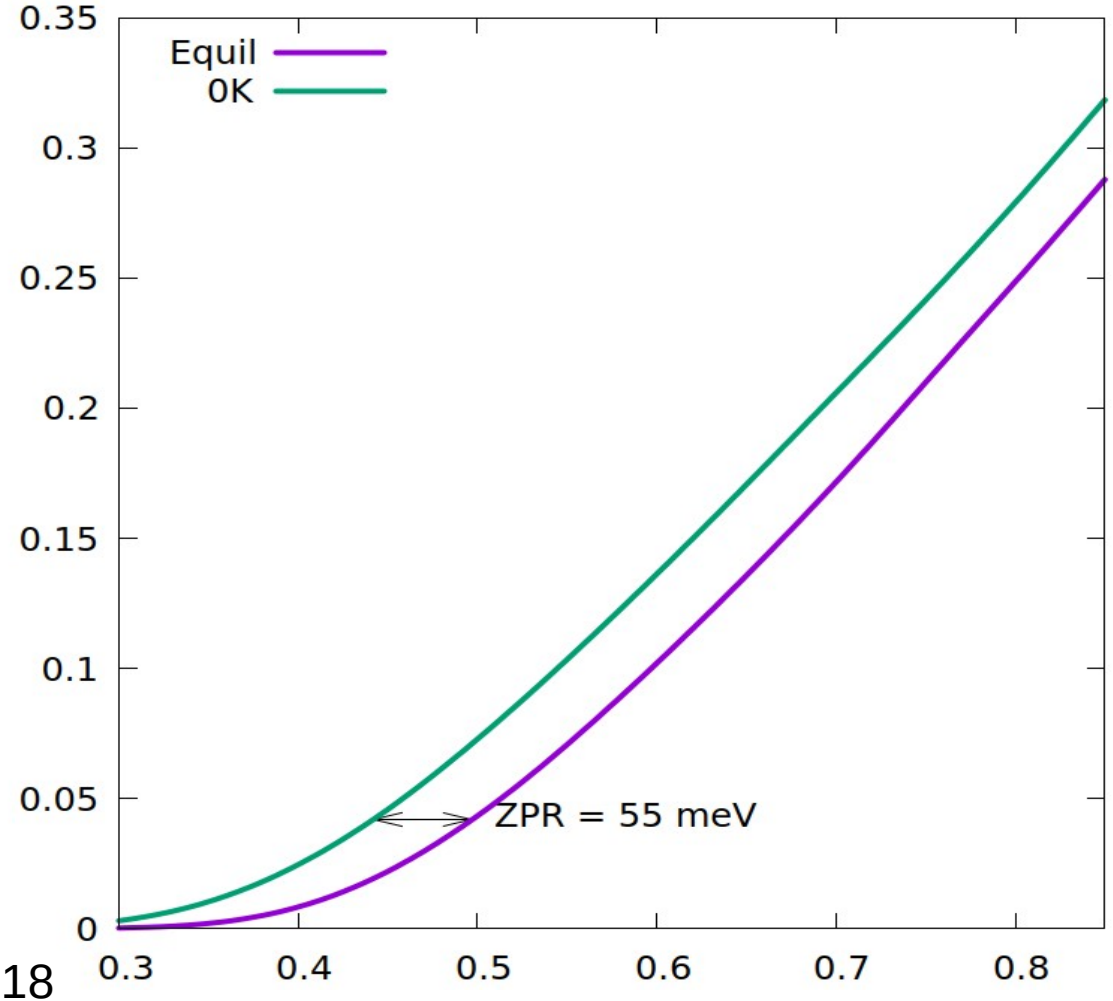
Where *xxx* is the supercell size

- single_phonon-displacements.dat
  By setting “single_phonon_displ = .true.”

```
 Anisotropic displacement tensor vs exact values:
Atom: 1
   Si     0.189030   0.192258   0.193426
        Exact values
   Si     0.190067   0.190067   0.190067
Atom: 2
   Si     0.188618   0.183368   0.193689
        Exact values
   Si     0.190063   0.190063   0.190063
```

ZG values get closer to the exact values by decreasing “error_thresh” flag

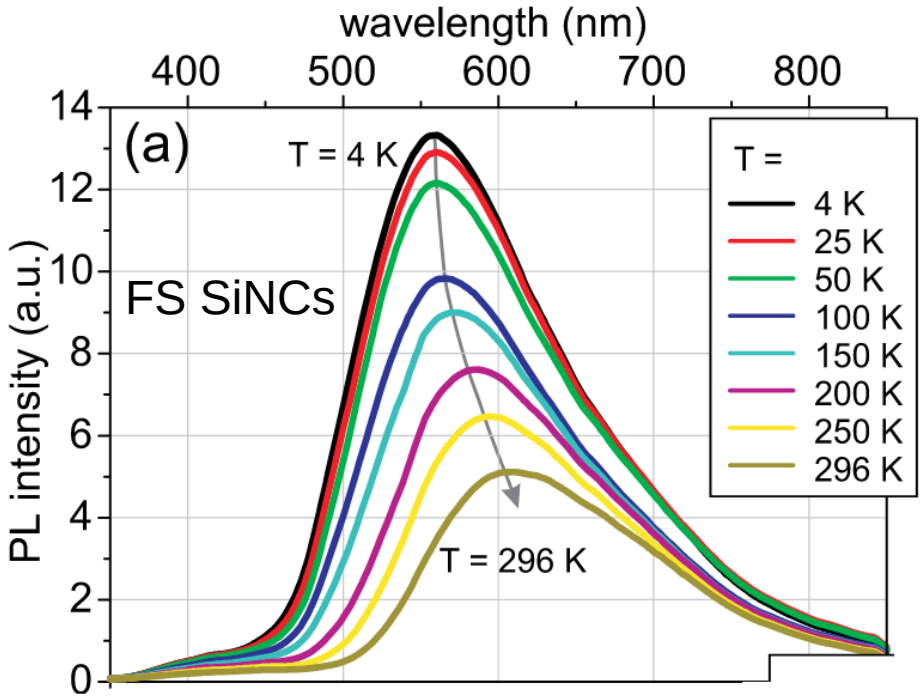
Example: zero-point renormalization using the JDOS

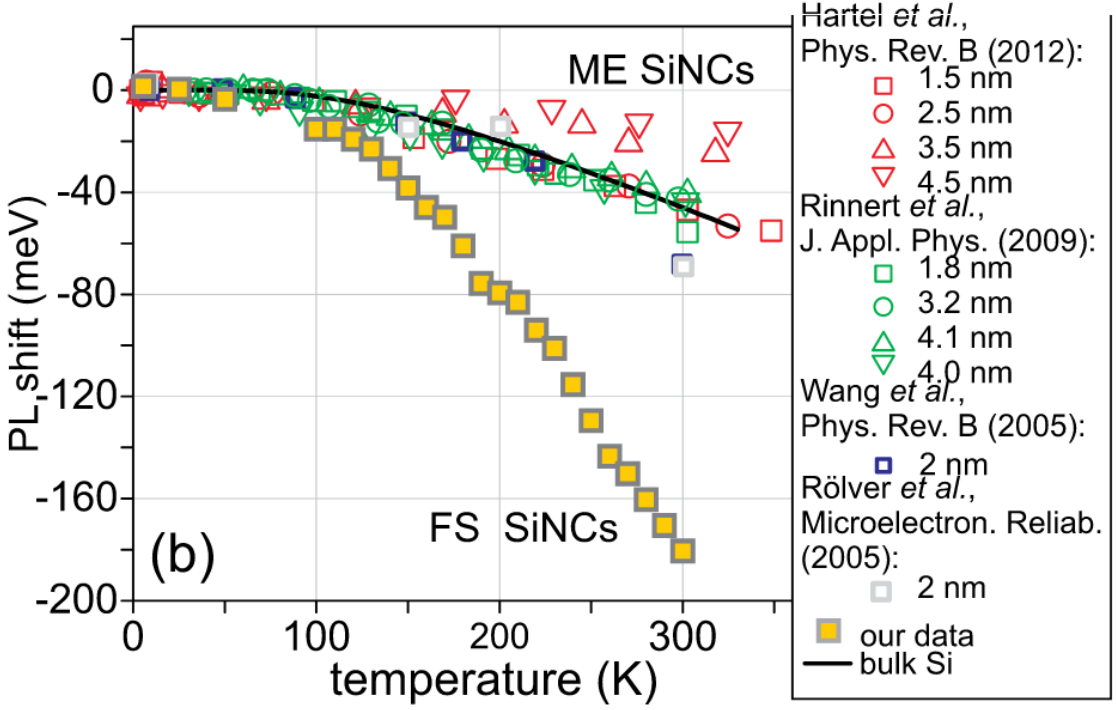


→ 5x5x5 ZG-configuration of Si at 0K

→ Zero-point renormalization very close to converged value of 57 meV

T-dependent PL peak energy from experiments: free standing (FS) and matrix embedded (ME) silicon nanocrystals (SiNCs)





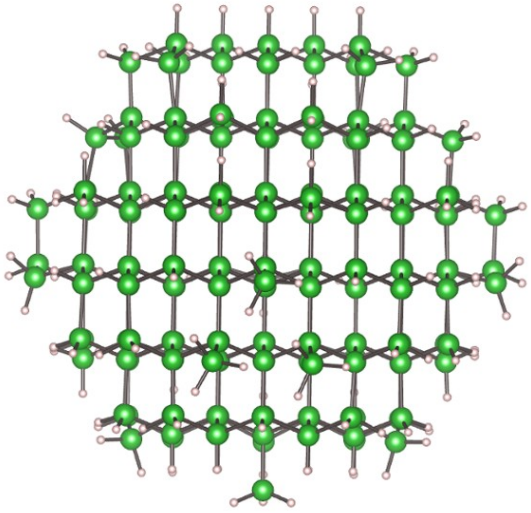
Interpretation ignores the effect of electron-phonon coupling

K. Kůsová, et al. Appl. Phys. Lett. 101, 143101 (2012).

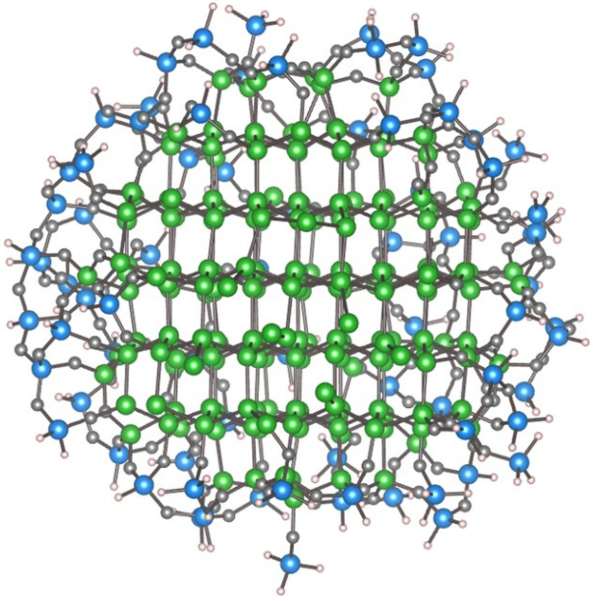
T-dependent band gap of SiNCs using SDM

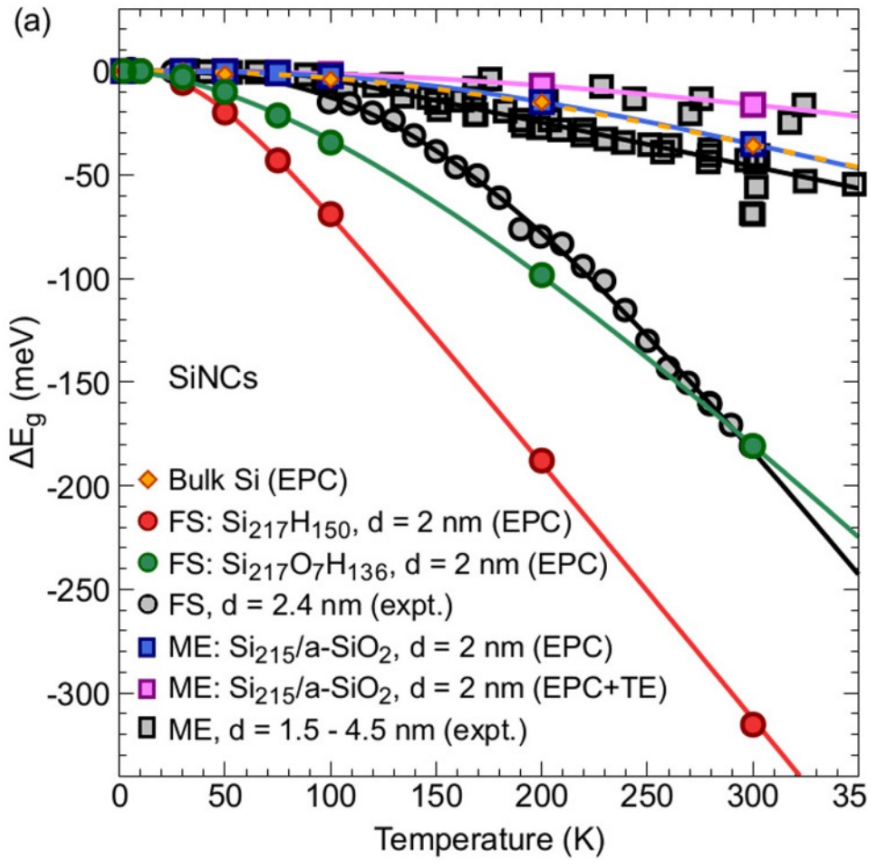
Homo - Lumo Gap

Free-Standing (FS)
$Si_{217}H_{150}$



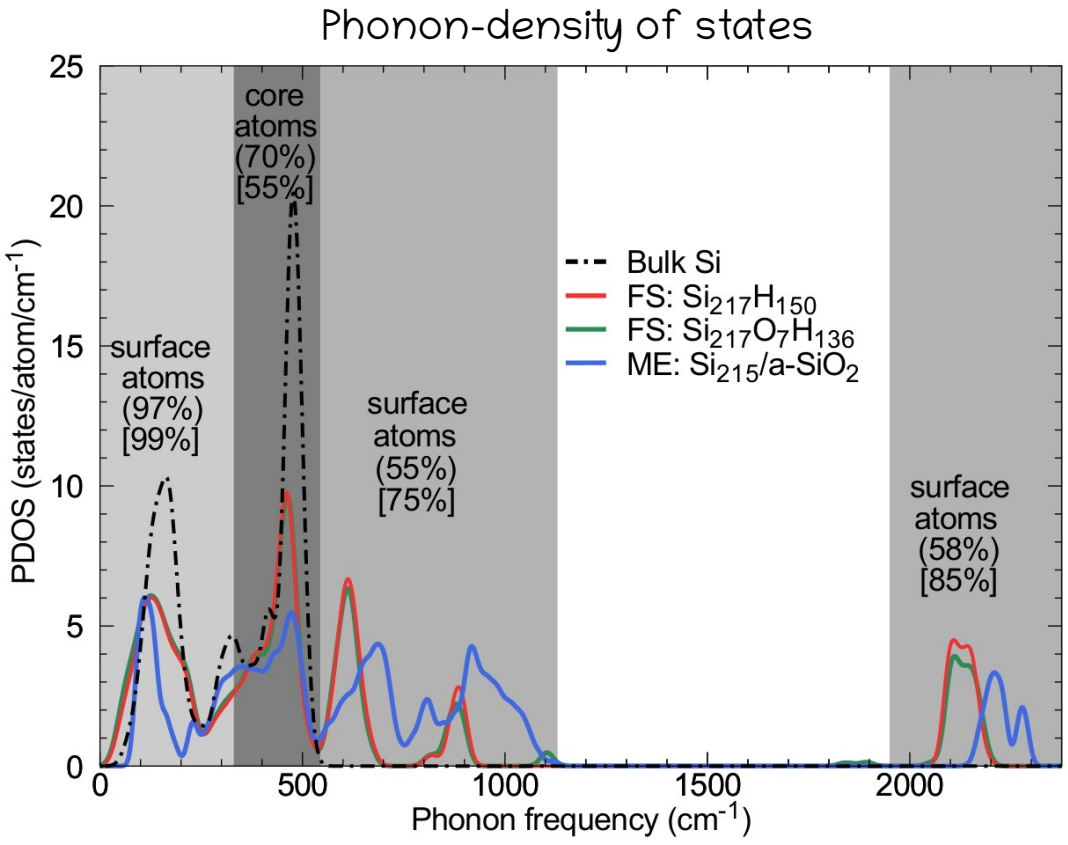
Matrix-Embedded (ME)
$Si_{215}/a\text{-}SiO_2$

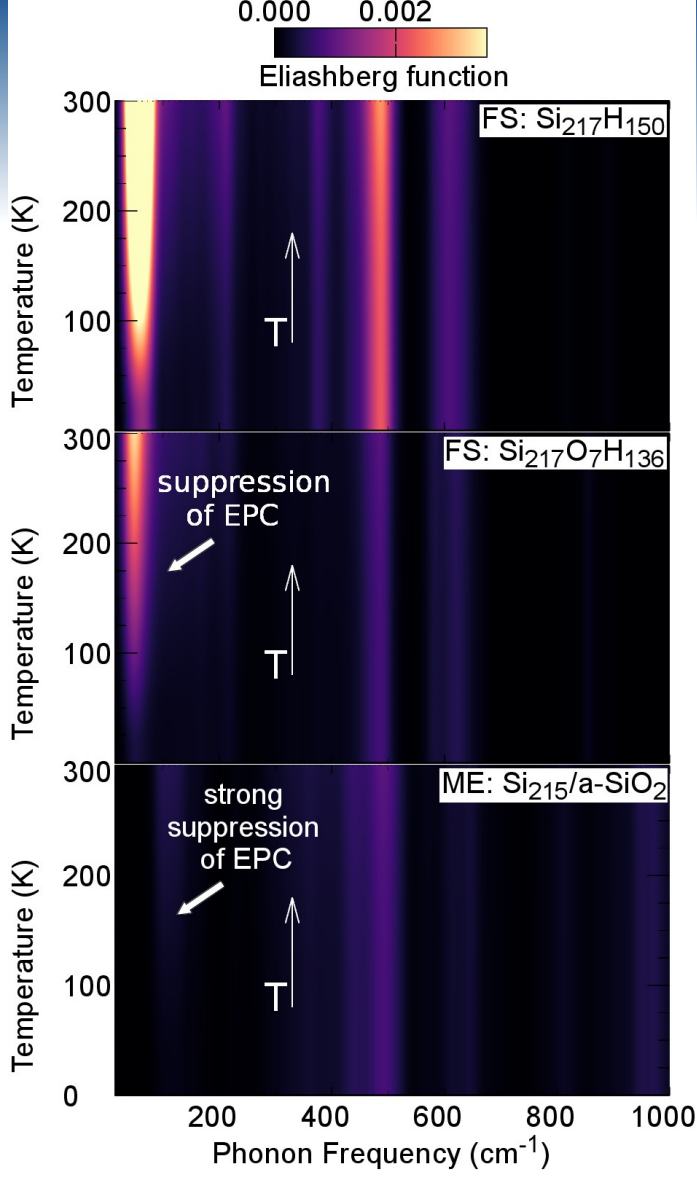




Marios Zacharias and Pantelis C. Kelires, Phys. Rev. B 101, 245122 (2020).
Calculations were performed using ***Cy-tera HPC system of CaSToRC***

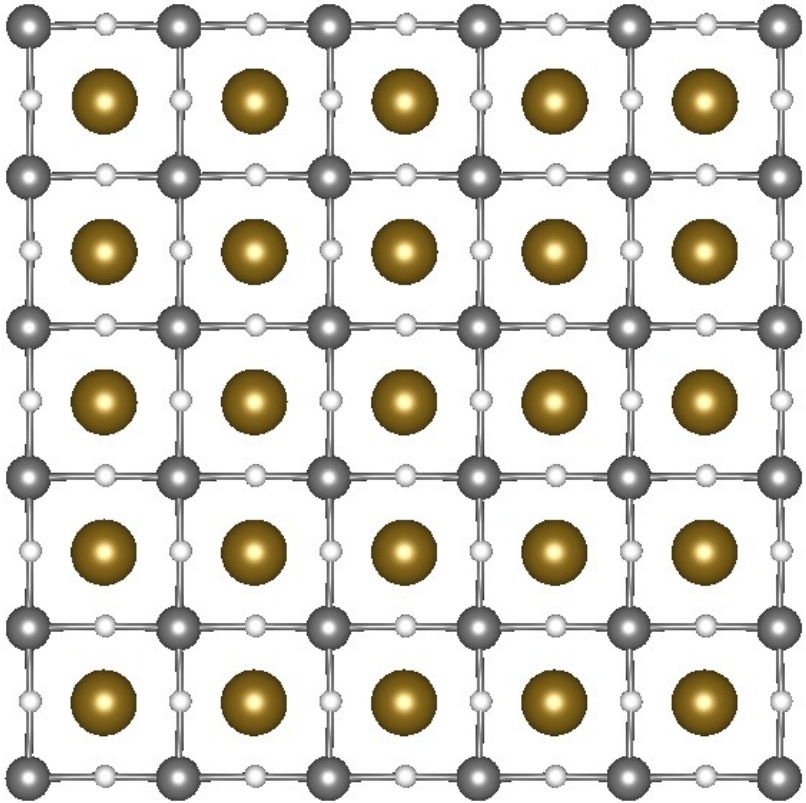
Phonon density of states and Eliashberg function of SiNCs by finite differences





Marios Zacharias and Pantelis C. Kelires, Phys. Rev. B 101, 245122 (2020).
Calculations were performed using ***Cy-tera HPC system of CaSToRC***

Nonperturbative stAVIC approach to the T-dependent band gap of perovskites: cubic $SrTiO_3$

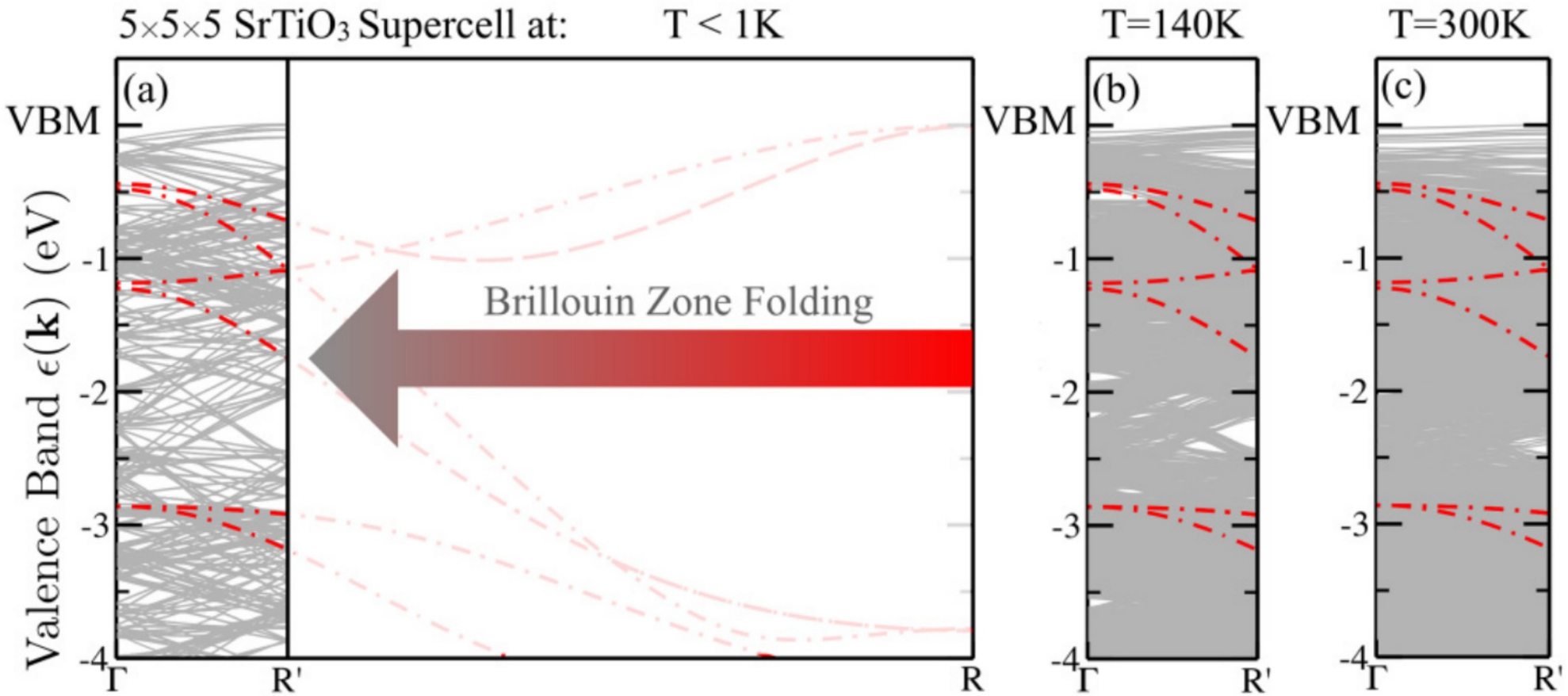


$SrTiO_3$

- Anharmonic material featuring soft modes in the harmonic approximation
- Exceptional high-T applications
- Thermoelectric waste-heat recovery
- Optical gas sensing
- Solid oxide fuel cells
- Tetragonal up to 105 K and Cubic up to 2300 K.

M. Zacharias, M. Scheffler, C. Carbogno, Phys. Rev. B102, 045126 (2020)

Nonperturbative stAVIC approach:
Band structure unfolding using numeric atom-centered orbitals



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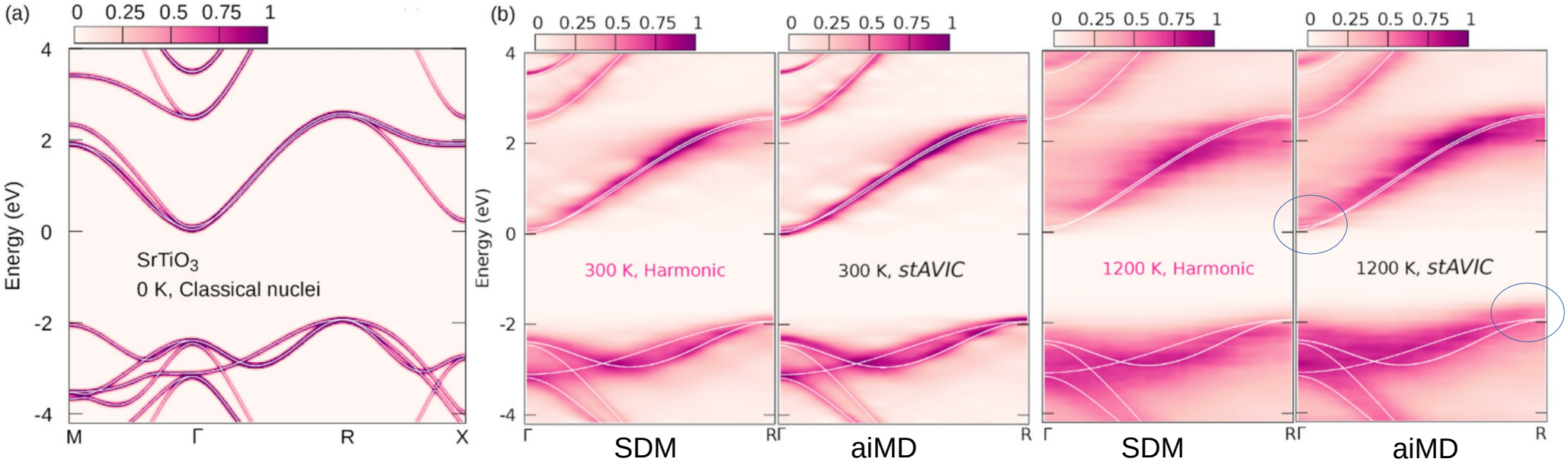
Nonperturbative stAVIC approach:
Band structure unfolding using numeric atom-centered orbitals

Momentum-resolved spectral functions:



Molecular Dynamics for anharmonic effects:

1) (N,V,T) ensemble and PBE-vdW (TS method)
2) 5x5x5 supercell
3) Average of 30 uncorrelated configurations
4) Thermal lattice expansion is included from ab-initio

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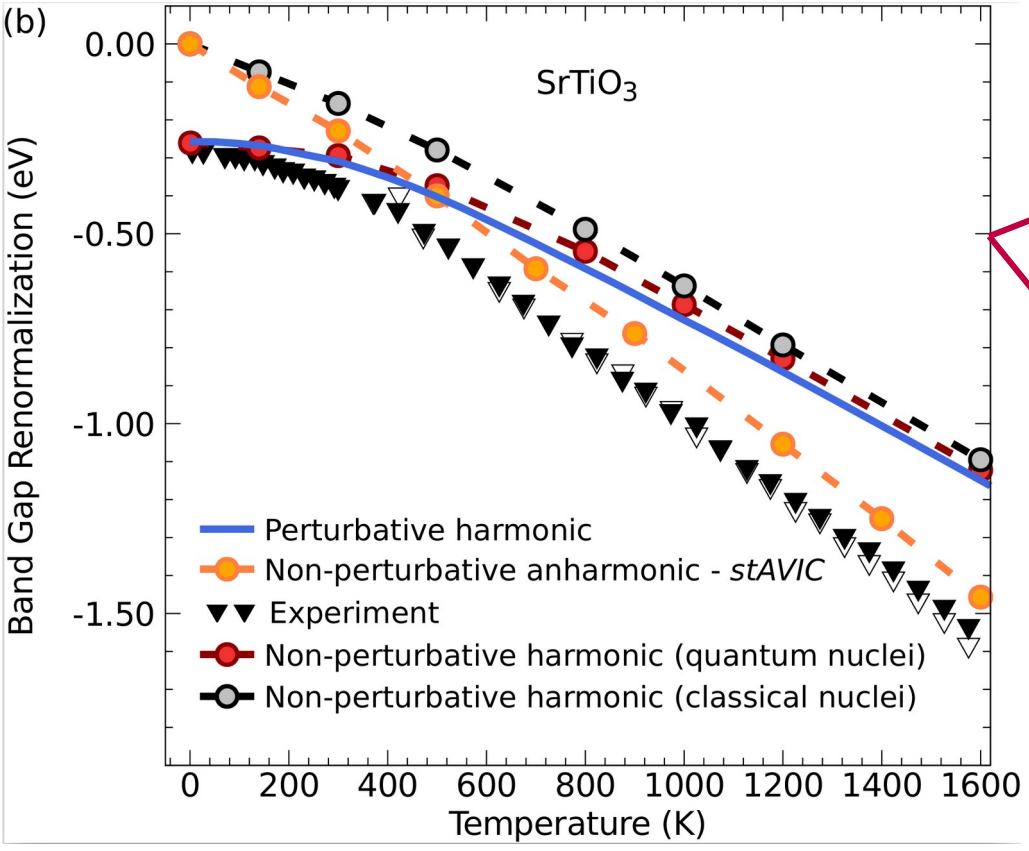
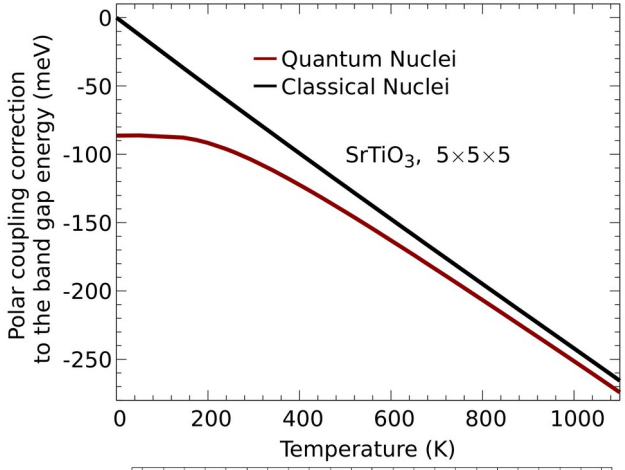
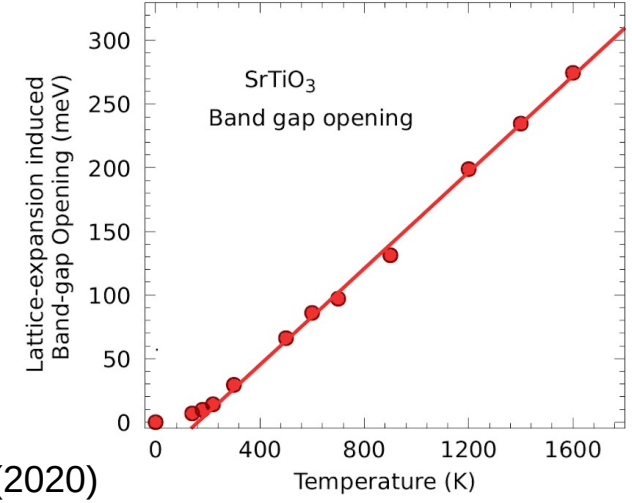
Nonperturbative stAVIC approach: Band gap renormalization including anharmonic effects







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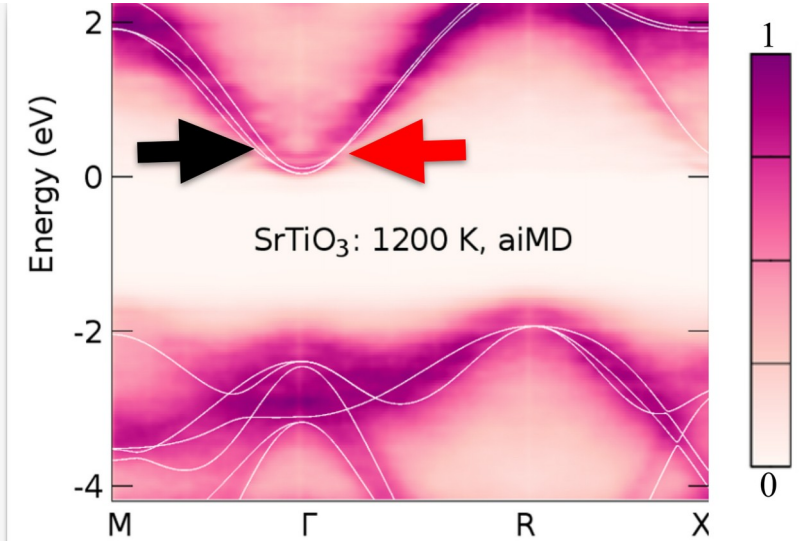
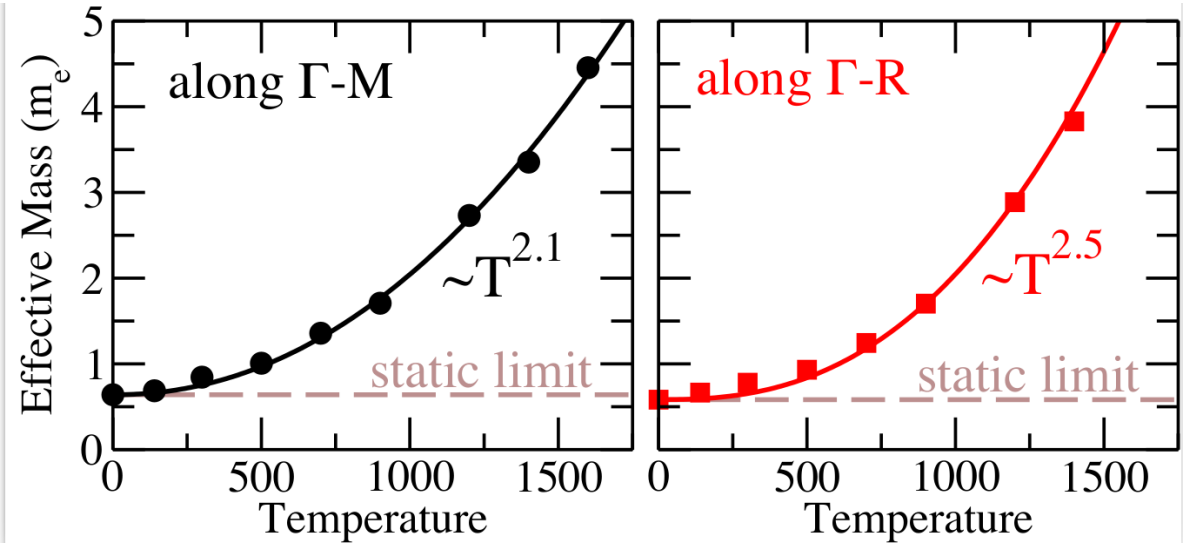
Nonperturbative stAVIC approach: Effective mass renormalization





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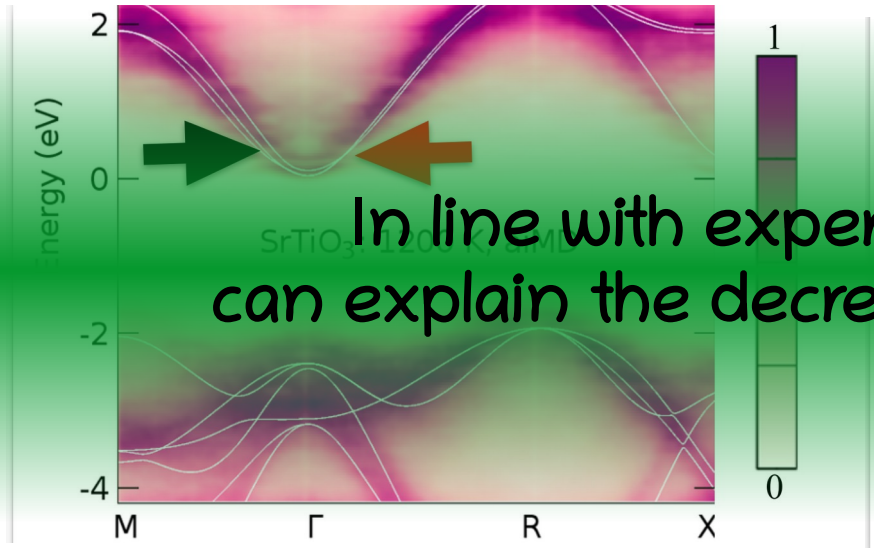
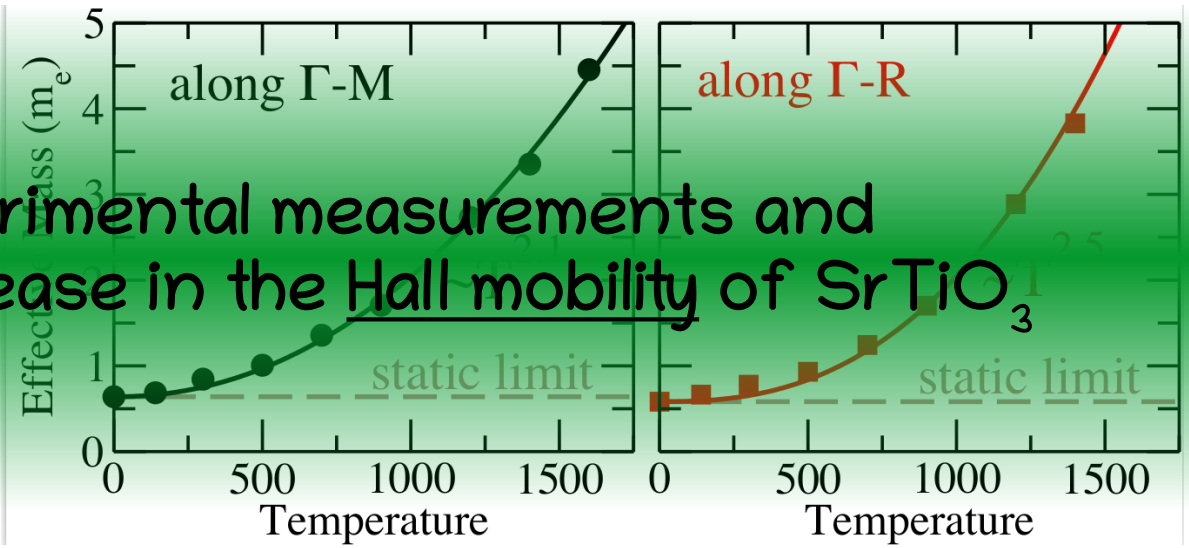
Nonperturbative stAVIC approach: Effective mass renormalization





In line with experimental measurements and can explain the decrease in the Hall mobility of $SrTiO_3$

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