Time dependent simulations in materials science

Electronic and ionic degrees of freedom

by

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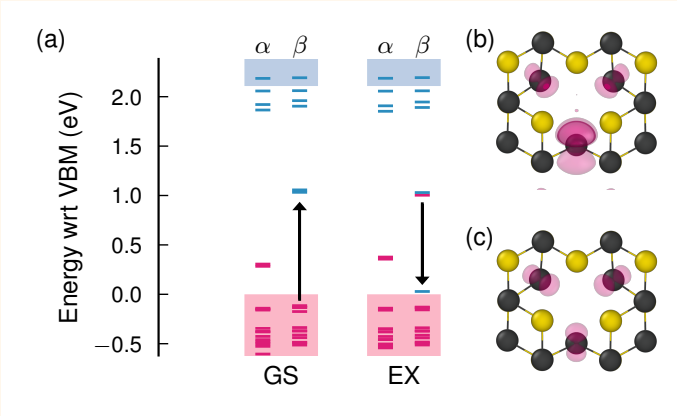
Contents

Introduction

Defects and quantum information

1. Disturb periodicity of a crystal by introducing irregularity
   $\rightarrow$ *localized* (correlated) states
2. Some can host *spin* qubits
3. Spin qubit + nuclear spin to get a two qubit system
4. In order to connect more qubits, need long range interaction (e.g., photons)

Examples, TM substitutional defects in oxide host (YAG, LuAG), vacancy complexes in diamond, SiC, carbon impurities in h-BN



What do we need to compute?

Whenever we want to assess the properties of a defect targeted for quantum information, we need to assess at least

- Electronic spectra
- Vibrational spectra
- Optical lineshape
- Lifetime of excited states
- Spin state

DFT

DFT is a many body method that can handle (imo) up to 10k electrons.

Map the full interacting system to a non-interacting system

Mean field method (electrons interact with themselves through the electron density)

Solve (SCF) for energy and single particle orbitals

A lot of people use it as a black box.

Input Atomic geometry

Output Total energy (and single particle props)

Can we use DFT for defects?

The first thing we want to know is the electronic spectra. But how?

DFT is *the* workhorse of computational condensed matter and it is exact! But ...

- We dont know the exact XC interaction
- Only electronic ground state is exact
- No multideterminant states
- No strongly correlated systems

Is a defect with say 4 dangling bonds + extra electrons in a very narrow region strongly correlated?

Effective models

The answer to whether we can use DFT is **yes** and **no**.

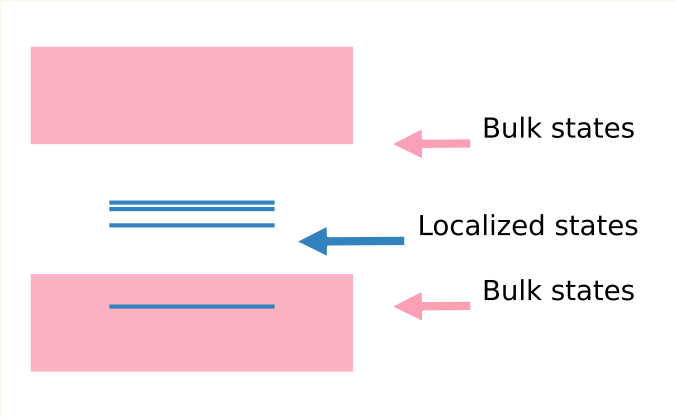
We need to make the connection between DFT and CC (or FCI) by parameterising the hamiltonian

$$h = \sum_{ij} t_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} U_{ijkl} c_i^\dagger c_j^\dagger c_k c_l \tag{1}$$

where *ijkl* are indices spanning a subspace (active space) of electronic single particle states.

Constrained RPA

Aim is to calculate U by removing screening from states in the active space

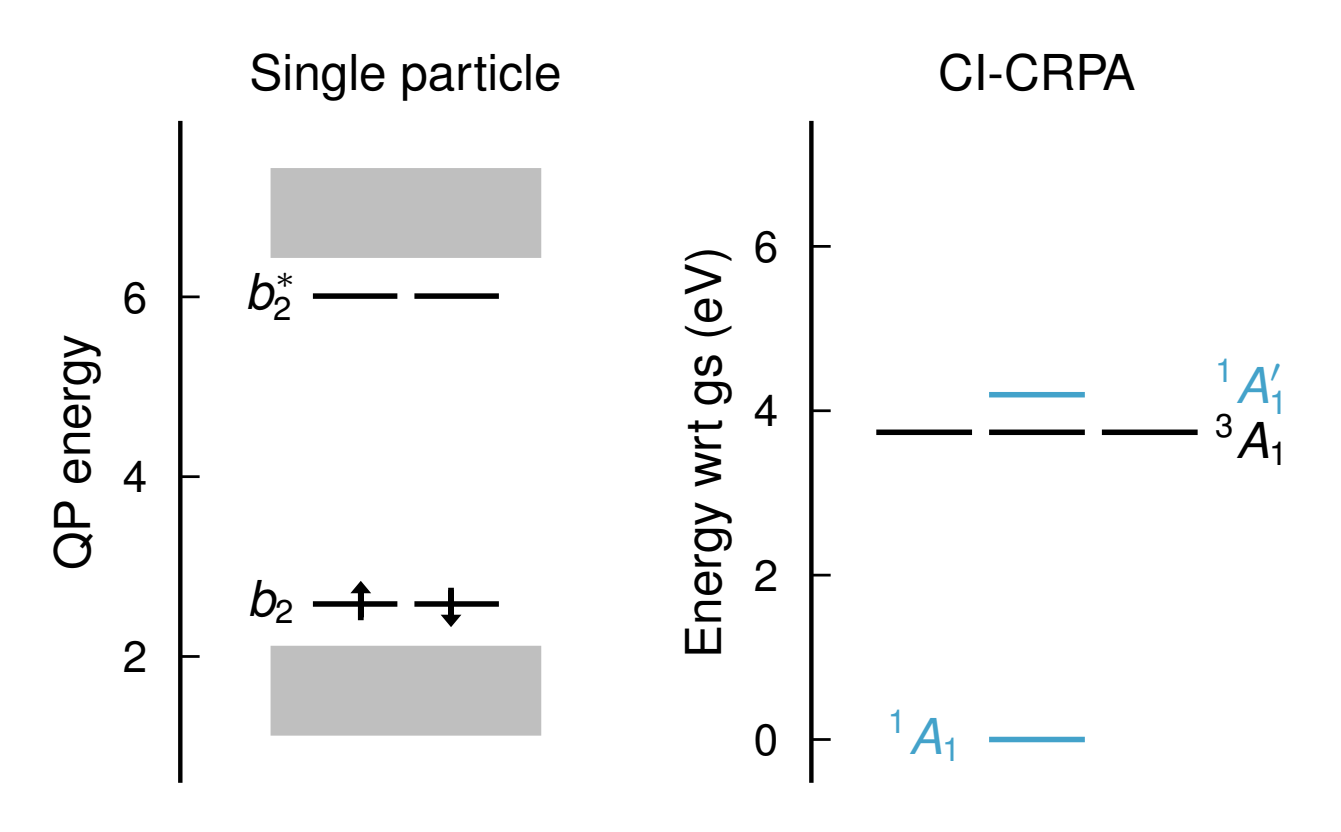


$U = (1 + Pv)^{-1}v$,
where $P = P_{\text{bulk+localized}} - P_{\text{localized}}$

Then we get U_{ijkl}, i.e., Coulomb interaction between states in the active space screened by the bulk

Comparison DFT and cRPA+FCI

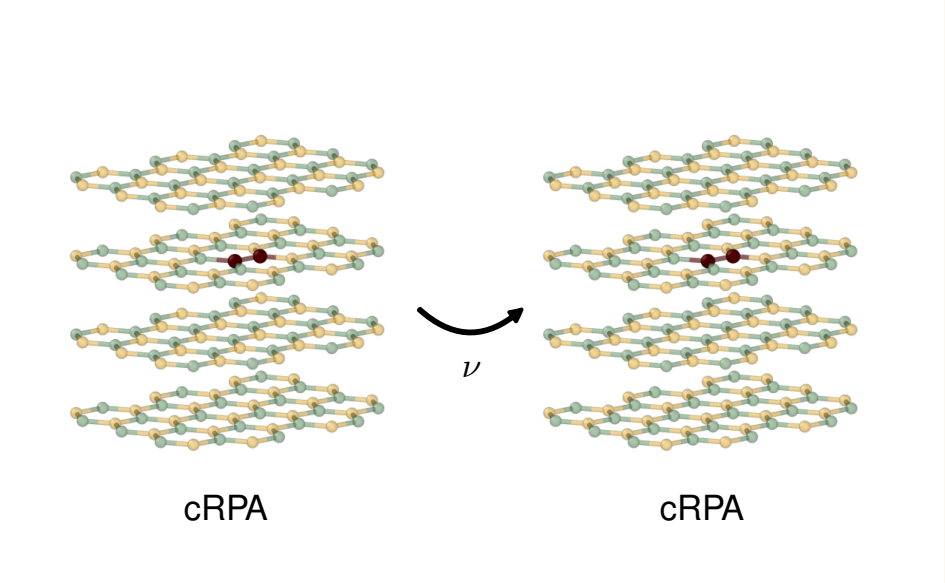
The level structure of the carbon dimer in h-BN (it is a simple defect)



Excitation energy differs by $\sim$ 0.7 eV.

Two carbon dimers

How can we connect two optical qubits?



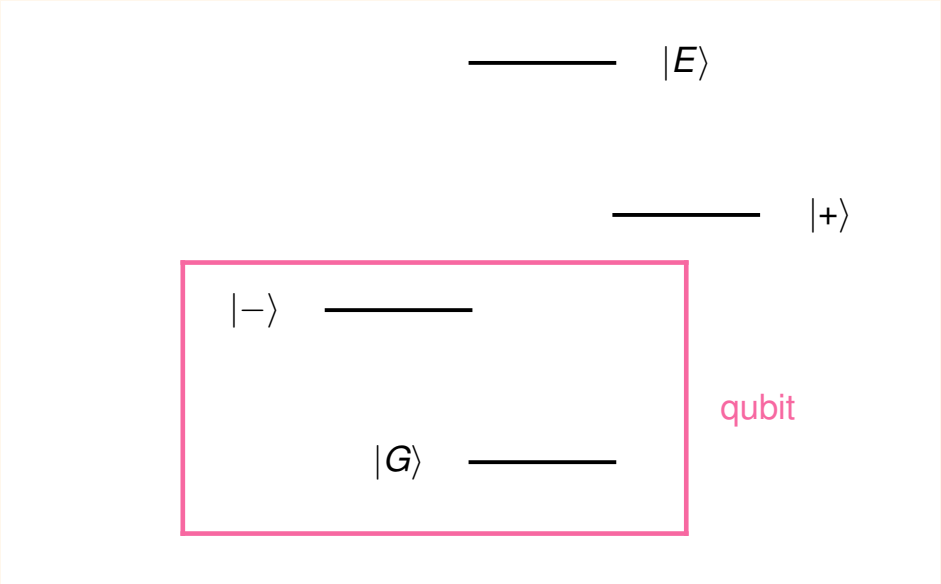
Resonant dipole-dipole interaction. Has been proposed for cold atoms etc.

Dipole-dipole interactions

Two two-level systems with basis $|g\rangle$, $|e\rangle$. Interaction is

$$H_{\mathrm{dip-dip}} = \nu|g_A e_B\rangle\langle e_A g_B| + \nu|e_A g_B\rangle\langle g_A e_B|, \tag{2}$$

diagonalizing this hamiltonian gives the following level structure



The splitting of $|-\rangle$ and $|+\rangle$ is 2ν.

Dynamical model

The model for two interacting defects coupled to an electric field is (in the composite many body basis)

$$i\frac{d}{dt}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = \begin{pmatrix} \epsilon_{gg} & \Omega_{\mathrm{A}} & 0 & 0 \\ \Omega_{\mathrm{A}} & \sigma_{eg} & \nu & 0 \\ 0 & \nu & \sigma_{eg} & \Omega_{\mathrm{B}} \\ 0 & 0 & \Omega_{\mathrm{B}} & \sigma_{ee} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{3}$$

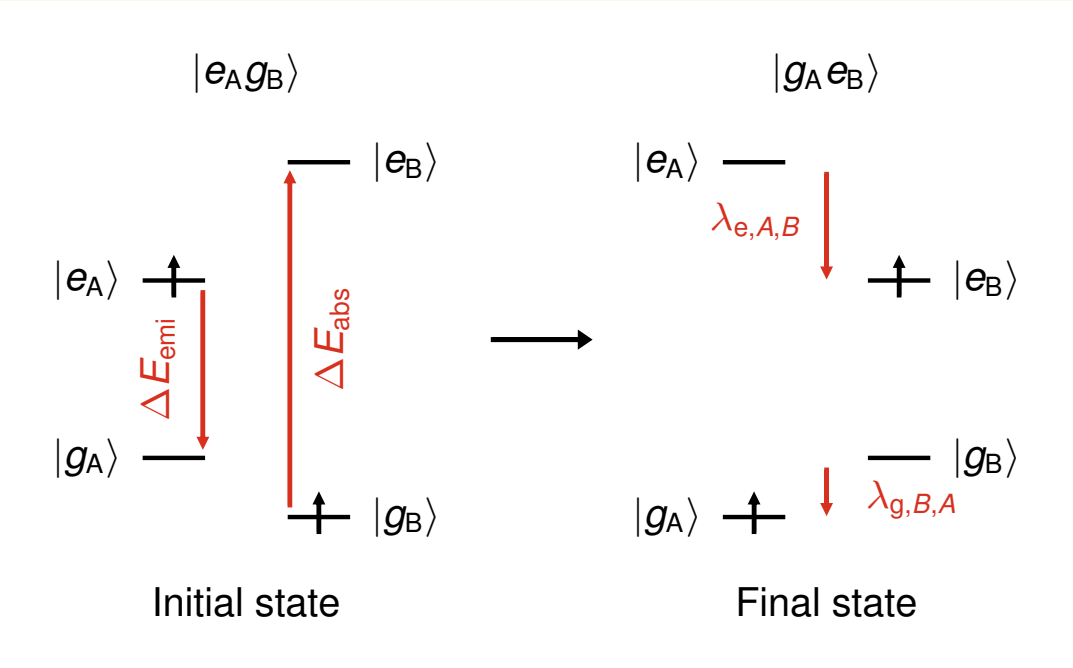
with

$$\Psi(t) = c_1(t)|g_{\mathrm{A}}g_{\mathrm{B}}\rangle + c_2(t)|g_{\mathrm{A}}e_{\mathrm{B}}\rangle + c_3(t)|e_{\mathrm{A}}g_{\mathrm{B}}\rangle + c_4(t)|e_{\mathrm{A}}e_{\mathrm{B}}\rangle. \tag{4}$$

The main problem is to determine interaction parameters for multideterminant states.

Phonon assisted energy transfer

The idea of a single parameter ν that governs the interaction is such a simplification. In reality, Stokes shift can make this a temperature activated process



This has been studied to some extent in connection with phosphors

Defects and optical lineshape

Empirics $\rightarrow$ machine learning

- Interested in integrating out *almost all* electronic DOF
- Usually done by some empirical functional form e.g., LJ w. 2 parameters per species
- Now machine learning potentials with thousands of parameters
- This gives us basically DFT level of accuracy to a fraction of the cost

Neural network potentials

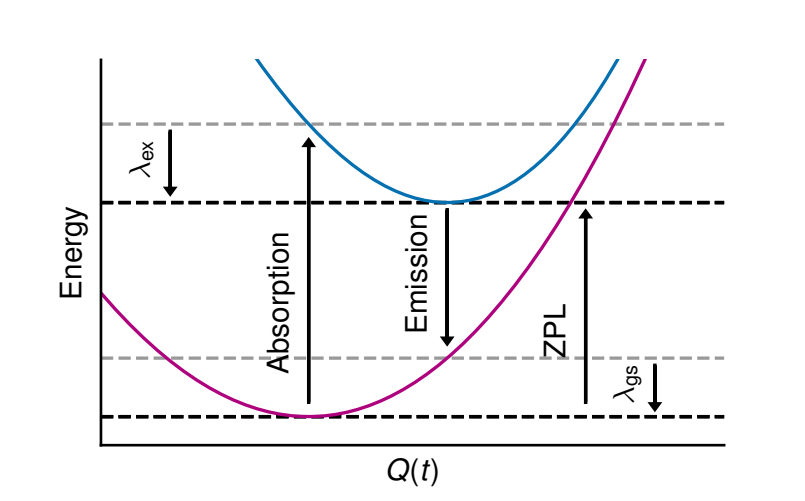
Analogous to classical force field $\Rightarrow$ rapid evaluation of energy as a function of Q.

Descriptors: Chebyschev, Legendre polynomials of relative coordinates

Input layer: descriptors
Output layer: site energies

Optical lineshape

The optical lineshape is the combination of the electronic transition and vibrational transitions



The optical lineshape is given by Fermis golden rule

$$I(\omega) \propto |\mu|^2 \delta(\omega - \omega_{eg}) \tag{5}$$

Where is the time dependence?

Fermis golden rule is transformed from the energy domain to the time domain by

$$\delta(\omega - \omega_{\mathrm{eg}}) \mapsto \frac{1}{2\pi} \int_{\infty}^{\infty} \exp[i(\omega - \omega_{\mathrm{eg}})t] dt, \tag{6}$$

by massaging the Fermis golden rule expression further we get

$$I(\omega) \propto \omega^n \int_{\infty}^{\infty} \mathrm{d}t \, \langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t) \rangle \exp(\mathrm{i}\omega t), \tag{7}$$

Expansion of ACF

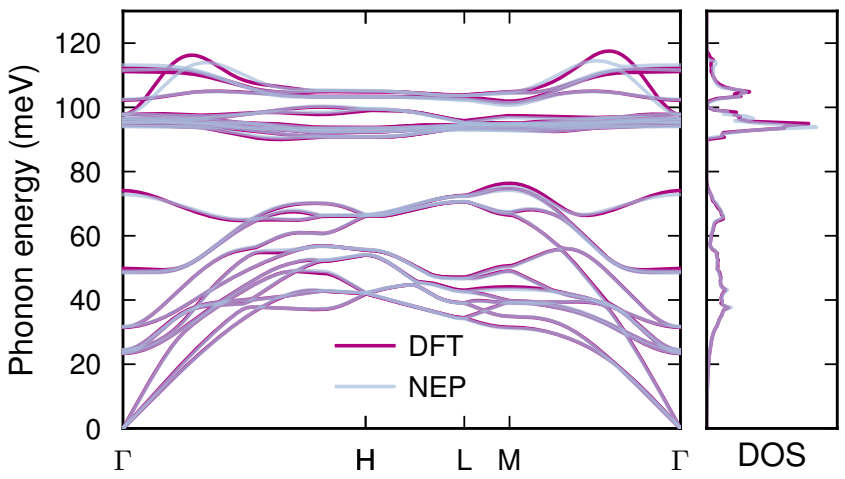
The ACF can be cast as an ordered exponential and then expanded so that the main thing to compute is the classical two-time ACF

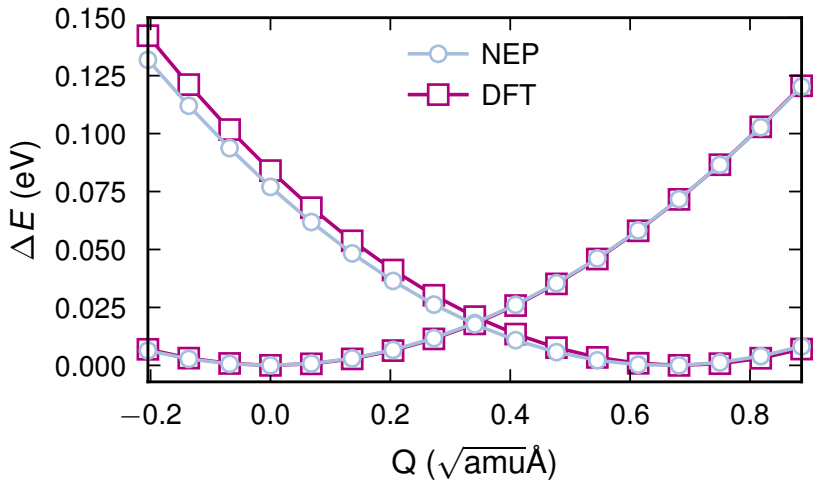
$$\langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t)\rangle \approx \exp\left(-\int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \left\langle \delta U(0)\, \delta U(t'')\right\rangle\right). \qquad (8)$$

And that is a proper time-dependent system that we can compute with MD.

The SiC divacancy

Trained potential on 1300 structures (300 atom)





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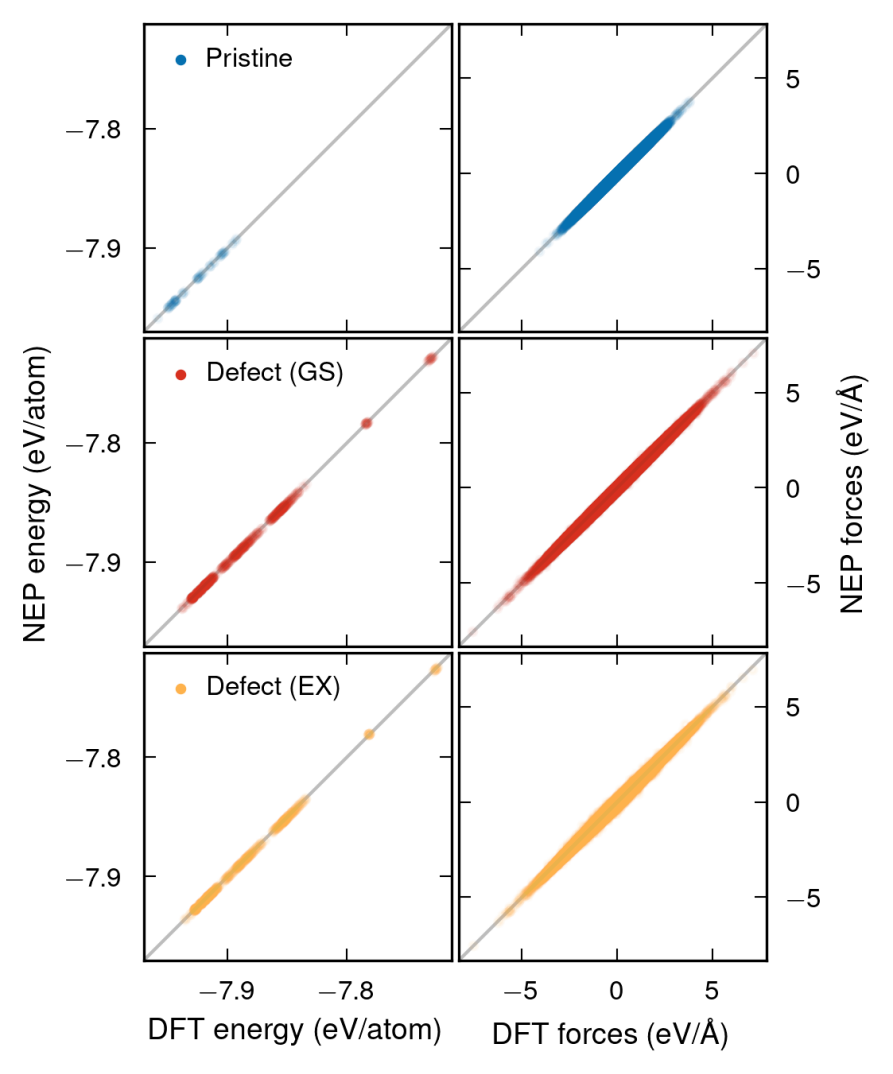
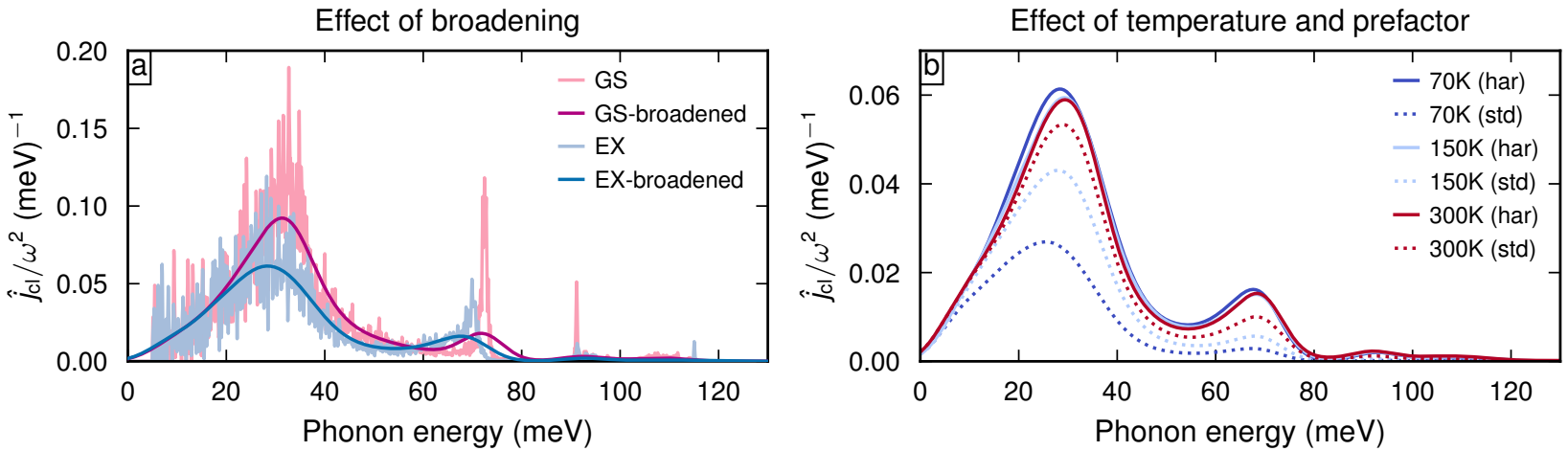


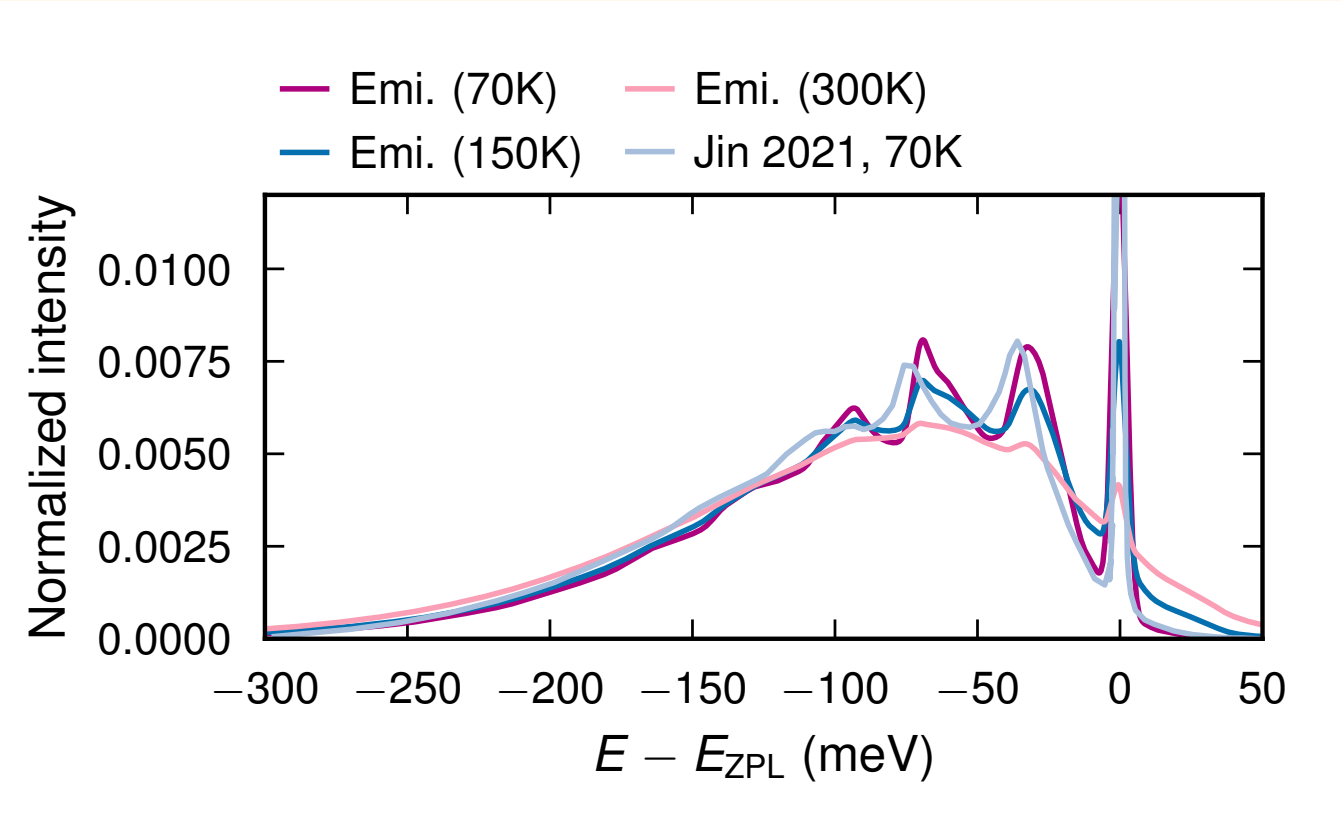
Spectral function

Which phonons have the largest coupling?



This simulation is done with a supercell consisting of 1 million atoms

Optical lineshape



In supergood agreement with experiments!