ICTP/Psi-k/CECAM School on Electron-Phonon Physics from First Principles

Trieste, 19-23 March 2018

Lecture Tue.1

Introduction to electron-phonon interactions

Feliciano Giustino

Department of Materials, University of Oxford

Department of Materials Science and Engineering, Cornell University

Lecture Summary

- Manifestations of the electron-phonon interaction
- Rayleigh-Schrödinger perturbation theory
- The electron-phonon matrix element
- Brillouin-zone integrals and Wannier interpolation
- The electron-phonon coupling constant
- Connection with molecular dynamics simulations

Where do electron-phonon interactions come from?

Ionic degrees of freedom in the Kohn-Sham equations

$$-\frac{\hbar^2}{2m_{\rm e}}\nabla^2\,\psi_n + V_{\rm SCF}\,\psi_n = E_n\,\psi_n$$

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$$V_{\rm SCF}(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0}\left[\,\sum\nolimits_\kappa \frac{Z_\kappa}{|\mathbf{r}-\boldsymbol{\tau}_\kappa|} - \int \frac{n(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\,\right] + V_{xc}[n(\mathbf{r})]$$

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Ionic degrees of freedom in the Kohn-Sham equations

The SCF potential depends parametrically on the ionic coordinates

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- Displace atoms from equilibrium sites, $\tau = \tau_0 + u$

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Perturbation Hamiltonian leading to EPIs

Some manifestations of electron-phonon interactions

- Electron mobility in monolayer and bilayer MoS_2

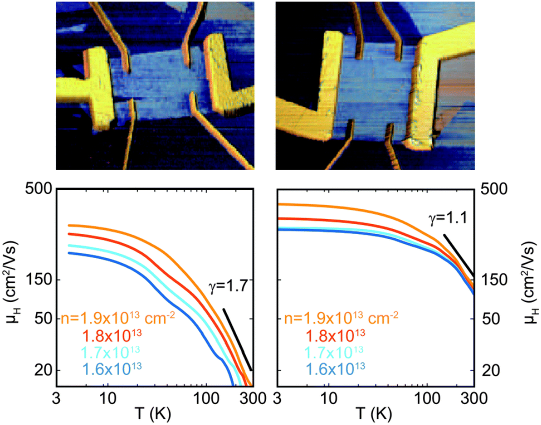
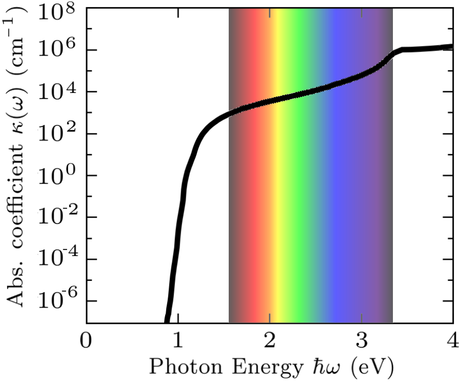


Figure from Baugher et al, Nano Lett. 13, 4212 (2013)

Some manifestations of electron-phonon interactions

- Phonon-assisted optical absorption in silicon



Data from Green et al, Prog. Photovolt. Res. Appl. 3, 189 (1995)

Some manifestations of electron-phonon interactions

- High-temperature superconductivity in compressed H_3S

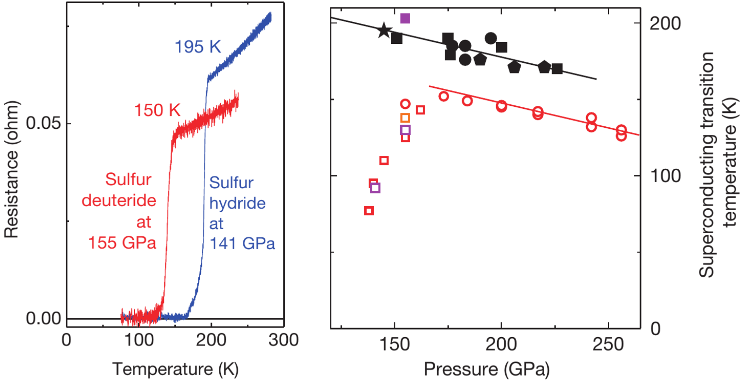
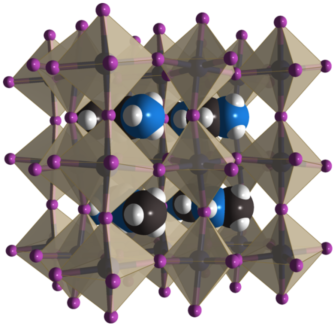


Figure from Drozdov et al, Nature 73, 525 (2015)

Some manifestations of electron-phonon interactions

- Temperature-dependent photoluminescence in hybrid perovskites



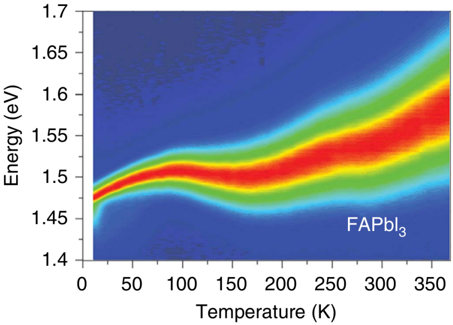


Figure from Wright et al, Nat. Commun. 7, 11755 (2016)

Some manifestations of electron-phonon interactions

- Electron mass enhancement in MgB_2

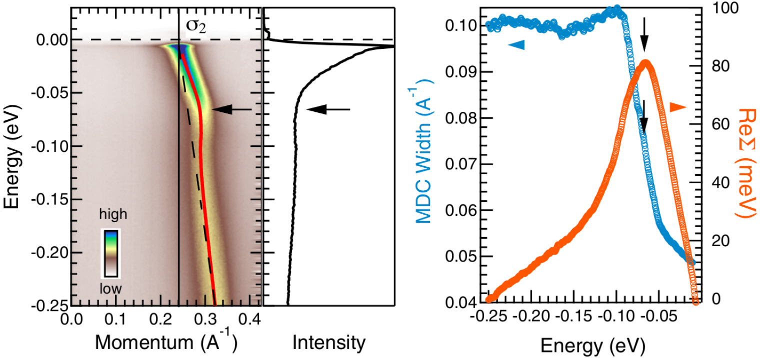


Figure from Mou et al, Phys. Rev. B 91, 140502(R) (2015)

Rayleigh-Schrödinger perturbation theory

$$\Delta \hat{H}_{\mathrm{ep}} = \frac{\partial V_{\mathrm{SCF}}}{\partial \tau}\, u + \frac{1}{2}\frac{\partial^2 V_{\mathrm{SCF}}}{\partial \tau^2}\, u^2 + \cdots$$

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- Energies $$\Delta E_n = \langle n|\, \frac{\partial V_{\rm SCF}}{\partial \tau} u \,|n\rangle$$

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- Transition rates $$\Gamma_{n\to m} = \frac{2\pi}{\hbar}|\langle m|\, \frac{\partial V_{\rm SCF}}{\partial \tau} u \,|n\rangle|^2 \;\delta(E_m - E_n - \hbar\omega)$$

Thermodynamic averages

What is the atomic displacement u in $\Delta\hat{H}_{\rm ep}$?

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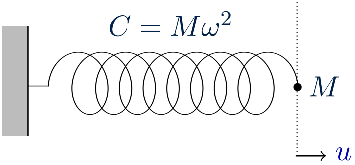

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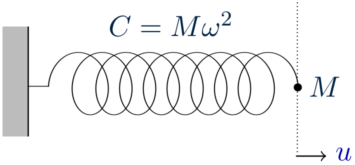

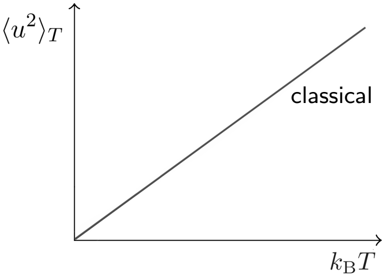

$$\langle u^2 \rangle_T = \frac{k_{\mathrm{B}}T}{M\omega^2}$$

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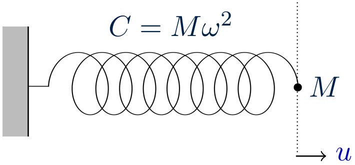

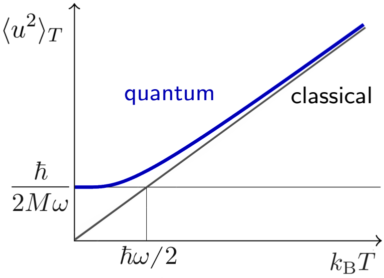

$$\langle u^2\rangle_T = \frac{k_{\rm B}T}{M\omega^2}$$

$$\langle u^2\rangle_T = \frac{\hbar}{2M\omega}\left[2\,n\left(\frac{\hbar\omega}{k_{\rm B}T}\right)+1\right]$$

Thermodynamic averages

$\langle \Delta E_n \rangle_T \longrightarrow$ Temperature-dependent band structures

$\langle \cdots \Delta\psi_n(\mathbf{r}) \cdots \rangle_T \longrightarrow$ Phonon-assisted optical absorption

$\langle \Gamma_{n\to m} \rangle_T \longrightarrow$ Phonon-limited carrier mobilities

Temperature-dependent band structures

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(Lecture Thu.2)

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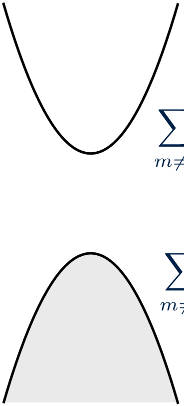
(Lecture Thu.2)

Temperature-dependent band structures



$$\sum_{m \neq c} \frac{|\cdots|^2}{E_c - E_m} < 0$$

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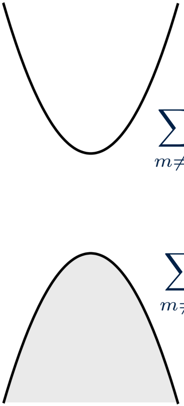
(Lecture Thu.2)

Temperature-dependent band structures



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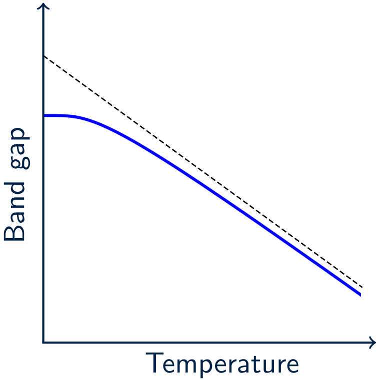
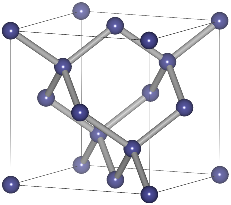


(Lecture Thu.2)

Temperature-dependent band structures

silicon



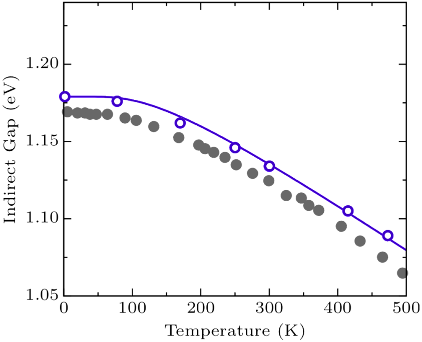


Figure from Zacharias et al, Phys. Rev. B 94, 075125 (2016)

Phonon-assisted optical absorption

$$\Delta\psi_n(\mathbf{r}) = \sum_{m\neq n} \frac{\langle m|\, \frac{\partial V_{\mathrm{SCF}}}{\partial \tau}\, u\, |n\rangle}{E_n - E_m}\psi_m(\mathbf{r})$$

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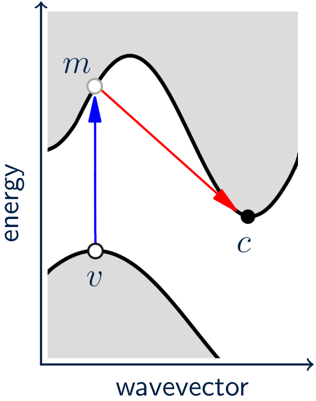
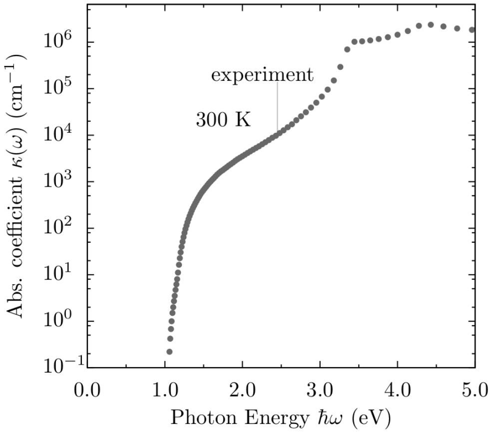


(Lecture Fri.1)

Phonon-assisted optical absorption



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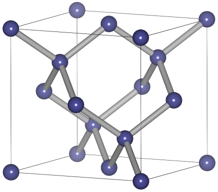
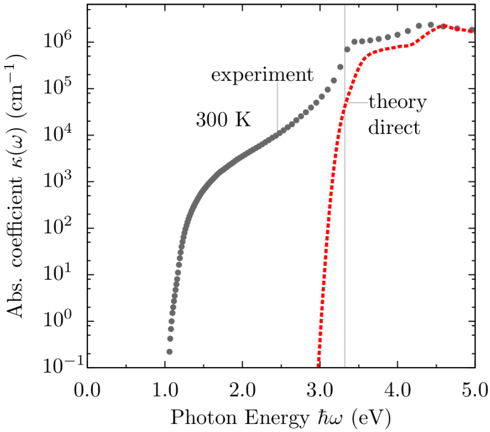


Figure from Zacharias et al, Phys. Rev. Lett. 115, 177401 (2015)

Phonon-assisted optical absorption



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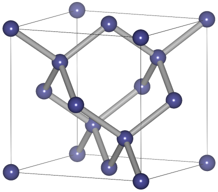

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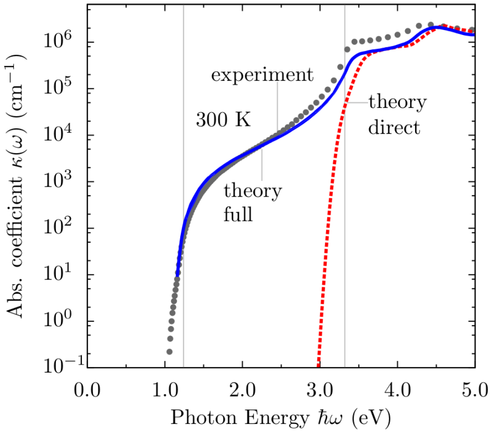

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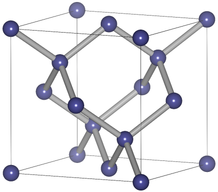

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Phonon-limited carrier mobilities

Carrier relaxation time

$$\frac{1}{\tau_n} = \sum_m \Gamma_{n \to m}$$

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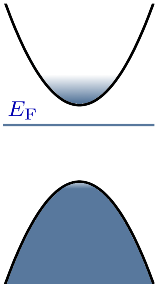
Electron mobility from Boltzmann equation (Lecture Wed.2)



$$\mu = \frac{e}{m} \left\langle \frac{1}{3}\, e^{-(E_n - E_{\mathrm{F}})/k_{\mathrm{B}}T} \frac{m|\mathbf{v}_n|^2}{k_{\mathrm{B}}T}\, \tau_n \right\rangle_{\mathrm{CB}}$$

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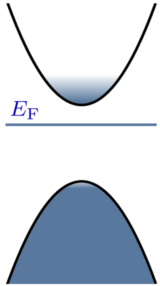

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$$\mu = \frac{e\langle\tau\rangle}{m}$$ Drude formula

The electron-phonon matrix element

Matrix element

$$\langle m | \frac{\partial V_{\rm SCF}}{\partial \tau} | n \rangle$$

Zero-point displacement

$$\langle u^2 \rangle_T = \frac{\hbar}{2M\omega}$$

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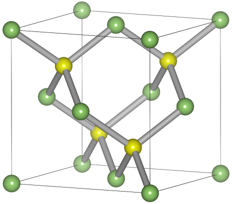
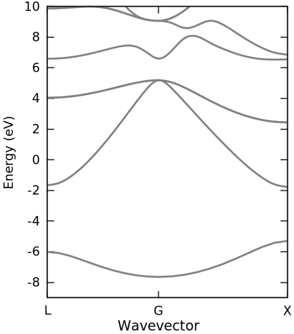


electrons in GaAs



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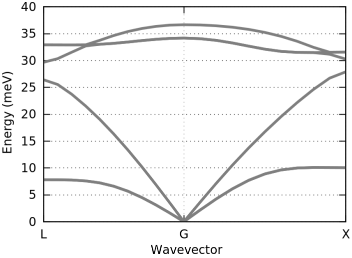

The electron-phonon matrix element

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} v_{\rm SCF} | u_{n\mathbf{k}} \rangle_{\rm uc}$$

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Lattice-periodic part of wavefunction

The electron-phonon matrix element

Variation of the Kohn-Sham potential

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Lattice-periodic part of wavefunction

$$\Delta_{\mathbf{q}\nu} v_{\mathrm{SCF}} = \sum_{\kappa\alpha p} e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_p)} \sqrt{\frac{\hbar}{2M_\kappa \omega_{\mathbf{q}\nu}}}\, e_{\kappa\alpha,\nu}(\mathbf{q}) \frac{\partial V_{\mathrm{SCF}}(\mathbf{r})}{\partial \tau_{\kappa\alpha p}}$$

κ Atom in the unit cell
α Cartesian direction
p Unit cell in the equivalent supercell

The electron-phonon matrix element

Variation of the Kohn-Sham potential

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Lattice-periodic part of wavefunction

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Zero-point amplitude

κ Atom in the unit cell
α Cartesian direction
p Unit cell in the equivalent supercell

The electron-phonon matrix element

Variation of the Kohn-Sham potential

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Brillouin-zone integrals

Example: electron lifetimes in metals, adiabatic approximation

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Wannier interpolation of electron-phonon matrix elements

Wannier functions (Lecture Tue.2)

$$\mathrm{w}_{mp}(\mathbf{r}) = \frac{1}{N_p} \sum_{n\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_p}\, U_{nm\mathbf{k}}\, \psi_{n\mathbf{k}}(\mathbf{r}),$$

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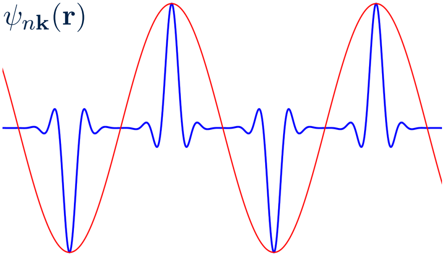

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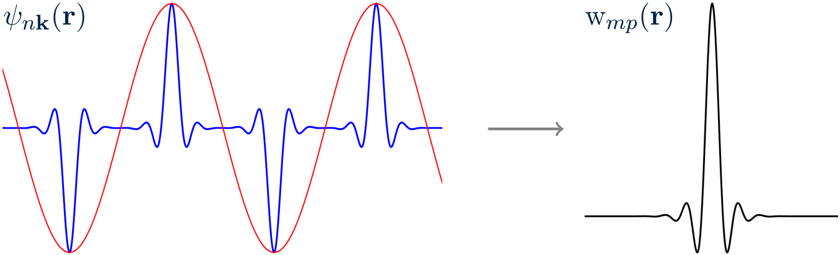

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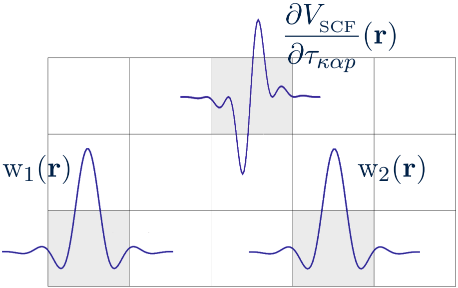

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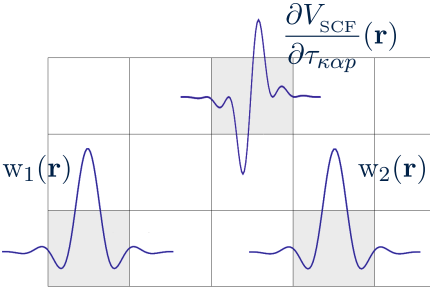

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2M_\kappa\omega_{\mathbf{q}\nu}}} \sum_{pp'} e^{i(\mathbf{k}\cdot\mathbf{R}_p+\mathbf{q}\cdot\mathbf{R}_{p'})} \left[U_{\mathbf{k+q}}\ \mathbf{g}(\mathbf{R}_p,\mathbf{R}_{p'})\cdot\mathbf{e}_{\mathbf{q}\nu}\ U^\dagger_{\mathbf{k}}\right]_{mn}$$

(Lecture Wed.3)

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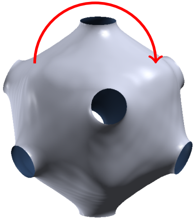

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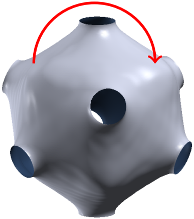

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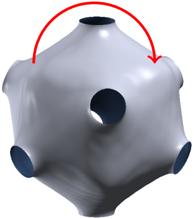

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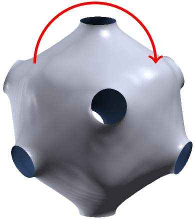

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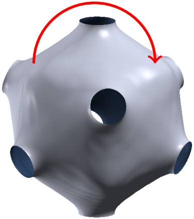

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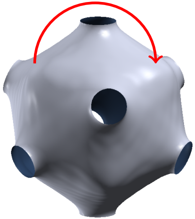

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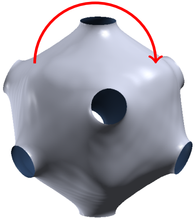

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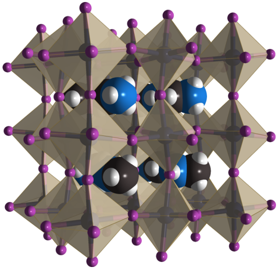
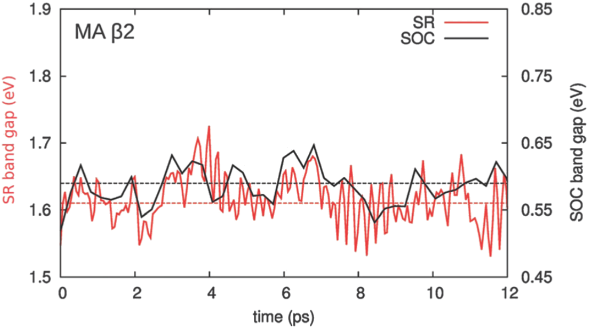
- Not meaningful for intrinsic semiconductors and insulators (Lecture Wed.1)

Molecular Dynamics vs. Rayleigh-Schrödinger

- Time-evolution of DFT band gap of $CH_3NH_3PbI_3$





Right figure from Quarti et al, Phys. Chem. Chem. Phys. 17, 9394 (2015)

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We have seen that DFT eigenvalues

depend parametrically on the ionic displacements

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- These two approaches are equivalent for harmonic systems

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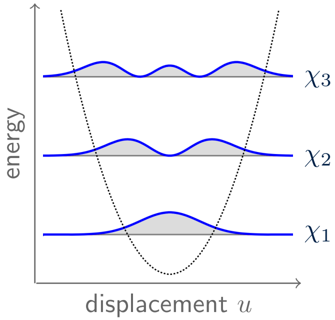
Probability distribution of ionic displacements (harmonic system)



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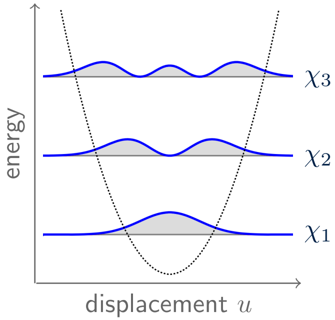

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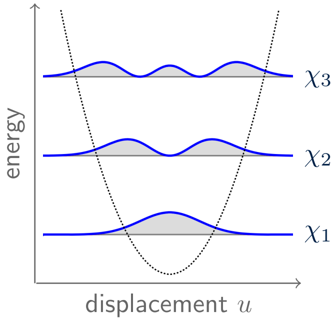
Meheler formula



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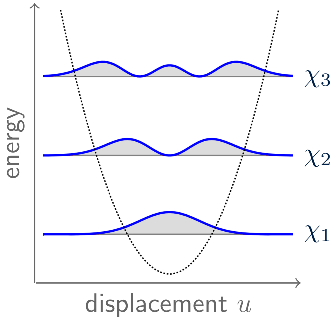

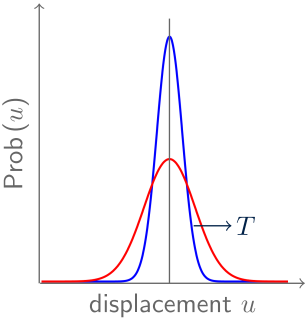

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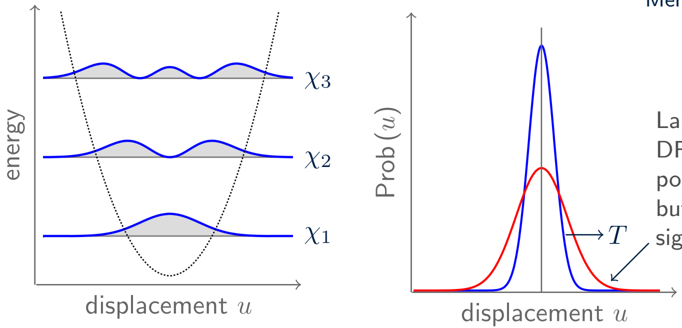

Large fluctuations of DFT eigenvalues are possible in MD, but statistically not significant

Take-home messages

- We can understand the basics of electron-phonon physics using elementary perturbation theory
- The calculations almost invariably require a fine sampling of the matrix elements across the Brillouin zone
- The electron-phonon coupling constant λ was introduced to study metals and superconductors
- Rayleigh-Schrödinger perturbation theory and MD simulations describe the same physics

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