2021 Virtual School on Electron-Phonon Physics and the EPW code

June 14-18 2021

Lecture Tue.1

Introduction to electron-phonon interactions

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Lecture Summary

- Heuristic approach to the electron-phonon interaction
- Examples of electron-phonon interactions
- Rayleigh-Schrödinger perturbation theory
- The electron-phonon matrix element
- Wannier interpolation

Where do electron-phonon interactions come from?

Ionic degrees of freedom in the Kohn-Sham equations

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

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Atom κ at position τ_κ

Heuristic approach to electron-phonon interactions

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Heuristic approach to electron-phonon interactions

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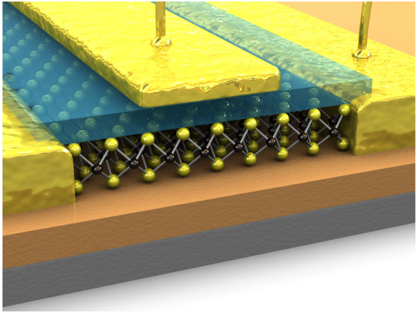
Perturbation Hamiltonian leading to EPIs

Manifestations of electron-phonon interactions

Electron mobility in monolayer MoS_2



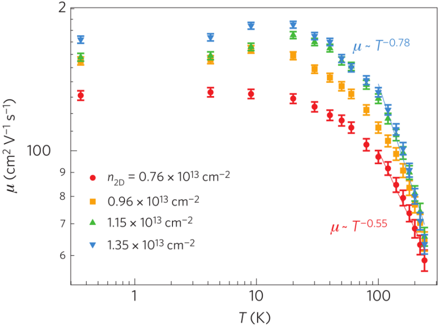
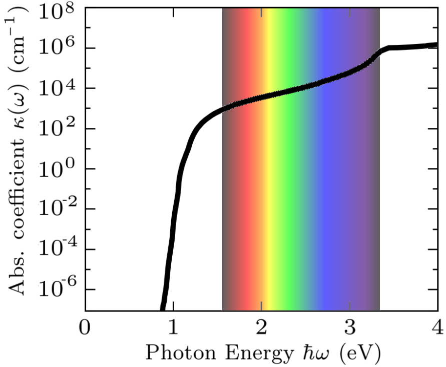


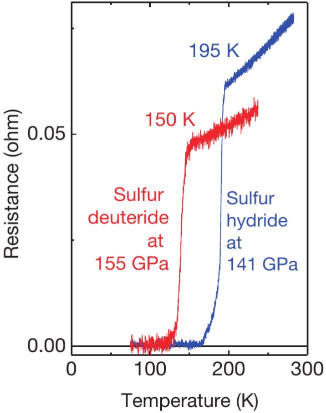
Figure from Radisavljevic and Kis, Nature Mater. 12, 815 (2013)

Phonon-assisted optical absorption in silicon



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

High-temperature superconductivity in compressed H_3S



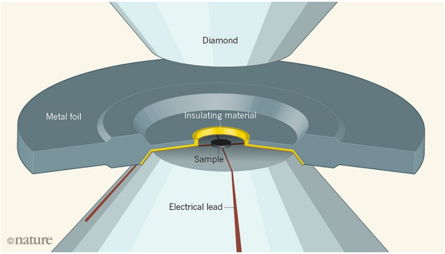
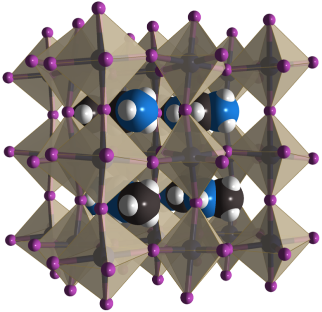


Figure from Drozdov et al, Nature 73, 525 (2015)

Temperature-dependent photoluminescence in hybrid perovskites



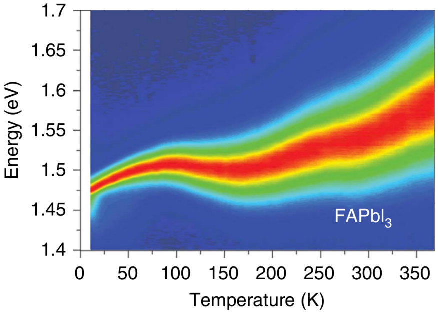
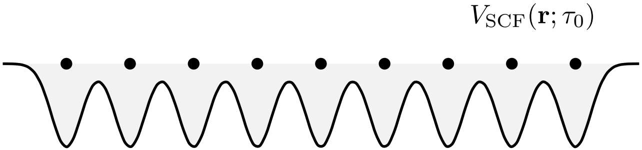


Figure from Wright et al, Nat. Commun. 7, 11755 (2016)

Perturbation Hamiltonian leading to EPIs



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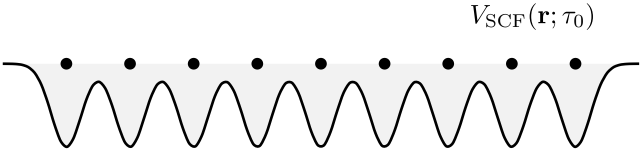

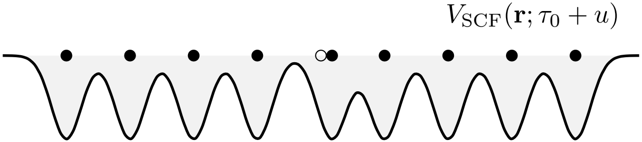

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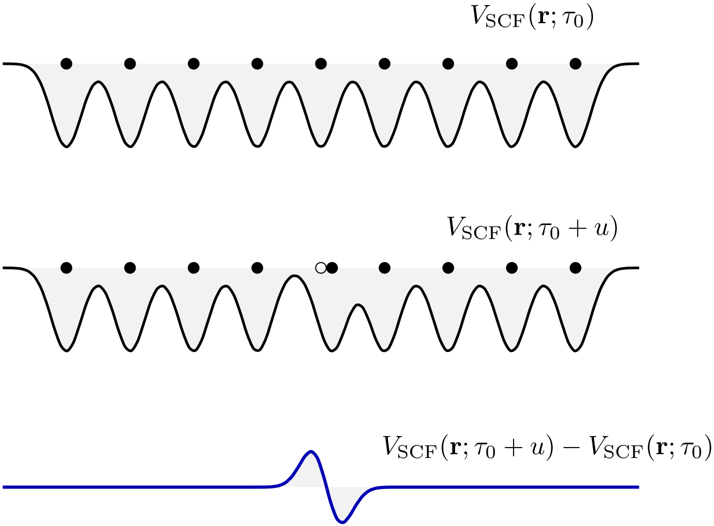

Rayleigh-Schrödinger perturbation theory

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Energy $$\Delta E_n = \langle n | \frac{\partial V_{\mathrm{SCF}}}{\partial \tau} u | n \rangle$$

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

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

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Temperature-dependent band structure

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Phonon-assisted optical processes and polarons

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Phonon-limited transport phenomena

Displacement amplitudes

What is the atomic displacement u in the perturbation Hamiltonian?

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equilibrium

e.g.: fixed temperature

out of equilibrium

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Mean square displacement amplitudes

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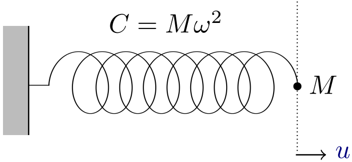
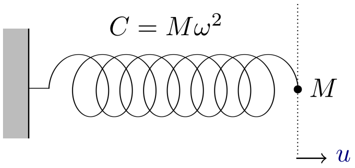
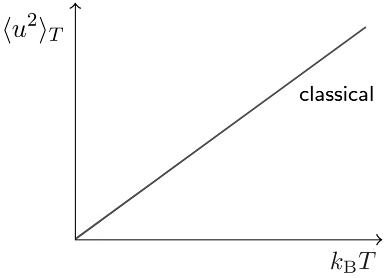
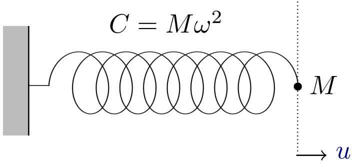


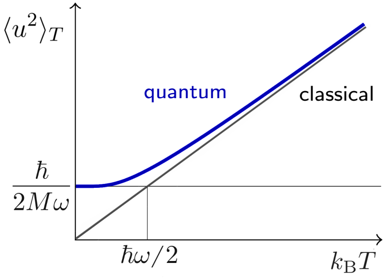
Mean square displacement amplitudes





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





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

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

Temperature-dependent band structures

Allen-Heine theory

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

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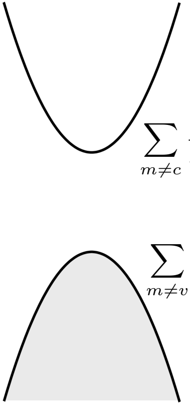
$$\langle \Delta E_n \rangle_T = \left[\sum_{m \neq n} \frac{\left| \langle m| \frac{\partial V_{\text{SCF}}}{\partial \tau} |n\rangle \right|^2}{E_n - E_m} + \frac{1}{2} \langle n| \frac{\partial^2 V_{\text{SCF}}}{\partial \tau^2} |n\rangle \right] \frac{\hbar}{2M\omega} (2\, n_T + 1)$$

Temperature-dependent band structures: Basic trends



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

$$\sum_{m\neq v} \frac{|\cdots|^2}{E_v - E_m} > 0$$

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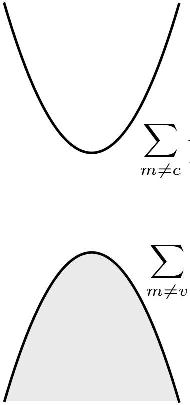

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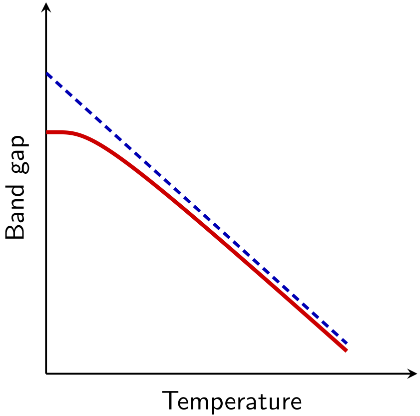

Example: Temperature-dependent bands of silicon

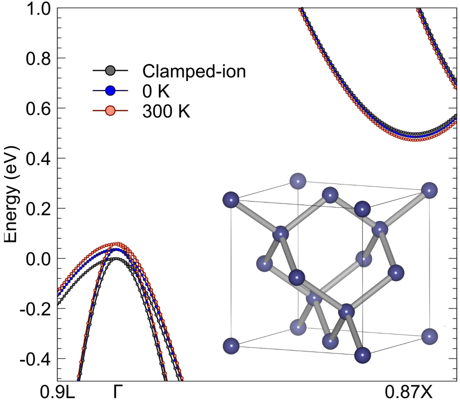

Figure from Zacharias et al, Phys. Rev. Research 2, 013357 (2020)

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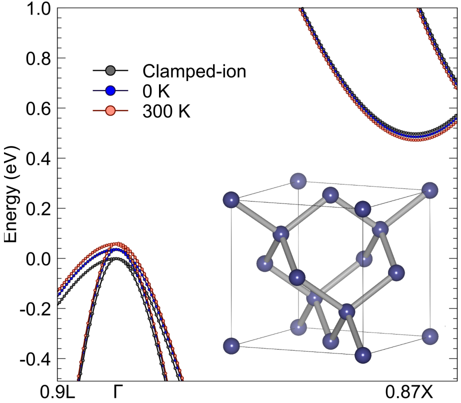

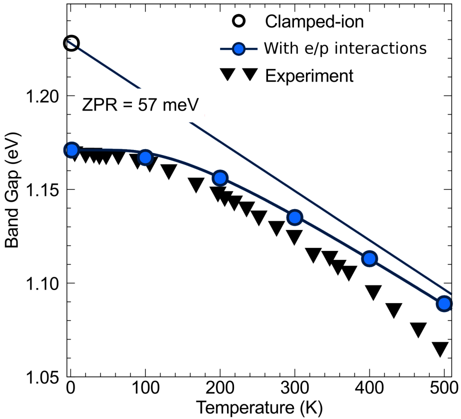

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Phonon-assisted optical absorption

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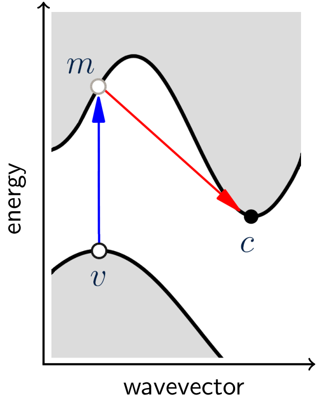
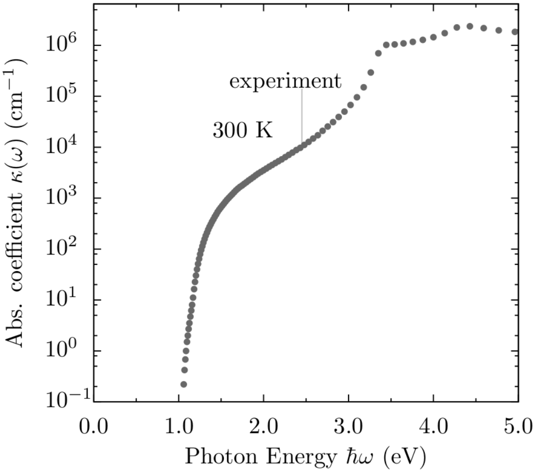


Example: Absorption spectrum of silicon



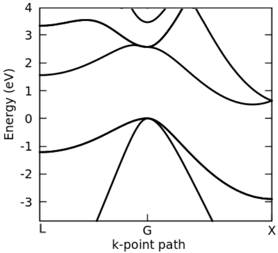
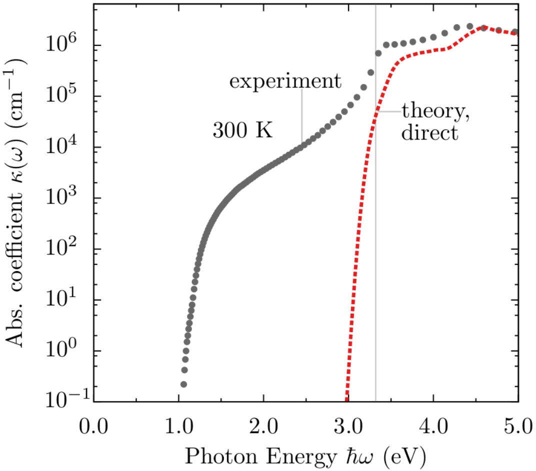
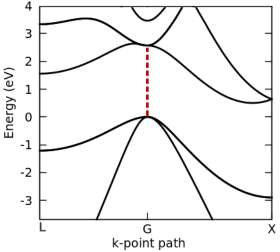


Figure from Zacharias et al, Phys. Rev. Lett. 115, 177401 (2015)

see also: Noffinger et al, Phys. Rev. Lett. 108, 167402 (2012)





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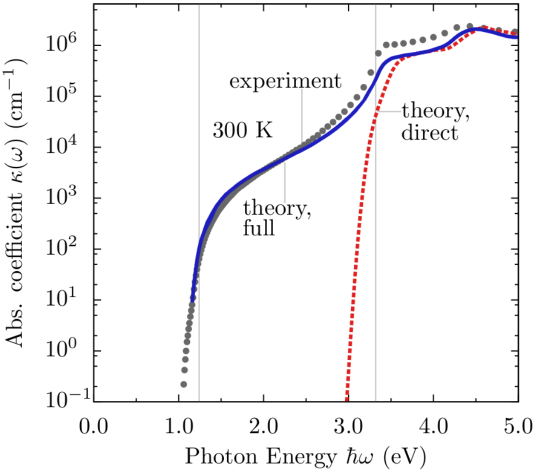

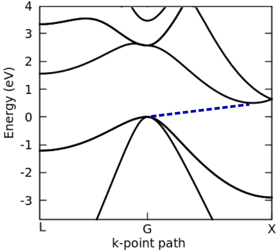

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Phonon-limited carrier mobilities

Carrier relaxation time

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

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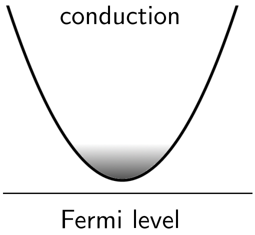
Electron mobility from Boltzmann equation (simplified)



$$\mu_\mathrm{e} = \frac{e}{m}\frac{1}{N_c}\sum_{n\in c}\frac{m|\mathbf{v}_n|^2}{3\,k_\mathrm{B}T}e^{-(E_n-E_\mathrm{F})/k_\mathrm{B}T}\,\tau_n$$

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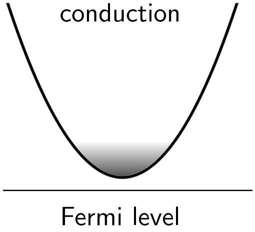

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$$\mu = \frac{e\langle\tau\rangle}{m}$$ Drude formula

Example: Mobility of lead-halide perovskite $MAPbI_3$

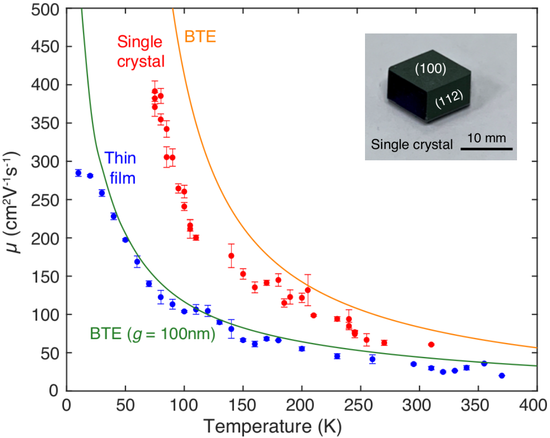

Figure from Xia et al, J. Phys. Chem. Lett. 12, 3607 (2021)

The electron-phonon matrix element

$$\langle \psi_m | \frac{\partial V_{\rm SCF}}{\partial \tau} | \psi_n \rangle \quad \longrightarrow \quad g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} v_{\rm SCF} | u_{n\mathbf{k}} \rangle_{\rm uc}$$

Baroni et al, Rev. Mod. Phys. 73, 515 (2001); Giustino, Rev. Mod. Phys. 89, 015003 (2017)

The electron-phonon matrix element

$$\langle \psi_m | \frac{\partial V_{\rm SCF}}{\partial \tau} | \psi_n \rangle \longrightarrow g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} v_{\rm SCF} | u_{n\mathbf{k}} \rangle_{\rm uc}$$

Lattice-periodic part of the wavefunction

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Zero-point amplitude

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Incommensurate modulation

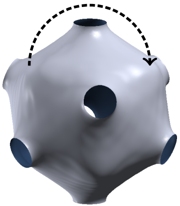
Phonon polarization

Baroni et al, Rev. Mod. Phys. 73, 515 (2001); Giustino, Rev. Mod. Phys. 89, 015003 (2017)

Brillouin Zone integrals

Example: electron lifetimes in metals (adiabatic, high temperature)

$$\frac{1}{\tau_{n\mathbf{k}}} = 2k_{\mathrm{B}}T\ \frac{2\pi}{\hbar}\sum_{m\nu}\int_{\mathrm{BZ}}\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}\frac{|g_{nm\nu}(\mathbf{k},\mathbf{q})|^2}{\hbar\omega_{\mathbf{q}\nu}}\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}})$$



Fermi surface of copper

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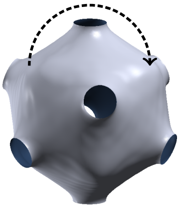
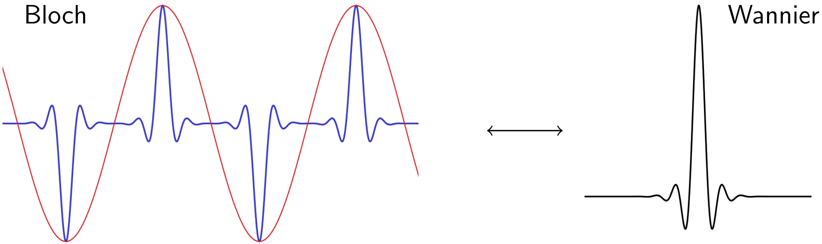


Fermi surface of copper

- The integral over the Brillouin zone can require grids with $100\times100\times100$ $\mathbf{q}$-points and more: expensive
- Each $\mathbf{q}$-vector requires a separate DFPT calculation: expensive

Wannier functions

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



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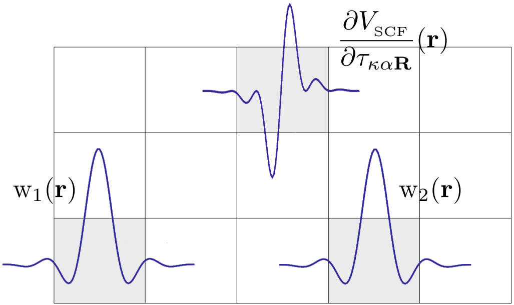
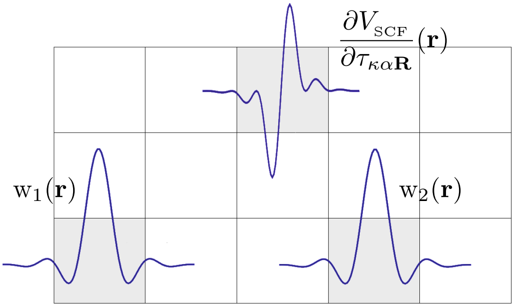


FG, Rev. Mod. Phys. 89, 015003 (2017)



$$\mathbf{g}_\nu(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2M_\kappa \omega_{\mathbf{q}\nu}}} \sum_{\mathbf{R}\mathbf{R}'} e^{i(\mathbf{k}\cdot\mathbf{R}+\mathbf{q}\cdot\mathbf{R}')} U_{\mathbf{k}+\mathbf{q}}\, \mathbf{g}(\mathbf{R},\mathbf{R}') \cdot \mathbf{e}_{\mathbf{q}\nu}\, U^\dagger_{\mathbf{k}}$$

FG, Rev. Mod. Phys. 89, 015003 (2017)

Example: Electron-phonon matrix elements of diamond

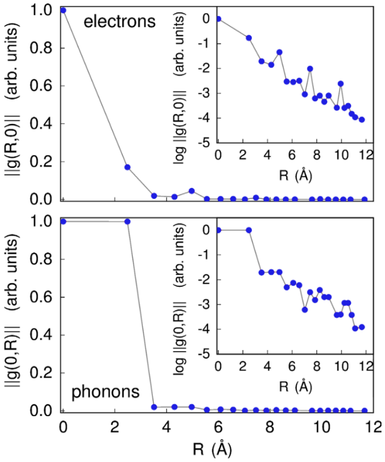
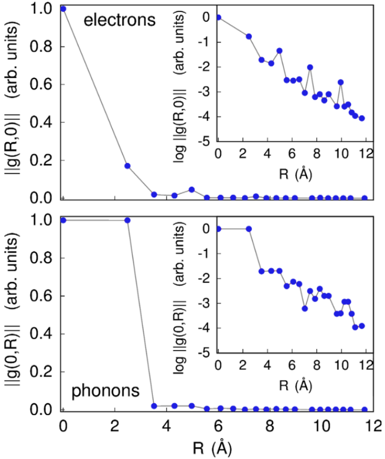
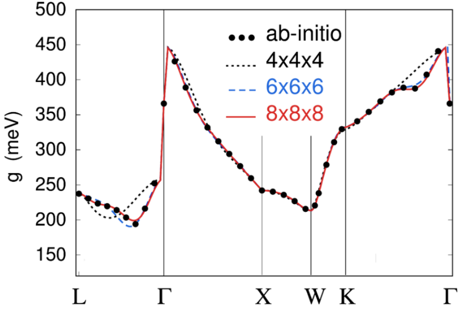


Figure from FG et al, Phys. Rev. B 76, 165108 (2007)

Example: Electron-phonon matrix elements of diamond





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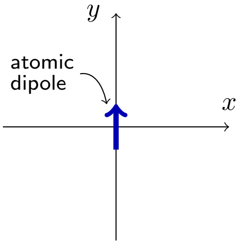
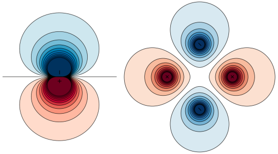
Spatial decay of induced potential



dipole quadrupole octupole

$$\frac{\partial V_{\mathrm{SCF}}}{\partial \tau}(\mathbf{r}) \sim \epsilon^{-1}\left[D_\alpha \frac{\hat{r}_\alpha}{r^2} + Q_{\alpha\beta}\frac{\hat{r}_\alpha \hat{r}_\beta}{r^3} + O_{\alpha\beta\gamma}\frac{\hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma}{r^4} + \cdots\right]$$



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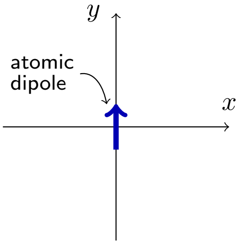

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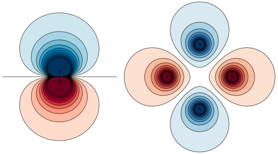
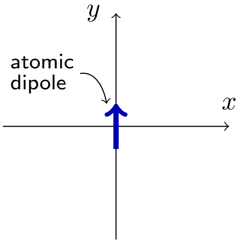


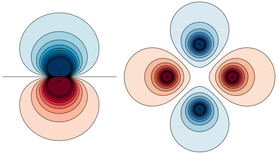
Fourier: $\frac{1}{q}$ $\quad 1 \quad$ q

Spatial decay of induced potential



dipole — quadrupole — octupole

$$\frac{\partial V_{\rm SCF}}{\partial \tau}(\mathbf{r}) \sim \epsilon^{-1}\left[D_\alpha \frac{\hat{r}_\alpha}{r^2} + Q_{\alpha\beta}\frac{\hat{r}_\alpha \hat{r}_\beta}{r^3} + O_{\alpha\beta\gamma}\frac{\hat{r}_\alpha \hat{r}_\beta \hat{r}_\gamma}{r^4} + \cdots \right]$$



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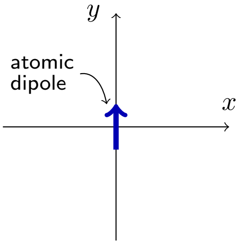
Metals: $\epsilon(q) = 1 + \dfrac{q_{\rm TF}^2}{q^2}$

Insulator: $\epsilon(q) = 1 + \dfrac{\epsilon_0 - 1}{1 + q^2/q_0^2}$



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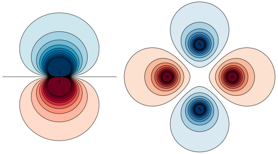
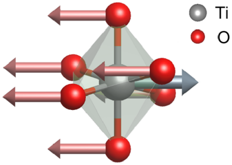


Fourier: $\frac{1}{q}$ $\quad 1 \quad$ q

Metals: $\epsilon(q) = 1 + \frac{q_{\rm TF}^2}{q^2}$ — smooth, smooth, smooth

Insulator: $\epsilon(q) = 1 + \frac{\epsilon_0 - 1}{1 + q^2/q_0^2}$ — singular, discontinuous, smooth

Example: Fröhlich interaction matrix element in TiO_2



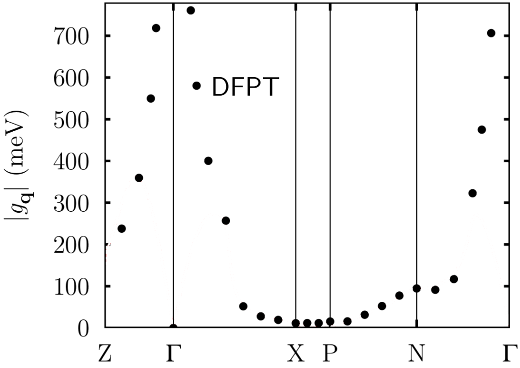


Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

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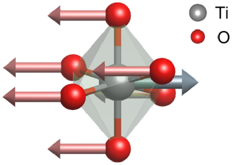

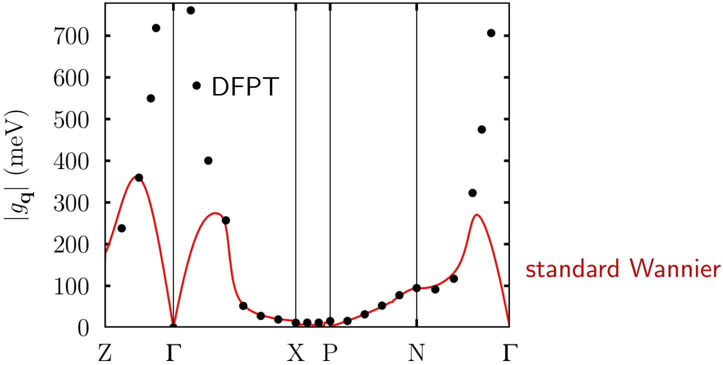

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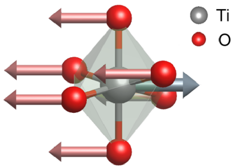

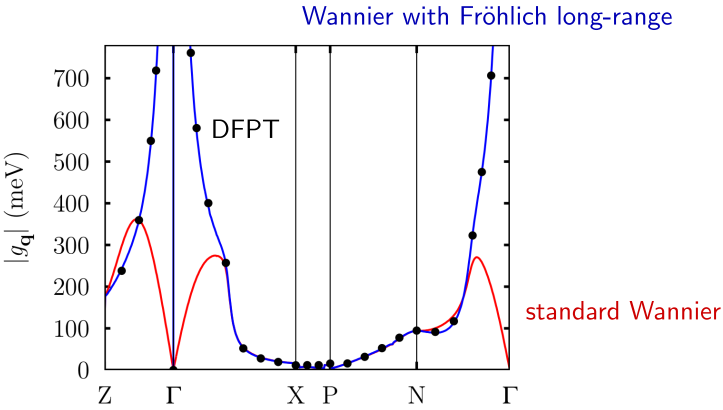

Figure from Verdi et al, Phys. Rev. Lett. 115, 176401 (2015)

Take-home messages

- We can understand the basics of electron-phonon physics using elementary perturbation theory
- Calculations of EPIs require a fine sampling of the electron-phonon matrix elements across the Brillouin zone
- The EPI matrix elements of metals and insulators behave very differently for long-wavelength phonons

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