Electron-phonon beyond Fröhlich : dynamical quadrupoles in polar and covalent solids

ABIDEV 2021

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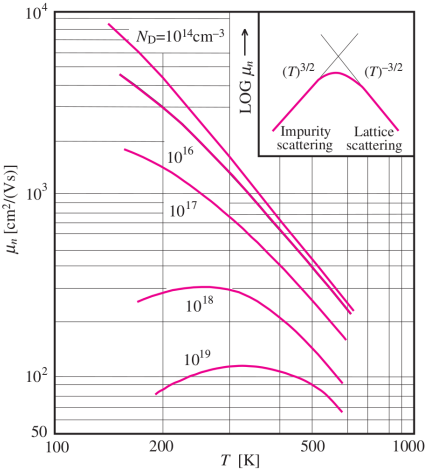
UCLouvain
Institute of Condensed Matter and Nanosciences

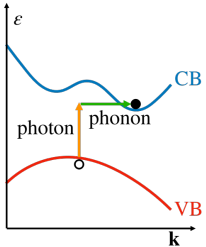
Electron-phonon coupling governs many phenomena

Phonon-limited mobility at high T

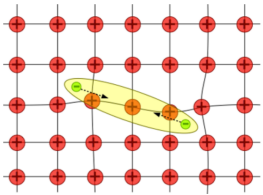


[Yu & Cardona, Fundamentals of Semiconductors]

Indirect light absorption



Conventional superconductivity



[Margine, EPW school 2018]

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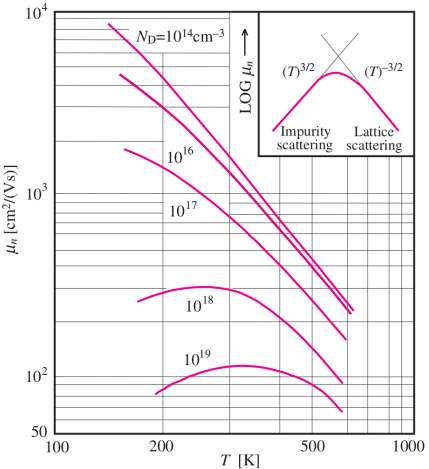

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In semiconductors, at high T or when the impurity concentration is very low, the mobility is governed by electron-phonon interactions.

Electronic lifetimes and phonon-limited mobility in the SERTA

Electron mobility in the **s**elf-**e**nergy **r**elaxation-**t**ime **a**pproximation to the Boltzmann transport equation :

$$\mu_{e,\alpha\beta} = \frac{-1}{\Omega n_e} \sum_{n \in CB} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \mathrm{v}_{n\mathbf{k},\alpha} \mathrm{v}_{n\mathbf{k},\beta} \tau_{n\mathbf{k}} \left. \frac{\partial f^0}{\partial \varepsilon} \right|_{\varepsilon_{n\mathbf{k}}}$$

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Electronic lifetimes due to the scattering by phonons :

$$\frac{1}{\tau_{n\mathbf{k}}} = \frac{2\pi}{\hbar} \sum_{m,\nu} \int_{\mathrm{BZ}} \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \times [(n_{\nu\mathbf{q}} + f_{m\mathbf{k}+\mathbf{q}}) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}\nu}) + (n_{\nu\mathbf{q}} + 1 - f_{m\mathbf{k}+\mathbf{q}}) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}\nu})]$$

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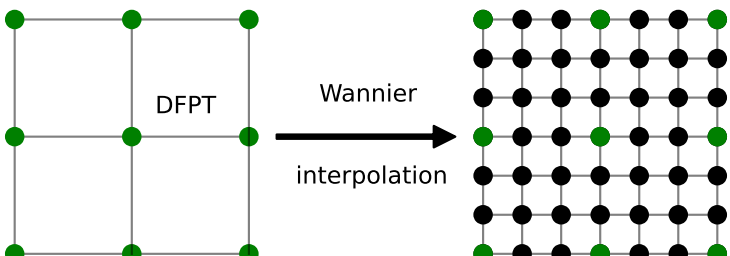
Solution : Wannier interpolation of the $g_{mn\nu}(\mathbf{k},\mathbf{q})$ obtained from DFPT $\Rightarrow$ *EPW approach*.



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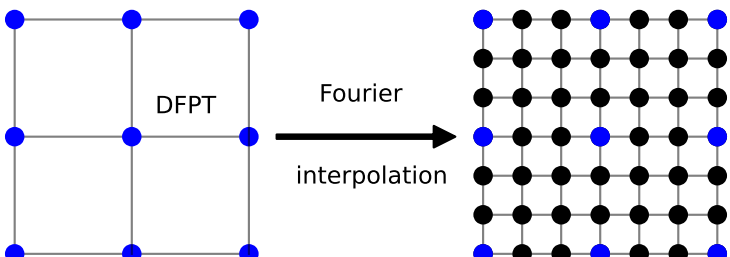
Problem : this integral converges very slowly ($\sim 100 \times 100 \times 100$ **q** mesh required).
Our solution : Fourier interpolation of the $\Delta_{\mathbf{q}\nu} V^{\mathrm{KS}}$ obtained from DFPT, and computation of $\psi^{\mathrm{KS}}_{m\mathbf{k}+\mathbf{q}}$.



Important physical interactions : dipoles (Fröhlich) and dynamical quadrupoles

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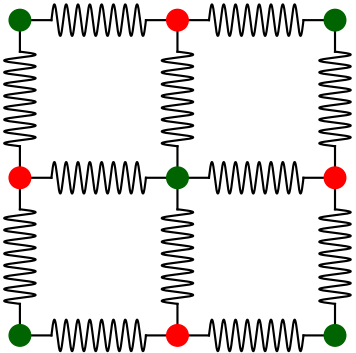
- Fröhlich interaction : in polar semiconductors, longitudinal optical phonons create **dipoles** and a long-range potential that interacts strongly with electrons.



[PRL **115**, 176401 (2015), PRB **92**, 054307 (2015)]

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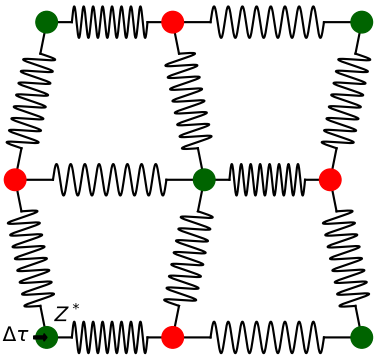

Dipole = $Z^* \Delta\tau \rightarrow$ electrostatic potential

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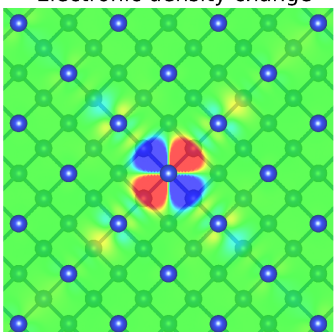
The scattering potentials $\Delta_{\mathbf{q}\nu} V^{\mathrm{KS}}$ describe how the phonons change the electronic properties.

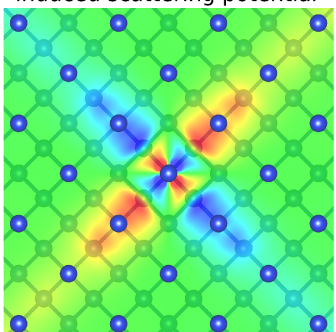
We need to consider different important interactions for a correct physical interpretation :

- Dipoles are not the only electrostatic effect appearing when atoms are displaced.
- Dynamical quadrupoles are also created, even in nonpolar semiconductors.

Electronic density change



Induced scattering potential



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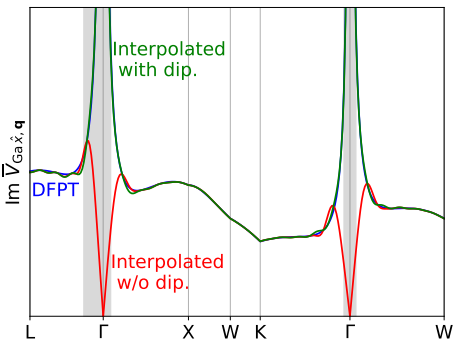
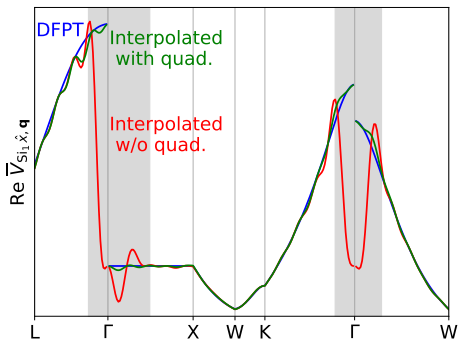
Fröhlich



Dynamical quadrupoles



How do we actually take the dynamical quadrupoles into account ?

The scattering potentials can be written in the phonon mode $(\mathbf{q}\nu)$ or atomic representation $(\mathbf{q}\kappa\alpha)$:

$$\Delta_{\mathbf{q}\nu} V^{\mathrm{KS}} = \frac{1}{\sqrt{2\omega_{\mathbf{q}\nu}}} \sum_{\kappa\alpha} \frac{e_{\kappa\alpha,\nu}(\mathbf{q})}{\sqrt{M_\kappa}} V_{\kappa\alpha,\mathbf{q}}(\mathbf{r}).$$

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The interpolation procedure is similar to what is done for the dynamical matrix to obtain phonon spectra :

1. Split the DFPT scattering potentials into long-range ($V^{\mathcal{L}}$) and short-range ($V^{\mathcal{S}}$) parts.
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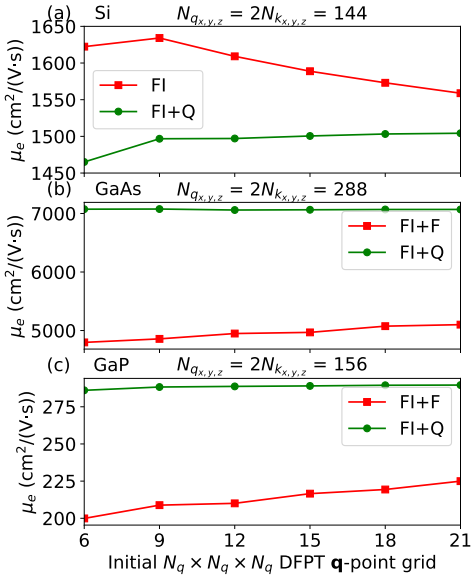
$$V^{D}_{\kappa\alpha,\mathbf{q}}(\mathbf{r}) \propto \frac{\mathbf{q}\cdot\mathbf{Z}^*}{\mathbf{q}\cdot\epsilon^\infty\cdot\mathbf{q}}$$

$$V^{Q}_{\kappa\alpha,\mathbf{q}}(\mathbf{r}) \propto \frac{\mathbf{q}\cdot\mathbf{Q}^*\cdot\mathbf{q}}{\mathbf{q}\cdot\epsilon^\infty\cdot\mathbf{q}}$$

Interpolating the scattering potentials without the dynamical quadrupoles interactions is bad



- We start from a given $N_q \times N_q \times N_q$ DFPT **q**-point grid and interpolate the scattering potentials on the fine meshes required to converge the mobility.
- Without including the dynamical quadrupoles, the interpolation converges slowly.
- Including them fixes the interpolation and the correct mobility can be obtained.

In-depth analysis : which modes are the most impacted by quadrupoles ?

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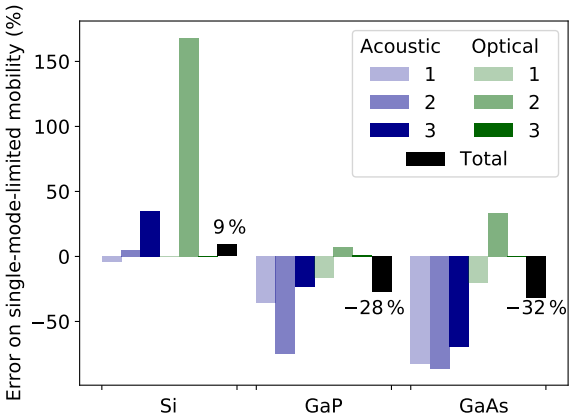
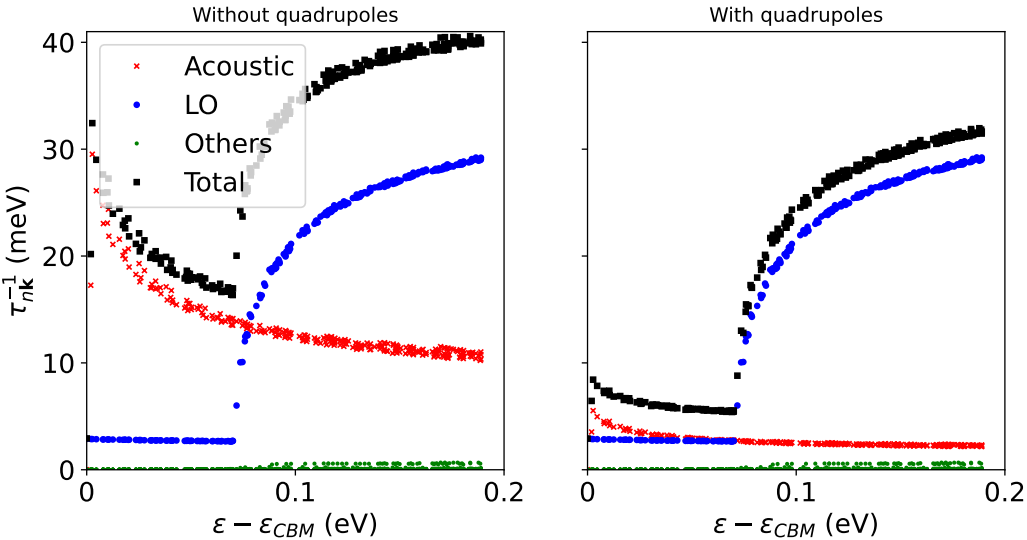


- Quadrupole acoustic sum rule for nonpolar semiconductors ⇒ larger impact on optical modes.
- Piezoelectric coupling in polar materials ⇒ larger impact on acoustic modes.

Dynamical quadrupoles seem particularly important for strongly piezoelectric systems

Example : ZnO



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- use a workflow to compute the mobility directly : all that is needed is the structure, pseudopotentials, and the size of the meshes, see `abipy/examples/flows/run_eph_mob.py`

Keep-home message

- The implementation in ABINIT to compute the phonon-limited lifetimes (`eph_task -4`) and transport tensors (`eph_task -4 or 7`) is ready and documented with a tutorial.
- Computations are rather optimized (many parallelization levels) and can be run through an AbiPy workflow.
- Dynamical quadrupoles are required for a correct interpolation of the e-ph scattering potentials. They can be computed with ABINIT as well ! Unphysical results can be obtained otherwise.
- Check our papers : Phys. Rev. Lett. **125**, 136601 (2020) and Phys. Rev. B **102**, 094308 (2020).

Thank you !