Electron-Phonon Coupling in Naphthalene

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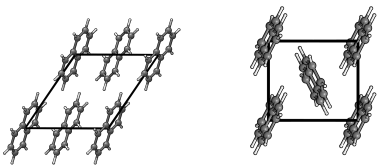
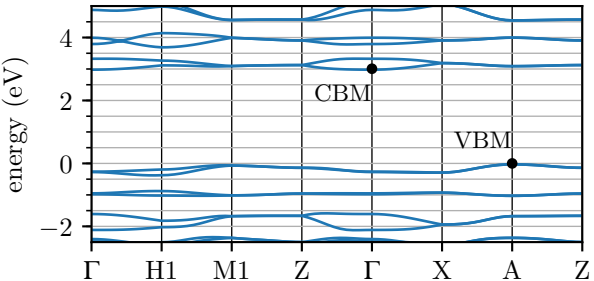
Outline

Naphthalene crystals

- Organic molecular crystal
- Good electrical conductivity
  - Solar cell
  - Field-effect transistors





- Zero-point renormalization (ZPR)
- Temperature-dependent band gap
- Electron and hole mobilities

Computing the electron-phonon self-energy

Fan self-energy

$$\Sigma^{\text{Fan}}_{\mathbf{k}n}(T,\omega) = \sum_{\mathbf{q}\nu}\sum_{m} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu}(T) + f_{\mathbf{k}+\mathbf{q}m}(T)}{\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q}m} + \hbar\omega_{\mathbf{q}\nu} + i\eta} + \frac{n_{\mathbf{q}\nu}(T) + 1 - f_{\mathbf{k}+\mathbf{q}m}(T)}{\varepsilon - \varepsilon_{\mathbf{k}+\mathbf{q}m} - \hbar\omega_{\mathbf{q}\nu} + i\eta} \right]$$

Separation into lower bands / higher bands contributions

$$\Sigma(T,\omega) = \sum_{\mathbf{q}\nu}\sum_{m\leq M} \Sigma_{\mathbf{q}\nu,m}(T,\omega) + \sum_{\mathbf{q}\nu}\sum_{m>M} \Sigma^{\text{Static}}_{\mathbf{q}\nu,m}(T,\varepsilon^0_{\mathbf{k}n})$$

Double-grid technique

$$\Sigma(T,\omega) = \sum^{\text{fine}}_{\mathbf{q}\nu}\sum_{m\leq M} \Sigma_{\mathbf{q}\nu,m}(T,\omega) + \sum^{\text{coarse}}_{\mathbf{q}\nu}\sum_{m>M} \Sigma_{\mathbf{q}\nu,m}(T,\varepsilon^0_{\mathbf{k}n})$$

Interpolating the phonon potential in polar materials

Long-range part of the phonon potential

$$V^L_{\kappa j}(\mathbf{q},\mathbf{r}) = i\frac{4\pi}{\Omega}\sum_{\mathbf{G}}\frac{e^{i(\mathbf{q}+\mathbf{G})\cdot(\mathbf{r}-\mathbf{R}_\kappa)}(\mathbf{q}+\mathbf{G})_{j'}\cdot Z^*_{\kappa,j'j}}{(\mathbf{q}+\mathbf{G})\cdot\varepsilon^\infty\cdot(\mathbf{q}+\mathbf{G})}$$

Fourier interpolation of the short-range part of the phonon potential

$$W^S_{\kappa j}(\mathbf{r}-\mathbf{R}_l) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_l}\Big[V_{\kappa j}(\mathbf{q},\mathbf{r}) - V^L_{\kappa j}(\mathbf{q},\mathbf{r})\Big]$$

The long-range part is then added to the interpolated potential

$$V_{\kappa j}(\tilde{\mathbf{q}},\mathbf{r}) \approx \sum_l W^S_{\kappa j}(\mathbf{r}-\mathbf{R}_l)e^{-i\tilde{\mathbf{q}}\cdot\mathbf{R}_l} + V^L_{\kappa j}(\tilde{\mathbf{q}},\mathbf{r})$$

Workflow

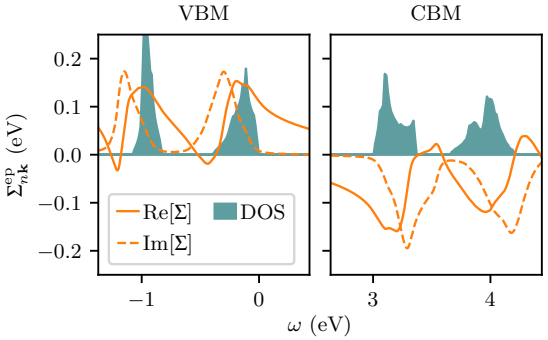
Computation	**Executable**	**Input variables**	**Files**
Eigenvalues at $\mathbf{k}$ and at $\mathbf{k}+\mathbf{q}$	`abinit`	`iscf=-2`	`EIG.nc`
DFPT calculation of all perturbations (atoms + electric field)	`abinit`	`rfphon=1`	`POTx` `DDB.nc`

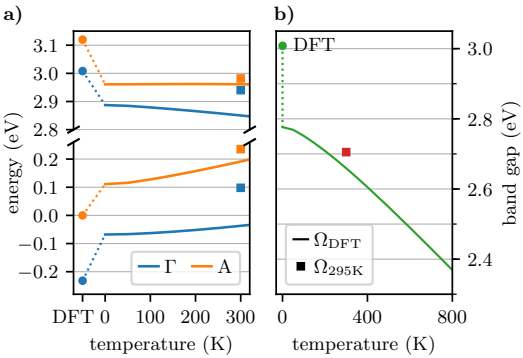
Non-self-consistent DFPT for upper bands contribution	`abinit`	`rfphon=1`
		`ieig2rf=5`
		`iscf=-2`
			`EIGR2D.nc`

Merging of phonon potential	`mrgdv`		`DVDB`
Interpolation of phonon potential	`abinit`	`eph_task=5`	`DVDB`
Merging of dynamical matrices	`mrgddb`		`DDB`
Interpolation of dynamical matrices	`anaddb`	`prtddb=1`	`DDB.nc`
El-ph coupling matrix elements	`abinit`	`eph_task=2`	`GKK.nc`
Self-energy	`ElectronPhonon-Coupling`		`EP.nc`

Temperature dependence of the band gap

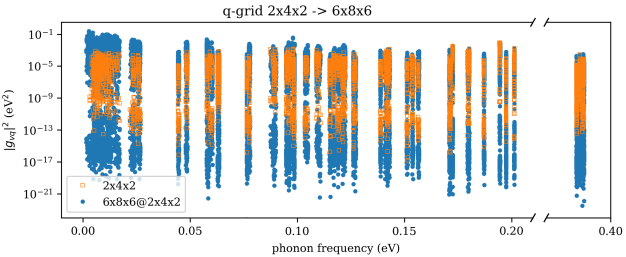
Band gap renormalization

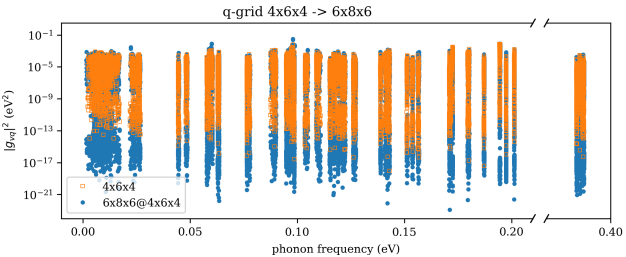




	Exp.	DFT	GW	GW+ZPR
Band gap (eV)	5.0	3.01	5.30	5.07

A word of warning

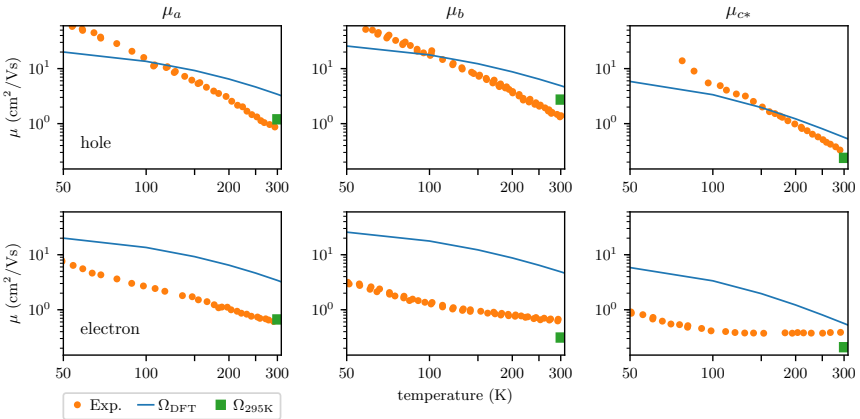




- Large errors in the interpolated potential with a $2 \times 4 \times 2$ coarse q-point grid

Electrical mobility

$$\mu_\alpha^{\mathrm{e,h}} = \frac{-e}{\rho_{\mathrm{e,h}}\Omega} \sum_n \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \frac{\partial f_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} |v_{n\mathbf{k},\alpha}|^2 \tau_{n\mathbf{k}}$$



Approximating the mobility

Using the density of states $D(\varepsilon)$

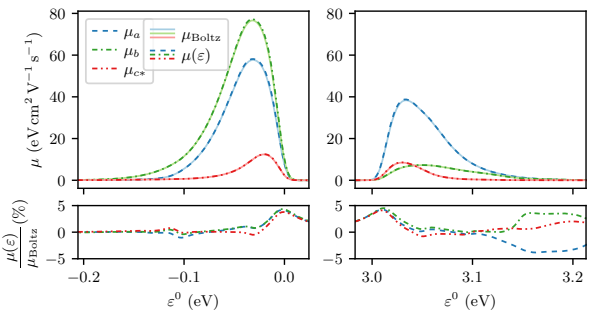
$$\mu_\alpha^{\mathrm{e,h}} \approx \frac{-e}{\rho_{\mathrm{e,h}}} \int d\varepsilon\, D(\varepsilon) f'(\varepsilon) v_\alpha^2(\varepsilon) \tau(\varepsilon)$$

Energy-resolved squared velocity

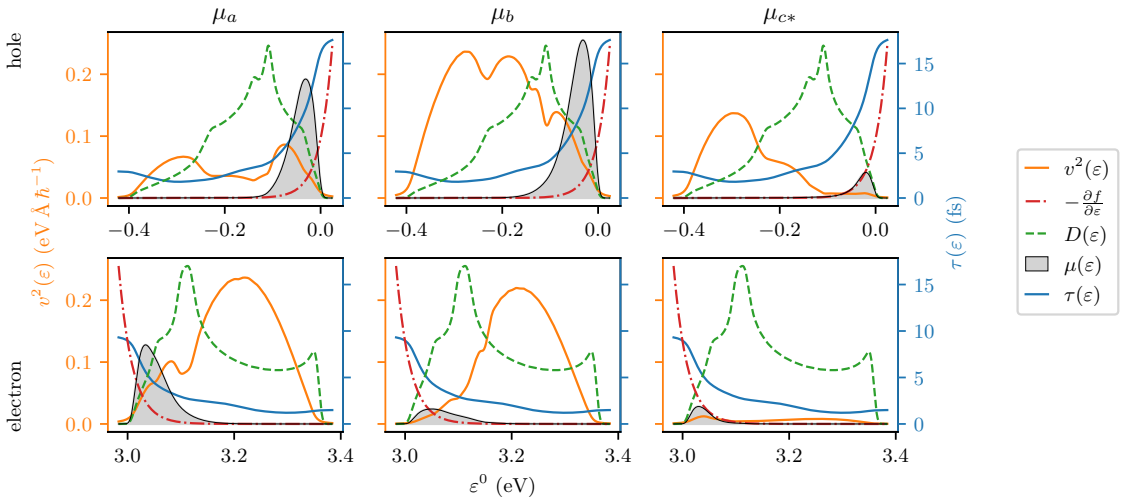
$$v_\alpha^2(\varepsilon) = \frac{1}{D(\varepsilon)} \sum_n \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} |v_{n\mathbf{k},\alpha}|^2 \delta(\varepsilon - \varepsilon_{n\mathbf{k}})$$

Energy-resolved lifetime

$$\tau(\varepsilon) = \frac{1}{D(\varepsilon)} \sum_n \int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} \tau_{n\mathbf{k}} \delta(\varepsilon - \varepsilon_{n\mathbf{k}})$$



Approximating the mobility



Self-consistency in the self-energy

Finding the quasiparticle energy

On-the-mass-shell approximation

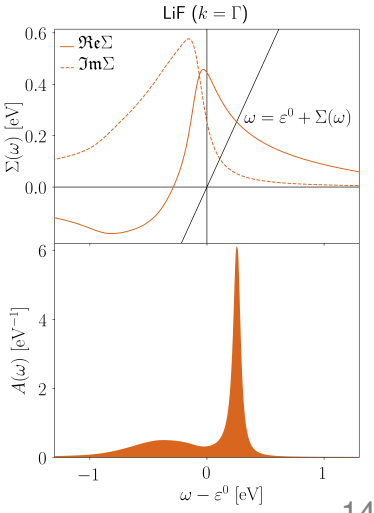
$$\varepsilon_{\mathbf{k}n}(T) = \varepsilon^0_{\mathbf{k}n} + \Re\Sigma_{\mathbf{k}n}(\varepsilon^0_{\mathbf{k}n}, T)$$

Quasiparticle energy

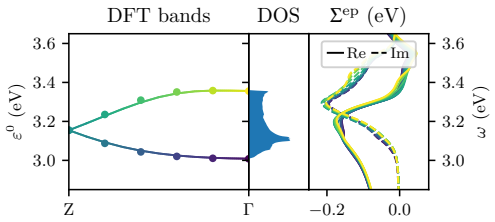
$$\varepsilon_{\mathbf{k}n}(T) = \varepsilon^0_{\mathbf{k}n} + \Re\Sigma_{\mathbf{k}n}(\varepsilon_{\mathbf{k}n}, T)$$

Spectral function

$$A_{\mathbf{k}n}(\omega, T) = \frac{1}{\pi}\Im G_{\mathbf{k}n}(\omega, T)$$
$$= \frac{1}{\pi}\frac{|\Im\Sigma_{\mathbf{k}n}(\omega, T)|}{[\omega - \varepsilon^0 - \Re\Sigma_{\mathbf{k}n}(\omega, T)]^2 + \Im\Sigma_{\mathbf{k}n}(\omega, T)^2}$$



Self-consistent scheme



The self-energy is largely k-independent

Iterative computation of the self-energy at Γ

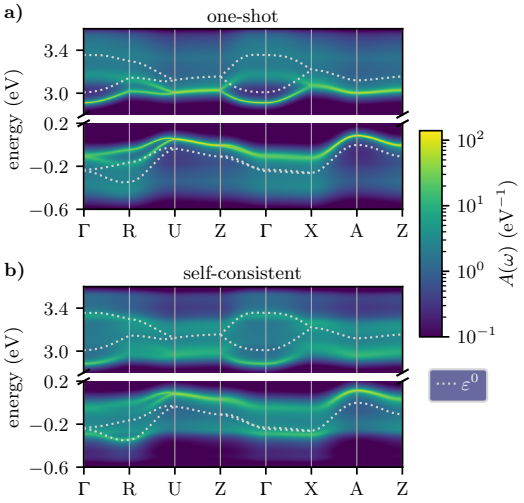
$$\varepsilon^1_{n\mathbf{k}} = \varepsilon^0_{n\mathbf{k}} + \Re\left[\Sigma_{n\Gamma}(\{\varepsilon^0_{n\mathbf{k}} - \varepsilon^0_{m\mathbf{k}+\mathbf{q}} \pm \omega_{\nu\mathbf{q}}\})\right]$$

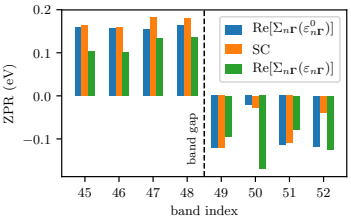
$$\varepsilon^2_{n\mathbf{k}} = \varepsilon^0_{n\mathbf{k}} + \Re\left[\Sigma_{n\Gamma}(\{\varepsilon^1_{n\mathbf{k}} - \varepsilon^1_{m\mathbf{k}+\mathbf{q}} \pm \omega_{\nu\mathbf{q}}\})\right]$$

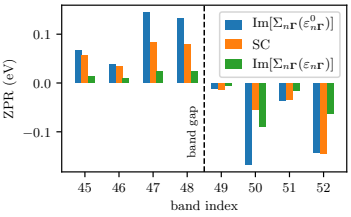
$$\dots$$

$$\varepsilon^i_{n\mathbf{k}} = \varepsilon^0_{n\mathbf{k}} + \Re\left[\Sigma_{n\Gamma}(\{\varepsilon^{i-1}_{n\mathbf{k}} - \varepsilon^{i-1}_{m\mathbf{k}+\mathbf{q}} \pm \omega_{\nu\mathbf{q}}\})\right],$$

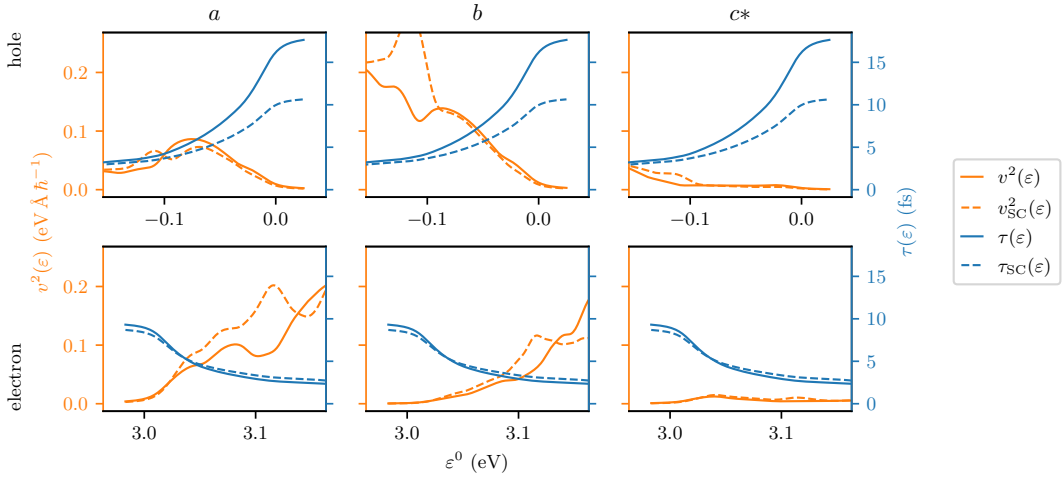
Self-consistent scheme







Effect of self-consistency on the mobility



Effect of self-consistency on the mobility

	Mobility at 295K					
	hole			electron		
	μ_a^{h}	μ_b^{h}	μ_{c*}^{h}	μ_a^{e}	μ_b^{e}	μ_{c*}^{e}
one-shot	1.20	2.73	0.24	0.67	0.31	0.21
SC	0.90	2.19	0.18	1.18	0.59	0.31
Exp.	0.79	1.34	0.31	0.58	0.63	0.39

Summary / Acknowledgments

- Efficient scheme for computing the electron-phonon self-energy
- Interpolation of the phonon coupling potential in real space
- Good agreement for the band gap and ZPR of Naphthalene
- Reasonable agreement for the electron and hole mobilities
- Important effect of lattice expansion on mobilities
- Self-consistent electron-phonon self-energy scheme
- On-the-mass-shell approximation better mimics self-consistency

Thank you for your attention!

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