Electron-Phonon Coupling in Naphthalene

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9th international Abinit developer workshop, May 2019
Outline

1 Introduction

2 Recent implementation in Abinit

3 Temperature dependence of the band gap

4 Electron and hole mobilities

5 Self-consistency in the self-energy
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

$$\Sigma_{\text{Fan}}^{kn}(T, \omega) = \sum_{q\nu} \sum_m |g_{mn\nu}(k, q)|^2 \left[ \frac{n_{q\nu}(T) + f_{k+q_m}(T)}{\epsilon - \epsilon_{k+q_m} + \hbar \omega_{q\nu} + i\eta} + \frac{n_{q\nu}(T) + 1 - f_{k+q_m}(T)}{\epsilon - \epsilon_{k+q_m} - \hbar \omega_{q\nu} + i\eta} \right]$$

Separation into lower bands / higher bands contributions

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

Double-grid technique

$$\Sigma(T, \omega) = \sum_{q\nu} \sum_{m \leq M} \Sigma_{q\nu, m}(T, \omega) + \sum_{q\nu} \sum_{m > M} \Sigma_{q\nu, m}(T, \epsilon_{kn}^0)$$
Interpolating the phonon potential in polar materials

Long-range part of the phonon potential

\[ V_{kj}^L(q, r) = i \frac{4\pi}{\Omega} \sum_G e^{i(q+G) \cdot (r - R_k)} (q + G) j' \cdot Z_{kj'j}^* (q + G) \]

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

\[ W_{kj}^S(r - R_l) = \sum_q e^{iq \cdot R_l} \left[ V_{kj}(q, r) - V_{kj}^L(q, r) \right] \]

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

\[ V_{kj}(\tilde{q}, r) \approx \sum_l W_{kj}^S(r - R_l) e^{-i\tilde{q} \cdot R_l} + V_{kj}^L(\tilde{q}, r) \]
## Workflow

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<td>iscf=-2</td>
<td>EIG.nc</td>
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<td>DFPT calculation of all perturbations (atoms + electric field)</td>
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<td>rfphon=1</td>
<td>POTx DDB.nc</td>
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<td>rfphon=1, ieig2rf=5, iscf=-2</td>
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<td>DVDB</td>
</tr>
<tr>
<td>Interpolation of phonon potential</td>
<td>abinit</td>
<td>eph_task=5</td>
<td>DVDB</td>
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<tr>
<td>Merging of dynamical matrices</td>
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<td>Interpolation of dynamical matrices</td>
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<td>prtddb=1</td>
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<td>El-ph coupling matrix elements</td>
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<td>ElectronPhonon-Coupling</td>
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<td>EP.nc</td>
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Temperature dependence of the band gap
Band gap renormalization

\[ \Sigma_{nk}^{ep} (\text{eV}) \]

\[ VBM \]

\[ \text{Re}\[\Sigma]\] \n\[ \text{Im}\[\Sigma]\] \n\[ \text{DOS}\]

\[ \text{CBM}\]

\[ \text{Exp.} \quad \text{DFT} \quad \text{GW} \quad \text{GW+ZPR}\]

| 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

\[ \mu_{e,h}^{\alpha} = \frac{-e}{\rho_{e,h}\Omega} \sum_n \int \frac{d\mathbf{k}}{\Omega_{\text{BZ}}} \frac{\partial f_{nk}}{\partial \varepsilon_{nk}} \left| V_{nk,\alpha} \right|^2 \tau_{nk} \]

![Graphs showing electrical mobility as a function of temperature for different materials and bands.](image-url)
Approximating the mobility

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

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

Energy-resolved squared velocity

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

Energy-resolved lifetime

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

\[ v^2(\varepsilon) (\text{eV} \cdot \text{Å} \cdot \text{fs}^{-1}) \]

\[ \tau(\varepsilon) (\text{fs}) \]

\[ \partial f / \partial \varepsilon \]

\[ D(\varepsilon) \]

\[ \mu(\varepsilon) \]

\[ \mu_a, \mu_b, \mu_c^* \]
Self-consistency in the self-energy
Finding the quasiparticle energy

**On-the-mass-shell approximation**

\[ \varepsilon_{kn}(T) = \varepsilon_{kn}^0 + \Re \Sigma_{kn}(\varepsilon_{kn}, T) \]

**Quasiparticle energy**

\[ \varepsilon_{kn}(T) = \varepsilon_{kn}^0 + \Re \Sigma_{kn}(\varepsilon_{kn}, T) \]

**Spectral function**

\[ A_{kn}(\omega, T) = \frac{1}{\pi} \Im G_{kn}(\omega, T) = \frac{1}{\pi} \frac{\Im \Sigma_{kn}(\omega, T)}{[\omega - \varepsilon^0 - \Re \Sigma_{kn}(\omega, T)]^2 + [\Im \Sigma_{kn}(\omega, T)]^2} \]
Self-consistent scheme

The self-energy is largely k-independent

Iterative computation of the self-energy at $\Gamma$

$$\varepsilon_{nk}^1 = \varepsilon_{nk}^0 + \Re \left[ \Sigma_{n\Gamma}(\{ \varepsilon_{nk}^0 - \varepsilon_{mk+q}^0 \pm \omega_{\nu q} \}) \right]$$

$$\varepsilon_{nk}^2 = \varepsilon_{nk}^0 + \Re \left[ \Sigma_{n\Gamma}(\{ \varepsilon_{nk}^1 - \varepsilon_{mk+q}^1 \pm \omega_{\nu q} \}) \right]$$

$$\ldots$$

$$\varepsilon_{nk}^i = \varepsilon_{nk}^0 + \Re \left[ \Sigma_{n\Gamma}(\{ \varepsilon_{nk}^{i-1} - \varepsilon_{mk+q}^{i-1} \pm \omega_{\nu q} \}) \right],$$
Self-consistent scheme

a) one-shot

b) self-consistent

\[ A(\omega) (\text{eV}^{-1}) \]

\[ ZPR (\text{eV}) \]

\[ \text{band index} \]

\[ \text{band gap} \]

\[ \text{Re}\left[\Sigma_n(\epsilon_{0n})\right] \]

\[ \text{SC} \]

\[ \text{Re}\left[\Sigma_n(\epsilon_n)\right] \]

\[ \text{Im}\left[\Sigma_n(\epsilon_{0n})\right] \]

\[ \text{Im}\left[\Sigma_n(\epsilon_n)\right] \]
Effect of self-consistency on the mobility

\[ v^2(\epsilon) \ (eV \cdot \AA^2 h^{-1}) \]

\[ \frac{\tau(\epsilon)}{(fs)} \]

\[ \frac{\tau_{SC}(\epsilon)}{(fs)} \]
## Effect of self-consistency on the mobility

<table>
<thead>
<tr>
<th></th>
<th>Mobility at 295K</th>
<th>hole</th>
<th>electron</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\mu_a^h$</td>
<td>$\mu_b^h$</td>
<td>$\mu_{c^*}^h$</td>
</tr>
<tr>
<td>one-shot</td>
<td>1.20</td>
<td>2.73</td>
<td>0.24</td>
</tr>
<tr>
<td>SC</td>
<td>0.90</td>
<td>2.19</td>
<td>0.18</td>
</tr>
<tr>
<td>Exp.</td>
<td>0.79</td>
<td>1.34</td>
<td>0.31</td>
</tr>
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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!