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DFTBephy: A DFTB-based Approach for Electron-Phonon Coupling Calculations

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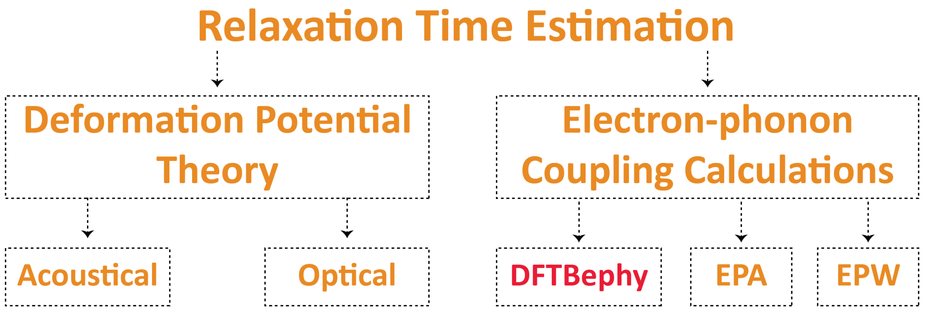
Motivation



Herein, we present a method for calculating the electron-phonon coupling matrix within the DFTB approach and demonstrate its implementation based on DFTB+ and phonopy. Exemplarily, we show results for γ-graphyne which was recently synthesized [Yiming Hu, Chenyu Wu, Qingyan Pan *et al* 2022 *Nat. Synth*]. Consistent with earlier predictions we obtain relaxation times on the order of 10^{-14} s at room temperature.

Electron-phonon Coupling

The deformed lattice is described in terms of the displacements $\vec{u}_{ls}$, as $\vec{R} \to \vec{R} + \vec{u}_{ls}$. The change in the Hamilton matrix elements and the overlap matrix elements can be defined by:

$$\delta H(\ell s, \ell' s') = \frac{\partial H(\ell s - \ell' s')}{\partial \vec{R}} \cdot (\vec{u}_{\ell s} - \vec{u}_{\ell' s'}) \ , \quad (1)$$

$$\delta S(\ell s, \ell' s') = \frac{\partial S(\ell s - \ell' s')}{\partial \vec{R}} \cdot (\vec{u}_{\ell s} - \vec{u}_{\ell' s'}) \ , \quad (2)$$

where the gradient is evaluated at the unperturbed positions. We first consider the two-center matrix elements:

$$H_{\mu,\nu}(\ell s, \ell' s') = \int dV \, \varphi^*_\mu(\vec{r} - \vec{R}_{\ell s}) \left[T_e + V(\vec{r} - \vec{R}_{\ell s}) + V(\vec{r} - \vec{R}_{\ell' s'}) \right] \varphi_\nu(\vec{r} - \vec{R}_{\ell' s'}) \ . \quad (3)$$

Then the first order change of H and S are calculated by noting that the two-center matrix elements depend on the distance vector and not the individual positions.

To find the electron-phonon coupling matrix, we consider the equation of motion of the electronic operator $\hat{c}_\nu$ in the Heisenberg picture:

$$\hbar \imath \partial_t \hat{c}_\nu = [\hat{c}_\nu, \mathcal{H}] = [S^{-1}]_\nu H \hat{c}_\cdot \longrightarrow \underbrace{\hbar \imath \partial_t \hat{c}_n(\vec{k}') = \varepsilon_n(\vec{k}') \hat{c}_n(\vec{k}')}_{\text{For the unperturbed system}} \quad (4)$$

The displacements in terms of phonon creation and annihilation operators are described as usual:

$$\vec{u}_{\ell s} = \sum_\lambda \sum_{\vec{q}} e^{\imath \vec{q} \cdot \vec{R}_{\ell s}} \vec{\xi}^\lambda_s(\vec{q}) \sqrt{\frac{\hbar}{2 N_c m_s \omega_\lambda(\vec{q})}} \left(\hat{b}^\dagger_\lambda(-\vec{q}) + \hat{b}_\lambda(\vec{q}) \right) \quad (5)$$

where $\vec{\xi}_s{}^\lambda(\vec{q})$ denotes the polarization vector of atom *s* in phonon branch λ at wave-vector $\vec{q}$. Then the equation of motion of the perturbed system can be written as

$$\hbar \imath \partial_t \hat{c}_n(\vec{k}') = \varepsilon_n(\vec{k}') \hat{c}_n(\vec{k}') + \sum_m \sum_{\vec{q};\lambda} g^\lambda_{nm}(\vec{k}' - \vec{q}, \vec{q}) \hat{c}_m(\vec{k}' - \vec{q}) \left(\hat{b}^\dagger_\lambda(-\vec{q}) + \hat{b}_\lambda(\vec{q}) \right) \quad (6)$$

where g^λ_{nm} is the electron-phonon coupling matrix:

$$g^\lambda_{nm}(\vec{k}, \vec{q}) = \sqrt{\frac{\hbar}{2 N_c \omega_\lambda(\vec{q})}} U^*(\vec{k} + \vec{q}) \left\{ \left[\frac{\partial H}{\partial \vec{R}}(\vec{k}) - \frac{\partial S}{\partial \vec{R}}(\vec{k}) \varepsilon_m(\vec{k}) \right] \cdot \frac{e^{\imath \vec{q} \cdot \vec{R}_0} \vec{\xi}^\lambda(\vec{q})}{\sqrt{m_s}} \right.$$
$$\left. - \left[\frac{\partial H}{\partial \vec{R}}(\vec{k} + \vec{q}) - \frac{\partial S}{\partial \vec{R}}(\vec{k} + \vec{q}) \varepsilon_m(\vec{k}) \right] \cdot \frac{e^{\imath \vec{q} \cdot \vec{R}_0} \vec{\xi}^\lambda(\vec{q})}{\sqrt{m}} \right\} U(\vec{k}) \quad (7)$$

Relaxation Time

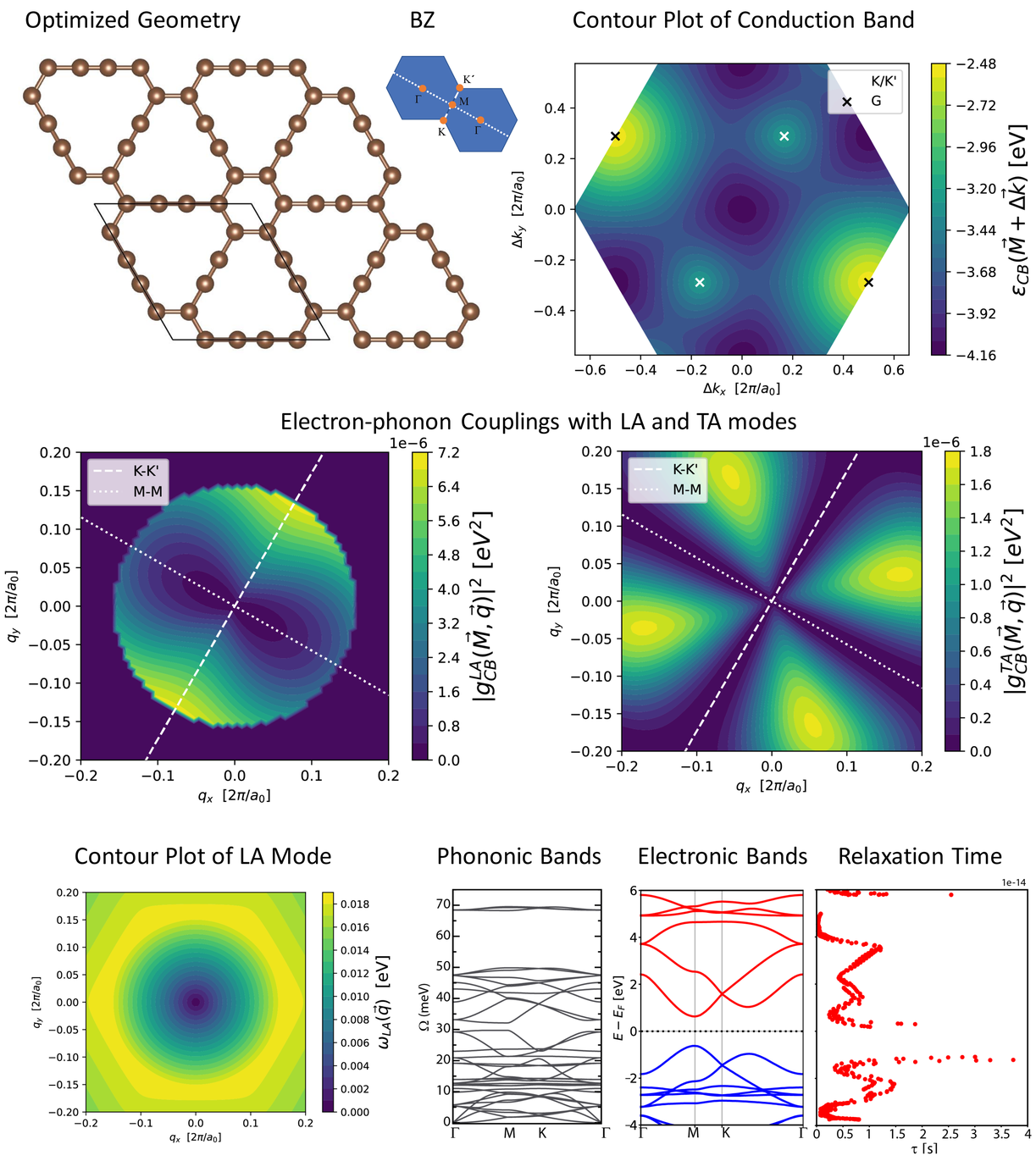
Here we use the self-energy relaxation time approximation (SERTA) [Samuel Poncé *et al* 2020 *Rep. Prog. Phys.* 83 036501] in which the scattering rate is defined as:

$$\tau_n^{-1}(\vec{k}) = \sum_m \int \frac{d^3 q}{\Omega_{BZ}} \tau^{-1}_{nm}(\vec{k}, \vec{k} + \vec{q}) \quad (8)$$

where $\tau_{nm}{}^{-1}(\vec{k}, \vec{k} + \vec{q})$ is the partial decay rate which is given in terms of the electron-phonon coupling matrix *g* and the occupation factors of the involved states:

$$\tau^{-1}_{nm}(\vec{k}, \vec{k} + \vec{q}) = \frac{2\pi}{\hbar} \sum_\lambda |g^\lambda_{mn}(\vec{k}, \vec{q})|^2 \left[\left(n_B(\omega_\lambda(\vec{q})) + 1 - f^0(\varepsilon_m(\vec{k} + \vec{q})) \right) \delta(\varepsilon_m(\vec{k} + \vec{q}) - \varepsilon_n(\vec{k}) + \hbar \omega_\lambda(\vec{q})) \right.$$
$$\left. + \left(n_B(\omega_\lambda(\vec{q})) + f^0(\varepsilon_m(\vec{k} + \vec{q})) \right) \delta(\varepsilon_m(\vec{k} + \vec{q}) - \varepsilon_n(\vec{k}) - \hbar \omega_\lambda(\vec{q})) \right] \ . \quad (9)$$

Results



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complexnano materials · DRESDEN concept · ULTIMATE ITN NETWORK

REFERENCES

DFTB+ · fhi · EPW · BoltzTraP2 · Phonopy · Phoebe