



Surface hopping dynamics in periodic solid-state materials with a linear vibronic coupling model

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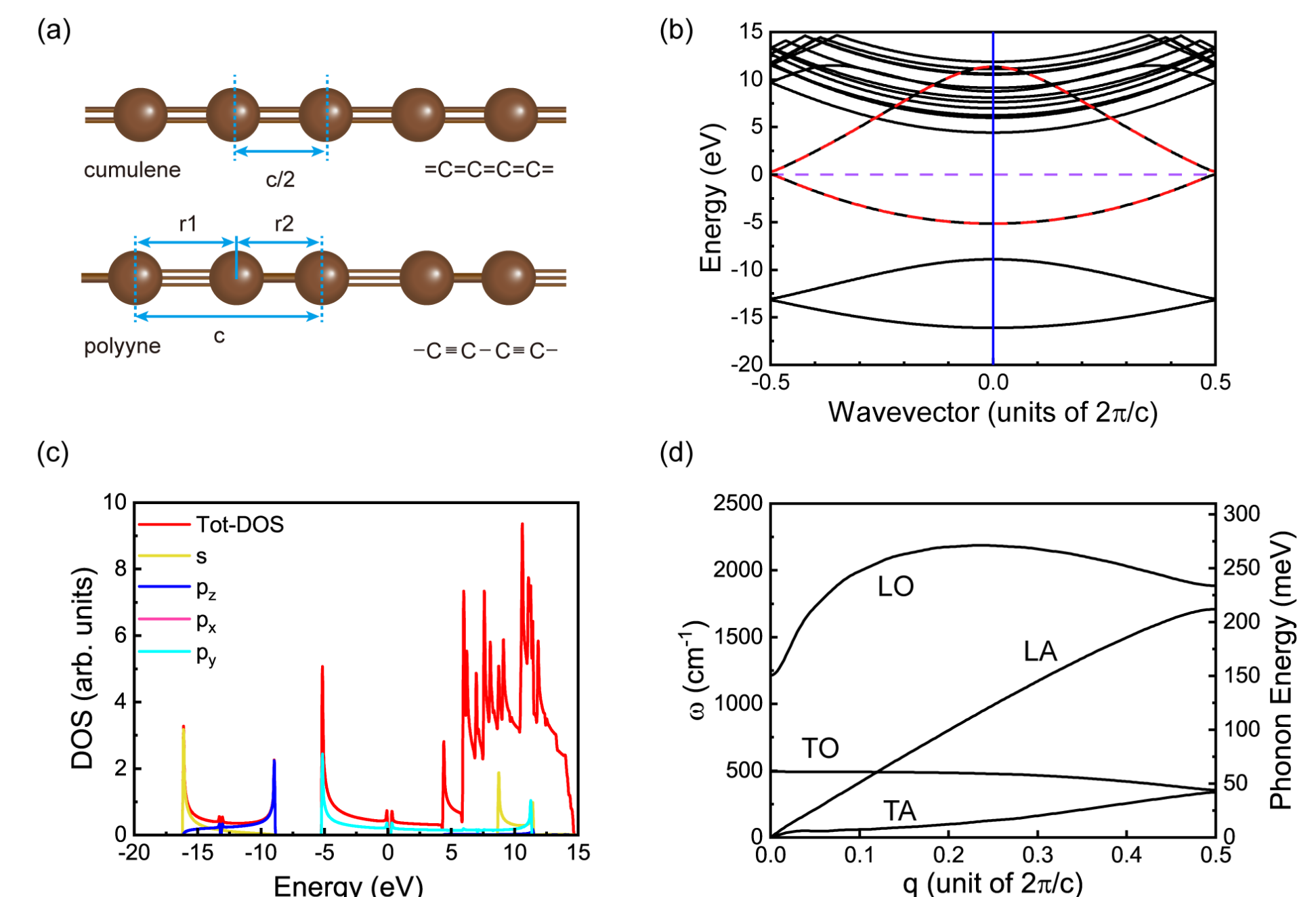
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Abstract

We report a surface hopping approach in which the implemented linear vibronic coupling Hamiltonian is constructed and the electronic wavefunction is propagated in the reciprocal space. The parameters of the linear vibronic coupling model, including onsite energies, phonon frequencies, and electron-phonon couplings, are calculated with density-functional theory and density-functional perturbation theory, and interpolated in fine sampling points of the Brillouin zone with maximally localized Wannier functions. Using this approach, we studied the relaxation dynamics of the photo-excited hot carrier in a one-dimensional periodic carbon chain. The results show that the completeness of the number of Hilbert space k -points and the number of phonon q -points play important roles in the hot carrier relaxation processes. By calculating the relaxation times of hot carriers under different reciprocal space sampling and extrapolating with the stretched-compressed exponential function, the relaxation times of hot electrons and holes in the quasi-continuous energy band are obtained. By considering the feedback effect in the hopping processes and analyzing the time-dependent phonon energy in different normal modes, we found that the long-wave longitudinal optical phonons play a major role in the relaxation dynamics of hot electrons and holes. We therefore provided herein an efficient and accurate approach for modeling the photophysical processes in periodic solid-state material systems.

Electron structure of infinite LCC



(a) Two possible structures of the ideal infinite carbon-atom chains: an equalized structure with double bonds (cumulene) and alternate single-triple bonds (polyene). (b) DFT calculated (black solid lines) and MLWFs interpolated (red dotted lines) band structure of infinite polyene. (c) The projected density of states of infinite polyene. (d) Phonon dispersion of the optimized infinite polyene.

Theory of fewest switches surface hopping in the LVC model for periodic system

In the second quantization form, when considering the first-order electron-phonon coupling, the Hamiltonian of the system can be written as:

$$H = \sum_{nk} \varepsilon_{nk} \hat{c}_{nk}^\dagger \hat{c}_{nk} + \sum_{q\nu} \hbar \omega_{q\nu} \left(\hat{b}_{q\nu}^\dagger \hat{b}_{q\nu} + \frac{1}{2} \right) + \frac{1}{\sqrt{N_p}} \sum_{\mathbf{k}, \mathbf{q}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} \left(\hat{b}_{q\nu} + \hat{b}_{-q\nu}^\dagger \right)$$

By convert the phonon creation and destruction operators ($\hat{b}_{q\nu}^\dagger$ and $\hat{b}_{q\nu}$) into the normal mode coordinate, $Q_{q\nu}$, in the harmonic approximation, the Hamiltonian can be rewritten as:

$$H(Q) = H_e(Q) + H_p(Q)$$

$$H_e(Q) = \sum_{nk} \varepsilon_{nk} \hat{c}_{nk}^\dagger \hat{c}_{nk} + \frac{1}{\sqrt{N_p}} \sum_{\mathbf{k}, \mathbf{q}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) \hat{c}_{m\mathbf{k}+\mathbf{q}}^\dagger \hat{c}_{n\mathbf{k}} Q_{q\nu} \sqrt{\frac{2\omega_{q\nu}}{\hbar}}$$

$$H_p(Q) = \sum_{q\nu} \left(\frac{1}{2} \omega_{q\nu}^2 |Q_{q\nu}|^2 + \frac{1}{2} |P_{q\nu}|^2 \right)$$

By diagonalizing the single electron Hamiltonian, $H_e(Q)$, in any normal mode coordinate, $\{Q\}$, we can get the adiabatic states, $\{|\Phi_i(Q)\rangle = \sum_{nk} P_{i,nk}(Q) |n\mathbf{k}\rangle\}$, in terms of the diabatic Bloch orbitals, and the corresponding energies, $\{E_i(Q)\}$, to construct the adiabatic potential energy surfaces (PES). Using Wannier interpolation^[2], we can get the Hamiltonian in any fine sampling points of the Brillouin zone. The excited electronic wavefunction can expressed in the adiabatic representation:

$$|\Phi(t)\rangle = \sum_i c_i(t) |\Phi_i(Q(t))\rangle$$

Substituting this wavefunction into the time-dependent electronic Schrodinger equation, the wavefunction coefficients are propagated as:

$$\dot{c}_i = \frac{1}{i\hbar} c_i E_i - \sum_{j \neq i} c_j \sum_{q\nu} \dot{Q}_{q\nu} \cdot d_{ij}^{q\nu}$$

where $d_{ij}^{q\nu} = \langle \Phi_i | \frac{\partial}{\partial Q_{q\nu}} | \Phi_j \rangle$ is the nonadiabatic coupling. The nuclear equations of motion are transformed into the normal coordinates and modeled by the Langevin equations to account for the system-bath coupling:

$$\ddot{Q}_{q\nu} = -\omega_{q\nu}^2 Q_{q\nu} - \frac{dE_a}{dQ_{q\nu}} - \gamma_{q\nu} \dot{Q}_{q\nu} + \xi_{q\nu}$$

where a indicates the active adiabatic PES, $\gamma_{q\nu}$ is the friction coefficient characterizing system-bath coupling strength and $\xi_{q\nu}$ is a Markovian Gaussian stochastic force. Both the electronic and normal mode differential equations can be solved with the standard fourth-order Runge-Kutta (RK4) method. Based on the Hellmann-Feynman theorem, we obtain:

$$d_{ij}^{q\nu} = \frac{1}{E_j - E_i} \sqrt{\frac{2\omega_{q\nu}}{\hbar N_p}} \sum_{mn, \mathbf{k}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) P_{i, m\mathbf{k}+\mathbf{q}}^* P_{j, n\mathbf{k}}$$

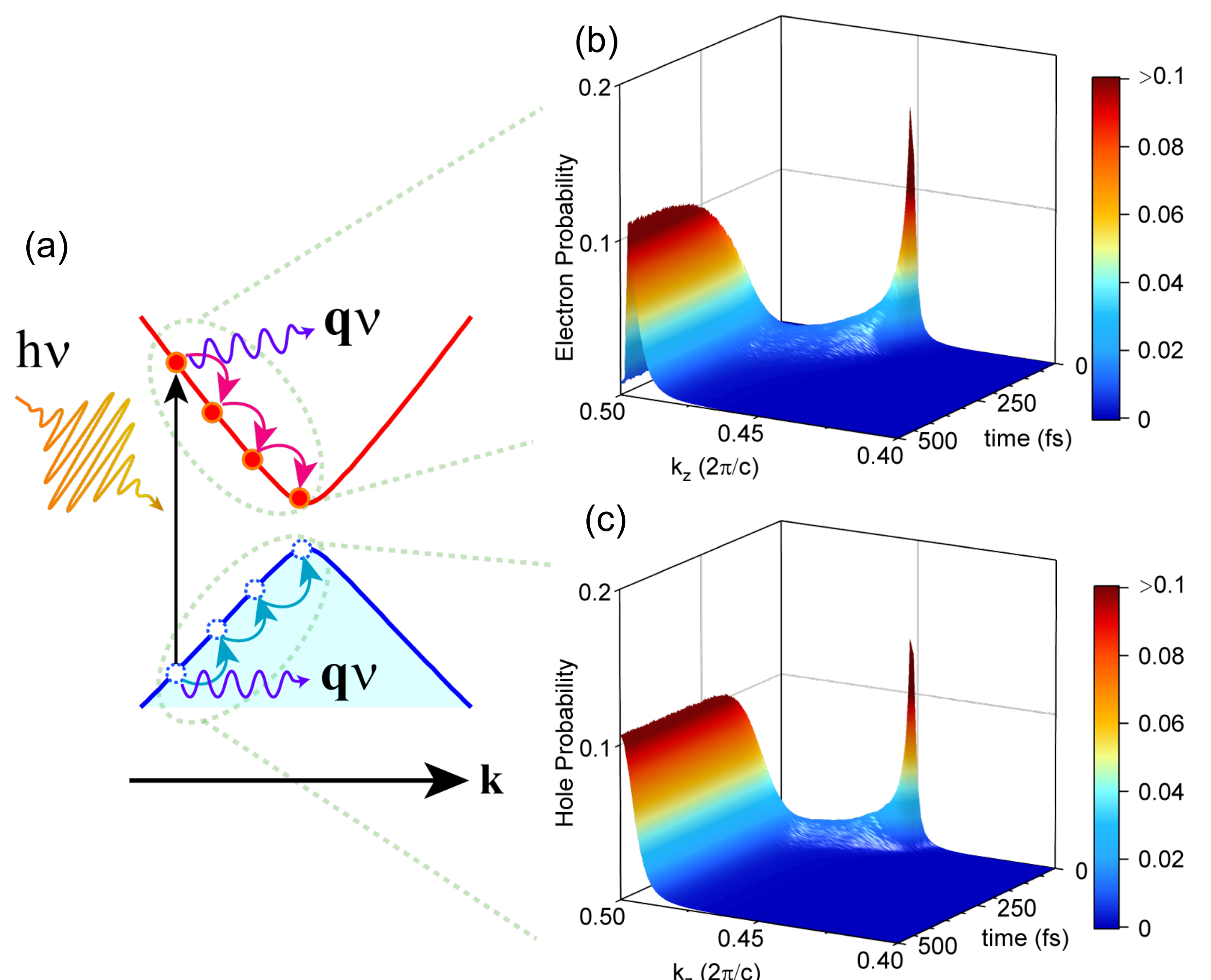
$$\frac{dE_i}{dQ_{q\nu}} = \sqrt{\frac{2\omega_{q\nu}}{\hbar N_p}} \sum_{mn, \mathbf{k}} g_{mn\nu}(\mathbf{k}, \mathbf{q}) P_{i, m\mathbf{k}+\mathbf{q}}^* P_{i, n\mathbf{k}}$$

$$\frac{d^2 E_i}{dQ_{q\nu} dQ_{q'\nu'}} = 2 \sum_{j \neq i} (E_j - E_i) (d_{ji}^{q\nu})^* d_{ij}^{q'\nu'}$$

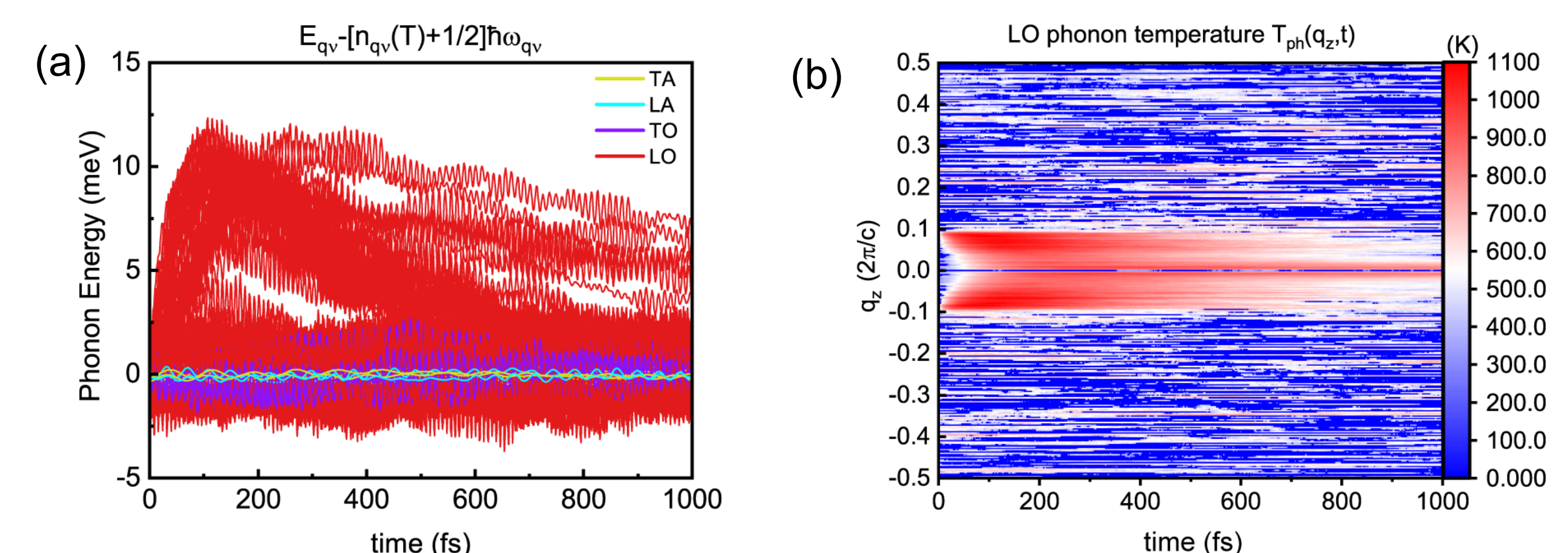
With Tully's FSSH algorithm^[3], the switching probability

$$g_{ai} = \frac{2 \text{Re} \left[c_a^* \sum_{q\nu} \dot{Q}_{q\nu} d_{ai}^{q\nu} \right]}{c_a^* c_a} \cdot dt$$

Hot carrier relaxation in polyene



(a) Schematic diagram of hot carrier generation and carrier relaxation by optical excitation with an energy of 2.0 eV in one-dimensional carbon lines. Probability of hot electron (b) and hole (c) over the conduction band states and valence band states.



(a) Phonon energy deviates from the average potential energy of thermal equilibrium. (b) Phonon temperature variation with time for longitudinal optical modes. The initial hot carriers are excited with the 2.0 eV energy laser, and then propagated at temperature 300 K. The Hamiltonian is built with the BvK supercell containing $N_p=480$ cells.

Reference

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