Intermediate Polaronic Charge Transport in Organic Crystals from a Cumulant plus Green-Kubo First-Principles Approach

Benjamin K. Chang,† Jin-Jian Zhou,† Nien-En Lee,† and Marco Bernardi†

†Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, California 91125, USA

Predicting the electrical properties of organic molecular crystals (OMCs) is challenging due to their complex crystal structures and electron-phonon (e-ph) interactions. Charge transport in OMCs is conventionally categorized into two limiting regimes – band transport, characterized by weak e-ph interactions and governed by low-energy intermolecular vibrations, and charge hopping, where strong e-ph interactions form localized polarons that diffuse slowly via thermally activated processes. However, between these two limiting cases there is a common, but less well understood intermediate transport regime where polarons are present but transport does not occur via hopping. Here we show accurate calculations of the carrier mobility in the intermediate transport regime, which contribute to shed light on its microscopic origin. We combine a finite-temperature cumulant method to describe the strong e-ph interactions and Green-Kubo transport calculations. Our study on naphthalene crystal demonstrates that we can accurately predict the electron mobility in the intermediate regime, within a factor of 1.5–2 of experiment between 100–300 K. Our analysis reveals that electrons couple strongly with both inter- and intramolecular phonons in the intermediate regime, as evidenced by the formation of a broad polaron satellite peak in the electron spectral function and by significant changes in the quasiparticle peak linewidth and spectral weight. These higher-order e-ph interactions make transport calculations based on the Boltzmann equation inadequate to describe the intermediate regime. Our study advances the understanding of the intermediate regime and paves the way for quantitative modeling of charge transport in complex organic crystals.

Organic molecular crystals (OMCs) possess complex crystal structures with an intricate interplay of electronic and structural degrees of freedom. Their electronic properties range from metallic to semiconducting or insulating, and they can host ferroelectricity [1], magnetism [2] and superconductivity [3]. OMCs are also versatile materials with broad applications, for example in electronics [4], light-emitting diodes [5, 6], spintronics [7, 8], batteries [9, 10] and solar cells [11–13]. The charge carrier mobility is a key figure of merit for organic materials in these devices [14–17]. Yet, understanding charge transport and accurately predicting the mobility in OMCs remain open challenges. Due to the presence of electron-phonon (e-ph) interactions ranging from weak to strong [18], the mobility varies dramatically among different OMCs, both in magnitude and temperature dependence [16]. Even in the same organic crystal, electron and hole carriers can exhibit different transport regimes, and the mobility can vary by orders of magnitude for different crystallographic directions.

Charge transport in OMCs is often classified into two limiting cases – the band transport and polaron hopping regimes, each entailing specific transport mechanisms [19]. In band transport, charge carriers are delocalized, the e-ph coupling is weak, and the mobility is correspondingly high (>10 cm²/Vs) and characterized by a power-law decrease with temperature. Band transport in OMCs is usually governed by scattering of carriers with low-energy acoustic and intermolecular phonons [18], with the corresponding e-ph interactions often modeled by the Peierls Hamiltonian [20]. Due to the weak coupling, these e-ph interactions can be described within lowest-order perturbation theory, and the mobility can be accurately predicted in the framework of the Boltzmann transport equation (BTE) [18, 21–23]. In the band regime, first-principles calculations that take into account all phonon modes have shed light on the charge transport mechanisms [18, 24]. In the polaron hopping regime, electrons interact strongly with the phonons, forming self-localized (small) polarons which are often modeled with the Holstein Hamiltonian to describe intramolecular e-ph interactions [25]. The resulting charge transport is dominated by thermally activated polaron hopping and is often described with Marcus theory [26, 27]. The mobility in the polaron hopping regime is relatively small, usually below 0.1 cm²/Vs.

Between these two limiting scenarios, OMCs also exhibit an intermediate transport regime, for which neither the band transport nor the polaron hopping pictures are fully adequate [19, 27]. In the intermediate regime the mobility exhibits a bandlike power-law temperature dependence [27–29], yet polarons can be present and low mobility values (<1 cm²/Vs) are common [19]. A signature of intermediate transport is the violation of the Mott-Ioffe-Regel limit [30], whereby the carrier mean-free-paths become smaller than the intermolecular distance [27], making the BTE description inadequate.

Various approaches have been employed to study intermediate transport in OMCs. These approaches start from either a Holstein Hamiltonian, a (Peierls-type) dynamical disorder Hamiltonian, or a combination of both, and obtain the mobility via linear-response theory [31–34], diffusion simulation [35, 36], surface hopping method [37], or transient localization calculation [38, 39]. These methods are highly valuable for studies of OMCs, although they usually rely on simplifying assumptions.
such as including only specific phonon modes and e-ph interactions, or fitting model parameters to experiments. To date, first-principles approaches to predict charge transport in the intermediate regime with quantitative accuracy are scarce, especially within rigorous treatments based on many-body perturbation theory.

Here we show accurate calculations of the mobility in the intermediate charge transport regime in OMCs. Focusing on naphthalene crystal as a case study, we employ a finite-temperature cumulant approach [28] to capture the strong e-ph interactions and polaron effects characteristic of the intermediate regime, and employ Green-Kubo theory to compute the electron mobility. All phonon modes are included and treated on equal footing. This cumulant plus Kubo (CK) approach is shown to predict the electron mobility in the intermediate regime with a high accuracy, within a factor of two of experiment between 100–300 K for crystallographic directions parallel to the naphthalene molecular planes. We additionally show the failure of the BTE to describe the mobility in the intermediate regime.

Our analysis of the electronic spectral functions reveals the presence of a broad satellite next to the quasiparticle (QP) peak, explaining the breakdown of the BTE and the band transport picture. Although the polaron satellite peak includes contributions from both inter- and intramolecular phonons, we find that the mobility is mainly limited by low-energy intermolecular phonons, similar to the band transport regime. Finally, for charge transport normal to the molecular planes, we find that both the BTE and CK approaches cannot correctly predict the mobility, which experimentally is nearly temperature independent and governed by small polaron hopping [40–42]. This finding restricts the applicability of the CK method to intermediate e-ph coupling strengths. Taken together, our treatment demonstrates the presence of polaron effects and the interplay of low- and high-energy phonon modes in the intermediate transport regime in OMCs. Our results provide a blueprint for studying transport in the bandlike and intermediate regimes in a wide range of organic crystals.

I. COMPUTATIONAL METHODOLOGY

We compute the ground state electronic structure of naphthalene crystal using plane-wave density functional theory (DFT) calculations with the QUANTUM ESPRESSO code [43, 44]. We employ the generalized gradient approximation [45] and norm-conserving pseudopotentials [46] from Pseudo Dojo [47]. The DFT band structure is refined using GW calculations (with the YAMBO code [48, 49]) to better capture dynamical screening effects. Maximally localized Wannier functions [50] are generated with the WANNIER90 code [51] following a procedure similar to Ref. [18]. We compute the e-ph interactions and charge transport separately at four temperatures (100, 160, 220, and 300 K), using different experimental lattice parameters at each temperature [52] and relaxing the atomic positions with DFT. After obtaining the lattice dynamics and e-ph perturbation potentials from density functional perturbation theory (DFPT) [53], we compute and interpolate the e-ph coupling matrix elements with the PERTURBO code [54]. Additional details on the numerical calculations are provided in the Methods section.

Using the computed e-ph interactions, we study charge transport in the BTE and CK frameworks with the PERTURBO code [54]. In the BTE, the mobility tensor \( \mu_{\alpha \beta} \) is computed using the relaxation time approximation (RTA):

\[
\mu_{\alpha \beta}(T) = \frac{2e}{n_c V_{uc}} \int dE \left( -\frac{\partial f(E,T)}{\partial E} \right) \times \sum_{nk} \tau_{nk}(T) v_{nk}^\alpha v_{nk}^\beta \delta(E - \varepsilon_{nk}),
\]

where \( \alpha \) and \( \beta \) are Cartesian directions parallel to the crystal principal axes, \( T \) is the temperature, \( e \) the electronic charge, \( n_c \) the carrier concentration, \( V_{uc} \) the unit cell volume, \( f \) the electronic Fermi-Dirac distribution and \( E \) is the electron energy. Here and below, \( n \) is the band index and \( k \) the crystal momentum of the electronic states. The BTE mobility depends on the electron band energies \( \varepsilon_{nk} \), the corresponding band velocities \( v_{nk} \), and the state-dependent e-ph relaxation times \( \tau_{nk} \) obtained within lowest-order perturbation theory [54, 55]. As a sanity check, we compute the mobility at 220 K by solving the full linearized BTE [54] with an iterative approach (ITA), and find that in naphthalene it gives results identical to the RTA, justifying our use of the RTA.

To properly treat strong e-ph interactions and include polaron effects on the mobility, we employ a finite-temperature cumulant approach in which the retarded electron Green’s function \( G_{nk}^R(t) \) is written using the exponential ansatz [28, 56–60]

\[
G_{nk}^R(t,T) = G_{nk}^{R,0}(t)e^{c_{nk}(t,T)},
\]

where \( G_{nk}^{R,0} \) is the non-interacting Green’s function and \( C_{nk} \) is the cumulant function, obtained here at finite temperatures from the lowest-order e-ph self-energy (see Methods). The electron spectral function is obtained from the Green’s function at each electron energy \( E \) using

\[
A_{nk}(E,T) = -\text{Im} G_{nk}^R(E,T)/\pi.
\]

In the CK method, the mobility tensor is computed directly from the spectral function using the linear-response Green-Kubo formula [28, 57, 61]:

\[
\mu_{\alpha \beta}(T) = \frac{1}{n_c e} \int dE \Phi_{\alpha \beta}(E,T),
\]

where integrand is referred to as the transport distribution function (TDF). Under the approximation of neglecting vertex corrections, the TDF can be written
FIG. 1. (a) Monoclinic crystal structure of naphthalene, with molecular a-b planes stacked in the plane-normal c* direction. (b) Band structure of naphthalene, showing the two lowest-energy electron (LUMO and LUMO+1) and hole (HOMO and HOMO-1) bands.

\[ \Phi_{\alpha\beta}(E,T) = \frac{\pi \hbar e^2}{V_{uc}} \sum_{nk} v_{nk}^\alpha v_{nk}^\beta |A_{nk}(E,T)|^2 \left( -\frac{\partial f(E,T)}{\partial E} \right), \]

where \( v_{nk} \) are the unperturbed electron band velocities, the same as those used in Eq. (1) [61]. The CK mobility defined in Eq. (4) is obtained from the cumulant spectral function, so it takes into account strong e-ph coupling and polaron effects. The CK calculations have been shown to provide results identical to the BTE-RTA in the limit of weak e-ph interactions (see Ref. [28] for a calculation on GaAs).

II. ELECTRON MOBILITY

The crystal structure of naphthalene consists of molecular planes in the a and b crystallographic directions stacked along the plane-normal c* direction [Fig. 1(a)]. We first discuss charge transport within the molecular planes. For hole carriers, we have previously shown that the in-plane mobility is bandlike and well described by the BTE [18]. In this work, we focus on the mobility of the electron carriers, which due to their flatter electronic bands with greater effective masses compared to holes [Fig. 1(b)] are expected to exhibit lower mobilities and a range of transport regimes. Only the electronic bands formed by the lowest unoccupied molecular orbital (LUMO) and the next-higher-energy orbital (LUMO+1) contribute to electron transport in the 100–300 K temperature range studied here, so we consider only these two bands in our mobility calculations.

Figure 2 shows the in-plane electron mobilities computed with the BTE and CK methods, and compares them with experimental data [40]. We fit each mobility curve with a \( T^{-n} \) power-law temperature trend and give the exponent \( n \) next to each curve. The results show clearly that the BTE predicts a much stronger temperature dependence of the mobility than in experiment, with errors in the computed exponents for transport along the a and b crystallographic directions (mobilities \( \mu_a \) and \( \mu_b \) in Fig. 2, respectively) of over 100% for \( \mu_a \) and 270% for \( \mu_b \) relative to the exponent \( n \) obtained by fitting the experimental results. Due to this error, the BTE greatly overestimates the mobility at low temperatures — for example, in the BTE \( \mu_a \) at 100 K is an order of magnitude greater than the experimental value. These results are a strong evidence of the failure of the Boltzmann equation to describe electron transport in naphthalene; the physical origin of this failure is further examined below. Note that this result is not due to our use of the RTA as the full solution of the BTE [54] gives results nearly identical to the RTA (see the ITA points at 220 K in Fig. 2). The fact that the mobility has a power-law temperature dependence but is not correctly predicted by the BTE is a hallmark of the intermediate transport regime [27, 29].

The CK calculations give significantly improved results (Fig. 2). The mobility values from the CK calculations are within a factor of 2 of experiment for \( \mu_a \) and 1.3 for \( \mu_b \) in the entire 100–300 K temperature range. The error in the \( T^{-n} \) exponent is reduced to 20% for \( \mu_a \) and 45% for \( \mu_b \) relative to experiment, a five-fold improvement in accuracy over the BTE results. Achieving this level of accuracy for quantitative predictions of the mo-
bility in OMCs has recently become possible in the band transport regime [18] but has so far remained challenging in the intermediate regime. As we discuss below, by combining the cumulant and Green-Kubo frameworks our CK approach can capture key polaron effects in the intermediate regime such as higher-order e-ph coupling and spectral weight transfer, resulting in improved mobility predictions. The accuracy of the CK method for studies of charge transport at intermediate e-ph coupling strengths, previously demonstrated for oxides [28], is now shown also for OMCs, opening new doors for quantitative studies of their transport properties.

III. ELECTRON SPECTRAL FUNCTION

The electron spectral function is central to the understanding of polaron effects [28] and charge transport in the intermediate regime. The spectral function can be viewed as the density of states of a single electronic state, and it integrates to one over energy due to a well-known sum rule [57]. In Fig. 3(a), we show the spectral function at three temperatures, using results obtained with our cumulant method for the electronic state at the conduction band minimum (CBM) [Γ point in Fig. 1(b)]. At 100 K, next to the main QP peak we can clearly identify a broad spectral feature associated with the combined excitation of an electron QP plus one or two phonons. This broad satellite combines contributions from multiple satellite peaks, as shown by the arrows in Fig. 3(a), and is a signature of polaron formation [28]. At higher temperatures, the QP and satellite peaks broaden and ultimately merge into a continuum at 300 K. The coexistence of a well-formed QP peak and broad satellites shows that large-polaron effects, characteristic of e-ph interactions with intermediate strength, are a key characteristic of the intermediate transport regime.

The spectral functions for various electronic states in the LUMO and LUMO +1 bands can be combined to obtain a cumulant band structure renormalized by the e-ph interactions. Figure 3(b) compares the band structures at 100 K computed with the GW method and with our cumulant calculations that use the GW band structure as input. The cumulant band structure, obtained by joining the QP peaks of the cumulant spectral functions at neighboring k-points, captures polaron effects such as QP mass and weight renormalization. At 100 K, where the QP peaks are well-defined, we find that the renormalized effective masses in the cumulant band structure are greater by 15−35% than in GW in the in-plane directions. This result shows that the cumulant approach can capture the band-narrowing due to e-ph interactions and polaron effects in OMCs [62].

The physical origin of the polaron satellite in Fig. 3(a) is of key importance. In the prototypical case of an inorganic polar material with strong e-ph coupling to longitudinal optical (LO) phonons, the satellite peaks are located at the LO-mode energy \( \omega_{LO} \) (and its multiples) relative to the QP peak [28, 63]. Here, due to the presence of a large number of phonon modes in OMCs (108 in napthalene), the satellites merge into a broad spectral feature resembling a long tail of the QP peak, with contributions from various phonon modes. To explain the origin of this broad satellite, in Fig. 3(c) we analyze the e-ph coupling strength for an electronic state near the CBM, as quantified by the absolute value of the gauge-invariant e-ph coupling, \( |g| \) (see Methods).

In naphthalene, the 12 lowest-energy phonon modes are intermolecular, and the remaining 96 modes are intramolecular vibrations [18]. In Fig. 3(a), the mode with the strongest e-ph coupling, an intramolecular phonon with energy \( \omega_1 \approx 0.1 \) eV, generates a satellite peak in the spectral function at energy \( \omega_1 \) relative to the QP peak. The intramolecular phonon with the second strongest e-ph coupling, with energy \( \omega_2 \approx 0.2 \) eV, gives a second contribution to the broad satellite, followed by a plateau at higher energy. Finally, the inflection point in the spectral function at energy \( \omega_1 + \omega_2 \) is due to higher-order e-ph coupling from the two modes with energies \( \omega_1 \) and \( \omega_2 \). The atomic displacements associated with these two intramolecular modes are shown in Fig. 3(d). Both modes involve vibrations of the hydrogen atoms, in one case in the carbon ring plane and in the other case normal to the carbon rings. Our analysis demonstrates that these intramolecular phonons are responsible for the formation of polarons in naphthalene. This strong coupling with intramolecular phonons and the associated satellite peak in the spectral function are consistent with recent results from the Holstein-Peierls model [33].

Interestingly, lowest-order theory is wholly inadequate to describe this polaronic regime with intermediate e-ph coupling strength. To show this result, we compute the Dyson-Migdal (DM) spectral function [see Eq. (A6)], which is obtained from the lowest-order e-ph self-energy and therefore does not include polaron effects. From the comparison of the cumulant and DM spectral functions in Fig. 3(a) it is clear that the DM spectral functions have a Lorentzian shape and lack any satellite structure. As a result, the subtle interplay between inter- and intramolecular phonons in the QP and satellite peaks cannot be captured in lowest-order theory. As we discuss below, this is the origin of the failure of the BTE to describe transport in the intermediate regime.

IV. FAILURE OF THE BOLTZMANN EQUATION

It is important to understand the microscopic origin of the failure of the BTE, and the success of the CK method, to describe transport in the intermediate regime. In the Green-Kubo framework, the mobility is given by an integral over electron energies [see Eq. (4)], which in principle combines contributions from all features of the spectral function. To quantify the contributions of the QP and satellite peaks to charge transport, we analyze the mobility integrand, the TDF in Eq. (5), and plot it together with the spectral functions in Fig. 3(a). We find that the TDF decays rapidly outside the QP peak, within energy
FIG. 3. (a) Spectral functions computed at three temperatures for the CBM electronic state. Results from the cumulant approach \( A_{CBM}^c \) are compared to the Dyson-Migdal spectral function \( A_{CBM}^{DM} \). The QP peak is chosen as the zero of the energy axis for each spectral function. The transport distribution function (TDF) in arbitrary units is also shown at each temperature. (b) Electron spectral function for the LUMO and LUMO+1 bands along a high-symmetry path, computed at 100 K using the cumulant method. The solid line is the GW band structure and the dashed line shows the renormalized cumulant band structure obtained by joining the QP peaks of the spectral functions. (c) Gauge-invariant e-ph coupling strength as a function of phonon energy. The energies \( \omega_1 \) and \( \omega_2 \) of the two phonon modes with strongest e-ph coupling are shown with vertical dashed lines. (d) Atomic displacements for the two intramolecular modes with the strongest e-ph coupling.

\( \omega_1 \) of the QP peak at low temperature and \( \omega_2 \) at 300 K. Spectral function features with energy greater than \( \omega_2 \) have no overlap with the TDF and cannot contribute to charge transport between 100–300 K. In this temperature range, although the mobility is mainly governed by the QP peak, polaron effects and the broad satellite also contribute in important ways.

First, due to higher-order e-ph coupling with intermolecular and low-energy intramolecular phonons, the QP peak linewidth in the cumulant spectral function is different than in the DM spectral function from lowest-order theory (see Fig. 4), where the linewidth corresponds to the scattering rate entering the BTE mobility calculation. The fact that the QP linewidth discrepancy is temperature and energy dependent (Fig. 4) explains why the BTE cannot correctly predict the value and temperature dependence of the mobility in the intermediate regime, corroborating our results in Fig. 2. In addition, the broad satellite in the cumulant spectral function limits the carrier mobility indirectly, by transferring spectral weight away from the QP peak (recall that the spectral function integrates to one over energy). The satellite peak at \( \omega_1 \) contributes directly to transport only above \( \sim200 \) K, where the QP peak broadens, merging with the satellite and overlapping with the TDF.

The picture that emerges is that electron transport in the naphthalene molecular planes is mainly governed by the scattering of QPs with renormalized weight, which couple directly with intermolecular and indirectly (via weight transfer) with higher-energy intramolecular phonons. The latter can also contribute directly to charge transport as the temperatures increases above 200 K. The ability of our CK approach to quantitatively describe these subtle e-ph interactions enables accurate predictions of the mobility and its temperature dependence in the intermediate regime, where the Boltzmann equation combined with lowest-order e-ph coupling fails as it cannot capture these essential polaron effects.
V. DISCUSSION

In naphthalene, measurements of the mobility in the direction normal to the molecular planes ($c^*$ direction in Fig. 1) point to a transport regime different from the in-plane directions. In experiments, the mobility along $c^*$ is less than 1 cm$^2$/Vs and is nearly temperature independent between 100−300 K [40–42]. These trends suggest that charge transport normal to the molecular planes may occur in the small-polaron hopping regime, where the quasiparticles are strongly localized and the e-ph interaction is so strong that a diagram-resummation technique such as the cumulant method is not expected to give accurate results.

We calculate the plane-normal mobility using both the BTE and CK methods, and compare the results with experiments in Fig. 5. The computed mobility decreases with temperature in both the CK and BTE approaches, deviating substantially from the nearly temperature independent mobility found in experiment. It is encouraging that the CK mobility agrees well with experiment at 100 K and its temperature dependence is weaker than in the BTE — fitting the temperature dependence with a $T^{-n}$ power law gives an exponent $n = 1.72$ in the CK and $n = 3.78$ in the BTE method, versus $n = 0.04$ in experiment. However, although the CK provides a significant improvement over the BTE, it is clear that neither method can accurately describe charge transport normal to the molecular planes.

The band dispersion in the GW electronic band structure is small along the plane-normal $c^*$-direction [$\Gamma$–Z direction in Fig. 3(b)], with large effective masses of order 15$m_e$ for the GW calculation done on the 100 K structure, and greater at higher temperature. Combined with the absence of a power-law temperature trend for the experimental mobility, this relatively flat band is a strong evidence that electrons are nearly localized to a single molecular plane and that transport in the plane-normal direction occurs via small-polaron hopping. The failure of the CK approach in this regime highlights the need for predictive first-principles approaches to study charge transport in the small-polaron hopping regime in OMCs.

VI. CONCLUSION

We investigated the electron mobility in naphthalene crystal as a paradigmatic case of intermediate charge transport regime in OMCs. Combining a finite-temperature cumulant method and Green-Kubo transport calculations, we demonstrated accurate predictions of the electron mobility and its temperature dependence in the intermediate regime. Our study reveals an interplay between low-energy intermolecular phonons responsible for limiting the mobility and intramolecular modes with strong e-ph coupling, which are responsible for the formation of polarons and their associated broad satellite peak in the spectral functions. The broad satellite removes spectral weight from the QP peak, modifying the mobility and its temperature dependence. By capturing these subtle polaron effects, our CK approach addresses the shortcomings of the BTE for modeling the intermediate transport regime. The limitations of the CK approach for studying polaron-hopping transport normal to the molecular planes are also analyzed. Taken together, our work sheds light on the microscopic mechanisms governing the intermediate transport regime and paves the way for accurate first-principles studies of charge transport in OMCs.

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Appendix A: Methods
1. First-principles calculations

We carry out first-principles density functional theory (DFT) calculations of the ground state and electronic structure of naphthalene using the QUANTUM ESPRESSO code [43, 44]. Thermal expansion of the lattice is taken into account by employing lattice constants [52] taken from experiments at four different temperatures of 100, 160, 220, and 300 K. All calculations are carried out separately at these four temperatures. The initial atomic positions are also taken from experiment [64, 65]. We use a kinetic energy cutoff of 90 Ry together with 2 × 4 × 2 and 4 × 4 × 4 k-point grids for self-consistent and non-self-consistent calculations, respectively. The Grimme van der Waals correction [66, 67] is included during structural relaxation of the atomic positions. To improve the description of dynamical electronic correlations, we correct the DFT electronic band structure with $G_0W_0$ calculations, which include 500 bands in the polarization function and a cutoff of 10 Ry in the dielectric screening using the Yambo code [49]. The WANNIER90 code [51] is employed to obtain Wannier functions and the corresponding transformation matrices, using the selected-columns-of-the-density-matrix method [68]. The lattice dynamics and e-ph perturbation potential are computed with density functional perturbation theory (DFPT) [53] calculations on a 2 × 4 × 2 q-point grid (here and below, q is the phonon wavevector). Using our PERTURBO code [54], the electron and phonon data are combined to form the e-ph coupling matrix elements [54]:

$$g_{mn\nu}(k, q) = \sqrt{\frac{\hbar}{2\omega_{\nu}q}} \sum_{\kappa \alpha} \frac{e^{\kappa\alpha}_{q\nu}}{M_\kappa} \langle mk + q|\partial_{q\alpha\nu}V|nk\rangle,$$

(A1)

where $|nk\rangle$ are electronic Bloch states, $\omega_{\nu}q$ are phonon energies, $\partial_{q\alpha\nu}$ are e-ph perturbation potentials, $e^{\kappa\alpha}_{q\nu}$ are phonon displacement vectors, and $M_\kappa$ is the mass of atom $\kappa$. The absolute value of the gauge-invariant e-ph coupling strength shown in Fig. 3(b) is computed for each phonon mode $\nu$ and phonon wavevector $q$ as [54]

$$|g_\nu(k=0, q)| = \sqrt{\sum_{mn} |g_{mn\nu}(k=0, q)|^2/N_b},$$

(A2)

where $N_b$ is the number of selected bands. The mobility calculations use a fine k-grid of 60 × 60 × 60 for the BTE and 30 × 30 × 30 for the CK method. Both methods use between $10^5$–$10^6$ randomly selected q-points.

2. Electron-phonon scattering rate

The relaxation time $\tau_{nk}$ used in the BTE is computed as the inverse of the scattering rate, defined as [55]

$$\Gamma_{nk}(T) = \frac{2\pi}{\hbar} \sum_{mn\nu} |g_{mn\nu}(k, q)|^2 \times \left[ (N_{\nu,q} + 1 - f_{mk+q})\delta(\varepsilon_{nk} - \varepsilon_{nk+q} - \omega_{\nu q}) \ight. \\
+ (N_{\nu,q} + f_{mk+q})\delta(\varepsilon_{nk} - \varepsilon_{nk+q} + \omega_{\nu q}) \right],$$

(A3)

where $f_{nk}$ and $N_{\nu,q}$ are electron Fermi-Dirac and phonon Bose-Einstein occupations in thermal equilibrium, respectively.

3. Cumulant method

The cumulant ansatz assumes that the retarded Green’s function in the time domain takes the exponential form in Eq. (2), where the cumulant function $C_{nk}$ is defined as [28, 56]

$$C_{nk}(t, T) = \int_{-\infty}^{\infty} dE \frac{|\text{Im}\Sigma_{nk}(E + \varepsilon_{nk}; T)|}{\pi E^2} (e^{-iEt} + iEt - 1).$$

(A4)

Here, $\varepsilon_{nk}$ is the electron band energy, $E$ the electron energy, and $\Sigma_{nk}$ is the lowest-order (Fan-Migdal) e-ph self-energy [57]:

$$\Sigma_{nk}(E, T) = \sum_{mn\nu} |g_{mn\nu}(k, q)|^2 \times \left[ \frac{N_{\nu,q} + f_{mk+q}}{E - \varepsilon_{nk+q} + \omega_{\nu q} + i\eta} + \frac{N_{\nu,q} + 1 + f_{mk+q}}{E - \varepsilon_{nk+q} - \omega_{\nu q} + i\eta} \right]$$

(A5)

whose temperature dependence is due to the occupation factors $N_{\nu,q}$ and $f_{nk}$. After Fourier-transforming the retarded Green’s function in Eq. (2) to the energy domain, we obtain the electron spectral function using Eq. (3). We compute $\text{Im}\Sigma_{nk}(E)$ off-shell, using a fine energy $E$ grid, and $\text{Re}\Sigma_{nk}$ on-shell at the band energy $\varepsilon_{nk}$ and use them as input to obtain the spectral function $A_{nk}$ [28] as a function of electron energy $E$. Due to the exponential form of $G_{nk}$, the cumulant Green’s function includes contributions from higher-order e-ph Feynman diagrams [57].

4. Dyson-Migdal spectral function

The Dyson-Migdal (DM) spectral function is given by

$$A_{nk}^{DM}(E, T) = \frac{-\text{Im}\Sigma_{nk}(T)}{[E - \varepsilon_{nk} - \text{Re}\Sigma_{nk}(T)]^2 + [\text{Im}\Sigma_{nk}(T)]^2},$$

(A6)
where $\Sigma_{nk}(T)$ is the lowest-order e-ph self-energy [Eq. (A5)] computed on-shell at the band energy $\varepsilon_{nk}$. The DM spectral function has a Lorentzian shape as a function of energy, with a linewidth of $2\text{Im}\Sigma_{nk}(T)$ which is proportional to the e-ph scattering rate in Eq. (A3), $\Gamma_{nk}(T) = 2\text{Im}\Sigma_{nk}(T)/\hbar$ [55].

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