Off-diagonal carrier-phonon coupling and polaron transport

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Abstract. A method extending the Munn-Silbey approach has been applied to obtain the temperature dependence of transport properties of a generalized Holstein model incorporating simultaneous diagonal and off-diagonal carrier-phonon coupling. The Hamiltonian is partially diagonalized by a canonical transformation, and optimal transformation coefficients are determined in a self-consistent manner. Effects of off-diagonal coupling on the optimal transformation coefficients and diffusion coefficients have been discussed in details. The off-diagonal coupling has been revealed as a localization factor as well as a transport mechanism. Moreover, momentum-space variation of the transformation coefficients are found to be responsible for enhanced transport due to off-diagonal coupling.

1. Introduction

Theory of organic molecular crystals was established to deal with the complexity of charge transport from as early as 1950s [1, 2], when the Holstein molecular crystal model was introduced to account for carrier-phonon coupling. Charge transport in organic semiconductors, often described by polaron and disorder models as reviewed recently in Ref. [3], is governed by a number of factors such as the electronic coupling and carrier-phonon interactions. Early theories on polaron transport include the phenomenological model [4] and the polaron effective mass approach [5]. Microscopic models for polaron transport were later developed by Yarkony, Munn and Silbey[6, 7, 8, 9, 10] in 1980s using a density matrix approach, capable to account for the effects of electronic coupling, diagonal and off-diagonal carrier-phonon interaction of arbitrary strength over a full range of temperatures. More recently, models using the generalized master equation approach[11, 12, 13] and dynamical mean-field theory[14] have also been developed.

The effect of off-diagonal coupling is more difficult to tackle than its diagonal counterpart, and as a result, off-diagonal coupling has not been extensively treated before[15]. Following up on the Munn-Silbey transformation, Zhao et al. [16] devised a self-consistent routine to determine the transformation coefficients, demonstrating substantial corrections of the polaron band structure thanks to a built-in momentum dependence of the transformation coefficients. In our recent work[17], a combination of the Munn-Silbey transformation and Zhao’s self-consistent routine has been shown to be a robust approach to provide new insights into charge transport in the presence of off-diagonal carrier-phonon coupling. To further account for the effect of off-diagonal coupling, a more systematic study will be performed in this paper.

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The rest of the paper is organized as follows. Theoretical formulations for charge transport are first introduced in Section II. In Section III numerical results on transport properties obtained with our approach are displayed and discussed in detail with a focus on the effect of off-diagonal coupling on polaron transport. Finally, the conclusions are drawn in Section IV.

2. Methodology
The generalized Holstein Hamiltonian and canonical transformation to partially diagonalize it have been described in detail previously by Munn and Silbey [8, 9, 10], and more detailed work combining the self-consistent routine devised by Zhao et al. [16] and the Munn-Silbey approach [8, 9, 10] has been documented elsewhere. Thus, in this Section we will only briefly introduce the formalism first constructed in Ref. [17]. The generalized Holstein Hamiltonian in the momentum-space representation looks more compact than its site-space counterpart due to translational symmetry

\[ H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \omega_q (b_q^\dagger b_q + 1/2) + N^{-1/2} \sum_{kq} \omega_q f_{-k}^q a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger), \]  

with \( \epsilon_k = \epsilon + J_k \), and

\[ J_k = \sum_m e^{ik \cdot (R_n - R_m)} J_{nm}, \]  

where the nearest-neighbor transfer integral \( J_{nm} = J(\delta_{n,m+1} + \delta_{n,m-1}) \) is taken, and \( \omega_q \) is the phonon frequencies.

The carrier-phonon coupling coefficients can also be written as:

\[ f_{k}^q = \sum_m e^{-ik \cdot (R_n - R_m)} f_{n-m}^q, \]  

with following coupling geometry:

\[ f_{k}^q = g - i\phi[\sin(k) - \sin(k - q)], \]  

which indicates that the antisymmetric type of coupling is used throughout the paper.

Now the transformation takes the following form in the momentum-space representation:

\[ U = e^{-N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^\dagger - b_q) a_{k+q}^\dagger a_k}, \]  

and

\[ A_{k}^q = \sum_m e^{-i(k-q) \cdot R_n} e^{ik \cdot R_m} A_{nm}^q = (A_{-k-q}^q)^*. \]  

The transformation can then also be written as:

\[ U = e^{\sum_{k k'} a_k^\dagger S_{k k'} a_{k'}}, \]  

with

\[ S_{k k'} = N^{-1/2} A_{k-k'} (b_{k'}^\dagger - b_{-k'}) \]  

where \( S_{k k'} \) is an operator creating a net phonon with momentum \( k' - k \). This operator is essential towards the evaluation of a series of important matrices, where

\[ a_k \rightarrow \sum_{k'} \theta_{k k'} a_{k'}, a_k^\dagger \rightarrow \sum_{k'} \theta_{k k'}^\dagger a_{k'}^\dagger, \]
with

\[ \theta_{kk'} = [\exp(-S)]_{kk'}, \theta_{kk'}^\dagger = [\exp(S)]_{kk'} \]  

(10)

where \( S \) stands for matrix \( S_{kk'} \). The transformed Hamiltonian can be partitioned into \( H_0 \) terms (zeroth order part) and the perturbative \( V \) terms. Thermal average of the \( \theta_{kk'} \) operator has the property:

\[ \langle \theta_{k,k+q}^\dagger \theta_{k',k'+q'} \rangle = \langle \theta_{k,k+q}^\dagger \theta_{k',k'+q} \rangle \delta_{qq'}, \]  

(11)

which ensures the correct thermal equilibrium behavior of \( H_0 \) by keeping it diagonal in excitation wave vector.

By applying the thermal average routine shown in Ref. [9], the transformed Hamiltonian can be written in a simpler form, which facilitates the numerical calculations. The zeroth order Hamiltonian \( H_0 \) now can be written as:

\[ \tilde{H}_0 = \sum_k \tilde{\epsilon}_k a_k a_k^\dagger + \sum_q \omega_q (b_q^\dagger b_q + \frac{1}{2}), \]  

(12)

and

\[ \tilde{\epsilon}_k = \epsilon + \tilde{J}_k - N^{-1} \sum_q |A_k^q|^2 \omega_q. \]  

(13)

The renormalized transfer integral in Eq. 13 is given by:

\[ \tilde{J}_k = \sum_{k'} \langle \theta_{kk'} \rangle^2 (\exp E_{kk'}^0)_{kk'} J_{kk'}, \]  

(14)

where the triadic \( E_{kk'}^0 \) is a quantity introduced to yield a simpler form of the transformed Hamiltonian, with following relationship:

\[ E_{kk'}^0 = N^{-1}(2n_{k-k'} + 1)(A_{k-k'}^*-A_{k-k'}), \]  

(15)

here \( n_q \) is the Bose-Einstein distribution, with \( 2n_q + 1 = \coth(\frac{\hbar}{2} \beta \hbar \omega) \).

With the form of \( A_k^q \) shown in Eq. 18, the perturbation part \( V \) of \( \tilde{H} \) can be written as:

\[ V = \sum_{kk'kk''} J_{kk'} T_{kk'',kk''} - 2N^{-1} \sum_q \omega_q f_{k-k'}^q A_{-k-q,k',k''} T_{k+q,k',k''-q} + N^{-1/2} \sum_q \omega_q f_{k-k'}^q T_{k+q,k',k''} (b_{-k-q}^\dagger a_{k'} + b_{-k-q} a_{k'}^\dagger). \]  

(16)

where

\[ T_{kk'',ww'} = \langle \theta_{kk'}^\dagger \theta_{ww'} \rangle - \langle \theta_{kk'}^\dagger \theta_{ww} \rangle, \]  

(17)

and \( A_k^q \) takes following form:

\[ A_k^q = \sum_{k'} f_{k-k'}^q \langle \theta_{kk'}^\dagger \theta_{k',k''} \rangle, \]  

(18)

to curb this possible uncontrolled growth of \( \theta_{kk'} \).

In this study, the transformation coefficients \( A_k^q \) (A-matrix) will be obtained numerically prior to the calculations of the transport properties. The detailed numerical variational procedures can be found in Ref. [16]. In performing the variational calculations, the transformation coefficients must satisfy following self-consistency equations together with Eq. 15:

\[ \langle \theta_{kk'} \rangle = \exp[-\frac{1}{2} \sum_{kk'} E_{kk'}^0], \]  

(19)

\[ A_k^q = \langle \theta_{k-q} \rangle \langle \theta_k \rangle \sum_{k'} f_{k'}^q \exp(E_{k'})_{kk'}. \]  

The self-consistency equations above follow the Munn-Silbey secular elimination scheme. In Ref. [9], this set of equations was solved upon further approximates on \( A_k^q \), whereas in this paper, it is solved numerically with an accuracy unavailable previously.

In the Munn-Silbey approach [9], the transformation coefficients \( A_k^q \) was at first approximated by the scaling parameters \( \xi \) and \( \eta \) as:

\[ A_k^q = g \xi - i \phi \eta [\sin(k) - \sin(k - q)]. \]  

Numerical evaluation of the Eqs. 15-20 is facilitated by rewriting the Eq. 21 with real matrices \( \xi_k^q \) and \( \eta_k^q \) in the following form:

\[ A_k^q = g \xi_k^q - i \phi \eta_k^q [\sin(k) - \sin(k - q)]. \]

In the equation above, the sine function leads to zero imaginary part along the line with \( q = 0, 2k \pm \pi \). In the numerical calculation, the lines with \( q = 0 \) and \( q = 2k \pm \pi \) are treated as removable singularities. Moreover, the values of \( \eta_k^q \) along these lines are chosen to be analytically connect with neighboring values [16]. The variational matrices \( \xi_k^q \) and \( \eta_k^q \) chosen can preserve the symmetry properties of \( A_k^q \) in a way such that \( \xi_k^q = \xi_{k-q} \) and \( \eta_k^q = \eta_{k-q} \).

The diffusion coefficient is closely related to the mean square displacement of an excitation in a given period of time. For the transformation scheme shown in this paper, the mean square displacement can be calculated from the excitation density matrix. The diffusion coefficient can then be expressed as [8, 10]:

\[ D = a^2 \langle \nu_k^2 / \Gamma_{kk} + \gamma_{kk} \rangle, \]

where \( a \) is the nearest neighbor distance, \( \mathbf{k} \) is the wave vector, and \( \nu_k = \nabla_k E_k \). The double bracket denotes the thermal average over the polaron states of energy \( E_k \), where \( \Gamma_{kk} \) and \( \gamma_{kk} \) are the scattering and hopping rates expressed as

\[ \Gamma_{kk'} = N^{-1} \sum_{k \neq k'} W_{k,k;k',k'}, \]

\[ \gamma_{kk} = \frac{1}{2} \nabla^2 \sum_k \text{Re} \left( \frac{1}{2} W_{k;k,k';q,k'+q} - W_{k,k+q;k',k'+q} \right)_{q=0}. \]

where \( W_{k,k+q;k',k'+q} \), crucial to the calculation of diffusion coefficient, are given by

\[
W_{k,k+q;k',k'+q} = \int_0^\infty dt \{ \langle V_{k'+q,k+q} V_{k,k'}(t) \rangle \exp[-i(E_{k'+q} - E_{k+q})t] + \langle V_{k'+q,k+q}(t) V_{kk'} \rangle \exp[-i(E_k - E_{k'})t] \},
\]

here the single angular bracket denotes the average of the residual interaction \( V_{kk'}(t) \) over phonon states. Using the formulism above, the evaluation of \( D \) will be done numerically here without introducing further approximations as in Ref. [8, 9]. With the diffusion coefficient \( D \), the mobility can be easily obtained with the Einstein relation \( \mu = eB \). As this work focus more on the numerical studies of off-diagonal coupling effect, one can refer to Ref. [17] for the details of correlation functions.
3. Results and Discussion
The numerical evaluation involves the solution of the self-consistency equations Eqs. 15, 19 and 20. Since the procedures for the evaluation of transformation coefficients $A_k^\phi$ have been detailed in Ref. [16, 17], here, we only concentrate on some of the important issues related to the transport properties, especially the role of off-diagonal coupling.

As demonstrated in Figs. 1(b)-(e), the A-matrix parameters $\xi_k^q$ and $\eta_k^q$ in Eq. 22 obtained with

**Figure 1.** (a) Polaron band structure with different values of off-diagonal coupling strength $\phi^2$ ranging from 0.0 to 0.7. A-matrix parameters $\xi_k^q$ and $\eta_k^q$ as functions of increasing off-diagonal coupling strength $\phi^2$ of (b)0.1, (c) 0.3, (d) 0.5 and (e) 0.7. The other parameters are: $J=0.1$, $g^2=0.3$ and $T=1.0$. 
In the vicinity of $q = 0$, $\xi_k^q$ is weakly structured and relatively flat with respect to $k$, while the wave vector dependence of $\eta_k^q$ is much more pronounced than that of $\xi_k^q$. Regardless of the coupling strength, the wave vector dependence of $\xi_k^q$ and $\eta_k^q$ has a characteristic “manta-ray” shape. As revealed from Figs. 1(b)-(e), the A-matrix parameters tend to have stronger wave vector dependence for larger $\phi$. It is also interesting to look into the change in the polaron band structure as a function of $\phi$. Greater wave vector dependence found for stronger off-diagonal coupling cases indicates that this parameter is responsible for the formation of bimodal shape of the polaron bands. It is however counterintuitive to see that the greater momentum-space variability of $\xi_k^q$ and $\eta_k^q$ due to larger $\phi$ translates into a narrower polaron band. The key towards a possible explanation lies in the binding energy being proportional to the average of $|A_k^q|^2$. The average binding energy obtained in the current approach is significantly larger while the average Debye-Waller factor is much smaller, leading eventually to the narrowing of the band. Further, the $\phi$ dependence in Fig. 1(a) can also be comprehended since a larger wave vector variation in $\xi_k^q$ and $\eta_k^q$ gets transformed into a weaker distortion of the energy band, an effect explained.

**Figure 2.** Diffusion coefficients $D$ versus scaled temperature $k_BT/\omega$ for a 1 dimensional chain with 6 sites, where the diagonal coupling strength $g^2$ takes (a) 0.1, (b) 0.3, (c) 0.5 and (d) 1.0. The off-diagonal coupling strength $\phi^2$ ranges from 0.0 to 0.7 for all figures. Finally, the transfer integral $J=0.1$ for all cases.
in detail in Ref. [16, 17].

Stronger \( \phi^2 \) leads to a smaller diffusion coefficient at very low temperatures as shown in Fig. 2. However, it is more interesting to note the nonmonotonic changes in the diffusion coefficient (i.e., a “hump”) as a function of the temperature in Fig. 2. This nonmonotonic behavior becomes even more pronounced when \( g^2 \) and \( \phi^2 \) are both large as indicated in Fig. 2(d), suggesting that the diffusion coefficient reaches its peak value at \( T \approx 0.5 \). Such behavior is a strong evidence that the off-diagonal carrier-phonon coupling can be a transport mechanism, which in turn suggests a competitive effect of the diagonal and the off-diagonal coupling by hindering and promoting transport respectively[10]. For a fixed value of \( g^2 \), the “hump” becomes more pronounced with an increase in \( \phi^2 \), which further supports the role of the off-diagonal coupling in enhancing transport. It has been shown[3, 10, 17] that the band-like transport dominates in the low temperature regime. Inclusion of carrier-phonon coupling will introduce phonon scattering that is deleterious to the band-like transport through the first term in Eq. 23. A decrease in the diffusion coefficients at low temperature regime with increasing \( \phi^2 \) is thus an evidence of localization role of the off-diagonal coupling via increasing phonon scattering. Although an increase in \( \phi^2 \) will lead to an increase in hopping contribution of the diffusion coefficient, the number of phonons that is greatly reduced at ultra-low temperature regime largely restricts the contribution from hopping transport. A combined effect of reduced band-like transport and slightly enhanced hopping transport at low temperature regime thus results in a decrease in the total diffusion coefficient.

While considering both Fig. 1 and Fig. 2(b) together, it needs be noted carefully that the first figure directly corresponds to the band structures and the A-matrix parameters for diffusion coefficients shown in the latter figure correspond to \( T = 1 \). An increase in \( \phi^2 \) leads to a greater momentum space variation of the A-matrix parameters, resulting in a higher value of \( D \) at \( T = 1 \). One may thus suspect that the greater momentum space variation in the A-matrix parameters should be responsible for larger value of \( D \) at the concerned temperature. More importantly, if one refers to Eq. 25 which corresponds to hopping rates, one may observe a \( q = 0 \) constraint when performing summation of the \( W \) quantities. This suggests that the variation of the A-matrix parameters along \( q = 0 \) line is important for those temperature regimes where hopping diffusion dominates. Further examination of Figs. 1(b)-(f) reveals an interesting \( k \)-dependence of \( \xi_k^q \) and \( \eta_k^q \) along the \( q = 0 \) line. It is also found that \( \xi_k^q \) are nearly \( k \)-independent and \( \eta_k^q \) have much greater variation along the \( q = 0 \) line, which is eventually reflected in the increased value of \( D \) for an increase in \( \phi^2 \) at a given \( T \). Such distinct \( k \)-dependence bolsters the role of off-diagonal coupling strength \( \phi \) in promoting hopping transport. Even more interestingly, the temperature regime for the nonmonotonic variations in the diffusion coefficient points to possible activated behavior of hopping transport owing to the simultaneous inclusion of the diagonal and the off-diagonal coupling, where the activation energy should be related to the diagonal polaron binding energy[10].

4. Conclusions
We have numerically computed the diffusion coefficients while taking into account the diagonal and the off-diagonal carrier-phonon coupling simultaneously for a wide range of temperatures following the Munn-Silbey approach. The structured transformation coefficients determined self-consistently are found to impose substantial influence on the transport properties. Effects of the off-diagonal carrier-phonon coupling strength have been discussed in detail via examination of the momentum space dependencies of the transformation coefficients and nonmonotonic variations in the temperature dependence of the diffusion coefficients. Importantly, off-diagonal coupling is revealed as a transport mechanism while also being an agent for polaronic localization. Inclusion of off-diagonal coupling in the current approach allows us to see the critical role it plays in determining both the polaron structures and the transport properties over a wide range of
temperatures. A greater momentum-space variability of $\xi_{\mathbf{k}}^q$ and $\eta_{\mathbf{k}}^q$ due to larger $\phi$ is shown to lead to a narrower polaron band and an obvious bimodal variation of polaron band structure $E(k)$. Moreover, strong $k$-dependence of $\eta_{\mathbf{k}}^q$ compared to $\xi_{\mathbf{k}}^q$ along the $q = 0$ line at given temperature can be regarded as a source to promote hopping transport. The nonmonotonic behavior in diffusion coefficient observed for an increase in temperature, is explained as a result of the competitive effect of diagonal coupling in hindering and off-diagonal coupling in promoting transport. Such an effect also suggests activated behavior of hopping transport with the activation energy being related to the diagonal polaron binding energy. At low temperatures, total diffusion coefficient is reduced owing to the phonon scattering that increases with off-diagonal coupling, and remains a major source of reduction in dominant band-like transport.

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