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Abstract

Organic/polymeric materials are of emerging importance for thermoelectric conversion. The soft nature of these materials implies strong electron-phonon coupling, often leading to carrier localization. This poses great challenges for the conventional Boltzmann transport description based on relaxation time approximation and band structure calculations. In this work, combining Kubo formula with finite-temperature time-dependent density matrix renormalization group (FT-TD-DMRG) in the grand canonical ensemble, we developed a nearly exact algorithm to calculate the thermoelectric power factor $PF = \alpha^2 \sigma$, where $\alpha$ is the Seebeck coefficient and $\sigma$ is electrical conductivity, and apply the algorithm to organic materials modeled by Holstein Hamiltonian with electron-phonon coupling. Our algorithm can provide a unified description covering the weak coupling limit described by bandlike Boltzmann transport to the strong coupling hopping limit.
1. Introduction

Organic/polymeric materials are potential candidates for next-generation high-performance thermoelectric materials because of their remarkable low thermal conductivity, relatively high electrical conductivity by doping, structural flexibility, light weight, low toxicity, and biocompatibility \(^1\)–\(^6\). Past decades witnessed rapid development in the field and a number of promising organic/polymeric thermoelectric materials have been synthesized, varying from small molecular systems \(^1\)\(^,\)\(^7\) to conducting polymers \(^8\)\(^,\)\(^9\). However, organic materials' thermoelectric figure of merit \(ZT\) is still low compared to the inorganic counterpart, mainly because of the low power factor \((PF)\). Theoretical understandings are essential for the development of novel high-performance thermoelectric materials. First-principle band structure calculations have been pivotal in such cases. Band structure theory assumes that both electron correlation and electron-phonon coupling are weak and thus the electrons are delocalized. Therefore, the charge transport process is wave-like with scatterings by phonons, impurities, disorders, etc. \(^10\)\(^,\)\(^11\). Combining Boltzmann transport equation with Matthiessen’s rule, insights into the thermoelectric transport process have been revealed for a number of systems \(^12\)–\(^16\). Meanwhile, it should be borne in mind that the most important characteristics of organic/polymeric materials lies in the structural flexibility and the disorders/impurities \(^17\)–\(^21\). From the perspective of device physics modeling, hopping theory has been widely employed to describe carrier transport. The origin of carrier localization relies on the assumption of strong electron-phonon coupling, and thus carriers travel through the system via a hopping process \(^22\)–\(^24\). With the assistance of numerical simulation, plenty of studies have been carried out in hopping limit \(^24\)–\(^26\).

However, the strength of electron-phonon coupling and charge transfer integral are comparable in most organic materials. This indicates a polaron transport mechanism that charge transports dressed with the lattice distortion it induced \(^27\)\(^,\)\(^28\), which is neither bandlike nor hopping \(^29\)\(^,\)\(^30\). Efforts have been devoted to going beyond the simple descriptions of hopping or band. Different time scales for inter-molecular vibration, intra-molecular vibration and inter-molecular charge transfer have been taken into
accounts\textsuperscript{28,31,32}. Since intra-molecular vibration is much faster than inter-molecular charge transfer, the intra-molecular electron-phonon coupling has been treated as a mean-field via polaron transformation\textsuperscript{33–35}, through which, the dependence of Seebeck coefficient on doping level (chemical potential), electron-phonon coupling strength and temperature has been unraveled\textsuperscript{36–38}. On the other hand, inter-molecular vibration is much slower than the inter-molecular charge transfer. Thus, it can often be approximated classical mechanically through mixed quantum-classical approaches\textsuperscript{32,39–41}. Combining numerical calculation and theoretical analysis, transient localization theory has been developed for organic materials’ charge transport\textsuperscript{42–45}, emphasizing the vital role of inter-molecular electron-phonon coupling in the charge transport of organic materials. Although these approaches provide insightful results in the regimes where the underlying assumption is valid, their accuracy remains unclear in the broad parameter regimes, especially the intermediate coupling regime which is believed to be relevant to high-performance organic materials. A general method for thermoelectric transport in organic materials is still absent. The main difficulty lies in the unavoidable many-body problem arising from comparable charge transfer integral and inter/intra-molecular electron-phonon coupling, which limits the accuracy of analytic approaches and numerical methods.

Density matrix renormalization group (DMRG) is a numerically accurate and robust method for many-body problems\textsuperscript{46}. Since the establishment by White in 1992\textsuperscript{47}, numerous algorithms have been developed, including time-evolution algorithms\textsuperscript{48,49}, finite temperature algorithms\textsuperscript{50}, etc. The rapid development of algorithms enables DMRG to tackle various problems, including strong correlation lattice models\textsuperscript{51}, ab-initio electronic structure\textsuperscript{52,53}, and excited state dynamics\textsuperscript{54}. The recent development of GPU acceleration algorithms\textsuperscript{55} and matrix product operator (MPO) auto-construction algorithms\textsuperscript{56} further broaden the application scope of DMRG in simulating the dynamics of complex systems. Very recently, Li \textit{et al.} presented a general picture of organic semiconductors’ mobility by combining time-dependent DMRG (TD-DMRG) with Kubo formula\textsuperscript{57,58}, indicating that TD-DMRG is a possible solution for organic thermoelectric transport in broad parameter space.
In this work, we develop an algorithm based on finite-temperature time-dependent density matrix renormalization group (FT-TD-DMRG) in the grand canonical ensemble to calculate the power factor of organic materials described by Holstein model. We demonstrate that FT-TD-DMRG is a powerful method for investigating the organic thermoelectric transport process, which can bridge the gap between hopping picture and band picture. Detailed theoretical framework and numerical outcomes are provided in the following sections.

2. Model and algorithm

2.1. Introduction of model

Holstein model is widely used to capture the effect of electron-phonon coupling in organic materials. We consider a one-dimensional molecular chain in this work, and the Hamiltonian is

\[ \hat{H} = \hat{H}_e + \hat{H}_{e-ph} + \hat{H}_{ph} \]  \hspace{1cm} (1)

where, the electronic part is

\[ \hat{H}_e = \sum_j \varepsilon_j \hat{a}_j^\dagger \hat{a}_j + \sum_j \tau_j (\hat{a}_{j+1}^\dagger \hat{a}_{j+1} + \hat{a}_j^\dagger \hat{a}_j) \]  \hspace{1cm} (2)

and the phonon part is

\[ \hat{H}_{ph} = \sum_{j,n} \hbar \omega_n \left( \hat{b}_{jn}^\dagger \hat{b}_{jn} + \frac{1}{2} \right) \]  \hspace{1cm} (3)

and the electron-phonon coupling term is

\[ \hat{H}_{e-ph} = \sum_{j,n} \hbar g_n \omega_n (\hat{b}_{jn}^\dagger \hat{b}_{jn} \hat{a}_j^\dagger \hat{a}_j) \]  \hspace{1cm} (4)

Here, \( \hat{a}_j^\dagger \) and \( \hat{a}_j \) are creation and annihilation operators of electron at site \( j \). \( \hat{b}_{jn}^\dagger \) and \( \hat{b}_{jn} \) are creation and annihilation operators of the \( n \)-th intra-molecular vibration mode at site \( j \) with coupling constant \( g_n \) and vibration frequency \( \omega_n \). \( \varepsilon_j \) and \( \tau_j \) are site energy at site \( j \) and charge transfer integral between site \( j \) and \( j+1 \). Reorganization energy \( \lambda = \sum_n g_n^2 \omega_n \) characterizes the strength of electron-phonon coupling.
The thermoelectric power factor $PF$ is defined as:

$$PF = \alpha^2 \sigma$$  \hspace{1cm} (5)

Conductivity $\sigma$ and Seebeck coefficient (thermopower) $\alpha$ can be calculated via the Kubo formula$^{37,60}$:

$$\begin{align*}
\sigma &= \frac{1}{k_B T} L_{11} \\
\alpha &= \frac{1}{T} \frac{L_{12}}{L_{11}}
\end{align*}$$  \hspace{1cm} (6)

Here, $k_B$ is Boltzmann constant and $T$ is temperature. $L_{11}$ and $L_{12}$ are defined as:

$$\begin{align*}
L_{11} &= \frac{1}{2V} \int_{-\infty}^{+\infty} C_1(t) dt = \frac{1}{V} \int_0^{+\infty} \text{Re} C_1(t) dt \\
L_{12} &= \frac{1}{2V} \int_{-\infty}^{+\infty} C_2(t) dt = \frac{1}{V} \int_0^{+\infty} \text{Re} C_2(t) dt
\end{align*}$$  \hspace{1cm} (7)

with correlation functions

$$\begin{align*}
C_1(t) &= \text{Tr} \left[ \hat{\rho}_0 e^{i\mathbf{R} t/\hbar} \hat{j}_e e^{-i\mathbf{R} t/\hbar} \hat{j}_e \right] \\
C_2(t) &= \text{Tr} \left[ \hat{\rho}_0 e^{i\mathbf{R} t/\hbar} \hat{j}_Q e^{-i\mathbf{R} t/\hbar} \hat{j}_e \right]
\end{align*}$$  \hspace{1cm} (8)

Where $J_e$ and $J_Q$ are the electric current and heat current operators, respectively, and $V$ is the volume: $V = N A \Omega$, where $N$ is the total site number, $A$ is the cross-section area and $\Omega$ is the lattice spacing. The density operator for the grand canonical ensemble is:

$$\hat{\rho}_0 = \frac{1}{Z} e^{-\beta (\mathbf{R} - \mu \hat{N}_e)}$$  \hspace{1cm} (9)

where $Z = \text{Tr} \left[ e^{-\beta (\mathbf{R} - \mu \hat{N}_e)} \right]$ is partition function and $\mu$ is chemical potential, $\beta = (k_B T)^{-1}$ and electron number operator $\hat{N}_e = \sum_j \hat{a}_j^\dagger \hat{a}_j$. In the grand canonical ensemble, the mean number of electrons in the system $n_e = \text{Tr} \left[ \hat{N}_e \hat{\rho}_0 \right]$ depends on $\mu$. We can adjust $\mu$ via the bisection method to reach the target $n_e$, considering $n_e$ increases monotonically with $\mu$. Here, we define doping ratio $c = n_e / N$ as the number of electrons in the system divided by the maximum number of electrons that the system can hold. Obviously, $c$ is related to the carrier concentration of the system.

The electric current operator $J_e$ and heat current operator $J_Q$ are derived through
commutator with Holstein Hamiltonian (see Supporting Information 1):

\[
\hat{J}_e = -\frac{i}{\hbar} e \Omega \sum_j \tau_j (\hat{a}^\dagger_{j+1} \hat{a}_j - \hat{a}^\dagger_j \hat{a}_{j+1})
\]

(10)

\[
\hat{J}_q = \hat{J}_q^I + \hat{J}_q^III
\]

(11)

\[
\hat{J}_q^I = -\frac{i}{\hbar} \Omega \sum_j \tau_j \tau_{j+1} (\hat{a}^\dagger_{j+2} \hat{a}_j - \hat{a}^\dagger_j \hat{a}_{j+2})
\]

(12)

\[
\hat{J}_q^III = -\frac{i}{\hbar} \sum_j \left[ \frac{1}{2} (\hat{E}_j + \hat{E}_{j+1}) - \mu \right] \tau_j (\hat{a}^\dagger_{j+1} \hat{a}_j - \hat{a}^\dagger_j \hat{a}_{j+1})
\]

(13)

Here, we define

\[
\hat{E}_j = \epsilon_j + \sum_n \hbar g_n \omega_n (\hat{b}^\dagger_n + \hat{b}_n)
\]

(14)

2.2. TD-DMRG algorithm and realization

2.2.1. MPS and MPO

The second generation of DMRG adopts a matrix product state (MPS) ansatz with a finite truncation of virtual bond dimension to approximate the exact wave function \( |\Psi\rangle \) efficiently:

\[
|\Psi\rangle \approx \mathcal{A}_1^{a_1} \cdots \mathcal{A}_L^{a_L} |\sigma_1 \cdots \sigma_L\rangle
\]

(15)

Here, \( \sigma_l \) is the physical index at site \( l \), ranging from 1 to \( d_l \). For electron or spin sites, \( d_l = 2 \), representing occupied and unoccupied state or spin-down and spin-up state. For phonon sites, \( d_l = d_H \), where \( d_H \) is the size of local phonon basis. Theoretically, \( d_H \) should be infinitely large while a reasonably finite \( d_H \) can provide rather accurate outcomes in most cases. \( a_i \) is the index of virtual bond between site \( l \) and site \( l + 1 \), ranging from 1 to \( D_l \). With a careful selection of the upper bound \( D \) of \( D_l \), the exact wave function \( |\Psi\rangle \) can be approximated efficiently with high accuracy.

The graphic illustration of MPS is presented in Fig. 1(a).

Similarly, the operator \( \hat{O} \) can be expressed as a matrix product operator (MPO) form exactly, as presented in Fig. 1(b).
\[ \hat{\mathcal{O}} = \sum_{\{a_1\}, \{\sigma_1\}, \{\sigma'_1\}} O_{a_1, \sigma_1} O_{a_2, \sigma'_2} \cdots O_{a_{L-1}, \sigma_{L-1}} |\sigma_1 \sigma_2 \cdots \sigma_L \rangle \langle \sigma'_1 \sigma'_2 \cdots \sigma'_{L-1}| \]  

(16)

Fig. 1 Schematic diagram of (a) MPS and (b) MPO. (c) Mapping a three-site system with two vibration modes per site into a one-dimensional chain structure.

There exist a number of schemes to construct MPO of a generic operator, and in this work, we adopted the graph-based automated construction algorithm developed by Ren et al.\textsuperscript{56} to obtain the most compact MPO with the minimum bond dimension. After defining MPS and MPO, the calculation of quantities such as expectation value simply becomes tensor contraction. For the Holstein model, we map the electron and phonon degrees of freedom (DoF) into a chain structure where the DoFs of one molecule are arranged together and phonons with lower frequency are closer to electron sites, as presented in Fig. 1(c).

2.2.2. Time evolution algorithm

Time-evolution is involved in calculating the correlation functions in Eq. (8). Various time evolution methods have been developed\textsuperscript{48,49,61,62}, including direct evolution and compression, time step-targeting, time-dependent variational principle, and so on. In this work, we adopt the time-dependent variational principle with projector-splitting algorithm (TDVP-PS) for time evolution, which has been proved efficient and robust, especially with the hybrid CPU-GPU heterogeneous algorithms\textsuperscript{49,55}. The basic idea of TDVP-PS is projecting \( \hat{H} |\Psi\rangle \) onto the tangent space of current
MPS via projection operator $\hat{P}$:

$$\frac{\partial |\Psi(t)\rangle}{\partial t} = -i\hat{H}|\Psi(t)\rangle$$  \hspace{1cm} (17)

$$\hat{P} = \sum_{l=1}^{L} \hat{P}[1: l - 1] \otimes \hat{I}_{l} \otimes \hat{P}[l + 1: L] - \sum_{l=1}^{L-1} \hat{P}[1: l] \otimes \hat{P}[l + 1: L]$$  \hspace{1cm} (18)

Here,

$$\hat{P}[1: l] = \sum_{\sigma_{1}, \sigma_{2}, \ldots, \sigma_{l} \vdash \sigma_{l-1}, \sigma_{l}, \ldots, \sigma_{1} \vdash \sigma_{l}, \ldots, \sigma_{1}} A_{\sigma_{1}}^{\sigma_{2}} \cdots A_{\sigma_{l-1}, \sigma_{l}}^{\sigma_{l}} A_{\sigma_{l}}^{\sigma_{l+1}} \cdots A_{\sigma_{l}, \sigma_{l+1}}^{\sigma_{l+1}} |\sigma_{1}, \ldots, \sigma_{l}\rangle \langle \sigma_{l}, \ldots, \sigma_{1}|$$  \hspace{1cm} (19)

$$\hat{P}[l: L] = \sum_{\sigma_{l}, \sigma_{l+1}, \ldots, \sigma_{L-1} \vdash \sigma_{l-1}, \sigma_{l}, \ldots, \sigma_{L-1}} B_{\sigma_{l}, \sigma_{l+1}}^{\sigma_{l}} \cdots B_{\sigma_{l-1}, \sigma_{l}}^{\sigma_{l}} B_{\sigma_{l}, \sigma_{l+1}}^{\sigma_{l+1}} \cdots B_{\sigma_{l-1}, \sigma_{l}}^{\sigma_{l+1}} |\sigma_{l}, \ldots, \sigma_{L}\rangle \langle \sigma_{l}, \ldots, \sigma_{L}|$$  \hspace{1cm} (20)

$$\hat{I}_{l} = \sum_{\sigma_{l}} |\sigma_{l}\rangle \langle \sigma_{l}|$$  \hspace{1cm} (21)

$$\hat{P}[1: 0] = \hat{P}[L + 1: L] = 1$$  \hspace{1cm} (22)

Here, tensors $A$ and $B$ are expressed in left-canonical and right-canonical forms, respectively.

For a tiny time step $\Delta t$, Eq. (17) can be solved as:

$$|\Psi(t + \Delta t)\rangle = e^{-i\hat{H}\Delta t/\hbar}|\Psi(t)\rangle,$$  \hspace{1cm} (23)

The propagator is split into multiple subterms through a second-order Trotter decomposition, each of which is applied successively in a sweep process. Time evolution step $\Delta t$ should be carefully chosen to balance accuracy and efficiency.

### 2.2.3. Finite-temperature algorithm for grand canonical ensemble

Temperature is introduced through a purification procedure for the thermal state. The latter is spanned in a direct product space of the physical space $P$ and an auxiliary space $Q$ chosen as an exact copy of $P$. Then the thermal ensemble average $\langle O \rangle$ at $T$ can be expressed as the expectation value of pure thermal state $|\Psi_{\beta}\rangle$ (we suppose $|\Psi_{\beta}\rangle$ is normalized and $\beta = (k_{B}T)^{-1}$):

$$\langle O \rangle = \text{Tr}[\hat{O} \hat{\rho}] = \langle \Psi_{\beta} | \hat{O} | \Psi_{\beta} \rangle$$  \hspace{1cm} (24)

By defining the maximally entangled state $|I\rangle$: 9
\[
|I\rangle = \prod_i \sum_{\sigma_i} \frac{1}{\sqrt{d_i}} |\sigma_i\rangle_p |\sigma_i\rangle_Q
\]  

(25)

And the thermal state can be obtained via imaginary time evolution on the maximally entangled state \(|I\rangle\) from \(t = 0\) to \(t = -i\beta/2\) \(^{48,64}\):

\[
|\Psi_\beta\rangle = e^{-\frac{\beta(\hat{H} - \mu \hat{N}_e)}{2}} |I\rangle
\]

(26)

Lower \(T\) (larger \(\beta\)) needs larger number of imaginary time evolution steps \(N_{\text{imag}}\). Note that in imaginary time evolution, the number of electrons \(n_e\) can change since the grand canonical ensemble is adopted.

2.2.4. Jordan-Wigner transformation for many-electron system

When constructing an MPO, to fulfill the antisymmetric property of electrons, Jordan-Wigner transformation is adopted\(^{65}\) to transform electron basis to spin basis:

\[
\begin{align*}
\hat{a}^\dagger_j &= \prod_{k=1}^{j-1} (-\sigma^z_k) \cdot \hat{a}^+_j \\
\hat{a}_j &= \prod_{k=1}^{j-1} (-\sigma^z_k) \cdot \hat{a}^-_j
\end{align*}
\]

Here, \(\sigma^z\), \(\sigma^+\) and \(\sigma^-\) are Pauli operators of spin basis, which commute for different sites:

\[
[\sigma^z_{l,+,\pm} \sigma^z_{m,+,\pm}] = 0, (l \neq m)
\]

(28)

2.2.5. algorithm flow chart

In summary, we can reformulate the correlation functions in Eq. (8) as follows and calculate \(\alpha\) and \(\sigma\) via the procedure presented in Fig. (2)

\[
\begin{align*}
C_1(t) &= Tr[\hat{\rho}_0 e^{i\hat{H}t} e^{-i\hat{J}_e} \hat{f}_e] = \langle \Psi_\beta | e^{i\hat{H}t} e^{-i\hat{J}_e} \hat{f}_e | \Psi_\beta \rangle \\
C_2(t) &= Tr[\hat{\rho}_0 e^{i\hat{J}_Q t} e^{-i\hat{H}t} \hat{f}_e] = \langle \Psi_\beta | e^{i\hat{J}_Q t} e^{-i\hat{H}t} \hat{f}_e | \Psi_\beta \rangle
\end{align*}
\]

(29)
As shown in Fig. 2, the maximally entangled state $|I\rangle$ ($\beta = 0$) is taken as the initial state. Thermal state $\Psi_{\beta}$ is obtained via several hundred steps of imaginary time evolution from $|I\rangle$. After obtaining $\Psi_{\beta}$, we calculate $\hat{J}_e \Psi_{\beta}$ by applying MPO $\hat{J}_e$ to $\Psi_{\beta}$. Through time evolution on bra $\langle \Psi_{\beta} |$ and ket $f_e |\Psi_{\beta}\rangle$, $\langle \Psi_{\beta} | e^{i\hat{H}t} \rangle$ and $e^{-i\hat{H}t} f_e |\Psi_{\beta}\rangle$ can be calculated. Finally, correlation functions $C_1(t)$ and $C_2(t)$ are calculated by contracting $\langle \Psi_{\beta} | e^{i\hat{H}t} \rangle$ and $e^{-i\hat{H}t} f_e |\Psi_{\beta}\rangle$ with MPO $\hat{J}_e$ and MPO $\hat{J}_Q$ separately. The evolution continues until correlation functions decay to zero, and then the electrical conductivity $\sigma$ and the Seebeck coefficient $\alpha$ can be obtained by integrating correlation functions as Eq.(6) and (7).
3. Results and discussions

In this work we focus on one-dimensional Holstein model with periodic boundary condition and assume $\tau_j \equiv \tau$ and $\epsilon_j \equiv \epsilon$ for all sites. Following the work of Wang and Zhao\(^{37}\), we choose carrier reorganization energy $\lambda = 125 \text{meV}$ (for typical organic semiconductor) and use 5 intra-molecular vibration modes, where $\{\omega_n\} = \{35.6 \text{meV}, 106.8 \text{meV}, 178.0 \text{meV}, 249.2 \text{meV}, 320.4 \text{meV}\}$ and $\{g_n\} = \{1.208, 0.617, 0.352, 0.179, 0.086\}$. The values are taken from the super-Ohmic spectral density function from Ref.\(^{37}\), following a discretization scheme (Supporting Information 2). For simplicity, we set site energy $\epsilon = 0$, cross area $A = 100 \text{a. u.}$ and lattice constant $\Omega = 10 \text{a. u.}$ in all the calculations.

3.1. Validity of TD-DMRG algorithm

As mentioned above, the number of imaginary time evolution steps $N_{\text{imag}}$, the size of bond dimension $D$, the size of local phonon basis $d_H$, the size of real time evolution step $\Delta t$ and the number of sites $N$ are essential parameters to assure the accuracy of calculations. In this work, we focus on the challenging intermediate parameter regime where $\tau$ is comparable to $\lambda$ and room temperature. In Supporting Information 3, we demonstrate that in this case, the converged and valid results can be obtained by TD-DMRG with a moderate computational cost. For most of the parameter regimes we are interested in, parameter set of $\Delta t = 50$, $N = 12$, $D = 48$ and $d_H = 9$ is enough for numerical convergence.

3.2. Comparison with polaron transformation

We now compare the correlation functions calculated by TD-DMRG with those obtained from Lang-Firsov Polaron Transformation\(^{36}\) (LF) and Variational Polaron Transformation\(^{37}\) (VPT) (Supporting Information 5) ranging from strong coupling regime, Figs. 3(a) and 3(b), intermediate coupling regime, Figs. 3(c-f), weak coupling regime, Figs. 3(g) and 3(h), to zero coupling limit, Figs. 3(i) and 3(j).
Fig. 3 Comparison of the real and imaginary parts of correlation functions $C_1(t)$ and $C_2(t)$ calculated by time-dependent density matrix renormalization group (TD-DMRG), Lang-Firsov polaron transformation (LF), and variational polaron transformation (VPT) in different regimes. (a) and (b) are in strong coupling regime where $\tau \ll \lambda$. (c), (d), (e) and (f) are in intermediate regime where $\tau$ and $\lambda$ are comparable. (g) and (h) are in weak coupling regime where $\tau \gg \lambda$. (i) and (j) are in zero coupling limit where $\lambda = 0$ indicates that $g_n = 0$ and no electron-phonon coupling exists. Here, we set $T = 300 \, K$, $N = 20$, $D = 48$, $d_H = 12$, $N_{imag} = 300$, and $\Delta t = 10.0$

It is known that LF/VPT theory is valid in the strong coupling regime. These polaron transformation methods can reproduce the hopping behavior as described by Fermi’s golden rule for $\tau \ll \lambda$. These can also reproduce the bandlike behavior as described by Boltzmann transport equation when $\lambda$ is negligible, as demonstrated
previously\textsuperscript{35,37} (see Supporting Information 5). As shown in Figs. 3(a), 3(b), 3(i), and 3(j), the correlation functions calculated by TD-DMRG coincide impressively with analytic solutions in both strong coupling regime and zero coupling limit, which proves TD-DMRG’s validity and accuracy. Meanwhile, the correlation functions calculated by TD-DMRG are quite different from analytic formula in intermediate regime plotted in Fig. 3(c)-3(f), and larger $\tau$ leads to more obvious difference. Recall Eq. (6), the large difference in correlation functions will lead to large difference in transport coefficients. In weak coupling regime plotted in Fig. 3(g) and 3(h), the difference in correlation functions calculated via different methods begins to disappear, and VPT performs better than LF. Considering the approximations adopted in polaron transformation approaches\textsuperscript{33}, these differences imply the limitation of LF/VPT in intermediate coupling region and the necessity of more accurate numerical methods such as TD-DMRG.

3.3. dependence of doping ratio

Fig. 4 (a) and (b) are the doping ratio dependence of conductivity $\sigma$, (c) and (d) are the doping ratio dependence of Seebeck coefficient $\alpha$, and (e) is the doping ratio dependence of power factor $PF$. The hopping behavior in (b) and (d) is obtained by the outcomes of Fermi’s golden rule presented in Supporting Information 5, and $\alpha_{HL} = \frac{k_B}{e} \ln \frac{c}{1-c}$. Band behavior in (d) is calculated
with $\tau = -240 \text{ meV}$ and $\lambda = 0$ by Boltzmann transport theory presented in Supporting Information 4.

The dependence of transport coefficients on the doping ratio $c$ is plotted in Fig. 4. As shown in Fig. 4 (a), the conductivity increases with increasing $c$ first, and then decreases. The maximum value of conductivity is reached when $c = 0.5$, corresponding to the half-filling case where most charge carriers are involved in charge transport. In the hopping limit, the conductivity satisfies\(^{22,27,37}\) $\sigma \propto \tau^2 c (1 - c)$ when $\tau \ll \lambda$ (Supporting Information 5 and 6), which is plotted in Fig. 4(b). The $\sigma \propto \tau^2 c (1 - c)$ is satisfied impressively when $\tau = -6 \text{ meV}$, and begins to fail as the transfer integral increases, which is attributed to the transition to band-like transport behavior in section 3.4. The dependence of $\alpha$ on $c$ is also plotted in Fig. 4(c). Seebeck coefficient $\alpha$ increases with $c$ and changes sign when $c = 0.5$, corresponding to the change of main carriers from electrons to holes. With a fixed $c$, the absolute value of $\alpha$ decreases slightly with increasing $\tau$. As reflected in Fig. 4(d), $\alpha_{HL} = -\frac{k_B}{e} \ln \frac{c}{1 - c}$ in hopping limit\(^{66-68}\) where $\tau \ll \lambda$ (Supporting Information 6).

While the dependence $\alpha = -\frac{k_B}{e} \ln \frac{c}{1 - c}$ no longer hold when $\tau$ increases. The behavior of $(\alpha - \alpha_{HL})$ in band theory (Supporting Information 4) with $\tau = -240 \text{ meV}$ is also plotted for comparison. The similarity of the case $\tau = -72 \text{ meV}$ and band behavior indicates the transition from hopping behavior to band behavior. The power factor $PF$ is also plotted in Fig. 4(e). Considering the fact that in the hopping limit:

$$PF = \alpha^2 \sigma \propto \tau^2 c (1 - c) \left( \ln \frac{c}{1 - c} \right)^2$$  \hspace{1cm} (30)

The maximum of $PF$ is reached when $c = 0.08$ and $c = 0.92$, corresponding to the electron and hole doping. This suggests that the optimal doping ratio in Holstein model when $\tau \ll \lambda$ is that HOMOs are 8% filled by holes or LUMOs are 8% filled by electrons. Besides, $PF$ increases with increasing $\tau$ monotonically. These all agree with Fig. 4(e).
3.4. Dependence on transfer integral

As shown in Fig. 5(a) and 5(b), in the strong electron-coupling regime where \( \tau \ll \lambda \), the behavior satisfies \( \sigma \propto \tau^2 \) and \( \alpha = -\frac{k_B}{e} \ln \frac{c}{1-c} \) (independent of \( \tau \)), indicating a hopping-like transport mechanism\(^{66,69}\). When \( \tau \) keeps increasing, both \( \sigma \) and \( \alpha \) depart from hopping-like behaviors in this intermediate regime. \( \sigma \) keeps increasing with increasing \( \tau \) but \( \sigma \propto \tau^2 \) no longer holds. Different from \( \tau \) irrelevance presented in the strong coupling regime, \( \alpha \) begins to decrease with increasing \( \tau \). Finally, when \( \tau > \lambda \), the transport behavior turns to band-like. On the one hand, conductivity roughly satisfies \( \sigma \propto \tau^2 \), which is considered as a typical band like behavior\(^{70}\). On the other
hand, $\alpha - \tau$ dependence becomes similar to $\alpha - \tau$ dependence calculated by Boltzmann transport equation. Note that the introduction of electron-phonon coupling contributes an additional decrease of $\alpha$ in band-like regime in Fig. 5 (b). Considering the wide bandwidth, the decrease of $\alpha$ with increasing $\tau$ in band limit can also be interpreted via Mott’s Formula because increasing $\tau$ leads to a smoother change in $D(E)$ (Supporting Information 6).

$$\alpha = \frac{\pi^2 k_B}{3 e k_B T} \frac{d \ln D(E)}{dE} \bigg|_{E=\mu}$$

(31)

The power factor $PF$ is also calculated in Fig. 5(c) to measure thermoelectric performance. We find that with other factors fixed, the increase of $\tau$ systematically increases $PF$, enhancing thermoelectric performance.

The crossover of transport behavior from hopping to band-like is also reflected in the mean free path $l_{mf\mu}^{72}$ shown in Fig. 5(d). Here,

$$l_{mf\mu} = v\theta$$

(32)

where the mean square velocity is calculated as:

$$v = \left[ \frac{1}{e^2 n_e C_1(0)} \right]^{1/2}$$

(33)

and coherence time is obtained as:

$$\theta = \int_0^{+\infty} dt \left| \frac{Re C_1(t)}{Re C_1(0)} \right|$$

(34)

In the strong coupling regime, $l_{mf\mu}/\Omega \ll 1$, indicating that electrons are totally localized in a single unit cell and the transport process is hopping-like. With the increase of $\tau$, $l_{mf\mu}$ becomes comparable to $\Omega$, corresponding to the intermediate regime. Finally, when $l_{mf\mu}/\Omega \gg 1$, electrons are more delocalized and band-like transport behavior appears.
4. Conclusions

In summary, we developed a numerically nearly exact method for calculating the power factor of organic thermoelectric materials modeled by electron-phonon (Holstein) model via combining Kubo formula with finite-temperature time-dependent density matrix renormalization group (FT-TD-DMRG) in the grand canonical ensemble. We demonstrated the validity and computational feasibility for a broad parameter range. We highlight the advantage of the present method for intermediate coupling regime, difficult for other approximate methods. Our method can bridge the gap between hopping transport described by Fermi’s golden rule and band transport described by Boltzmann transport equation, providing a unified picture for organic materials’ thermoelectric transport process. We find that (i) electric conductivity and Seebeck coefficient strongly depend on doping ratio and present impressive symmetry about \( c = 0.5 \) in room temperature; (ii) increasing transfer integral changes the transport mechanism from hopping to band-like and enhances power factor monotonically. By merely changing the exact form of Hamiltonian and current operators, it is straightforward to take other factors into account in our framework, such as off-diagonal dynamic disorder, Coulombic interaction, static disorder, and so on.

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References:


(37) Wang Y.-C., Zhao Y. Variational polaron transformation approach toward the


(50) Verstraete F., Murg V., Cirac J. I. Matrix product states, projected entangled pair


(61) White S. R., Feiguin A. E. Real-time evolution using the density matrix


