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Zhigang Shuai,^{1,a)} Weitang Li,¹ Jiajun Ren,¹ Yuqian Jiang,² and Hua Geng³

AFFILIATIONS

¹MOE Key Laboratory of Organic OptoElectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, 100084 Beijing, People's Republic of China

²Laboratory for Nanosystem and Hierarchy Fabrication, National Center for Nanoscience and Technology, Chinese Academy of Sciences, 100084 Beijing, People's Republic of China

³Department of Chemistry, Capital Normal University, 100048 Beijing, People's Republic of China

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a) Author to whom correspondence should be addressed: zgshuai@tsinghua.edu.cn

ABSTRACT

Marcus theory has been successfully applied to molecular design for organic semiconductors with the aid of quantum chemistry calculations for the molecular parameters: the intermolecular electronic coupling V and the intramolecular charge reorganization energy λ . The assumption behind this is the localized nature of the electronic state for representing the charge carriers, being holes or electrons. As far as the quantitative description of carrier mobility is concerned, the direct application of Marcus semiclassical theory usually led to underestimation of the experimental data. A number of effects going beyond such a semiclassical description will be introduced here, including the quantum nuclear effect, dynamic disorder, and delocalization effects. The recently developed quantum dynamics simulation at the time-dependent density matrix renormalization group theory is briefly discussed. The latter was shown to be a quickly emerging efficient quantum dynamics method for the complex system.

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I. INTRODUCTION

Organic semiconductors have become an important component in electronics for information display and energy materials.¹ Carrier transport has been the bottleneck for such applications. Recent progress in molecular design and material processing has led to a rapid increase for mobility in molecular and polymeric devices.² In solid state physics, carrier transport is usually described by the Boltzmann transport equation as wavepacket diffusion accompanied by scatterings with impurity and lattice vibration, and very often, the constant relaxation time approximation is assumed.³ Such a description is most appropriate for well delocalized bandlike motion, for instance, in most of the inorganic crystals such as silicon crystals. For molecular materials, due to the light weight of carbon as well as disorder/impurity, typical for organic systems, bandlike description

is often not enough: charge localization, quantum nuclear nature, and disorder/impurity could dominate the charge transport processes. In this context, about 20 years ago, Brédas *et al.* first proposed to use Marcus theory to describe the charge transport process in organic semiconductors.⁴ Particularly, Heeger presented in his Nobel lecture the basic understanding of charge transport in polymeric and organic conductors by referring to the electron transfer process of Marcus theory.⁵ This opened a novel avenue toward better understanding the charge transport in organic materials, in sharp contrast to the conventional bandlike transport. In fact, long ago, the local electron-phonon model had been employed to describe mobility by Holstein.⁶ Later, non-local electron-phonon effects have been explored and highlighted by a number of authors,⁷ including the Holstein-Peierls type model.⁸ Then, the carrier transport has been described as non-adiabatic electron dynamics from the

bottom level such as Ehrenfest dynamics,^{9–11} then the surface hopping (SH) dynamics,^{12–14} to more sophisticated quantum dynamics.^{15–17} The advantage of dynamics simulation lies in the comprehensive consideration of polaronic size effect: full localized charge corresponds to an extremely small polaron. The difficulty of dynamics simulation, more than often mixed quantum–classical nature, is the long-time diffusion behavior specifically required by transport and the quantum nature of nuclear motion, which was shown to be essential for electron dynamics. This is very different from ultrafast dynamics for which initial short time behavior is essential. There has been impressive progress in recent years for the quantum dynamics in the complex system, from surface hopping to centroid molecular dynamics¹⁸ and ring polymer molecular dynamics,¹⁹ to the state-of-the-art [multilayer (ML)] multiconfiguration time dependent Hartree (MCTDH) approach,²⁰ and to the very recent development of the nearly exact time-dependent density matrix renormalization group theory (TD-DMRG), much more conveniently and efficiently recast in the matrix product states (MPS) formalism.²¹ Since the mobility is long time behavior, considering the quantum nuclear effect only in the initial samplings is certainly not enough for the carrier quantum dynamics. Thus, the TD-DMRG is expected to be the most promising method for carrier mobility. These advances can gain a better understanding of the charge transport in organic semiconductors, which is really a challenge for quantum dynamics in the complex system, mingling electron–phonon interaction, static and dynamic disorders, and quantum nuclear nature, and possibly with electron–electron correlation for high carrier concentration cases, the latter often ignored to avoid further complexity. Thus, there will be a large space to extend the Marcus theory to more complicated situations.

II. EFFECTS OF QUANTUM NUCLEAR NATURE

Bredas and collaborators first proposed to use the Marcus semiclassical theory to describe the carrier motion in organic semiconductors, where the charge carrier is assumed to be fully localized on one single molecule, and the transport was described as sequential charge hopping from one molecule to another, with rate expressed as

$$k = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda k_B T}\right). \quad (1)$$

In Eq. (1), the electronic coupling term V can be assumed to be the intermolecular hopping integral. Specifically, the charge state is approximately regarded as a frontier molecular orbital, the HOMO for hole transport and the LUMO for electron transport. There have been a number of quantum chemistry methods to calculate V from the simplest one of evaluating the frontier orbital energy level splitting for a molecular dimer to more complicated intermolecular overlap correction. λ is the charge reorganization energy defined as the free energy change associated with the relaxation of the molecular dimer. Often, it can be assumed to be a sum of the reorganization energy for two individual molecules by ignoring the intermolecular relaxation energy. ΔG^0 is the total Gibbs free energy change. The exponential term in the Marcus formula corresponding to the “inverted region” is first proposed in the study

of radiationless transitions in a crystal by Kubo and Toyozawa in 1955²² whose idea can be traced back to the pioneering work of Huang and Rhys.²³ Although nowadays it is well-known that the radiationless transitions are closely related to charge transfer reactions, this progress in solid state physics does not make immediate impact on the study of charge transfer reactions. In 1956 and 1958, Marcus and Hush published their representative work on the charge transfer reaction in solution, respectively.^{24,25} They both concluded that the rate of the charge transfer reaction takes the form of the Arrhenius equation $k \propto Z \exp[-E_A/k_B T]$; however, the form of E_A differs in their works, as a consequence of their focus on an explicit form of λ based on their particular physical model. Nevertheless, their results can be unified by $E_A = (\Delta G^0 + \lambda)^2/4\lambda$ once ΔG^0 and λ are properly defined in their model.^{26,27} The Marcus formula in the same form as Eq. (1) is derived by Levich and Dogonadze based on Landau–Zener theory around 1960.²⁸ At the same time, Holstein reached a similar result independently based on small-polaron motion in solids.⁶ The rate formula by Holstein assumes $\Delta G^0 = 0$, which is common for carrier transport. In this case, the reaction barrier is simply $\lambda/4$ for thermal activation. Thus, V and λ are the two important molecular parameters governing charge transport, regardless of the transport mechanism. These are the most important molecular descriptors for searching high mobility organic semiconductors and have been applied in machine learning for molecular design.²⁹

It should be noted that Eq. (1) is valid for $V \ll \lambda$ where the charge transfer occurs in the non-adiabatic transition regime where the charge is fully trapped by the molecular reorganization process. The second assumption is that under high temperature ($\omega \ll k_B T$), the environmental fluctuation can be treated classically. Thus, the thermal activation vanishes at low temperature, while experiments indicated otherwise.³⁰ In the original Marcus theory for the ferrous–ferric charge transfer reaction, the environment is the solvent polarization motion, which was treated classically.³¹ In fact, for organic semiconductors, both intramolecular and intermolecular vibrational modes serve as the environment for electron transfer. For instance, for the conjugated organic molecules, more than often, the most relevant vibrational mode is the C–C bond stretching mode strongly coupled with charge transfer, with $\omega \gg k_B T$. Even the zero point fluctuation of such vibrational mode can cause a noticeable effect for charge transfer, which can explain widely observed finite conductivity in organic materials at extreme low temperature.

Since the original Marcus–Hush theory is semiclassical where nuclear motion is classic, a number of efforts have then been devoted to take the quantum nature of nuclei into consideration, for instance, by Bixon, Jortner and co-workers.^{32–37} By virtue of Fermi’s golden rule (FGR), under the Condon approximation, the charge transfer rate is

$$k = \frac{2\pi}{\hbar^2} V^2 \sum_{v,v'} P_{iv} |\langle \Theta_{fv'} | \Theta_{iv} \rangle|^2 \delta(\omega_{fv',iv}). \quad (2)$$

Here, P is the Boltzmann distribution for the v th vibrational quanta in the initial state and Θ is the vibration wavefunction. Under the displaced harmonic oscillator approximation, it can be expressed as³⁸

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp\left\{it\omega_{fi} - \sum_j S_j [(2n_j + 1) - n_j e^{-it\omega_j} - (n_j + 1)e^{it\omega_j}]\right\}, \quad (3)$$

where ω_{fi} is the adiabatic transition energy, n_j is the population for the j th vibrational mode with circular frequency ω_j , and S_j is its Huang–Rhys factor, characterizing the coupling strength of carrier motion with the j th mode. The relevant parameters and charge transfer rate with the quantum nuclear effect can be calculated from first-principles by MOMAP (Molecular Materials Property Prediction Package), a distributed computational chemistry program developed by us for evaluating the molecular materials property.^{39,40} The quantum nature for the charge transfer rate formula [Eq. (3)] is embodied in the vibration mode considered as a quantum harmonic oscillator. This corresponds to a full quantum mode expression of the Bixon–Jortner formula where one mode was considered as quantum and the rest as classical.^{34,35,41,42} Suppose the quantum mode is labelled l , then the Bixon–Jortner formula reads

$$k = \frac{V^2}{\hbar} e^{-S_l} \sum_{j=0}^{\infty} \frac{S_l^j}{j!} \sqrt{\frac{\pi}{\lambda' k_B T}} \exp\left[-\frac{(\lambda' + j\hbar\omega_l + \Delta G^0)^2}{4\lambda' k_B T}\right], \quad (4)$$

where $\lambda' = \sum_{j \neq l} S_j \hbar\omega_j$ is the reorganization energy of the classical modes. The advantage of the direct application of the full-mode quantum rate [Eq. (3)] is the full consideration of the discreteness nature of molecular vibrational modes along with the electron–vibration couplings being computed from quantum chemistry, without any assumption on the spectral function.

It should be noted that even for the original ferrous–ferric charge transfer rate Marcus investigated, the quantum nature of the water solvent has been examined. For instance, by using quantum Monte-Carlo simulation to treat water solvent quantum mechanically, Bader, Kuharski, and Chandler demonstrated quite remarkable hydrogen nuclear tunneling effects,⁴³ which was confirmed later by Song and Marcus.⁴⁴ In the context of polaron transport, Emin proposed the concept of polaron quantum tunneling.⁴⁵ All these indicated the importance of nuclear quantum effects in the charge transfer reaction. In fact, in the strong coupling limit ($S \gg 1$), we can apply the short time approximation: $e^{-it\omega_j} \approx 1 - it\omega_j + \frac{1}{2i}(it\omega_j)^2$ in Eq. (2), and at the high temperature limit, $\hbar\omega_j \ll k_B T$, the phonon population can be approximated as $n_j \approx \hbar\omega_j/k_B T$. By noting that the charge reorganization can be expressed by vibrational mode relaxation: $\lambda = \sum_j \lambda_j = \sum_j S_j \hbar\omega_j$, it is straightforward to show that Eq. (2) goes back to Eq. (1). It can be proven that Eq. (2) reduces to Eq. (4) using similar techniques.

Applying Eq. (2) to prototypical organic semiconductors such as tetracene, pentacene, and rubrene, coupled with a random walk simulation of the carrier diffusion, and relating the carrier mobility to the diffusion constant by the Einstein relationship, $\mu = \frac{eD}{k_B T}$, we found that the temperature dependence is usually governed by the $1/T$ prefactor, namely, decreasing behavior, instead of the thermal activation-like.³⁸ This seems to be quite paradoxical since the decrease with temperature ($d\mu/dT < 0$) would be considered as “bandlike,” whereas the charge is localized in one single molecule. Such an exotic behavior was indeed found in the experiment of

Sakanoue and Sirringhaus that for 6,13-Bis(triisopropylsilylethynyl)pentacene, the mobility vs temperature from electrical measurement looked “bandlike” ($d\mu/dT < 0$), but the optical measurement indicated otherwise, namely, from their *in situ* charge modulation spectroscopy on the device, the charge induced absorption occurring at the same position as that from the electrochemical doping in solution, that is to say, the charge carrier in the solid state device is the same as in a single molecule.⁴⁶ Even more, both features are independent of temperature, which seem to rule out the possibility of temperature induced localization as claimed from the off-diagonal dynamic disorder mechanism.⁴⁷ Combining quantum chemistry calculation for TIPS-pentacene, Geng *et al.* found that TIPS substitutions can (i) largely reduce the intermolecular coupling V to only one tenth of that for pentacene and (ii) double the reorganization energy λ , and when partitioning it into vibrational mode relaxation, it was found that the high frequency modes dominate. These clearly indicated that the charge transport in TIPS-pentacene could be described as localized but enabled by quantum nuclear tunneling.⁴⁸

Next, we looked at how the dynamic disorder, arising from non-local electron–phonon coupling, would influence in such a transport model. We then perform molecular dynamics simulation at room temperature to get a large amount of snap-shots, and at each of which, quantum chemistry calculations are carried out for all the molecular dimers.⁴⁹ The electronic coupling V is now a function of time, which can be Fourier transformed into time series,

$$V(t) = \langle V \rangle + \sum_{i=0}^{N/2} \text{Re}(V_i) \cos(\omega_i t + \varphi_0) + \sum_{i=0}^{N/2} \text{Im}(V_i) \sin(\omega_i t + \varphi_0), \quad (5)$$

where N is the total number of snapshots and the phase factor φ_0 is chosen as a random number for different dimers. The flow chart for evaluating mobility is sketched in Fig. 1.⁵⁰

Figure 2 demonstrates that (i) the quantum nature of vibration with high frequency dominates; (ii) only at very high temperature can Marcus rate approach the quantum model; and (iii) the “bandlike” decreasing temperature behavior is reproduced here, but the dynamic disorder does not show any appreciable influence on the mobility, in sharp contrast to the common perception.⁹ The discrepancy between the viewpoints is solved recently by general methods applicable at different charge transport regimes.^{12,14,17} It is concluded that in the hopping regime, dynamic disorder could enhance mobility, whereas with weaker electron–phonon interaction, dynamic disorder tends to limit charge transport. In the particular case of TIPS pentacene, the thermal averaged electronic coupling is found to be around 15 meV, far less than the reorganization energy of 217 meV.⁴⁸ Thus, TIPS pentacene lies in the hopping regime, and the effect of dynamic disorder is different from theories based on a delocalized charge picture.⁴⁷ Our study based on the hopping model found that for one dimensional chain, the presence of any disorder, being static or dynamic, can suppress the transport. When going to higher dimension, dynamic disorder would not limit transport, and in the extremely localized limit, it can even enhance mobility.⁴⁹

It is worthwhile to mention that our numerical diffusion simulations based on the rates evaluated for all the molecular dimers indicated that crystal packing with uniform intermolecular coupling V 's is favorable for carrier transport. Taking the annealed

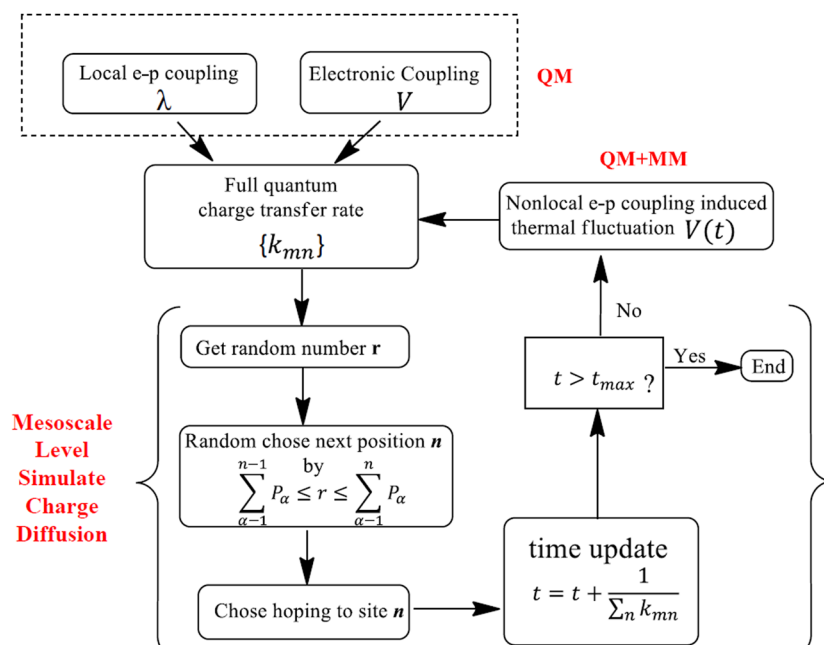


FIG. 1. Multiscale modeling of carrier diffusion considering dynamic disorder for the nuclear tunneling enabled hopping model. Reproduced with permission from Shua *et al.*, Chem. Soc. Rev. **43**, 2662 (2014). Copyright 2014 Royal Society of Chemistry.

β -trithiophenes as an example, the crystal packing of compound **1** is arranged as a sandwich-herringbone structure, while compound **2** is normal herringbone. The crystal structure and the corresponding electronic couplings are shown in Fig. 3. There exists a much larger V for one dimer in the former case, while the latter shows more uniform but much smaller values of V 's. According to the V^2 prefactor in Marcus theory, the charge transfer rate in the former case should be much larger than in the latter. However, the diffusion simulation indicated that the charge spent enormous amount of time oscillating within the dimer with large V , without any appreciable contribution to the current.^{51,52} Eventually, the calculated mobility of the latter is about 50 times as large as the former, in good agreement with the measurement. The conclusion that intermolecular coupling anisotropy is not favorable for

high mobility organic semiconductors is also drawn from theories other than the hopping model, such as the Boltzmann transport theory or the recent transient localization theory.⁵³ The aforementioned two theories further take into account the relative phase of intermolecular coupling, which is absent in the hopping mechanism though.

Most interestingly, in a somewhat different field, the electrical conductivity for heavily doped polymers, there have been quite hot debates over the conducting mechanism. To our surprise, even though the conducting polymer was discovered in 1977 and awarded Nobel Prize in Chemistry in 2000 for Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, the conducting mechanism has not been fully understood. In 2009, Heeger and co-workers⁵⁴ suggested that the one-dimensional Luttinger liquid model proposed

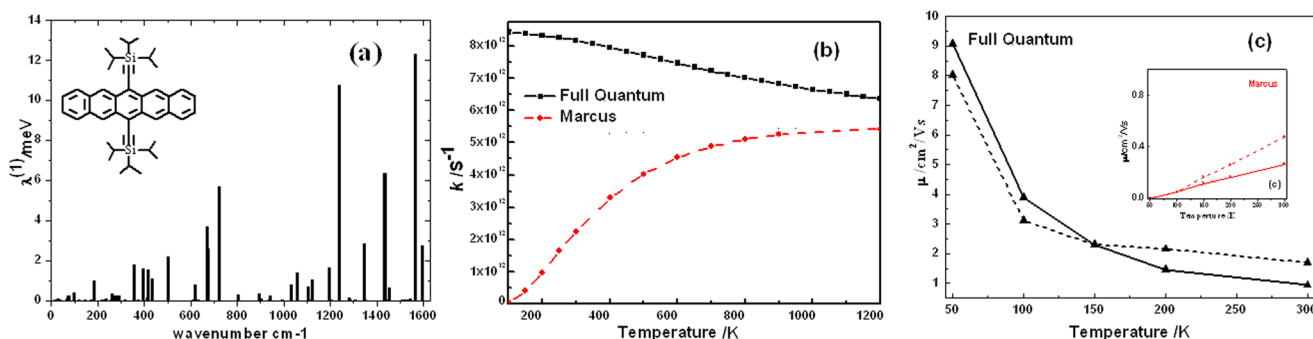


FIG. 2. Tunneling enabled hopping model case study for TIPS-pentacene. (a) Partition of reorganization energy into normal mode relaxation. (b) Temperature dependence of the charge transfer rates. (c) Hole mobility as a function of temperature: dashed line for dynamic disorder and solid line for dynamically averaged static V 's. The inset is the Marcus rate. Adapted with permission from Geng *et al.*, Adv. Mater. **24**, 3568 (2012). Copyright 2012 Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

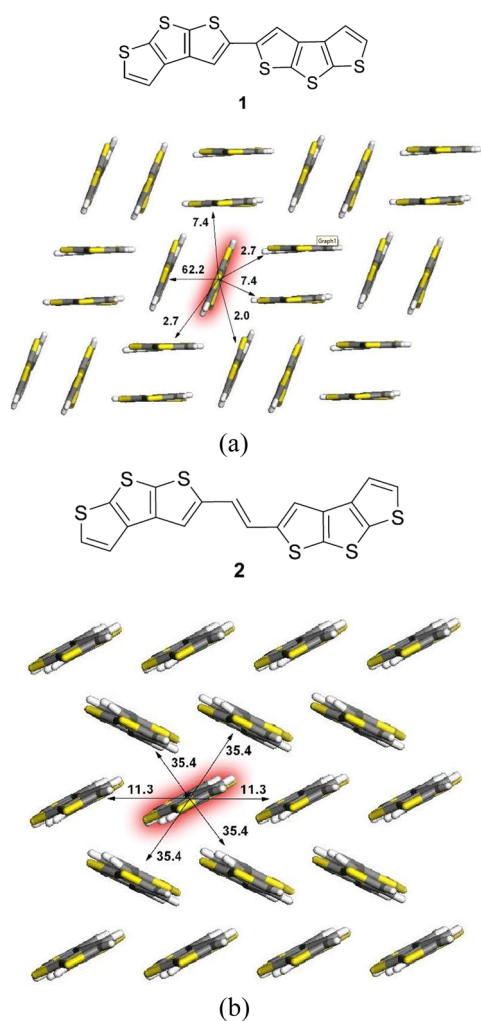


FIG. 3. Uniformed stacking network is favorable for transport taking annelated β -trithiophenes crystals as an example: (a) for sandwiched herringbone packing and (b) normal herringbone packing. Adapted with permission from Wang *et al.*, *Chem. Soc. Rev.* **39**, 423 (2010). Copyright 2010 Royal Society of Chemistry.

by Haldane in the early 1980s⁵⁵ would be most appropriate to fit the $J(V, T)$ curve for a doped donor–acceptor type of polymer, except some deviations at low temperature. Heeger *et al.* claimed that this is universal for all polymers. The obvious three-dimensional spaghetti morphology shown by atomic force microscopy seems to be a clear evidence to oppose such a one-dimension model. Hence, different models have been put forth for alternative mechanisms.^{56–59} Among these, the localized hopping mediated by nuclear tunneling has been found to be universal for all polymers measured recently by de Leeuw *et al.*^{58,59} Furthermore, such a model was even employed to explain the transport behavior in the molecular junction.⁶⁰

A straightforward inference for the nuclear quantum effect would be the negative isotope effect.⁶¹ Specifically, from Eq. (2),

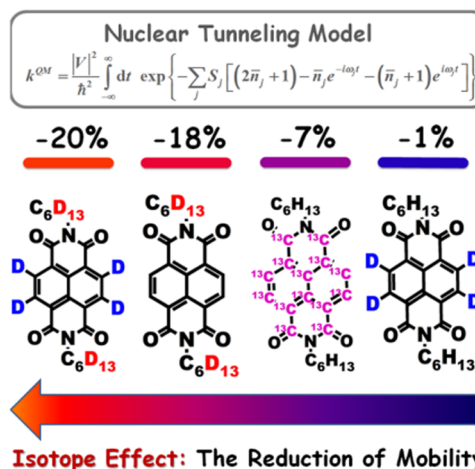


FIG. 4. Isotope effect for the electron mobility of naphthalene diimide derivatives. Adapted with permission from Jiang *et al.*, *J. Phys. Chem. Lett.* **5**, 2267 (2014). Copyright 2014 American Chemical Society.

it is easily seen that upon decreasing vibrational frequency ω , the Huang–Rhys factor increases because the reorganization energy is kept constant, and V is also independent on the isotope. The first-principles evaluated molecular parameters plugged into the above-mentioned mobility evaluation scheme (Fig. 1) for the electron transport materials of naphthalene diimide derivatives gave the isotopic behaviors shown in Fig. 4. The experiment carried out by Frisbie and co-workers immediately confirmed such a negative isotope behavior.⁶²

III. DELOCALIZATION EFFECT

Fully localized charge is certainly too simple to account for the full spectrum of organic semiconductors. The hopping model simply assumes localization of charge, which could arise not only from electron–phonon coupling but also from static disorder or impurities, typical for the organic system. That is why in the charge modulation experiment of Sakanoue and Sirringhaus, the measured peak position for the charge induced absorption is independent of temperature:⁴⁶ if localization had been originated from the electron–phonon mechanism, the peak position would shift with temperature. Nevertheless, from a theoretical point of view, the charge delocalization effect is of great importance. In the context of the charge transfer reaction where the Marcus theory initially formulated, the delocalization effect is introduced by Piepho, Krausz, and Schatz (PKS model) when discussing the spectra of the Creutz–Taube ion in which the charge is found to be completely delocalized over the two Ru cations.⁶³

In this section, we present two schemes to look at the electron–phonon model for charge transport. One is based on the Haken–Strobl type approach; the time-dependent wavepacket diffusion (TDWPD)^{16,64} method for the following model Hamiltonian:

$$H(t) = \sum_i (\varepsilon_{ii} + F_i(t)) |i\rangle\langle i| + \sum_{i>j} (\varepsilon_{ij} + V_{ij}(t)) |i\rangle\langle j|, \quad (6)$$

where $|i\rangle$ is the electronic state of the i th site (frontier orbital) and F_i and V_{ij} represent the fluctuation part for the site energy ε_{ii} and electronic coupling ε_{ij} , respectively. We employed a spectral density for the diagonal electron–phonon interaction,

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{\chi_j^2}{\omega_j} \delta(\omega - \omega_j), \quad (7)$$

where j is the index of the vibrational mode and χ_j^2 is proportional to the Huang–Rhys factor. The time-dependent Schrödinger equation is solved to obtain the electron dynamics using a Chebyshev polynomial expansion technique.⁶⁵ Once the wavefunction is obtained as $\psi(t) = \sum_i c_i(t) |i\rangle$, the diffusion constant is evaluated

as $D = \lim_{t \rightarrow \infty} \frac{\sum_i r_i^2 \langle c_i(t) | c_i(t) \rangle}{2dt}$ (d is the spatial dimension). The initial position is assumed to be at the origin $R = 0$. Averaging over hundreds of trajectories, the D is shown to be constant after enough long time. The TDWPD approach is very simple to account for the polaronic size effect in addition to the quantum nuclear effect because the spectral function characterizes the coupling between electronic state and harmonic oscillators. For real world molecules, all the parameters can be obtained from density functional theory (DFT) calculation, much as described in Sec. II. For the sake of simplicity, we did not consider the dynamic disorder here for the TDWPD simulation.⁶⁶

In the fully delocalized band limit, an approach based on the Boltzmann transport equation coupled with the acoustic phonon deformation potential (DP) approximation has been extremely efficient and reliable, as demonstrated for graphene and graphdiyne.⁶⁷ It can also be applied to a closely packed organic crystal.⁶⁸ DP theory assumed the longitudinal acoustic phonon being dominant, as in traditional silicon crystals. We found that if there exists plane mirror symmetry for the layered structure, the DP approximation is quite satisfactory compared with a more sophisticated approach taking all the phonon scatterings into account.⁶⁹ Thus, so far, we can evaluate the carrier mobility at four levels: the Marcus semi-classical theory, the Marcus theory with the quantum nuclear effect, TDWPD, and the bandlike DP theory, and all of these approaches can be applied in the first-principles level. Thus, it is ready to make a comparison for the theoretical room temperature mobility values, for example, for the five organic semiconductors, shown in Fig. 5. As discussed at the beginning of this section, for high mobility crystalline organic semiconductors, the hopping model is severely limited. The reason why the results are included is for comparison with other methods. The experimental crystal structures are employed for the starting structure. Figure 5(b) shows the mobility anisotropy, and Fig. 5(c) demonstrates the charge population density with delocalization length (L). The mobility values are presented in Table I.

Recently, the fragment orbital-based surface hopping (FOB-SH) approach has been demonstrated to be successful in calculating the carrier mobilities and delocalization lengths for pentacene, rubrene, and DATT.¹⁴ The delocalization lengths have been found to be around 10, in good agreement with the TDWPD results shown

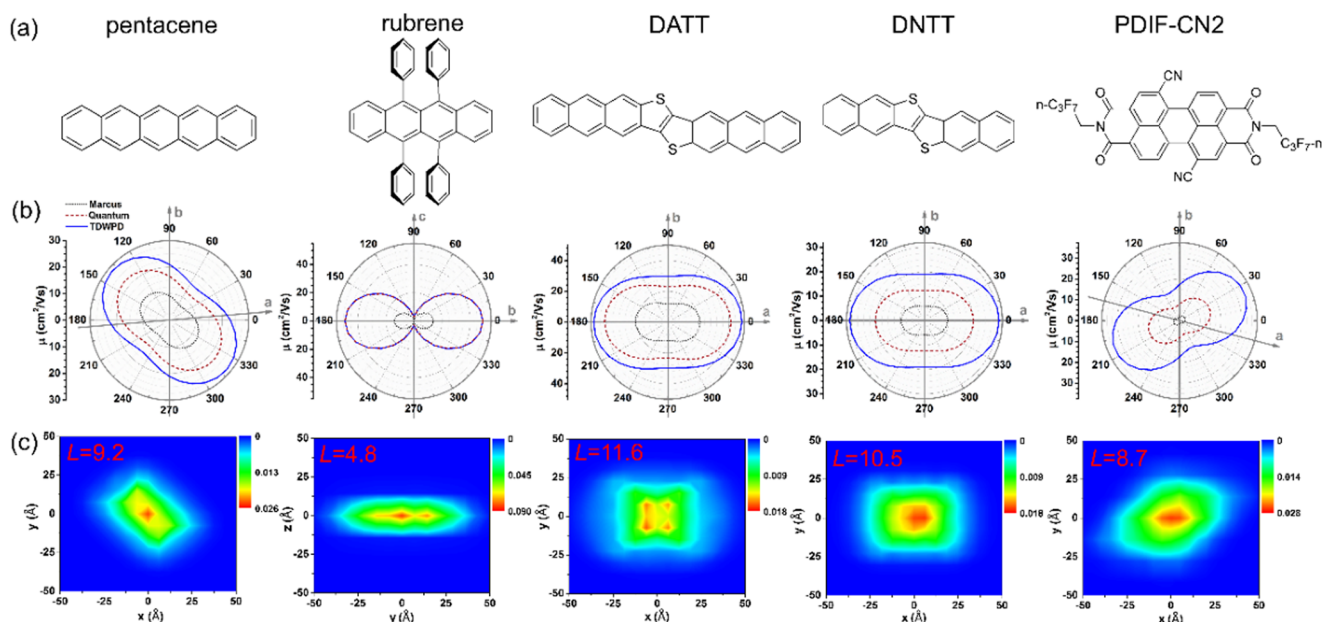


FIG. 5. (a) The molecular structures of the five systems; (b) the anisotropic mobilities from Marcus, quantum nuclear tunneling, and TDWPD methods; and (c) the distributions of charge population from TDWPD method and the corresponding 2D electronic delocalization lengths (L). Adapted with permission from Jiang *et al.*, *Nanoscale Horiz.* 1, 53 (2016). Copyright 2016 Royal Society of Chemistry.

TABLE I. The theoretical mobilities ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) along *a*, *b*, or *c* directions and the 3D-averaged (AVG) mobility resulted from Marcus, quantum nuclear tunneling, TDWPD, and DP methods. Partly adapted with permission from Jiang *et al.*, *J. Phys. Chem. Lett.* **5**, 2267 (2014). Copyright 2014 Royal Society of Chemistry.

	Marcus	Quantum	TDWPD	DP
Pentacene	<i>a</i> : 9.4	<i>a</i> : 16.9	<i>a</i> : 21.8	<i>a</i> : 58.0
	<i>b</i> : 9.3	<i>b</i> : 16.7	<i>b</i> : 21.1	<i>b</i> : 44.0
	AVG: 6.7	AVG: 11.8	AVG: 15.1	
Rubrene	<i>b</i> : 13.8	<i>b</i> : 48.9	<i>b</i> : 49.0	<i>b</i> : 242.6
	<i>c</i> : 0.8	<i>c</i> : 2.8	<i>c</i> : 3.2	<i>c</i> : 72.7
	AVG: 4.9	AVG: 17.2	AVG: 17.4	
DATT	<i>a</i> : 21.2	<i>a</i> : 41.3	<i>a</i> : 48.3	<i>a</i> : 322.6
	<i>b</i> : 11.6	<i>b</i> : 23.0	<i>b</i> : 29.6	<i>b</i> : 19.1
	AVG: 10.6	AVG: 21.1	AVG: 25.2	
DNNT	<i>a</i> : 9.5	<i>a</i> : 20.2	<i>a</i> : 30.7	<i>a</i> : 137.7
	<i>b</i> : 5.8	<i>b</i> : 12.2	<i>b</i> : 19.0	<i>b</i> : 76.4
	AVG: 5.1	AVG: 10.7	AVG: 16.3	
PDIF-CN2	<i>a</i> : 2.3	<i>a</i> : 12.1	<i>a</i> : 25.9	<i>a</i> : 132.8
	<i>b</i> : 1.5	<i>b</i> : 8.0	<i>b</i> : 17.4	<i>b</i> : 91.2
	AVG: 1.4	AVG: 7.5	AVG: 16.1	

in Fig. 5(c). Based on the numerical data in Table I, it is seen that (i) in general, the bandlike DP values are much larger than others and usually well overestimation for the experiment; (ii) the quantum nuclear effects represent a significant correction to the Marcus theory; and (iii) TDWPD, in principle, can consider both quantum nuclear effect and delocalization effect, while numerical data indicated that the latter effect is much less pronounced than the former. It is intriguing why this is the case given the localization lengths ~ 10 for these compounds are substantially larger than the fully localized value of 1. A plausible explanation will be given below when we move to the nearly exact solution from TD-DMRG.

TDWPD is based on the simple Haken–Strobl type of approximation, thus very efficient for large molecular systems, but the truncations to the stochastic Schrödinger equation could lead to uncontrolled errors. There are a number of wavefunction propagation approaches to describe charge mobility, from Ehrenfest mean-field dynamics, trajectory surface hopping, real-time time dependent DFT (TDDFT), and even at the MCTDH level, with the latter typically applied to ultrafast dynamics,^{70,71} instead of long time diffusion behavior for mobility. Trajectory surface hopping has become a promising method to study charge transport using mixed quantum–classical dynamics.⁷² An advantage of the method is the possibility to cooperate with fully atomistic non-harmonic potential instead of model Hamiltonian.^{73–76} For the carrier non-adiabatic dynamics in organic solids, there occur many surface crossing (from molecule to molecule). The trivial crossings between uncoupled and weakly coupled electronic states lead to severe problems in general extended systems.⁷² Recently, it has been pointed out that the widely used decoherence corrections further enhance the difficulty in treating trivial crossings and can easily lead to artificial long-range charge transfer, inducing enormous errors.^{77,78} In the

past few years, lots of efforts have been devoted to improving the performance of surface hopping simulations. To reduce the negative effects of decoherence corrections when the charge has already hopped to an improper electronic state, Wang and co-workers proposed a restricted decoherence approach, which applies the decoherence corrections only when the population of the active state is greater than a critical value.⁷⁹ To effectively deal with multiple trivial crossings during a single time step, they also proposed the crossing-corrected surface hopping algorithm, which classifies the surface crossings into four general types by state tracking and self-consistently corrects the hopping probabilities.⁸⁰ Moreover, a subspace with only important adiabatic states can be constructed for surface hopping simulations and greatly simplifies the surface crossings. These general approaches are compatible with different surface hopping algorithms. In systems with thousands of molecular sites and different strengths of electron–phonon couplings, converged charge transport dynamics has been achieved with a large time step size of 1 fs. Both the traditional hopping and band-like pictures of charge transport have been reproduced. The intrinsic charge localization length can be extracted from surface hopping trajectories and determines the mechanism of charge transport. Particularly, it is shown that the famous hopping-to-band crossover already occurs for charge carriers that spread over only a few molecular sites.

Oberhofer *et al.* have recently made a quite comprehensive assessment on the computational methods for carrier mobility of organic semiconductors.⁸¹ In addition to those, here, we add our very recent development of the time-dependent density matrix renormalization group (TD-DMRG) to solve the electron–phonon coupling problem for the molecular aggregate.^{21,82} This is especially challenging since most of the modern quantum dynamics methods for the complex system are most appropriate for ultrafast dynamics up to picosecond because the errors can be accumulated in time evolution. Mobility is a steady state property, which needs longtime behavior to the diffusion limit. Dynamic simulation is very hard to reach such a limit, except Ehrenfest or surface hopping dynamics. The typical (and original) Holstein Hamiltonian for the molecular aggregate reads

$$H = V \sum_n (c_{n+1}^\dagger c_n + h.c.) + \sum_{n,m} \omega_m b_{n,m}^\dagger b_{n,m} + \sum_{n,m} g_m \omega_m (b_{n,m}^\dagger + b_{n,m}) c_n^\dagger c_n, \quad (8)$$

where *n* is the index for molecule and *m* for the intramolecular vibrational mode and *g_m* is the coupling constant between the *m*th mode with the electronic degree of freedom. TD-DMRG is nearly exact, especially when the time-dependent variational principle with the projector-splitting algorithm (TDVP-PS) and graphical processing units (GPUs) are employed to accelerate the tensor contractions, the computational efficiency has been greatly enhanced, rendering TD-DMRG a quickly emerging method for quantum dynamics in the complex system, comparable to the state-of-the-art multi-layer multiconfiguration time-dependent Hartree (ML-MCTDH), with even more versatility, e.g., for flexible quantum state manipulations due to the matrix product structure as well as efficient finite temperature algorithms.⁸³ Taking rubrene as an example, quantum chemistry calculations are performed for *V*, ω_m , and *g_m*, and these showed

a strong anisotropy that the intermolecular electronic coupling in the stacking direction is much larger than the others. Hence, a one-dimensional chain is considered here with $V = 83$ meV, and we keep only nine molecular vibrational modes with the most significant reorganization energy $\lambda = 2 \sum_m \lambda_m = 2 \sum_m g_m^2 \omega_m = 151$ meV.

The carrier mobility is evaluated with the Kubo formula, $\mu = \frac{1}{2k_B T e_0} \int_{-\infty}^{\infty} \langle \hat{j}(t) \hat{j}(0) \rangle dt \equiv \frac{1}{2k_B T e_0} \int_{-\infty}^{\infty} C(t) dt$, where the current operator is $\hat{j} = \frac{e_0 V R}{i\hbar} \sum_n (c_{n+1}^\dagger c_n - c_n^\dagger c_{n+1})$. The temperature effect is introduced by thermal field dynamics or called purification method by expanding the thermal equilibrium density matrix of any mixed state in physical space P to the enlarged direct product $P \otimes Q$ space, where Q is auxiliary space to be traced over and the thermal density operator can be expressed as $\hat{\rho}_\beta = \frac{e^{-\beta \hat{H}}}{Z} = \frac{\text{Tr}_Q |\Psi_\beta\rangle \langle \Psi_\beta|}{\text{Tr}_Q |\Psi_\beta\rangle \langle \Psi_\beta|}$, where Z is the partition function.⁸⁴ $|\Psi_\beta\rangle$ expressed in the direct product space is a pure quantum state, which can be represented by a matrix product state (MPS) and can be obtained by evolution in the imaginary time space starting from $\beta \equiv \frac{1}{k_B T} = 0$ where all the states are equally populated (identity density matrix $|I\rangle$), to any finite temperature $\beta/2$,

$$|\Psi_\beta\rangle = e^{-\beta \hat{H}/2} |\Psi_{\beta=0}\rangle = e^{-\beta \hat{H}/2} |I\rangle, \quad (9)$$

where $\hat{H} = \hat{H} \otimes \hat{I}_Q$ and $|\Psi_{\beta=0}\rangle = \sum_i |i\rangle_P |i\rangle_Q$ at infinitely high temperature. The current-current correlation function at $t = 0$ now can be calculated as $C(0) = \langle \Psi_\beta | \hat{j}(0) \hat{j}(0) | \Psi_\beta \rangle$. The real time evolution for the current-current correlation function is obtained at each temperature by

$$C(t) = \langle \Psi_\beta | e^{i\hat{H}t} \hat{j}(0) e^{-i\hat{H}t} \hat{j}(0) | \Psi_\beta \rangle / Z(\beta). \quad (10)$$

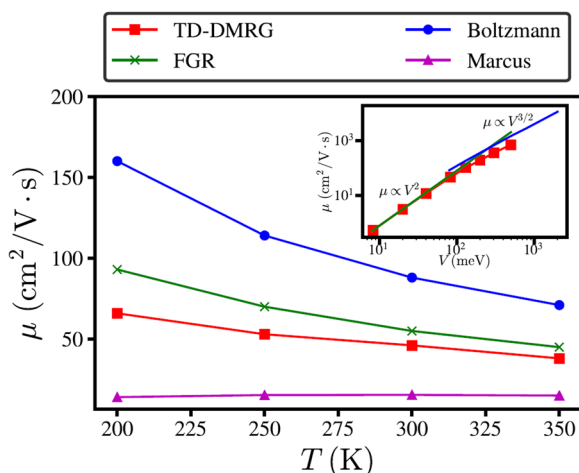


FIG. 6. Comparison of the numerical assessed hole mobility in rubrene as a one-dimensional chain by a different approach. The inset shows the dependence on the electronic coupling constant V from V^2 in perturbation to $V^{3/2}$ in large V for bandlike.

The TDVP-PS algorithm is employed for both imaginary time evolution [Eq. (9)] and real time evolution [Eq. (10)]. The GPU can be very helpful to accelerate the numerical computations.⁸⁵ The evaluated hole mobility as a function of temperature is depicted in Fig. 6, in comparison with Marcus theory, the Fermi's golden rule, and the bandlike Boltzmann theory. Marcus theory is a thermal activation process (which is pretty flat in the temperature range and the scale is large to display the bandlike value), and all others show a “bandlike” decreasing behavior. It is noted that Fermi's golden rule curve is above the TD-DMRG. This is quite paradoxical since the former assumed a localized charge state hopping assisted by nuclear quantum fluctuation and the latter assumed a finite size polaron with delocalization, favorable for charge transport, which would be above the former. In fact, in FGR, the transfer rate is proportional to V^2 from first-order perturbation. As shown in the inset of Fig. 6, for the nearly exact TD-DMRG, as V increases, dependence deviates from quadratic, approaching to $V^{3/2}$, the real bandlike limit. Thus, the V^2 assumption can overestimate the mobility.

IV. PERSPECTIVES

There exist a vast number of publications on the theoretical and computational work for carrier mobility of organic semiconductors. It is the least motivation of this Perspective to give a comprehensive discussion on the vast literature. Instead, we present some of our own understandings of the problem in a step by step way. It should be noted that the phenomenological simulation pioneered by Bäessler had played essential roles in organic electronic device physics under which the organic materials, being small molecule or polymer, were described by disorder with certain distribution (Gaussian type, for instance) and empirical distribution of density of states, and the charge (or exciton) transport follows the hopping process as a function of carrier density and external field.⁸⁶ There exists vast literature along this line and from the comparison with experiments; the mechanism related to charge recombination, separation, and migration could be deduced.⁸⁷ However, it is difficult to provide insight into materials design from such models because the microscopic nature of disorder at the molecular level is ill-defined. Recent advances based on stochastic models try to derive the nature of morphology and disorders from molecular dynamics simulation for amorphous organic materials.⁸⁸ When combined with first-principles evaluation of mobility, it can present more comprehensive understandings from both molecular design and device physics perspectives, which deserve further investigations. TD-DMRG is a promising tool to study the microscopic charge transport mechanism due to its high accuracy and unbiased nature. As far as TD-DMRG is concerned, the major problem arises from the constraint on the dimensionality of the model because the number of MPS variational parameters required for two or three dimensions is much more than that of one-dimension. Plausible avenues to reduce the computational cost include treating low-frequency molecular vibrations classically, adopting a more generalized tensor renormalization ansatz, and then incorporating machine learning techniques into the TD-DMRG time evolution. It remains a big challenge to make a balance of high accuracy and complex problem.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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