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Quantum dynamic localization in the Holstein Hamiltonian at finite temperatures

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It is shown that dynamic localization of the charge carrier is present in the simple Holstein Hamiltonian (fully quantum and without random variables) if the polaron binding energy is sufficiently small and the small polaron is not formed at high temperature. Previously, this idea was only explored in semiclassical models of organic semiconductors. Band renormalization cannot be used in the presence of dynamic localization, which is best studied with a vibronic basis set introduced here. The lifetime of these vibronic states can be estimated using second-order renormalized perturbation theory. In the regime of dynamic localization the diffusivity displays a transition between metal-like and insulator-like transport as the temperature increases, similar to that predicted and observed in the nonadiabatic regime.

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I. INTRODUCTION AND BACKGROUND

Numerous investigations in the charge transport properties of organic semiconductors have pointed out their peculiarity with respect to their inorganic counterparts.[1,2] The most striking feature is the presence of narrow bands[3,4] and strong electron-phonon coupling,[5,6] two elements that prompted the study of *dynamic localization* in organic materials. These investigations are semiclassical in nature, i.e., the nuclei are treated classically at finite temperature and the charge carrier is described quantum mechanically.[7–10] It was noted that the electronic Hamiltonian computed at frozen nuclear configuration is that of a disordered system, because the translational symmetry, at each given time, is broken by the nuclear motions, and the instantaneous eigenfunctions are therefore localized[11] (a fraction of them may still be delocalized[12]). The time evolution of such localized wave function have characteristics compatible with the experimental observation and lead to a satisfactory evaluation of the absolute charge mobility without the need of adjustable parameters.[13]

The fully quantum descriptions of the electron-phonon Hamiltonian,[14] however, do not include any dynamic localization feature (its eigenfunctions must be translationally invariant[15]), making the semiclassical description of dynamic localization a concept disconnected with most of the work done on electron-phonon systems in the past years. In this paper we try to remedy to this limitation discussing an alternative approach to the (quantum) electron-phonon problem that incorporates the effect of dynamic localization and that has, at sufficiently high temperature, the same qualitative features of the semiclassical model. We plan to illustrate the effect of quantum dynamic localization on one of the simplest and most studied model Hamiltonian, to allow a better comparison with the existing literature and to prove that dynamic localization is a general feature of Hamiltonians with electron-vibron coupling and it is not related to more complicated features of organic semiconductors (e.g., Peierls electron-phonon coupling, multiple optical modes and electronic bands), which will be neglected here.

A milestone for the study of the electron dynamics in molecular crystal is provided by the work of Holstein[16] whose one-dimensional model Hamiltonian is the starting point of many investigations, including ours

$$H=\sum_j\left(a_j^\dagger a_j+\frac{1}{2}\right)+\sum_j \varepsilon_j c_j^\dagger c_j+\sum_j V_0(c_j^\dagger c_{j+1}+\text{H.c.})+\sum_j \lambda c_j^\dagger c_j(a_j^\dagger+a_j). \qquad (1)$$

Here $a_j^\dagger/a_j$ ($c_j^\dagger/c_j$) are the creation/annihilation operators for the phonon (electron), λ the electron-phonon coupling parameter, ε_j the on-site electronic energy, and V_0 the nearest-neighbor electronic coupling. The (dispersionless) phonon energy $\hbar\omega$ is taken as the energy unit of the Hamiltonian which implies one electronic and one localized phonon state per lattice site j.

Holstein's discussion of the Hamiltonian above clarified that there are two limit cases, easy to deal with, and a very difficult intermediate regime investigated by many researchers for five decades after the original paper.[14,17,18] The best way to describe the conventional limiting cases is by performing the Lang-Firsov[19] transformation. The transformed Hamiltonian takes the form

$$\tilde{H}=\sum_j\left(a_j^\dagger a_j+\frac{1}{2}\right)+\sum_j(\varepsilon_j-\lambda^2)c_j^\dagger c_j+\sum_j V_0(c_j^\dagger c_{j+1}e^{\lambda[(a_j^\dagger-a_j)-(a_{j+1}^\dagger-a_{j+1})]}+\text{H.c.}). \qquad (2)$$

Before the transformation [Eq. (1)] the Hamiltonian is represented by a set of wave functions $\{\phi_j\prod_{k\neq j}\Lambda_{v_k}(x_k)\}$, where ϕ_j is the electronic wave function localized on j and $\{\Lambda_{v_k}(x_k)\}$ are the vibrational wave functions in the absence of charge (v_k is the quantum number, x_k the displacement and Λ the harmonic oscillator wave function). The transformation consists in the use of another diabatic basis set where the electronic wave function ϕ_j is multiplied by the same vibrational wave functions for $k\neq j$ and by a vibrational wave function displaced by $\lambda\sqrt{\frac{2\hbar}{m\omega}}$ for $k=j$. The notation $\{|j;v_1\ldots v_k\ldots\rangle\}$ will be used in the following sections to indicate this latter basis set. We note that this diabatic basis set corresponds to the exact eigenfunctions in the limit of vanishing V_0.

The first limiting case is for low electron-phonon coupling or temperature, when one can assume that the phonons, in thermal equilibrium, modulate weakly the electronic Hamiltonian. In this limit one can substitute the complicated electron-phonon coupling term with its thermal average, i.e.,

$$\begin{aligned}\tilde{V} &= V_0 c_j^\dagger c_{j+1} e^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]} \\ &\sim \langle V_0 e^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]}\rangle_T c_j^\dagger c_{j+1}. \end{aligned} \tag{3}$$

The average is defined as $\langle\tilde{V}\rangle_T = \Sigma_\alpha \exp(-\beta E_\alpha)\langle\alpha|\tilde{V}|\alpha\rangle / \Sigma_\alpha(\exp -\beta E_\alpha)$, where $\{|\alpha\rangle\}$ are states with all possible distributions of phonon energies. Qualitatively, one is considering a system where the mixing between states with different phonon occupation number is not important. The average in Eq. (3) can be evaluated analytically[20]

$$\langle V_0 e^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]}\rangle_T = V_0 e^{-2\lambda^2(1/2+N)} \equiv V_T^{eff} \tag{4}$$

with temperature-dependent $N=(e^{1/T^*}-1)^{-1}$ and reduced temperature $T^*=k_B T/\hbar\omega$. The formula above expresses the "band-narrowing" with temperature, i.e., the reduction in the average intersite coupling to an effective value V_T^{eff} due to the vibronic interaction and the consequent increase in effective mass. The charge carrier described in this limit is delocalized and its mobility decreases with temperature (because the scattering time decreases as the number of phonons increases with temperature). Many recent contributions in the field of organic electronics are based on a generalization of this scheme to three-dimensional Hamiltonians with more phonons and electronic states per unit cells[21] and can be now based on accurate *ab initio* calculations of the Hamiltonian parameters.[22,23]

The opposite limiting case occurs at high temperature, high electron-phonon coupling. Here the electron can be considered completely localized on one site because all the polaronic band states are degenerate, and the process of hopping from one site to another can be studied in a model two-site Hamiltonian

$$\begin{aligned}\tilde{H}_{1,2} = &\sum_{j=1,2}\left(a_j^\dagger a_j + \frac{1}{2}\right) + \sum_{j=1,2}(\varepsilon_j - \lambda^2)c_j^\dagger c_j \\ &+ V_0(c_1^\dagger c_2 e^{\lambda[(a_1^\dagger - a_1)-(a_2^\dagger - a_2)]} + \text{H.c.})\end{aligned} \tag{5}$$

for which it is possible to express the hopping rate in the high-temperature limit[16] as

$$k_{hop} = \omega V_0^2\left(\frac{\pi}{2T^*\lambda^2}\right)^{1/2}\exp\left(-\frac{\lambda^2}{2T^*}\right). \tag{6}$$

This is also used by several authors[24–27] in conjunction with electronic-structure calculations, although it appears that there are fewer molecular crystalline materials for which the assumptions leading to Eq. (6) are valid. When Eq. (6) is valid, e.g., for the study of transport in several insulating metal oxides,[28,29] the mobility increases with temperature. A crucial feature of this limit case is that the charge mobility can be entirely determined by the parameters of Hamiltonian (1) while, in the delocalized case, the polaron is scattered by impurities (or other mechanisms) which are not included in the model Hamiltonian.

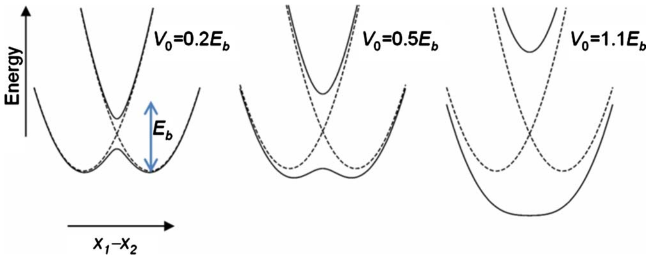

FIG. 1. (Color online) Dashed lines represents the energy of two localized states in the Holstein Hamiltonian with two sites and $V_0=0$ (diabatic states) as a function of the relative displacement. Solid lines are the adiabatic (Born-Oppenheimer) states for different values of the coupling V_0 relative to the classical polaron binding energy E_b ($E_b \sim \lambda^2$ in the notation of this paper) For V_0 larger than E_b there are no localized states. The only localization possible is due to thermal disorder and this is the regime investigated in this paper.

The existence of many materials which appeared to be far from both limiting cases[30,31] prompted the investigation of the crossover between polaron band transport and small polaron incoherent hopping which was approached with many methods[32–43] covering almost the totality of the theoretical solid-state physics methodologies. Since the charge dynamics can be described by a suitable separation between zeroth-order Hamiltonian and a small perturbation, the two limiting cases of the Holstein Hamiltonian can be seen as two different choices of the zeroth-order Hamiltonian suitable at low and high temperature, respectively. It was therefore natural to search for a temperature-dependent analog of the Lang-Firsov transformation which make the off-diagonal terms of the Hamiltonian sufficiently small at finite temperature. This avenue, followed by Silbey and co-workers,[32–34] always involves a thermal average of the phonon degrees of freedom [analog to Eq. (4)] which assumes the presence of a polaron band in the system, i.e., a quasiparticle with a well-defined crystal momentum and dispersion relation. Most of the alternative approaches to the intermediate cases (including dynamic mean-field theory[35] and quantum Monte Carlo approaches[36–38]) build a dispersion relation for the polaron and involve at some point an averaging out of the phonon degrees of freedom that decouple the electron and the boson part of the Hamiltonian. The variational method proposed by Bonča *et al.*[39] also searches for a delocalized (Bloch-type) ground state, linear combination of localized vibronic wave functions and a similar ansatz it is found in alternative variational calculations.[40–42] Diagrammatic techniques have been used to study the situation where there is a coexistence of polaronic band and incoherent hopping.[43]

However, the small polaron incoherent hopping limit [Eq. (9)] is not the only high-temperature limit. As already recognized in the original Holstein paper, the coupling V_0 should be smaller than the polaron binding energy in order to form a small polaron localized on one site. When the two-site Holstein problem is represented in the configuration coordinate (Fig. 1) one can appreciate how, for small V_0, one can use perturbation theory to study the hopping between the potential-energy wells, for larger V_0, the hopping occurs adiabatically in the lowest potential-energy surface and for even larger V_0 the two localized potential-energy minima merge into a single delocalized minimum. In this regime, where there is the largest disagreement between the different methods,[44] the source of localization at high temperature is not the formation of a small polaron but dynamic localization.

Dynamic localization is a concept well defined, so far, only in the semiclassical limit. The semiclassical limit of the Holstein Hamiltonian corresponds to a one-dimensional chain of energy levels whose on-site energy is linearly modulated by the displacement of classical harmonic oscillators. When the oscillators are displaced from the equilibrium at finite temperature, the eigenfunctions of such a system are localized at each given instant and they break the translational symmetry of the problem. While the (translationally invariant) quantum description is obviously always valid, in the semiclassical limit this would be very inconvenient and, although one could express the dynamics in terms of superposition of translationally invariant states, it is best to separate electronic and nuclear degrees of freedom and describe the latter classically. If we assume that the correspondence principle is valid as the nuclear degrees of freedom become more classical (for example, increasing the temperature or decreasing their frequency), there must be a transition regime where the description in terms of localized electronic states starts becoming more convenient than a description based on translationally invariant states. We would like to propose a description of the charge dynamics in the Holstein Hamiltonian which acts as a bridge between the polaronic description valid for high-frequency modes and the dynamic disorder description valid in the semiclassical limit, when a small polaron cannot be formed.

We propose in this paper that this intermediate regime between localized and delocalized transport can be studied using a suitable *localized vibronic basis* set which allows to incorporate the effect of dynamic disorder originally devised for semiclassical models.

II. BREAKDOWN OF THE BAND NARROWING APPROXIMATION

In the transformed Hamiltonian of Eq. (2) the electronic and nuclear modes are coupled together by the term $V_0 c_j^\dagger c_{j+1} e^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]}$ which makes the Hamiltonian not exactly diagonalizable. Substituting this coupling with its thermal average, as done in Eq. (4), is a classic way to decouple electronic and nuclear degrees of freedom and to introduce the idea that the band narrows as the temperature increases. However, this averaging is meaningful as long as the distribution of $Ve^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]}$ around its average value is sufficiently narrow.

A rapid way to estimate the validity range of the band-narrowing concept is to plot the standard deviation σ_V of $V_0 e^{\lambda[(a_j^\dagger - a_j)-(a_{j+1}^\dagger - a_{j+1})]}$ for phonon distributions at different temperature alongside the thermally averaged coupling V_T^{eff} as done in Fig. 2 for a particular value of λ. It is evident that, already at relatively low temperatures, the standard deviation of the coupling becomes of the same order of magnitude of its average value, i.e., if we fix the phonon occupation number and build the corresponding electronic Hamiltonian the elements of latter will be "disordered." In particular, for fixed phonon occupation numbers at high temperature the Hamiltonian of Eq. (2) will lead to a one-dimensional electronic Hamiltonian with *off-diagonal disorder*. To better appreciate the parameter range where the disorder due to the phonons is relevant we defined the reduced temperature $T_{0.5}^*$ at which $\sigma_V / V_T^{eff} = 0.5$, i.e., the disorder in the coupling is very high, and we plotted this temperature as a function of the electron-phonon coupling parameter λ in Fig. 3. For $\lambda \sim > 0.4$ the reduced temperature at which the disorder is very high approaches the unity. This result should not be surprising as this is precisely the parameter range where the electron-phonon coupling term [in the transformed Hamiltonian of Eq. (2)] is of the same order of magnitude of the other terms and the thermal averaging procedure of Eq. (4) hides part of the physics. The presence of a large σ_V / V_T^{eff} ratio can be considered indicative of the presence of dynamic localization, i.e., the phonon distribution creates sufficient disturbance to the electronic Hamiltonian to cause localization of the wave function also if the electron-phonon coupling is not leading to the formation of a small polaron.

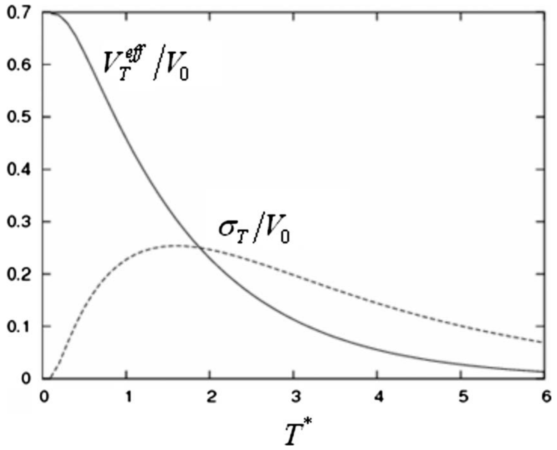

FIG. 2. Temperature-averaged intersite coupling [Eq. (4)] and standard deviation of the actual coupling between states for $\lambda = 0.6$ as a function of the reduced temperature.

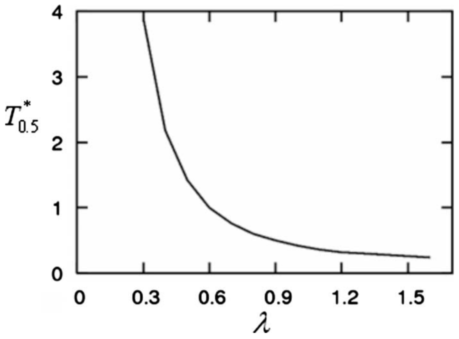

FIG. 3. Reduced temperature $T_{0.5}^*$ at which $\sigma_V / V_T^{eff} = 0.5$ as a function of λ.

In this paper we wish to describe the wave function in such a way that it behaves as a conventional polaronic wave function at low temperature and as a dynamically localized wave function at high temperature, so that we can put the semiclassical concept of dynamic localization on a firmer ground. Since the fully quantum description is translationally invariant while the semiclassical description breaks the translational symmetry, the transition between the two should be described in the lower symmetry. More specifically one should modify the semiclassical description to make it approach the polaron description in the quantum limit, while the opposite process would not work. In the semiclassical limit one evaluates the electronic Hamiltonian at given nuclear configurations and neglects the nuclear dynamics. To be able to approach this limit while keeping a quantum description of the nuclear modes one has to assume that a good description of the electronic Hamiltonian derives again from neglecting nuclear dynamics, which, in the quantum description of the nuclei, corresponds to fixing the vibrational quantum numbers while evaluating the electronic Hamiltonian.

More specifically, we considered the basis set $\{|j;v_1 \ldots v_k \ldots\rangle\}$ used to represent the Hamiltonian in Eq. (2) (see above) where each basis function is the product of an electronic state localized on site j and M vibrational wave functions localized on the M sites of the system. We therefore defined subsets of this complete basis set containing a fixed vector of quantum numbers $\{v_1 \ldots v_k \ldots\}$ and all the electronic states $j=1,\ldots,M$, and we computed the electronic wave function diagonalizing the Hamiltonian of size M. These partially diagonalized vibronic wave functions (PDVW) are therefore a linear combination of the localized vibronic wave function all with the same vibrational quantum numbers, i.e.,

$$\psi^{(l)}_{\{v_1 \ldots v_k \ldots\}} = \sum_j C^{(l)}_j |j;v_1 \ldots v_k \ldots\rangle \tag{7}$$

with l running over all the M eigenvalues. The $\psi^{(l)}_{\{v_1 \ldots v_k \ldots\}}$ are the quantum analogs of the instantaneous electronic wave functions considered in semiclassical models where they are obtained by diagonalizing the electronic Hamiltonian at fixed nuclear configurations.[10]

Diagonalization can be repeated for various sets of vibrational quantum numbers randomly chosen from the Bose-Einstein distribution and the results can be analyzed to study, for example, (i) the density of electronic states as a function of temperature and (ii) the average localization length as a function of temperature and energy as done in Fig. 4 for the coupling parameters λ=0.6, $V_0=4.0$. Finite chains of 200 sites have been used for this and the subsequent analyses. The density of states (DOS) and localization length of one-dimensional chains in the presence of off-diagonal disorder have been studied extensively,[45,46] with particular emphasis on the unexpected differences with respect to the (more common) models with disorder in the diagonal matrix elements of the electronic Hamiltonian. Albeit the distribution of the random component of the Hamiltonian is different in the present case, the results are qualitatively similar. The density of states [Fig. 4(a)] starts departing from that of the periodic chain already at $T^*=0.6$, while a discontinuity at $E=0$ develops at higher temperatures (higher disorder) in agreement with other one-dimensional disorder models in literature.[45] The localization length ξ is computed from the expectation value of the (square) position operator as $\xi=(\langle x^2\rangle-\langle x\rangle^2)^{1/2}$ and reported in Fig. 4(b). As expected, the localization length decreases with increasing temperature and possess a similar discontinuity at $E=0$ which is extensively discussed elsewhere (it will not have any impact on our discussion).[47]

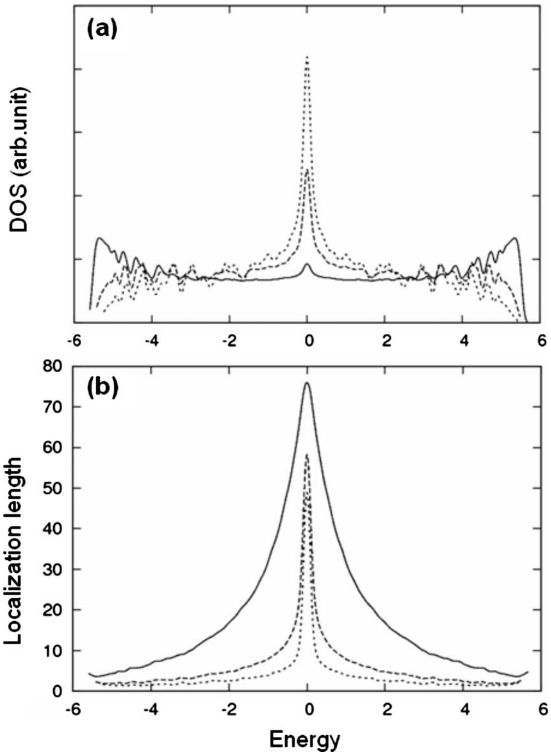

FIG. 4. Density of states (a) and localization length (b) as a function of electronic energy for a model with λ=0.6, $V_0=4.0$ and $T^*=0.6$ (solid), 1.0 (dashed), 1.4 (dotted).

A more compact illustration of the parameter range where dynamic localization can be important is given by a map of the Boltzmann averaged localization length as a function of the reduced temperature and the electron-phonon coupling (given in Fig. 5). The behavior is rather simple for λ<1 and $T^*<2$ showing an expected decrease in localization length

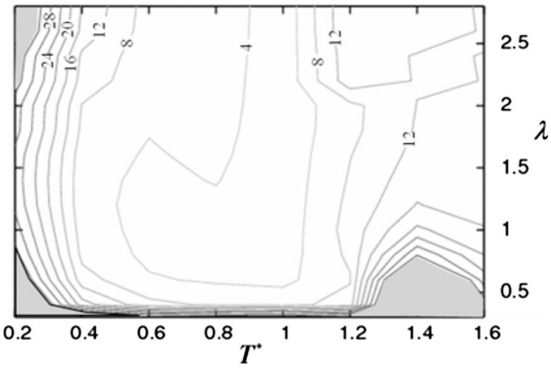

FIG. 5. Map of the average localization length as a function of the reduced temperature and electron-phonon coupling.

with increase in T^* or increase in λ. The complicated behavior for $\lambda > 2$ (not investigated in detail here) is due to the complex pattern of Franck-Condon integrals, $\langle v_j | e^{\lambda(a_j^\dagger - a_j)} | v_j \rangle$, in this parameter range. The essential point of Fig. 5 is that there is a very broad range of parameters where the PDWF are localized in less than eight sites and in this regime, we are arguing, the charge transport should be described by a suitable localized basis set. It should be stressed that the eigenfunctions of Hamiltonian (1) are certainly delocalized and translationally invariant and we do not claim a symmetry breaking of the eigenfunctions (which is forbidden by a theorem discussed in Ref. 15). On the other hand, when the bandwidth vanishes (i.e., at high temperature), one can argue that it is not useful to describe the dynamic of the system in a delocalized basis of Bloch wave functions. Whether the high-temperature limit is the small polaron or dynamic disorder, the band structure is "washed out," as recognized by Holstein,[16] and the polaron states are no longer Bloch states.[44] In this limit the localized and delocalized representations become equivalent, and the localized basis offers a more convenient description of the electron dynamics.

III. CHARGE DIFFUSION IN THE DYNAMIC LOCALIZATION REGIME

Basis functions for dynamic localization. We can now compare the regime of dynamic disorder with the classical limit cases of the Hamiltonian in Eq. (2). In the low temperature or low electron-phonon coupling regime, the approximation of Eq. (3) holds and one can write a zero-order Hamiltonian with translational symmetry and a well-defined dispersion relation for a delocalized polaron where the polaron wave vector is a good quantum number. At higher temperatures, however, the translational symmetry of the electronic Hamiltonian is lost and with that the possibility of defining a polaron and of using its wave vector as a good quantum number for the electronic wave function. In this regime of dynamic localization, the system is also very far from the opposite limit of activated hopping transport, where the matrix elements of $\tilde{V}$ are small and can be treated as a small perturbation. In dynamic localization these matrix elements are still comparable to V_0 and it is their *variation from site to site* that causes the charge to localize not their smallness. The two conventional limits of the Holstein Hamiltonian, characterized by two different sets of zero-order eigenfunctions used to describe charge transport, are therefore entirely inappropriate for the dynamic localization regime. It is proposed that, in this latter regime, the PDVW basis set given in Eq. (7) is the most suitable basis to describe transport because it takes into account the effect of localization due to disorder and it allows the evaluation of each state's lifetime. We should stress that, differently from other works on the effect of disorder in model Hamiltonians the "disorder" here is entirely due to finite temperature and electron-phonon coupling, i.e., there is no random variable[48–51] or phenomenological dephasing[52] in the model.

Lifetime of partially diagonalized vibronic wave functions. The wave functions defined in Eq. (7) are not eigenfunctions of the Hamiltonian but become asymptotically the correct eigenfunctions of the Hamiltonian in the limit of high temperature. They form our zeroth-order set of wave functions, which are corrected with a perturbative methods in this section. Each PDVW $\psi^{(l)}_{(v_1 \ldots v_k \ldots)}$, with average localization length ξ, is coupled to the family of all states $\{\psi^{(l)}_{(v_1 \ldots v_k \ldots)}\}$ with different distribution of vibrational quantum numbers and it has therefore a characteristic lifetime $\tau = \hbar/\Gamma$ (Γ is the imaginary component of the self-energy). Since a state can be only coupled to states localized close to it, the one-dimensional diffusion coefficient for the charge should be on the order of $\xi^2 \Gamma / 2\hbar$.

To evaluate the self-energy we use second-order renormalized perturbation theory[53] adopted in the classical work of Abou-Chacra *et al.*[54] to study static electronic disorder and identify the condition for localization. A similar method was used by Logan and Wolynes for the study of vibrational energy flow,[55] and, to some extent, this paper can be considered a combination of the methods of Refs. 54 and 55. The self energy is also used as an indicator of dynamic localization-delocalization in the work of Hotta and Takada on infinite-dimensional Hubbard-Holstein model (Ref. 56). Since each state is coupled to many states, which in turn are coupled to many other states, a useful approximation is to assume that the network of couplings behaves as a self-avoiding Cayley's tree and, in such case, the imaginary component of the self-energy of state i can be written as

$$\Gamma_i = \sum_j |\langle \psi_i | V | \psi_j \rangle|^2 \frac{\Gamma_j}{(\mathcal{E}_i - \mathcal{E}_j)^2 + \frac{1}{2}\Gamma_j^2}, \tag{8}$$

where $\mathcal{E}_i$ and $\mathcal{E}_j$ are the total energy of states i and j (the real component of the self-energy is neglected). To adapt this approach to our case we assume that the self energy can be written as a function of the electronic energy $[\Gamma_i \approx \Gamma(E_i)]$, essentially an average of the individual self-energies defined as

$$\Gamma(E) \equiv \sum_k \Gamma_k \delta(E - E_k) / \sum_k \delta(E - E_k). \tag{9}$$

In the transition from state i to state j, let w be the difference in total vibrational energy (also the difference in total vibrational quanta which are taken as energy units of our Hamiltonian). Equation (8) can be modified as follows:

$$\Gamma(E_i) = \sum_w \sum_{j(w)} |\langle \psi_i | V | \psi_j \rangle|^2 \frac{\Gamma(E_j)}{(E_i - E_j - w)^2 + \frac{1}{2}\Gamma(E_j)^2}. \tag{10}$$

The summation $j(w)$ is extended over all states j with w vibrational quanta more than in state i ($w = 0, \pm 1, \pm 2$, etc.). The energies E_j, E_i are purely electronic energies. It is convenient to define an average coupling between states with different electronic energy and a given difference in vibrational quanta as

$$\widetilde{V}_w^2(E',E) \equiv \sum_i \delta(E_i - E') \sum_{j(w)} |\langle \psi_i | V | \psi_j \rangle|^2 \times \delta(E_j - E) / \sum_i \delta(E_i - E') \tag{11}$$

which allow to rewrite Eq. (10) as

$$\Gamma(E') = \sum_w \int \widetilde{V}_w^2(E',E) \frac{\Gamma(E)}{(E' - E - w)^2 + \frac{1}{2}\Gamma(E)^2} dE. \tag{12}$$

To evaluate Eq. (10) one has to compute $\widetilde{V}_w^2(E',E)$ by a sufficiently accurate sampling of the coupling between PDVW states, which can be carried out numerically (see below). Then the integral is solved iteratively by initializing $\Gamma(E)$ to some arbitrary constant value. In this paper we solved Eq. (12) by discretizing the energy variables in 19 bins between the edges of the electronic DOS and initializing $\Gamma(E)$ to $0.1V_0$.

Evaluation of the coupling between PDVWs. The evaluation of $\widetilde{V}_w^2(E',E)$ is the most demanding part of the calculation and was carried out for a range of temperatures with $V_0=4$ and $\lambda=0.6$. At each given temperature the vibrational quanta $\{v_k^0\}$ are distributed according to the Bose-Einstein distribution and the electronic Hamiltonian is diagonalized to give the initial basis set $\psi^{(l)}_{\{v_1^0 \ldots v_k^0 \ldots\}}$ of Eq. (7). For each state l we compute all the non-negligible couplings with the other vibronic states $\psi^{(l')}_{\{v_1^m \ldots v_k^m \ldots\}}$, which should be, in principle, include all possible distributions of vibrational quanta $\{v_k^m\}$. Fortunately, the number of distributions $\{v_k^m\}$ to be considered is large but limited as one can appreciate by writing explicitly the coupling between two PDVWs corresponding to distinct distributions of vibrational quanta,

$$\begin{aligned}\langle \psi^{(l)}_{\{v_k^0\}} | \widetilde{V} | \psi^{(l')}_{\{v_k^m\}} \rangle &= \sum_{jj'} C_j^{(l)} C_{j'}^{(l')} \langle j; \{v_k^0\} | \widetilde{V} | j'; \{v_k^m\} \rangle \\ &= V_0 \sum_j C_j^{(l)} C_{j+1}^{(l')} \langle v_j^0 | e^{\lambda(a_j^\dagger - a_j)} | v_j^m \rangle \\ &\quad \times \langle v_{j+1}^0 | e^{-\lambda(a_{j+1}^\dagger - a_{j+1})} | v_{j+1}^m \rangle \prod_{j' \neq j, j+1} \delta_{v_j^0, v_j^m}.\end{aligned} \tag{13}$$

Only a reduced sets of vibrational quanta distributions $\{v_k^m\}$ give rise to wave functions $\psi^{(l')}_{\{v_1^m \ldots v_k^m \ldots\}}$ that can be coupled to $\psi^{(l)}_{\{v_1^0 \ldots v_k^0 \ldots\}}$. More in detail:

(i) if $\{v_k^0\}$ and $\{v_k^m\}$ differ only in one site, i.e., $v_{\bar{j}}^0 \neq v_{\bar{j}}^m$ and $v_j^0 = v_j^m$ for $j \neq \bar{j}$ the coupling is

$$\begin{aligned}\langle \psi^{(l)}_{\{v_k^0\}} | \widetilde{V} | \psi^{(l')}_{\{v_k^m\}} \rangle &= V_0 C_{\bar{j}}^{(l)} C_{\bar{j}+1}^{(l')} \langle v_{\bar{j}}^0 | e^{\lambda(a_{\bar{j}}^\dagger - a_{\bar{j}})} | v_{\bar{j}}^m \rangle \langle v_{\bar{j}+1}^0 | e^{-\lambda(a_{\bar{j}+1}^\dagger - a_{\bar{j}+1})} \\ &\quad \times | v_{\bar{j}+1}^0 \rangle + V_0 C_{\bar{j}-1}^{(l)} C_{\bar{j}}^{(l')} \langle v_{\bar{j}-1}^0 | e^{\lambda(a_{\bar{j}-1}^\dagger - a_{\bar{j}-1})} | v_{\bar{j}-1}^0 \rangle \\ &\quad \times \langle v_{\bar{j}}^0 | e^{-\lambda(a_{\bar{j}}^\dagger - a_{\bar{j}})} | v_{\bar{j}}^m \rangle,\end{aligned} \tag{14}$$

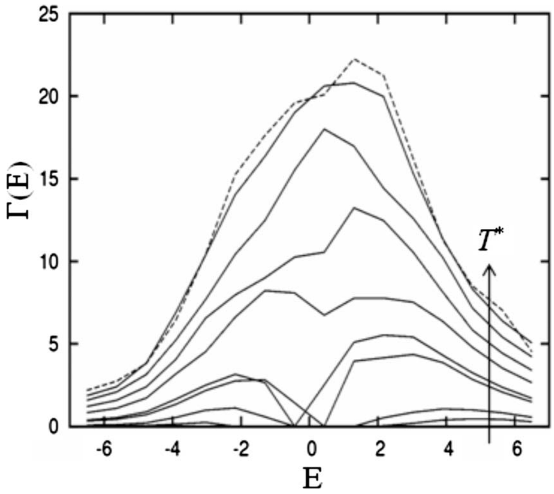

FIG. 6. $\Gamma(E)$ computed from Eq. (10) for a model with $\lambda=0.6$, $V_0=4.0$ and various temperatures $T^*=0.35$, 0.40, 0.45, 0.50, 0.55, 0.60, 0.80, 1.40 (solid line) and $T^*=2.10$ (dashed line).

(ii) if $\{v_k^0\}$ and $\{v_k^l\}$ differ in two consecutive sites, i.e., $v_{\bar{j}}^0 \neq v_{\bar{j}}^l; v_{\bar{j}+1}^0 \neq v_{\bar{j}+1}^l$ and $v_j^0 = v_j^l$ for $j \neq \bar{j}, \bar{j}+1$ the coupling is

$$\langle \psi^{(l)}_{\{v_k^0\}} | \widetilde{V} | \psi^{(l')}_{\{v_k^m\}} \rangle = V_0 C_{\bar{j}}^{(0)} C_{\bar{j}+1}^{(l)} \langle v_{\bar{j}}^0 | e^{\lambda(a_j^\dagger - a_j)} | v_{\bar{j}}^m \rangle \langle v_{\bar{j}+1}^0 | e^{-\lambda(a_{j+1}^\dagger - a_{j+1})} \times | v_{\bar{j}+1}^m \rangle, \tag{15}$$

(iii) if $\{v_k^0\}$ and $\{v_k^l\}$ differ in two nonconsecutive sites or in more than two sites the coupling is zero

Moreover, the following two considerations further reduce the number of couplings to be considered: (iv) the quantum numbers that differs must be in a region of j where the wave function $\psi^{(l)}_{\{v_1^0 \ldots v_k^0 \ldots\}}$ is localized. (v) The Franck-Condon overlap $\langle v_j^0 | e^{\lambda(a_j^\dagger - a_j)} | v_j^m \rangle$ decreases exponentially with the difference between the vibrational quantum numbers and so one can limit the allowed values of v_j^m as $|v_j^0 - v_j^m| \leq \Delta v_{\max}$ ($\Delta v_{\max}$ was set to 8 for the calculations with $\lambda=0.6$).

To summarize, $\Gamma(E)$, i.e., the average inverse lifetime of states with electronic energy E, is computed in the following way. An initial set of vibrational quanta distribution $\{v_k^0\}$ is set and the PDVW $\psi^{(l)}_{\{v_k^0\}}$ are computed. A set of alternative vibrational quanta distribution $\{v_k^m\}$ whose corresponding PDVWs could couple to the initial set is defined and, for each set, the corresponding PDVWs $(\psi^{(l)}_{\{v_k^m\}})$ are computed together with the coupling $\langle \psi^{(l)}_{\{v_k^0\}} | \widetilde{V} | \psi^{(l')}_{\{v_k^m\}} \rangle$ (only if there is sufficient overlap between the electronic wave functions). These matrix elements are the input for Eq. (11) that is used to define $\widetilde{V}_w^2(E',E)$. $\Gamma(E)$, is computed from Eq. (12). To improve the statistics of the results, the procedure is repeated with four initial sets of vibrational states.

Results. The computed $\Gamma(E)$ is illustrated in Fig. 6 for several reduced temperatures and coupling parameters set to $\lambda=0.6$, $V_0=4.0$ for the rest of our discussion. The spanned energy range is the same seen in Fig. 4(a), corresponding to

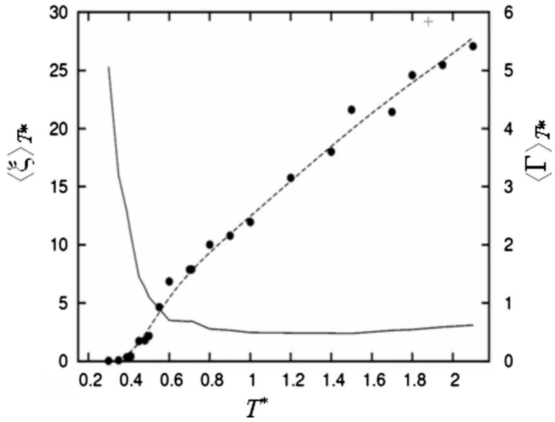

FIG. 7. Temperature-averaged localization length (solid line) and self-energy (full circles) for the same model parameters of Fig. 6 (these two quantities are defined in the text).

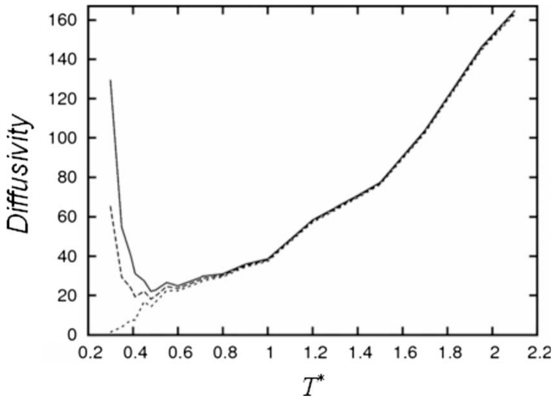

FIG. 8. Estimate of the (adimensional) charge diffusivity [Eq. (17)] using an additional phenomenological self-energy $\Gamma^p=0.2$ (solid), 0.1 (dashed), 0.0 (dotted, i.e., in the absence of the Γ^p correction).

the purely electronic energy (rigorously defined for PDVWs but not for the exact wave function). For $T^*>1.4$, $\Gamma(E)$ is almost temperature dependent and peaked at mid band. For $T^*<0.3$, $\Gamma(E)$ is effectively zero, i.e., the disorder is so modest that the basis functions are very close to the exact eigenstates of the system and the self-consistent procedure of Eq. (12) converges to $\Gamma(E)=0$. The temperature averaged $\langle\Gamma\rangle_{T^*}$ can be defined as

$$\langle\Gamma\rangle_{T^*}=\int\Gamma(E)e^{-E/T^*}dE\Big/\int e^{-E/T^*}dE, \tag{16}$$

where the integration extends within the range of nonvanishing electronic DOS. A plot of $\langle\Gamma\rangle_{T^*}$ versus T^* is given in Fig. 7 which clearly illustrates the existence of two regimes. Between $T^*=0.3$ and $T^*=0.6$ a rapid increase in $\langle\Gamma\rangle_{T^*}$ is observed because in this temperature region the disorder becomes sufficiently strong that the PDVW start departing from the true eigenfunctions and they acquire a finite lifetime. At higher temperature an almost linear increase in $\langle\Gamma\rangle_{T^*}$ is observed and this is due to the population of electronic states toward the center of the band which are characterized by slightly larger inverse lifetimes. Figure 7 also shows, for the same parameter set, the temperature-averaged localization length $\langle\xi\rangle_{T^*}=\int\xi e^{-E/T^*}dE/\int e^{-E/T^*}dE$. Figure 7 describe in the language of PDVW a scenario similar to that presented by Holstein model in the limit of existence of small polarons. At low temperature we find delocalized (translationally invariant) wave functions with a very long lifetime, i.e., rare scattering events (typically not included in the model Hamiltonian, like impurities) are responsible for the charge dynamics. At high temperature we find localized wave functions (which are not small polarons in this case) with a finite lifetime which is entirely determined by the model Hamiltonian (i.e., there is no need to include the effect of impurities or other scattering mechanisms). The low-temperature limit has the expected property of diverging localization length and vanishing self-energy but the actual $T^*\to 0$ limit cannot be taken accurately within this numerical approach which works well only in the presence of a certain degree of localization.

The process of charge diffusion in the regime of dynamic localization can be seen as a series of transitions in time $\sim\hbar/\Gamma$ of states with localization $\sim\xi$ into other states with similar localization length and partially overlapping with them. It is therefore natural to estimate the diffusion coefficient as $\langle\Gamma\zeta^2\rangle_T/2\hbar$. This estimate would be correct at high temperature when the electron-phonon interaction included in the Hamiltonian is the main mechanism behind the charge dynamics. At low temperatures, $\Gamma(E)$ goes to zero and the system appears to have no dynamics because the basis set is too close to the exact eigenfunctions. For an assessment of the model one should add a phenomenological lifetime $\hbar/\Gamma^p$ taking into account other scattering mechanisms outside the model Hamiltonian and evaluate the diffusivity as

$$D\cong\langle(\Gamma+\Gamma^p)\zeta^2\rangle_T/2\hbar. \tag{17}$$

The estimated dependence of the diffusivity with temperature for different Γ^p is given in Fig. 8. At low T^*, the diffusivity decreases with increasing T^* because of the decrease in localization length; at high T^* the localization length is approximately constant and the diffusion coefficient increases due to the increase in the inverse lifetime Γ. The mobility can be also readily estimated from the Einstein relation. The regime of dynamic localization appears therefore as an intermediate regime between delocalized metal-like transport (diffusivity decreasing with increasing temperature) and hopping insulatorlike transport (diffusivity increasing with increasing temperature). While the transition regime is qualitatively similar to the crossover between large polaron and incoherent hopping,[35,43] the high-temperature limit in our case is very different. The high-temperature states are localized by disorder not by the formation of a small polaron (the coupling V_0 is large compared to the polaron binding energy). In this regime the hopping mobility expression proposed within the Lang-Firsov-Hostein context would lead to completely inaccurate results and, by extension, it is not possible to compare this result with existing crossover theories valid in less adiabatic regime. We do not investigate here the possible effect of dynamic disorder in the case of larger polaron binding energy but we can hypothesize that this effect is negligible in the nonadiabatic limit[57] (confirming the validity of the classic works) and possibly more important as the system becomes more adiabatic.

Comparison with other approaches. It useful to consider what the advantage is of considering PDVW to study the Holstein Hamiltonian in the presence of many alternative methods.[32–42] We can compare the physics depicted in this paper, for example, with the results of very accurate calculations such as quantum Monte Carlo algorithms[36] (also following the Lang-Firsov transformation[58]) or Bonča *et al.*'s variational method.[39] The key results of these works are the polaron spectrum, its effective mass (typically as a function of the electron-phonon coupling parameters) and the extent of the lattice deformation. The former are zero-temperature theories and, as such, they do not incorporate the effect of phonon population. The description in terms of delocalized polarons is correct as long as the effective mass is not too high. As the effective mass goes to infinity the polaronic states become degenerate and will be localized by any random disturbance including, as we have seen, the thermal distribution of vibrational quanta. At high effective mass a localized representation is always more convenient than a delocalized one even though it breaks the translational invariance of the Hamiltonian. For example, the dynamic of a particle in a symmetric double well should be described in a localized representation if the mass of the particle is sufficiently high that the tunneling between the two potential wells is much slower that the thermally activated hopping. Our theory does not allow the definition of the effective mass, preventing a direct comparison with polaronic band theories, as it starts from a localized representation, but has conventional polaronic theory as a limit case at low temperature giving by construction the results of Holstein theory (Bloch-type functions) for $T \rightarrow 0$. This last characteristics is very important because, although we have constructed our zeroth-order wave function from the high-temperature limit, we described the vibrons quantum mechanically at all temperatures and, therefore, we avoided the artifacts of other adiabatic theories that neglect the kinetic energy of the nuclei[59] and predict self-trapped polarons at low temperature and self-trapping phase transitions.[15] We believe that our theory is advantageous with respect to the existing models in a well-defined parameter range (illustrated in Fig. 4 and always involving finite temperature) where dynamic localization makes unhelpful the description in terms of polaron. Whenever a delocalized basis is more convenient, our approach is unsuitable due to the large number of coupled states that one has to consider [Eq. (13)] and, more generally, because the chosen basis does not properly exploit the translational symmetry of the system. In agreement with Ref. 34 we therefore also conclude that the ideal basis set for the study of Hamiltonians with electron-phonon coupling at finite temperature should be temperature dependent. It should be noted however that, any polaronic band theories (including finite-temperature theories[60]), cannot describe the effect of dynamic localization because it is the polaronic ansatz that impose the absence of dynamic disorder, i.e., in the regime of dynamic disorder the polaron band language may be inappropriate.

IV. CONCLUSION

The idea that dynamic localization of charge carrier may take place in narrow band materials is certainly not new[61] but only recently it was translated into viable models for the study of transport in organic semiconductors.[7,11] These models are semiclassical in nature and, as such, are difficult to put in the traditional framework of fully quantum model Hamiltonians. The original motivation of this paper was to study dynamic localization in one of the most studied model Hamiltonians at finite temperature and, to do so, we have defined partially diagonalized vibronic wave functions PDWV obtained by diagonalizing the electronic Hamiltonian while the number of vibrational quanta in each oscillator is kept constant in a distribution compatible with the Bose-Einstein distribution. This definition suggested by the correspondence principle turned out to be particularly useful. In fact, not only PDWVs allow the evaluation of the parameter range where we can expect dynamic disorder but they also form a natural basis for the study of charge transport in this regime. We showed that it is possible to compute the finite lifetime for these wave functions and to relate it to the diffusivity of the electron in the lattice. Dynamic localization seems to provide the appropriate framework when the polaron binding energy is small and the high-temperature limit of transport is not small polaron incoherent hopping. Interesting, also in dynamic localization, as the temperature increases the electron diffusivity first decreases and then increases again, giving the same qualitative behavior of the transition between delocalized metal-like transport and localized insulatorlike transport described by Holstein in a different coupling regime. There is a growing number of experiments that point to localized charge carrier (including electron paramagnetic resonance measurements,[62,63] terahertz spectroscopy,[64] and charge modulated spectroscopy[65]) on samples of molecular crystals displaying metal-like mobility. Many of these molecular crystals have very small polaron binding energy (~ 0.05 eV) and relatively large intermolecular coupling ($\sim 0.2-0.02$ eV).[30] Understanding the nature of the carrier in these experiments is ultimately the driving reason to search for the origin of localized states in translationally invariant defect-free systems.

This work establishes that charge diffusion limited by dynamic disorder is a feature of the basic Holstein Hamiltonian and it is not limited to cases of dynamic off-diagonal disorder or to semiclassical descriptions. Moreover, it creates a link between the theory of localization in disordered systems and the theory and Hamiltonians with electron-phonon coupling opening interesting avenues for future investigations. For example, it is expected that additional physics can be observed for even narrower band, such that the state at mid-band with very large localization length can be populated as the temperature is increased.

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