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Formation and hopping motion of molecular polarons

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This paper addresses polaron formation and intermolecular hopping of a carrier confined to molecules immersed within a polar medium. Three types of polaron state are possible: (i) The carrier can encompass all equivalent sites of the occupied molecule. (ii) The carrier can be localized at a single atomistic unit of the molecule. (iii) If the carrier's interactions with the medium's ions are strong enough, the self-trapped carrier can be localized among a subset of the molecule's equivalent sites. High-temperature intermolecular hopping requires the formation of a coincidence configuration in which the carrier is shared between the jump's two molecules. The hop's activation energy depends on the *expansion* of a molecule's carrier as it approaches a coincidence from its minimum-energy configuration. The carrier's *intramolecular* motion in response to atoms' motions also reduces these atoms' vibrational frequencies thereby lowering their vibrational free energy. This carrier-induced vibrational softening affects the temperature-independent coefficient of the Arrhenius jump rate. Thus carrier's intrasite motion, ignored in Holstein's model, can significantly affect small-polaron formation and hopping.

I. INTRODUCTION

Discussions of small-polaron formation and hopping in molecular solids are often based on Holstein's ''molecular crystal model.''[1] The model envisions a regular array of molecules. An atomic deformation parameter is assigned to each molecule. These deformation parameters are assumed to vibrate harmonically about their equilibrium positions. Small-polaron formation corresponds to a carrier being confined to one of the molecular sites. The energy of the confined carrier is presumed to be simply proportional to the deformation parameter of the occupied site. As a result, the carrier's presence only induces a shift of the equilibrium position of the deformation parameter of the occupied site.

The Holstein model and equivalent treatments[2–9] implicitly assume the wave function of a carrier on a molecule to be ''rigid.'' In particular, the model ignores shifts of the carrier's wave function in response to atomic displacements. Such polarization of the carrier's wave function introduces contributions to the carrier's energy that depend nonlinearly on the deformation parameters.[10–13] The model also ignores dependencies of electronic transfer energies on the atomic displacement parameters.

The Holstein model was originally proposed as a conceptual aid to describe a type of small polaron that may be formed when a carrier is confined to a transition-metal ion of a transition-metal oxide.[14] The deformation parameter provides a simplified description of a collective optical vibration (e.g., breathing mode) of the anions adjacent to the transition-metal ion. Thus the ''molecule'' of Holstein's molecular crystal model was initially envisioned as only a construct to describe a carrier localized on a small cation surrounded by displaced ligands.

Self-trapped carriers in molecular solids are frequently much larger than those envisioned in the molecular crystal model. In particular, the self-trapped carrier of a molecular solid often encompasses many atoms. As a result, properties of a carrier on a real molecule differ from those assumed by the molecular-crystal model. In particular, rather than being confined to a point, a carrier on a real molecule generally sloshes amongst its atoms in response to their motions.[10] This effect causes the electronic energy of a localized carrier to depend nonlinearly on atomic displacements. As a result, a localized carrier generally softens the stiffness constants of the deformational modes to which it is coupled. This polarization effect grows with the size of the localized electronic state since the polarizability of an electronic state is comparable to its volume.

This paper addresses the self-trapping and semiclassical (high-temperature) inter-molecular hopping of carriers self-trapped on molecules, ''molecular polarons.'' Attention is focused on how the size and concomitant polarizability of a self-trapped state affects polaron formation and hopping.

The body of the paper begins in Sec. II A, where a model of a carrier restricted to a molecule embedded within a polar medium is presented. For simplicity, the molecule is represented as just providing a potential well that confines the carrier. In addition, all atoms' vibrations are represented as a collection of equivalent Einstein oscillators. Contributions to the carrier-related free energy arise from the carrier's confinement, the carrier-induced displacements of the oscillators' equilibrium positions, and the carrier-induced reductions of oscillators' stiffness constants. The minimum of the total free energy defines the polaron state. The minimum free energy is expressed in terms of an eigenstate of the localized carrier.

In Sec. II B the free-energy of the polaron state is examined as a function of the spatial extent of the electronic carrier. A scaling argument is used to determine how each contribution to the polaron's free energy depends on the characteristic length of its localized carrier. The spatial extent of the polaron's carrier depends on parameters governing the carrier's confinement energy as well as its interactions with the atoms. Depending on the values of these parameters a molecular polaron's carrier may either (i) extend over the entire molecule, (ii) be confined to only a por-

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tion of the molecule, or (iii) collapse to a single atomistic unit.

Section III addresses the intermolecular hopping of the polaron between equivalent molecules. The jump rate depends upon the difference between the polaron free energy and the free energy of the minimum-energy state for which the carrier is shared equally between initial and final sites of the hop. The electronic eigenstate of the lowest-energy coincidence state is described as a superposition of the local electronic states associated with the initial and final sites of the hop. Section III A obtains the free energy of the minimum-energy coincidence in terms of a local electronic wave function.

In Sec. III B the free-energy difference associated with a hop is studied as a function of the polaron radius and the radius of the local electronic function of a coincidence. The activation energy for a hop is reduced by the tendency of the radius of the coincidence electronic state to be larger than that of the ground state. In addition, the softening of vibrational frequencies produced by carrier's deformability provides an entropic factor that affects the temperature-independent (pre-exponential) factor of the high-temperature jump rate. Both of these effects are absent in prior works that presume the electronic state to be rigid. Simple examples indicate that a carrier's deformability significantly affects its hopping rate.

The paper concludes in Sec. IV with a discussion and summary of its principal findings. The results apply to carriers localized in molecular orbitals associated with dopants and defects as well as to carriers confined to bona fide molecules. The larger the size of the carrier's state, the greater the importance of its deformability and the relative importance of its interactions with ions through the long-range (Frohich) electron-lattice interaction.

II. FORMATION OF A MOLECULAR POLARON

A. Free energy of a molecular polaron

The first goal of this paper is to address the formation of a polaron by a carrier occupying a molecule immersed in a polar medium. This carrier interacts with the atomic displacements of both the occupied molecule and the surrounding medium. For clarity, the molecule, the atomic vibrations and the electron-lattice interactions are modelled most simply.

The molecule is viewed as just providing an attractive potential for the carrier, $V_m(\vec{r})$. This potential only serves to constrain the carrier to the molecule. As such, a molecule is modelled as providing a delineated region of low yet constant electronic potential.

The atomic vibrations of both the molecule and the enveloping medium are represented as being collections of equivalent Einstein oscillators. Each oscillator is characterized by the atomic effective mass M stiffness parameter k, and vibrational frequency $\omega = \sqrt{k/M}$. The deformation parameter of the oscillator at location $\vec{u}$ is $\Delta(\vec{u})$.

The electron-lattice interaction depicts the dependence of the potential energy of a carrier on deformations of the Einstein oscillators. The potential energy of a carrier at position $\vec{r}$ is presumed to depend linearly on the deformation of an oscillator at position $\vec{u}$ with a magnitude and range that is described by the electron-continuum interaction function, $Z(\vec{r},\vec{u})$.

The momentum operators conjugate to the carrier's position and to the atomic deformation parameter are defined as $\hat{p}_r$ and $\hat{P}_\Delta$, respectively. The Hamiltonian for this model is then written as

$$H = \frac{\hat{p}_r^2}{2m} - \frac{1}{V_c}\int d\vec{u}Z(\vec{r},\vec{u})\Delta(\vec{u}) + V_m(\vec{r}) + \frac{1}{V_c}\int d\vec{u}\left(\frac{\hat{P}_\Delta^2}{2M} + \frac{k}{2}\Delta^2(\vec{u})\right), \tag{1}$$

where m is the carrier's mass and V_c is the volume associated with the separation between oscillators, a ($V_c \equiv a^3$).

The eigenstates of the carrier on a molecule immersed within a deformable medium are described within the adiabatic approach. Within the adiabatic approximation the eigenstate is written as the product of an electronic eigenfunction that depends upon the carrier's position and the deformation parameters, $\Psi_\varepsilon[\vec{r},\Delta(\vec{u})]$, and an atomic eigenfunction describing the atomic motion when the electronic state is occupied, $\Theta_{n,\varepsilon}[\Delta(\vec{u})]$: $\Psi_\varepsilon[r,\Delta(\vec{u})]\Theta_{n,\varepsilon}[\Delta(\vec{u})]$. The electronic function is the solution of the electronic eigenvalue equation:

$$\left[\frac{\hat{p}_r^2}{2m} - \frac{1}{V_c}\int d\vec{u}Z(\vec{r},\vec{u})\Delta(\vec{u}) + V_m(\vec{r})\right]\Psi_\varepsilon[\vec{r},\Delta(\vec{u})] = \varepsilon[\Delta(\vec{u})]\Psi_\varepsilon[\vec{r},\Delta(\vec{u})], \tag{2}$$

where ε is the eigenvalue. The associated atomic motions are described by

$$\left[\frac{1}{V_c}\int d\vec{u}\left(\frac{\hat{P}_\Delta^2}{2M} + \frac{k}{2}\Delta^2(\vec{u})\right) + \varepsilon[\Delta(\vec{u})]\right]\Theta_{n,\varepsilon}[\Delta(\vec{u})] = E_n\Theta_{n,\varepsilon}[\Delta(\vec{u})], \tag{3}$$

where E_n is the eigenvalue. The adiabatic approach is valid if the time required for a carrier to traverse its eigenstate is much less than the time characterizing motion of the atoms to which the carrier is coupled. The adiabatic theory is typically applied to molecules that are not too large.

The lowest-energy electronic state for a static polaron, $\Psi_s(\vec{r})$, is found by minimizing $\langle\Psi_s(\vec{r})|H|\Psi_s(\vec{r})\rangle$ with respect to the deformation parameter, $\Delta(\vec{u})$. Deformations of the lowest-energy state are described by

$$\Delta_s(\vec{u}) \equiv \frac{1}{k}\int d\vec{r}Z(\vec{r},\vec{u})|\Psi_s(\vec{r})|^2. \tag{4}$$

Vibrations of the atoms about the minimum-energy configuration are governed by the interatomic stiffness constants. These stiffness constants, and therefore the vibrational frequencies, are affected by a carrier's presence. In particular, the strain energy is generally given by

$$\frac{1}{V_c^2}\int d\vec{u}\int d\vec{u}'\frac{k'(\vec{u},\vec{u}')}{2}D(\vec{u})D(\vec{u}'), \tag{5}$$

where $D(\vec{u})\equiv\Delta(\vec{u})-\Delta_s(\vec{u})$ is the deviation of the deformation parameter from its equilibrium value and the stiffness tensor in the presence of the carrier is obtained from the second derivative of the total energy evaluated at the minimum-energy configuration:

$$k'(\vec{u},\vec{u}')=kV_c\delta(\vec{u}-\vec{u}')-\int d\vec{r}Z(\vec{r},\vec{u})\frac{\partial|\Psi_s(\vec{r})|^2}{\partial\Delta(\vec{u}')}\Big|_{\Delta_s(\vec{u}')}. \tag{6}$$

The carrier-induced change of the stiffness tensor measures the sensitivity of the self-trapped carrier's state to alteration of the deformation parameter. In other words, carrier-induced softening is associated with the adjustment of the carrier's wave function to the movement of surrounding atoms. This effect vanishes in models that approximate the self-trapped state as being rigid.

Standard perturbation theory has been utilized to express the carrier-induced softening in terms of the wave functions and eigenvalues of the self-trapped carrier at the minimum-energy configuration:[11,12]

$$k'(\vec{u},\vec{u}')=kV_c\delta(\vec{u}-\vec{u}')-\sum_{n\neq s}\frac{\int d\vec{r}\Psi_s^*(\vec{r})Z(\vec{r},\vec{u})\Psi_n(\vec{r})\int d\vec{r}'\Psi_n^*(\vec{r}')Z(\vec{r}',\vec{u}')\Psi_s(\vec{r}')+\text{c.c.}}{\epsilon_n-\varepsilon_s}, \tag{7}$$

where ε_n is the electronic energy labeled by index n and ε_s is the energy of the electronic ground state. The carrier induced change in the vibrational stiffness shifts the set of vibrational eigenfrequencies from $\{\omega_i\}$ to $\{\Omega_i\}$.

The change of the free energy produced by inserting a charge carrier into the lowest adiabatic state is expressed as the sum of a contribution from the entropy of mixing, F_{mix}, and a contribution from the carrier's interactions, F_s: $\Delta F\equiv F_{mix}+F_s$. This entropic contribution is associated with the number of ways carriers can be distributed among states of nearly equivalent energies, $\lesssim\kappa T$. The contribution to the free energy arising from a carrier's interactions, F_s, is the sum of (i) the carrier's energy, (ii) the strain energy associated with carrier induced shifts of atomic equilibrium positions, and (iii) the change of the vibrational free energy arising from carrier induced shifts of the vibrational frequencies:

$$\begin{aligned}F_s={}&\left(\frac{\hbar^2}{2m}\right)\int d\vec{r}|\nabla\Psi_s(\vec{r})|^2\\&-\frac{1}{2V_ck}\int d\vec{u}\int d\vec{r}Z(\vec{r},\vec{u})|\Psi_s(\vec{r})|^2\\&\times\int d\vec{r}'Z(\vec{r}',\vec{u}')|\Psi_s(\vec{r}')|^2+\int d\vec{r}V_m(\vec{r})|\Psi_s(\vec{r})|^2\\&+\kappa T\sum_i\ln\left[\frac{\sinh(\hbar\Omega_i/2\kappa T)}{\sinh(\hbar\omega_i/2\kappa T)}\right].\end{aligned} \tag{8}$$

For an harmonic lattice, the strain energy associated with carrier induced shifts of atomic equilibrium positions is half the lowering of the electronic potential associated with these shifts. Combining these two effects introduces the factor 2 in the denominator of the second contribution to F_s.

The vibrational contribution to F_s may be rewritten when the carrier induced shifts in the phonon energies are sufficiently small, $(\Omega_i-\omega_i)\ll\omega_i$:

$$\begin{aligned}F_s={}&\left(\frac{\hbar^2}{2m}\right)\int d\vec{r}|\nabla\Psi_s(\vec{r})|^2\\&-\frac{1}{2V_ck}\int d\vec{u}\int d\vec{r}Z(\vec{r},\vec{u})|\Psi_s(\vec{r})|^2\\&\times\int d\vec{r}'Z(\vec{r}',\vec{u})|\Psi_s(\vec{r}')|^2+\int d\vec{r}V_m(\vec{r})|\Psi_s(\vec{r})|^2\\&+\sum_i\left[\frac{\hbar(\Omega_i-\omega_i)}{2}\right]\coth(\hbar\omega_i/2\kappa T).\end{aligned} \tag{9}$$

In the low-temperature limit, $T\rightarrow 0$, the vibrational contribution to F_s is just the carrier induced reduction of the zero-point vibrational energy. At sufficiently high temperatures, $\coth(\hbar\omega_i/2\kappa T)\rightarrow 2\kappa T/\hbar\omega_i$, the vibrational contribution to F_s depicts the carrier induced increase of vibrational entropy.

The vibrational contribution to the free energy may be expressed in terms of electronic parameters. To accomplish this task, first note that the sum of the squares of the vibrational eigenfrequencies is simply related to the net value of the diagonal elements of the stiffness constants:

$$\sum_i\Omega_i^2=\frac{\frac{1}{V_c}\int d\vec{u}k'(\vec{u},\vec{u})}{M}. \tag{10}$$

This equality can be combined with that for the carrier free system to obtain

$$\sum_i(\Omega_i^2-\omega_i^2)=\frac{\frac{1}{V_c}\int d\vec{u}[k'(\vec{u},\vec{u})-k]}{M}. \tag{11}$$

For small enough shifts of the vibrational frequencies this relationship becomes

$$\sum_i\omega_i(\Omega_i-\omega_i)=\frac{\frac{1}{V_c}\int d\vec{u}[k'(\vec{u},\vec{u})-k]}{2M}. \tag{12}$$

Focusing attention on optical modes and describing the optical spectrum as an Einstein spectrum, $\omega_i = \omega = \sqrt{k/M}$, the sum rule becomes

$$\sum_i (\Omega_i - \omega) = \omega \frac{\frac{1}{V_c}\int d\vec{u}[k'(\vec{u},\vec{u}) - k]}{2k}. \tag{13}$$

Thus the net carrier induced shift of vibrational frequencies is directly related to the sum of the carrier induced shifts of the diagonal components of the stiffness tensor.

The carrier induced reduction of the diagonal components of the stiffness tensor can be expressed in terms of the electronic eigenstates:

$$k'(\vec{u},\vec{u}) - k = -2\sum_{n\neq s} \frac{\left|\int d\vec{r}\Psi_s^*(\vec{r})Z(\vec{r},\vec{u})\Psi_n(\vec{r})\right|^2}{\varepsilon_n - \varepsilon_s} \tag{14}$$

$$= -2\sum_{n\neq s} \frac{\int d\vec{r}[\Psi_s^*(\vec{r})\Psi_n(\vec{r})]\int d\vec{r}'[\Psi_s^*(\vec{r}')\Psi_n(\vec{r}')]^* Z(\vec{r},\vec{u})Z(\vec{r}',\vec{u})}{\varepsilon_n - \varepsilon_s}. \tag{15}$$

With this relationship, the carrier induced shift of the free energy is written in terms of the electronic eigenstates:

$$F_s = \left(\frac{\hbar^2}{2m}\right)\int d\vec{r}|\nabla\Psi_s(\vec{r})|^2 - \int d\vec{r}|\Psi_s(\vec{r})|^2\int d\vec{r}'|\Psi_s(\vec{r}')|^2 I(\vec{r}-\vec{r}') + \int d\vec{r}V_m(\vec{r})|\Psi_s(\vec{r})|^2$$

$$-\hbar\omega\coth(\hbar\omega/2\kappa T)\sum_{n\neq s}\frac{\int d\vec{r}[\Psi_s^*(\vec{r})\Psi_n(\vec{r})]\int d\vec{r}[\Psi_s^*(\vec{r}')\Psi_n(\vec{r}')]^* I(\vec{r}-\vec{r}')}{\varepsilon_n - \varepsilon_s}, \tag{16}$$

where the carrier self-energy arising from the electron-lattice interaction is[15]

$$I(\vec{r}-\vec{r}') \equiv \frac{1}{2V_c k}\int d\vec{u}Z(\vec{r},\vec{u})Z(\vec{r}',\vec{u}). \tag{17}$$

The electron-lattice interaction for the carrier is generally the sum of short-range and long-range components.[16] The short-range component describes the dependence of the electronic energy of a carrier on the positions of the atoms responsible for its bonding. The long-range component models the dependence of a carrier's potential energy on displacements of the polar medium's distant ions. The contributions to a carrier's potential from displacing the medium's anions and cations are combined so that the net long-range interaction is described as that of carriers with deformable dipoles.[17] The sum of the carrier's contact interaction with the atoms and its interaction with dipoles of the surrounding medium becomes[15]

$$Z(\vec{r},\vec{u}) = AV_c\delta(\vec{r}-\vec{u}) + \frac{e}{\pi^{3/2}}\frac{\sqrt{k\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)V_c}}{|\vec{r}-\vec{u}|^2}. \tag{18}$$

Here ϵ_0 and ϵ_∞ are the medium's static and optical and static dielectric constants, respectively, and e is the elemental charge.

Evaluating $I(\vec{r}-\vec{r}')$ for a three-dimensional medium yields[15]

$$I(\vec{r}-\vec{r}') = E_b V_c\delta(\vec{r}-\vec{r}') + \frac{e^2}{2|\vec{r}-\vec{r}'|}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right) + \frac{\sqrt{2E_b\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{e^2}{\pi^3}V_c}}{|\vec{r}-\vec{r}'|^2}, \tag{19}$$

where $E_b \equiv A^2/2k$. The first and second contributions to $I(\vec{r}-\vec{r}')$ arise from the short-range and long-range components of electron-lattice interaction, respectively. The final contribution is a cross term between the short-range and long-range components of the electron-lattice interaction. The cross term results from evaluating the long-range component of the electron-lattice interaction at the carrier's location. However, the long-range interaction envisions a carrier interacting with electric dipoles beyond the carrier's charge distribution.[17] Thus this representation of the cross term is somewhat artificial. Furthermore, the cross term plays no significant role in the forthcoming considerations. For these reasons, the cross term shall be ignored henceforth.

Employing this model, the carrier induced change in the free energy of the solid becomes

$$
\begin{aligned}
F_s = {} & \left(\frac{\hbar^2}{2m}\right)\int d\vec{r}\,|\nabla\Psi_s(\vec{r})|^2 - E_b V_c\int d\vec{r}\,|\Psi_s(\vec{r})|^4 \\
& - \frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int d\vec{r}\int d\vec{r}\,'\frac{|\Psi_s(\vec{r})|^2|\Psi_s(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} \\
& + \int d\vec{r}\,V_m(\vec{r})|\Psi_s(\vec{r})|^2 \\
& - \hbar\omega\coth(\hbar\omega/2\kappa T)\sum_{n\neq s}\frac{1}{\epsilon_n-\epsilon_s}\int d\vec{r}\,[\Psi_s^*(\vec{r})\Psi_n(\vec{r})] \\
& \times\int d\vec{r}\,'[\Psi_s^*(\vec{r}\,')\Psi_n(\vec{r}\,')]^*\Bigg[E_b V_c\,\delta(\vec{r}-\vec{r}\,') \\
& + \frac{e^2}{2|\vec{r}-\vec{r}\,'|}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\Bigg].
\end{aligned}
\tag{20}
$$

The free energy of the static polaron is thus expressed in terms of the carrier's electronic eigenstates $\Psi_s(\vec{r})$ and $\Psi_n(\vec{r})$, and eigenvalues ϵ_s and ϵ_n.

B. Size of a molecular polaron

The ground-state electronic wave function $\Psi_s(\vec{r})$ is defined as corresponding to the state of lowest energy. Altering the spatial extent of the wave function by the dimensionless scaling parameter R therefore necessarily raises the energy. Thus the minimum of the energy as a function of R is defined as occurring at $R=1$. Examining the possible minima of the energy as a function of the scaling parameter is an efficacious way of elucidating features of competing free-energy minima.[16] The free-energy scaling functional obtained by changing the spatial extent of the electronic wave function by the dimensionless factor R while retaining the wave function's normalization is

$$
f_s(R)\equiv\frac{T}{R^2}-\frac{V_S}{R^3}-\frac{(V_L+\Delta F_{\text{vib,S}})}{R}-\Delta F_{\text{vib,L}}R-v_m(R),
\tag{21}
$$

where

$$
T\equiv\left(\frac{\hbar^2}{2m}\right)\int d\vec{r}\,|\nabla\Psi_s(\vec{r})|^2,
\tag{22}
$$

$$
V_S\equiv E_b V_c\int d\vec{r}\,|\Psi_s(\vec{r})|^4,
\tag{23}
$$

$$
V_L\equiv\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int d\vec{r}\int d\vec{r}\,'\frac{|\Psi_s(\vec{r})|^2|\Psi_s(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|},
\tag{24}
$$

$$
\Delta F_{\text{vib,S}}\equiv E_b\hbar\omega\coth(\hbar\omega/2\kappa T)V_c\sum_{n\neq s}\frac{\int d\vec{r}\,|\Psi_s^*(\vec{r})\Psi_n(\vec{r})|^2}{\epsilon_n-\epsilon_s},
\tag{25}
$$

$$
\begin{aligned}
\Delta F_{\text{vib,L}}\equiv {} & \left[\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]\hbar\omega\coth(\hbar\omega/2\kappa T) \\
& \times\sum_{n\neq 0}\frac{1}{E_n-E_0}\int d\vec{r}\int d\vec{r}\,' \\
& \times\frac{[\Psi_s^*(\vec{r})\Psi_n(\vec{r})][\Psi_s^*(\vec{r}\,')\Psi_n(\vec{r}\,')]^*}{|\vec{r}-\vec{r}\,'|}
\end{aligned}
\tag{26}
$$

and the excitation energies are presumed to scale as $1/R^2$.

The final contribution to the carrier induced change of the free energy $v_m(R)$ comes from the potential that binds the carrier on the molecule. After a change of variable, the average molecular potential experienced by a carrier whose spatial extent is expanded by the factor R can be written as

$$
v_m(R)\equiv\int d\vec{r}\,V_m(\vec{r}R)|\Psi_s(\vec{r})|^2.
\tag{27}
$$

This contribution vanishes in the limit that the spatial extent of the electronic state greatly exceeds the range of the molecular potential, a length comparable to the molecule's radius. That is, $v_m(R)\rightarrow 0$ as $R\rightarrow\infty$. Alternatively, $v_m(R)$ saturates at constant value when the electronic state is fully confined within the molecule. Details of this saturation effect depend upon specifics of both the electronic wave function and the molecular potential. However, this saturation effect can be simply modeled by replacing $v_m(R)$ by the constant $v_m(0)$ when the scaling parameter is less than that for which the radius of the electronic state equals the molecule's radius, $R\leqslant R_{molecule}$. That is, a carrier confined to a molecule experiences the constant potential $v_m(0)$.

The continuum theory breaks down, and the contributions from the electron-lattice interactions saturate, when the carrier's spatial extent falls below that of an elemental atomistic unit (atom or bond). Thus $f_s(R)$, as described by Eq. (21), is only meaningful when the scaling parameter exceeds the value corresponding to the electronic state's radius equaling the radius of the elemental atomistic unit, $R\geqslant R_{atom}$.

Incorporating these two size restrictions, the free-energy function for a carrier confined to a deformable molecule embedded within a medium of displaceable atoms becomes

$$
f_s(R)=\frac{T}{R^2}-\frac{V_S}{R^3}-\frac{(V_L+\Delta F_{\text{vib,S}})}{R}-\Delta F_{\text{vib,L}}R,
\tag{28}
$$

where $R_{atom}\leqslant R\leqslant R_{molecule}$. The R-independent term $v_m(0)$ has been dropped since this constant is irrelevant to forthcoming arguments. Thus the effect of the carrier's confinement to a molecule is represented solely by the restriction: $R\leqslant R_{molecule}$.

It is now useful to comment on the magnitudes of the various contributions to $f_s(R)$. Consider the case when the electronic state is confined to a single atomistic unit, $R=R_{atom}$. Then, the first two contributions to $f_s(R_{atom})$ are typically of the order of an electron volt. The third contribution, V_L/R_{atom}, is also of the order of an electron volt if the medium is ionic, $\epsilon_0\gg\epsilon_\infty$. Even if the medium has very little polar character, $\epsilon_0\gtrsim\epsilon_\infty$, the residual contribution of the long-range electron-lattice interaction, V_L/R_{atom}, will usually be sufficient to overwhelm $\Delta F_{\text{vib,S}}$ ($\approx 10^{-2}$ eV). There-

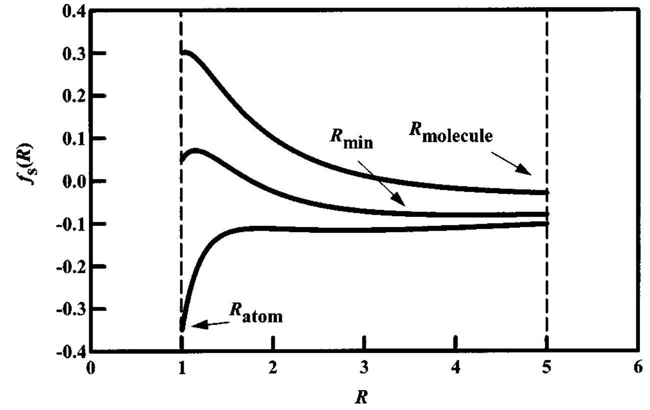

FIG. 1. The free energy of a molecular polaron, $f_s(R)$, is plotted as a function of the carrier's spatial extent R for three sets of parameters. The carrier is constrained to be no smaller than an atom and no larger than the occupied molecule: $R_{atom}<R<R_{molecule}$. The minimum of the uppermost curve resides at $R_{molecule}$ thereby indicating that it is energetically favorable for the carrier to encompass the entire molecule. The minimum of the middle curve resides at R_{min} thereby indicating that it is energetically favorable for the carrier to encompass a finite number of the molecule's atomic sites. The minimum of the lowest curve resides at R_{atom} thereby indicating that it is energetically favorable for the carrier to collapse on to a single atomistic unit of the molecule.

fore $\Delta F_{\mathrm{vib,S}}$ will henceforth be ignored. The fourth term's contribution is typically $\lesssim 10^{-2}$ eV when $R=R_{atom}$. However, the fourth term becomes significant for large states, $R \gg R_{atom}$.

In the absence of the fourth term, the minimum of the function $f_s(R)$ is at

$$R_{\mathrm{min}}=\frac{T+\sqrt{T^2-3V_SV_L}}{V_L}. \tag{29}$$

The existence of this minimum requires that V_S be small enough for the argument of the square root to be positive: $T^2>3V_SV_L$. Then $(T/V_L)<R_{\mathrm{min}}<2(T/V_L)$. In addition, V_L must be large enough to ensure that this minimum resides within the acceptable range, $R_{\mathrm{min}}\leqslant R_{molecule}$. Thus the existence of this minimum requires that the short-range interaction be sufficiently small and the long-range interaction be sufficiently large. Otherwise the minimum of $f_s(R)$ occurs at either R_{atom} or $R_{molecule}$.

The plots of $f_s(R)$ versus R depicted in Fig. 1 illustrate that the absolute minimum of $f_s(R)$ within the domain $R_{atom}\leqslant R\leqslant R_{molecule}$ is either at one of the boundaries of the permitted domain, R_{atom} or $R_{molecule}$, or at R_{min}. The minimum at R_{atom} corresponds to the carrier being localized at an atom on the molecule to form an "atomic small polaron." The minimum at R_{min} represents the carrier extending over a number of the molecule's atoms. The minimum at $R_{molecule}$ depicts the carrier being delocalized over the entire molecule. The latter two instances describe a "molecular small polaron" since the carrier occupies a multiatomic state confined to a single molecule.

The fourth term in $f_s(R)$ denotes the net reduction of the vibrational free-energy arising from carrier induced softening. Since this term, $-\Delta F_{\mathrm{vib,L}}R$, becomes increasingly negative as R is increased, it fosters expansion of the electronic state. To compute this shift, the derivative of $f_s(R)$ with respect to R is first set equal to zero. The resulting equation is then linearized with respect to the shift of the position of the minimum, defined as r, and to $\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}$. To first order in $\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}$, the shift of the position of the minimum is

$$\begin{aligned} r&=\frac{\Delta F_{\mathrm{vib,L}}}{\left.\dfrac{\partial f_s^2(R)}{\partial R^2}\right|_{R_{\mathrm{min}}}}\\ &=\frac{\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}^2}{3\times 2\dfrac{T}{R_{\mathrm{min}}^2}-4\times 3\dfrac{V_S}{R_{\mathrm{min}}^3}-2\dfrac{V_L}{R_{\mathrm{min}}}}\\ &=\frac{\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}^2}{\dfrac{V_L}{R_{\mathrm{min}}}-3\dfrac{V_S}{R_{\mathrm{min}}^3}}, \end{aligned} \tag{30}$$

where the formula after the second equality exploits the relation that determines R_{min}:

$$2\frac{T}{R_{\mathrm{min}}^2}-3\frac{V_S}{R_{\mathrm{min}}^3}-\frac{V_L}{R_{\mathrm{min}}}=0. \tag{31}$$

The divergence of r occurs when V_S becomes large enough for the existence of a minimum near R_{min} to be tenuous $(T^2\simeq 3V_SV_L)$. Then a modest change of the free-energy can have a major effect on the minimum's position or very existence. Away from this divergence

$$r\simeq\frac{\Delta F_{\mathrm{vib,L}}}{V_L}R_{\mathrm{min}}^3. \tag{32}$$

The shift of the minimum with these parameters increases strongly with the size of the molecular state since $r\propto R_{\mathrm{min}}^3$. Furthermore, the position of the minimum of $f_s(R)$ increases with rising temperature through the explicit temperature dependence of $\Delta F_{\mathrm{vib,L}}$ shown in Eq. (26).

To first order in $\Delta F_{\mathrm{vib,L}}$, the carrier induced change of the free energy at this molecular small polaron minimum is

$$\begin{aligned} f_s(R_{\mathrm{min}}+r)&\cong f_s(R_{\mathrm{min}})+\left.\frac{\partial f_s(R)}{\partial R}\right|_{R_{\mathrm{min}}} r\\ &\cong\frac{T}{R_{\mathrm{min}}^2}-\frac{V_S}{R_{\mathrm{min}}^3}-\frac{V_L}{R_{\mathrm{min}}}-\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}\\ &=-\frac{V_L}{2R_{\mathrm{min}}}+\frac{V_S}{2R_{\mathrm{min}}^3}-\Delta F_{\mathrm{vib,L}}R_{\mathrm{min}}, \end{aligned} \tag{33}$$

where it is first noted that $\partial f_s/(R)/\partial R|_{R_{\mathrm{min}}}=0$. Equation (31) is then used to obtain the final equality of Eq. (33).

Several conclusions can be drawn from the final expression for the free energy of a molecular polaron, Eq. (33). With increasing size, R_{min}, the contribution to the free energy arising from the long-range interaction, $-V_L/2R_{\mathrm{min}}$, increasingly dominates that from the short-range interaction, $V_S/2R_{\mathrm{min}}^3$. In addition, the lowering of the free energy arising from carrier induced reduction of the frequencies of ionic vibrations grows in importance with the carrier's radius, R_{min}.

These features differ from those of the small polaron formed by the collapse of the carrier to an atomic size. In particular, the free energy of an atomic small polaron is

$$f_s(R_{atom}) \cong \frac{T}{R_{atom}^2} - \frac{V_S}{R_{atom}^3} - \frac{V_L}{R_{atom}}. \tag{34}$$

The condition that this be at least a relative minimum is that $\partial f_s(R)/\partial R > 0$ at $R = R_{atom}$. This existence condition imposes an upper bound on the free energy of this minimum: $f_s(R_{atom}) < 2V_S/R_{atom}^3 - T/R_{atom}^2$. Thus the formation of a stable atomic small polaron, $f_s(R_{atom}) < 0$, requires a sufficiently large short-range component of the electron lattice interaction: $2V_S/R_{atom}^3 > T/R_{atom}^2$. Furthermore, the ratio of the contributions to the free energy from the short-range and long-range components of the electron-lattice, $(V_S/R_{atom}^3)/(V_L/R_{atom})$, is at its maximum for an atomic small polaron. Finally, as noted previously, above Eq. (29), the contribution to the atomic small polaron's free energy from carrier induced softening is neglectable.

III. ADIABATIC SMALL POLARON HOPPING

A. Free energy of the minimum-energy coincidence state

The vibratory motion of a solid's atoms provides a charge carrier with opportunities to hop between molecules. When that atomic motion is classical, an intermolecular jump can only occur as atoms pass through a configuration for which the carrier is shared equally between the two molecules involved in the hop. This configuration is termed a ''coincidence configuration.''[1]

If the electronic transfer energy that links the two molecules is sufficiently large, a carrier's intermolecular motion is fast enough to always adjust to the atomic motion. Then the hopping is termed ''adiabatic.''[1] The jump rate for such adiabatic hopping is the rate at which atoms assume a configuration corresponding to a hop. The rate for a jump from an initial site i to a final site f has the form[4,8]

$$R_{i\to f} = \nu\left(\frac{N_c}{N_s}\right)\exp\left(-\frac{\Delta F}{kT}\right). \tag{35}$$

Here ν represents a suitable average of atomic vibrational frequencies and ΔF is the difference between the free energy associated with coincidences and that associated with a static carrier. Attention is generally restricted to the lowest-energy coincidence and polaron configurations. Then, ΔF depicts the difference between the free energy representing atomic vibrations about the lowest-energy coincidence configuration and the free energy for vibrations about a static polaron's minimum-energy configuration: $\Delta F \equiv F_c - F_s$. The ratio of the number of ways of forming equivalent coincidences to the number of ways of forming equivalent static polarons is denoted as N_c/N_s. Simple models of adiabatic hopping give $N_c/N_s = 1$.[4,8]

In analogy with the static polaron's free energy, the free energy for the lowest-energy coincidence between two equivalent molecules (centered at the origin and a site centered at $\vec{s}$) is

$$F_c = \left(\frac{\hbar^2}{2m}\right)\int d\vec{r}\,|\nabla\chi_c(\vec{r})|^2 - \int d\vec{r}\,|\chi_c(\vec{r})|^2 \int d\vec{r}\,'|\chi_c(\vec{r}\,')|^2 I(\vec{r}-\vec{r}\,') + \int d\vec{r}\,[V_m(\vec{r})+V_m(\vec{r}-\vec{s})]|\chi_c(\vec{r})|^2$$
$$-\hbar\omega\coth\left(\frac{\hbar\omega}{2\kappa T}\right)\sum_{n\neq 0}\frac{\int d\vec{r}\,[\chi_c^*(\vec{r})\chi_{c,n}(\vec{r})]\int d\vec{r}\,'[\chi_c^*(\vec{r}\,')\chi_{c,n}(\vec{r}\,')]^* I(\vec{r}-\vec{r}\,')}{\epsilon_{c,n}-\epsilon_{c,0}}. \tag{36}$$

Here $\chi_c(\vec{r})$ and $\epsilon_{c,0}$ are the electronic wave function and electronic energy of the lowest-energy coincidence state. Using analogous notation, $\chi_{c,n}(\vec{r})$ and $\epsilon_{c,n}$ are the wave function and electronic energy of a carrier in the nth excited electronic state of the coincidence configuration, respectively.

The electronic wave function of the coincident state between two sites can be expressed in terms of their local functions. In particular, the electronic wave function of a carrier shared between equivalent sites centered at the origin and at $\vec{s}$ takes the form

$$\chi_c(r) = \frac{\Psi_c(\vec{r})+\Psi_c(\vec{r}-\vec{s})}{\sqrt{2(1+O)}}. \tag{37}$$

Here $O(\vec{s})$ is the overlap between the two normalized local functions of the coincidence state, $\Psi_c(\vec{r})$ and $\Psi_c(\vec{r}-\vec{s})$, each of which is taken to be real.

The coincidence free energy is expressed in terms of the local functions by inserting Eq. (37) into Eq. (36). If, for simplicity, all overlaps between local functions and potentials from different molecules are ignored:

$$\begin{aligned} F_c = {} & \left(\frac{\hbar^2}{2m}\right)\int d\vec{r}\,|\nabla\Psi_c(\vec{r})|^2 \\ & -\frac{1}{2}\int d\vec{r}\,|\Psi_c(\vec{r})|^2\int d\vec{r}\,'|\Psi_c(\vec{r}\,')|^2[I(\vec{r}-\vec{r}\,') \\ & +I(\vec{s}+\vec{r}-\vec{r}\,')] + \int d\vec{r}\,V_m(\vec{r})|\Psi_c(\vec{r})|^2 \\ & -\frac{1}{2}\hbar\omega\coth\left(\frac{\hbar\omega}{2\kappa T}\right)\sum_{n\neq 0}\frac{1}{\epsilon_{c,n}-\epsilon_{c,0}} \\ & \times\int d\vec{r}\,[\Psi_c^*(\vec{r})\Psi_{c,n}(\vec{r})]\int d\vec{r}\,'[\Psi_c^*(\vec{r})\Psi_{c,n}(\vec{r})] \\ & \times[I(\vec{r}-\vec{r}\,')+I(\vec{s}+\vec{r}-\vec{r}\,')], \end{aligned} \tag{38}$$

where $\Psi_c^*(\vec{r})$ and $\Psi_{c,n}(\vec{r})$ are the local electronic functions associated with the nth excited coincidence state. To obtain Eq. (38), equivalent contributions to the free energy from the two molecules are combined. In addition, a change of variable has been used to rewrite contributions to the free energy that link the two sites. In these instances, the origin of an electronic integration is shifted by $\vec{s}$ thereby introducing an $\vec{s}$ dependence into the associated interaction functions $I(\vec{s}+\vec{r}-\vec{r}\,')$.

When the separation between the centroids of the hops' two local functions greatly exceed their radii,

$$I(\vec{s}+\vec{r}-\vec{r}\,')\rightarrow I_c(\vec{s})\equiv\frac{e^2}{2|\vec{s}|}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right), \tag{39}$$

where, as above Eq. (20), the cross term between long- and short-range components of the interaction function $I(\vec{r}-\vec{r}\,')$, has again been dropped. Replacing $I(\vec{s}+\vec{r}-\vec{r}\,')$ by $I_c(\vec{s})$ in Eq. (39) yields

$$F_c=\left(\frac{\hbar^2}{2m}\right)\int d\vec{r}|\nabla\Psi_c(\vec{r})|^2-\frac{1}{2}\int d\vec{r}|\Psi_c(\vec{r})|^2\int d\vec{r}\,'|\Psi_c(\vec{r}\,')|^2 I(\vec{r}-\vec{r}\,')-\frac{1}{2}I_c(\vec{s})+\int d\vec{r}V_m(\vec{r})|\Psi_c(\vec{r})|^2$$
$$-\frac{1}{2}\hbar\omega\coth(\hbar\omega/2\kappa T)\sum_{n\neq 0}\frac{\int d\vec{r}[\Psi_c^*(\vec{r})\Psi_{c,n}(\vec{r})]\int d\vec{r}\,'[\Psi_c^*(\vec{r})\Psi_{c,n}(\vec{r})]I(\vec{r}-\vec{r}\,')}{\epsilon_{c,n}-\epsilon_{c,0}}, \tag{40}$$

where use has been made that $\Psi_c(\vec{r})$ is normalized and that $\Psi_c^*(\vec{r})$ and the $\Psi_{c,n}(\vec{r})$ are orthogonal to one another.

The formal expression for F_c, Eq. (40), differs from that for F_s, Eq. (16), in two aspects. First, the coefficients of electron-lattice-interaction contributions to F_c are half those of corresponding contributions to F_s. Second, F_c contains the $\vec{s}$-dependent contribution: $-I_c(\vec{s})/2$. These two effects will be seen to produce the free energy difference, ΔF, associated with a hop.

B. A hop's free energy difference, ΔF

The coincidence-state free-energy is expressed in terms of the coincidence's local functions in Eq. (40). A scaling analysis of Eq. (40) is now employed to investigate how the coincidence free energy depends on the spatial extent of the coincidence's local functions. The free-energy difference associated with a hop, ΔF, is then written in terms of the spatial extents of a static polaron and of the local states of the minimum-energy coincidence.

The scaling analysis of the coincidence state proceeds in direct analogy with the scaling analysis of a static polaron. The scaling functional for the coincidence states is

$$f_c(R)=\frac{T_c}{R^2}-\frac{V_{c,S}}{2R^3}-\frac{V_{c,L}}{2}\left(\frac{1}{R}+\frac{1}{S}\right)-\frac{\Delta f_{c,\mathrm{vib,L}}}{2}R, \tag{41}$$

where $R_{atom}\leqslant R_c\leqslant R_{molecule}$ and $I_c(\vec{s})$ is written as

$$I_c(\vec{s})=\frac{V_{c,L}}{S}, \tag{42}$$

where S is the intermolecular separation expressed in units of the characteristic length of $V_{c,L}$. The constants of the scaling analysis of coincidence states are formally analogous to those of the scaling analysis of the static polaron albeit with the local electronic functions being $\Psi_c(\vec{r})$ rather than $\Psi_s(\vec{r})$:

$$T_c\equiv\left(\frac{\hbar^2}{2m}\right)\int d\vec{r}|\nabla\Psi_c(\vec{r})|^2, \tag{43}$$

$$V_{c,S}\equiv E_b V_c\int d\vec{r}|\Psi_c(\vec{r})|^4, \tag{44}$$

$$V_{c,L}\equiv\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int d\vec{r}\int d\vec{r}\,'\frac{|\Psi_c(\vec{r})|^2|\Psi_c(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}, \tag{45}$$

and

$$\Delta f_{c,\mathrm{vib,L}}\equiv\left[\frac{e^2}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\right]\hbar\omega\coth(\hbar\omega/2\kappa T)\sum_{n\neq 0}\frac{1}{E_n^c-E_0}\int d\vec{r}\int d\vec{r}\,'\frac{[\Psi_c^*(\vec{r})\Psi_{c,n}(\vec{r})][\Psi_c^*(\vec{r}\,')\Psi_{c,n}(\vec{r}\,')]^*}{|\vec{r}-\vec{r}\,'|}. \tag{46}$$

As in the analysis of the static polaron, there are three possibilities for the lowest value of F. The most-localized possible solution has each of the two local electronic functions of the coincidence confined to a single atom R_{atom}. The least-localized possible solution has each of the two local electronic functions of the coincidence extending over the entire molecule $R_{molecule}$. The third possible solution has each of the two local electronic functions having a spatial extent of intermediate size $R_{c,\mathrm{min}}$. The value of R that minimizes $f_c(R)$ is defined as R_c.

The free-energy difference that characterizes the hop of a polaron between molecular units, $\Delta F\equiv F_c-F_s$, depends upon the sizes of the local electronic state at equilibrium and at the coincidence:

$$\Delta F=\left[\frac{T_c}{R_c^2}-\frac{V_{c,S}}{2R_c^3}-\frac{V_{c,L}}{2}\left(\frac{1}{R_c}+\frac{1}{S}\right)-\frac{\Delta f_{c,\mathrm{vib,L}}}{2}R_c\right]$$
$$-\left[\frac{T}{R_s^2}-\frac{V_S}{R_s^3}-\frac{V_L}{R_s}-\Delta f_{\mathrm{vib,L}}R_s\right]. \qquad (47)$$

Equating the corresponding energy parameters that result when the static polaron's electronic state and the coincidence's local electronic function both collapse to the atomistic limit yields $T_c=T$, $V_{c,S}=V_S$, $V_L^c=V_L$, and $\Delta f_{c,\mathrm{vib,L}}=\Delta f_{\mathrm{vib,L}}$. With these relations the free energy characterizing an adiabatic semiclassical polaron hop becomes

$$\Delta F=V_S\left(\frac{1}{R_s^3}-\frac{1}{2R_c^3}\right)+V_L\left(\frac{1}{R_s}-\frac{1}{2R_c}-\frac{1}{2S}\right)$$
$$-T\left(\frac{1}{R_s^2}-\frac{1}{R_c^2}\right)+\Delta f_{\mathrm{vib,L}}\left(R_s-\frac{R_c}{2}\right). \qquad (48)$$

The final contribution to ΔF is the change of the vibrational free energy associated with a hop. However, Eq. (48) is derived using the coincidence approach. This semiclassical treatment is only valid at sufficiently high temperatures for atoms' vibrational motion to be treated classically, $\kappa T>\hbar\omega/2$. In this high-temperature regime $\Delta f_{\mathrm{vib,L}}$, defined in Eq. (26), is proportional to temperature since $\hbar\omega\coth(\hbar\omega/2\kappa T)\rightarrow 2\kappa T$, when $\hbar\omega/2\kappa T\rightarrow 0$. Hence the contribution to the jump rate, Eq. (35), from this contribution to ΔF, $\exp[-\Delta f_{\mathrm{vib,L}}(R_s-R_c/2)/\kappa T]$, is independent of temperature at the high temperatures at which this semiclassical approach is valid. Furthermore, this temperature-independent factor augments the jump rate when $R_c>2R_s$ and reduces the jump rate when $R_c<2R_s$.

There are many possible hopping scenarios. In particular, there are three possible states of a static polaron, characterized by the radii R_{atom}, $R_{\min}$, and $R_{molecule}$. In addition, there are three possible coincidence states, characterized by local functions with radii of R_{atom}, $R_{c,\min}$, and $R_{molecule}$. However, the radius of the coincidence state, R_c, will tend to exceed that of a static polaron, R_s, since the coefficient of the contribution to the coincidence free-energy from the electron-lattice interaction is half that of the corresponding contribution to the free energy of a static polaron. Thus there are six hopping scenarios for which $R_c\geqslant R_s$. These jump processes are depicted schematically in Fig. 2.

For three of the six possible situations the spatial extents of the static carrier and the local function of the coincidence are limited by geometric constraints. In these cases both R_c and R_s are restricted to two values, R_{atom} or $R_{molecule}$.

The prototypical small polaron hop envisions a hop with $R_s=R_c=R_{atom}$:[1]

$$\Delta F_{atom,atom}=\frac{V_S}{2R_{atom}^3}+\frac{V_L}{2}\left(\frac{1}{R_{atom}}-\frac{1}{S}\right)+\frac{\Delta f_{\mathrm{vib,L}}R_{atom}}{2}. \qquad (49)$$

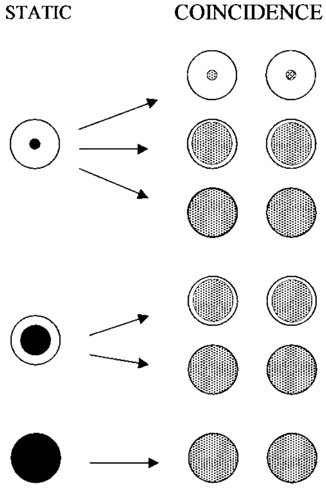

FIG. 2. The six processes by which a static polaron can hop to another site are schematically illustrated. The static polaron's charge carrier can either (i) collapse to a single atomistic unit, (ii) occupy a finite subset of the molecule's atomic sites, or (iii) extend over the entire molecule. In making a hop the carrier passes through a coincidence configuration in which it is shared between initial and final sites. The spatial extent of the carrier in the coincidence state is never smaller than that of the static polaron.

Here the minimal size of the electronic state ensures that the contribution to ΔF from the deformation energy associated with the short-range component of the electron-lattice interaction, $V_S/2R_{atom}^3$, has its greatest relative significance. By contrast, the temperature-independent reduction of the jump rate from vibrational softening, $\exp[-\Delta f_{\mathrm{vib,L}}R_{atom}/2\kappa T]$, is minimal in this situation.

The forms of the first two contributions to the activation energy for small polaron hopping have been obtained previously. In particular, the contribution to the hopping activation energy from the short-range component of the electron-lattice interaction was found to be inversely proportional to the electronic state's volume.[5,6]

Furthermore, it has previously been argued that the contribution to the hopping activation energy from the long-range component of the electron-lattice interaction depends on the separation between the states involved in the hop in the manner described by Eq. (49).[18]

For a hop between molecular states, $R_s=R_c=R_{molecule}$:

$$\Delta F_{molecule,molecule}=\frac{V_S}{2R_{molecule}^3}+\frac{V_L}{2}\left(\frac{1}{R_{molecule}}-\frac{1}{S}\right)$$
$$+\frac{\Delta f_{\mathrm{vib,L}}R_{molecule}}{2}. \qquad (50)$$

Increasing the size of the electronic state so that it encompasses the entire molecule minimizes the contribution of the short-range component of the electron-lattice interaction. However, the reduction of the contribution from the long-range component of the electron-lattice interaction as the electronic state expands, $\propto 1/R_{molecule}$, is much less severe than that from the short-range component of the electron-lattice interaction, $\propto 1/R_{molecule}^3$. Thus the relative significance of the long-range component of the electron-lattice interaction increases with the size of the electronic state. Finally, it is noted that expanding the electronic state to envelop the entire molecule maximizes the reduction of the jump rate from vibrational softening.

A molecule's electronic wave function tends to expand as a coincidence is achieved. This tendency has been thwarted by geometrical constrains in the two jump process that have been considered so far. However, a molecule's carrier is permitted to expand in the four remaining hopping scenarios depicted in Fig. 2. The dilation of a carrier during a coincidence can significantly affect ΔF.

Consider the expansion of the carrier of an atomic small polaron to encompass the entire molecule at the coincidence: $R_s = R_{atom}$ and $R_c = R_{molecule}$. The free-energy difference, Eq. (48), for such a hop becomes

$$\begin{aligned}\Delta F_{atom,molecule} = {} & V_S\left(\frac{1}{R_{atom}^3} - \frac{1}{2R_{molecule}^3}\right) \\ & + V_L\left(\frac{1}{R_{atom}} - \frac{1}{2R_{molecule}} - \frac{1}{2S}\right) \\ & - T\left(\frac{1}{R_{atom}^2} - \frac{1}{R_{molecule}^2}\right) \\ & + \Delta f_{\mathrm{vib,L}}\left(R_{atom} - \frac{R_{molecule}}{2}\right). \qquad (51)\end{aligned}$$

The short-range and long-range deformational contributions to ΔF grow with the expansion of the coincidence state. However, this effect is countered by the reduction of the carrier's confinement energy, the contribution proportional to T. Furthermore, the contribution to $\Delta F_{atom,molecule}$ from vibrational softening becomes negative when $R_{molecule} > 2R_{atom}$. In this circumstance, vibrational softening enhances the magnitude of the high-temperature jump rate.

An important circumstance occurs for hopping between molecules immersed in a strong dipolar medium. The free energies of both the static polaron and of the coincidence state may then be dominated by the long-range component of the electron-lattice interaction. In this case, $R_s = R_{\min} = 2T/V_L$ and $R_c = R_{c,\min} = 4T/V_L$. With these relations the free-energy difference associated with a semiclassical hop, Eq. (48), becomes

$$\Delta F_{LR} = \frac{V_L}{2}\left(\frac{3/4}{R_{\min}} - \frac{1}{S}\right), \qquad (52)$$

where, for simplicity, $V_S = 0$.

Equation (52) differs from the Austin-Mott formula for the activation energy of an equivalent situation, small polaron hopping in an ionic medium.[19] In particular, the Austin-Mott formula replaces the factor of 3/4 in the numerator of the first contribution within the curved brackets of Eq. (52) with 3/2. This discrepancy arises because Austin and Mott neglect the lowering of the hopping activation energy produced by the reduction of the carrier's confinement energy: $-T(1/R_s^2 - 1/R_c^2) = -3T/4R_{\min}^2 = -3V_L/8R_{\min}$. This lowering of a carrier's confinement energy at a coincidence significantly affects the activation energy for a hop. The hopping activation energy is less than half the Austin-Mott value.

IV. SUMMARY AND DISCUSSION

Polaron phenomena are based on a charge carrier's interactions with the atoms that surround it. Nonetheless, studies of small polaron formation and hopping motion frequently approximate the carrier's wave function as ''rigid,'' unaffected by atomic motion.[1] The dependence of the carrier's energy on atoms' positions then arises solely through the expectation value of the carrier's potential energy with respect to the rigid wave functions. In particular, a linear electron-lattice interaction (a linear dependence of the carrier's potential on atomic positions) yields a linear dependence of the carrier's energy on atoms' locations. A nonlinear dependence of the carrier's energy on atomic displacements results from proceeding beyond the rigid wave function approximation.

The breakdown of the rigid wave-function approximation grows with the carriers' polarizability.[11,12] The polarizability of an electronic state P_e rises rapidly with its radius: $P_e \approx R_e^4/a_B$, where R_e is the radius of the electronic state and a_B is the Bohr radius. Thus breakdown of the rigid-wavefunction is expected to be much more significant for carriers localized on large molecules ($R_e \sim 1$ nm) than for carries confined to cations ($R_e \lesssim 0.1$ nm).

Herein the theory of the formation and semiclassical hopping motion of small-polarons has been extended beyond the rigid wave-function approximation so as to apply to small-polarons with relatively large electronic states. In particular, this work models a carrier confined to large molecules embedded within an ionic medium. The carrier interacts with an occupied molecule's atoms via a short-range electron-lattice interaction (akin to the deformation potential of a covalent semiconductor). The carrier also interacts with the solid's ions via the long-range (Frohlich) electron-lattice interaction.

As in prior works, carrier induced displacements of atoms' equilibrium positions reduce the system's potential energy. This relaxation energy falls with the size of the carrier's state. The short-range component of the electron-lattice interaction produces a relaxation energy that is inversely proportional to the *volume* of the carrier's state. By contrast, the long-range component of the electron-lattice interaction drives an atomic relaxation whose energy only falls inversely as the carrier's *radius*. Thus long-range relaxation increases in importance relative to short-range relaxation as the carrier's radius increases. As a result, relaxation-related properties of molecular polarons tend to be especially sensitive to the ionicity of the medium about them.

Beyond the rigid wave-function approximation, the electronic state of the carrier adjusts to the motions of the material's atoms. This intramolecular charge flow reduces the stiffness constants of the atomic vibrations that are coupled to the carrier. This effect reduces the vibrational frequencies and vibrational free energy. Carrier induced vibrational softening thereby contributes to the polaronic binding of a carrier. By inducing a reduction of vibrational frequencies, a carrier also increases vibrational entropy. The carrier induced change of vibrational entropy contributes to the Seebeck coefficient,[13] the entropy transported with a charge carrier divided by the carrier's charge. As such, the Seebeck coefficient can provide a measure of carrier induced vibrational softening.

Carrier induced vibrational softening affects atomic vibrations of the embedding medium as well as those of occupied molecules. The reduction of the vibrational free energy that is driven by the short-range electron-lattice interaction is *inversely proportional* to the carrier's radius. By contrast, the reduction of the vibrational free energy that is driven by the long-range (ionic) electron-lattice interaction is *proportional* to the carrier's radius. Therefore the contribution of vibrational softening to polaron binding is greatest for large (multiatomic) carriers within ionic media.

Minimization of the system's energy with respect to the carrier's radius yields three distinct types of minima. The carrier can spread out over all equivalent sites of the molecule. Alternatively, the carrier can be localized at a single atomistic unit of the molecule. Finally, if the interaction with the medium's ions is sufficiently strong, the carrier can be localized among a subset of the molecule's equivalent atoms. Thus there are three distinct types of self-trapped state for a carrier on a molecule.

Intermolecular hopping has also been considered. Attention is focused at high enough temperatures for atoms' vibratory motion to be treated as classical. Then, intermolecular hopping requires the formation of a coincidence configuration in which the carrier is shared between the two molecules involved in the jump. The hopping activation energy is the minimum energy required to form a coincidence. Three types of minimum-energy coincidence, analogous to the three types of polaron, can form. Since a carrier expands as it approaches a coincidence, there are six distinct types of intermolecular hop. A significant contribution to a hop's activation energy can come from the electronic kinetic energy associated with the change of the carrier's size.

Furthermore, a hop is generally accompanied by a change of vibrational entropy [e.g., $\Delta f_{vib,L}(R_s - R_c/2)/T$ in Eq. (48)]. The entropy contribution, like the hopping activation energy, is of second order in the electron-lattice coupling strength. As such, the entropy contribution is proportional to the hopping activation energy. The Meyer-Neldel ''compensation'' effect, $\Delta F = E_A - E_A(T/T_0)$, results when $R_c > 2R_s$ in Eq. (48).[20]

All told, the ability of a carrier to move about an occupied molecule in response to atomic motions can significantly affect the formation and hopping of even a simple molecular polaron. These effects will be embellished for multicomponent molecules with intricate shapes. The theory also applies to carriers that occupy multiatomic defect centers in semiconductors.

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