Translationally invariant polarons in conjugated conducting polymers

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A simple effective Hamiltonian for the electron-phonon coupling in the conjugated polymers is derived from the Su-Schrieffer-Heeger model with quantized lattice motions. Phonons correspond to lattice quantum fluctuations around the dimerized positions. Both acoustic and optical modes are considered. The energy-momentum relation for the polaron is calculated variationally, with the aid of Lee-Low-Pines transformation. The discrete translational invariance of an ideal conjugated polymer is explicitly enforced. Analytical expression for the polaron effective mass m^* is obtained. m^* turns out to be, in general, much larger than the conduction-band effective mass. [S0163-1829(97)05920-1]

I. INTRODUCTION

Since the pioneering works of Lee, Low, and Pines[1] and Feynman[2] the problem of polarons in a coupled electron-phonon system has attracted constant attention.[3] Conventionally, the term ''polaron'' refers to a conduction electron coupled to the optical phonons in polar crystals described by the Fröhlich Hamiltonian.[4] Conjugated polymers, as an important class of coupled electron-phonon system, are one-dimensional covalent chains, in which the electron-phonon coupling has more of a deformation than a polar origin. Consequently, for conjugated polymers the Fröhlich Hamiltonian is not a suitable model, and the results of the conventional polaron theory do not apply. Furthermore, in the Fröhlich Hamiltonian phonons are quantum fluctuations around the equilibrium positions of the lattice by itself, regardless of the electron-lattice coupling. On the other hand, the equilibrium position of the lattice is dimerized in conjugated polymers due to Peierls instability caused by the π-electron delocalization. Phonons, therefore, correspond to the quantum lattice fluctuations around the dimerized positions determined by the electron-lattice coupling.[5] Electron-phonon coupling and polarons in a dimerized chain are a theoretical problem not yet fully explored. The importance of the theory of polarons in conjugated polymers, especially the calculation of their effective mass, is closely related to the potential application of polymer-based electro-optical devices. The effective mass, combined with the mean free time, determines the polaron mobility.[4] Mobility and other transport properties of polarons, which are believed to be the principal charge carriers, are crucial to the performance of those devices. For example, in light-emitting diodes, the electrons and holes have to be transported through the material after injection in order to meet each other and recombine.

Solitons are first identified as one of the ''nonlinear excitations'' in the Su-Schrieffer-Heeger (SSH) model for conjugated polymers.[6] Polarons and bipolarons in the SSH model were studied by Campbell, Bishop, and Fesser with the frozen valence-band approximation,[7] and later with the fully relaxed valence band.[8] While successful in explaining the optically and dopant-induced absorption spectra, the SSH model is not likely to be as ideal for the study of the charge transport properties for some fundamental reasons discussed below. The SSH Hamiltonian itself has the usual discrete translational symmetry of a one-dimensional crystal. However, all the nonlinear excitations are not translationally invariant. In fact, the lattice positions are treated as configuration parameters, and the local deviations from perfect dimerization accompanied with all the excitations can happen around any one of the unit cells with equal total energies. In other words, the translational invariance of the system is broken and the ground state becomes infinitely degenerate, which implies a constant energy-momentum relation and infinite effective mass. In such a case, the crystal momentum is no longer a good quantum number to label those excitations, as it should be for a full quantum theory. The notion of polarons in such a context is quite different from the conventional sense as defined for the Fröhlich Hamiltonian mentioned above.[1,2,4] In particular, the polaron energy-momentum relation cannot even be defined for a theory without translational symmetry. However, the curvature of the energy-momentum relation is fundamental to the determination of the polaron effective mass, which in turn determines the polaron mobility. Even though the polaron effective mass is given based on purely classical kinetic energy considerations,[7,8] it is not clear how it can be identified with the effective mass appearing in the mobility for a quantum theory.[4] After all, the classical mass obtained by Campbell *et al.* is not the same quantity as the quantum-mechanical mass we are considering, even if both models can be solved exactly. Consider the limit where the carbon atom mass goes to infinity. The classical mass, determined by the carbon atom motion, would go to infinity as well. On the other hand, the quantum-mechanical mass will go to the band mass (no renormalization). The reason for the latter is that at such a limit, the lattice does not respond to the electron, and it becomes rigid as experienced by the moving electrons. This feature is built in for our effective Hamiltonian. Further discussions on the difference between these two masses are postponed to the final section.

In this paper, we develop a fully quantum-mechanical and translationally invariant theory for the polaron problem in conjugated polymers. Starting with the SSH Hamiltonian with quantized lattice positions and momenta, we derive an effective Hamiltonian for a conduction electron interacting with phonons. It turns out that, unlike the polar coupling case, both the optical and acoustic phonon couplings are present and important. The total crystal momentum is conserved in such a Hamiltonian. A generalized Lee-Low-Pines transformation[1] is used to reduce the Hamiltonian to a subspace with particular total momentum. A variational method based on phonon coherent states is used to calculate the polaron energy spectrum. We obtain an analytical expression for the polaron effective mass. Numerical values are calculated for parameters suitable for polyacetylene.

In Sec. II, we derive the effective Hamiltonian. The polaron energy spectrum and the effective mass are calculated in Sec. III. We conclude with some critical remarks in the final section.

II. EFFECTIVE HAMILTONIAN

In order to derive the effective Hamiltonian for the polaron in conjugated polymers, we take cis-polyacetylene as an example, and start with the SSH Hamiltonian:[6]

$$H_{SSH} = -\sum_{n,s} t_{n+1,n}(C_{n+1,s}^\dagger C_{n,s} + C_{n,s}^\dagger C_{n+1,s})$$
$$+ \frac{K}{2}\sum_n (u_{n+1}-u_n)^2 + \frac{\hbar^2}{2M}\sum_n p_n^2. \quad (1)$$

$C_{n,s}$ is the annihilation operator of π electrons with spin s at site n, u_n is the displacement of the carbon atom at site n, and p_n is the conjugate momentum of u_n. K is the spring constant for the σ bonds, M is the mass of the carbon atom plus side group (monomer). $t_{n+1,n}$ is the hopping integral and is given by

$$t_{n+1,n} = t_0 - t_1(-1)^n - \alpha(u_{n+1}-u_n). \quad (2)$$

α is the electron-lattice coupling constant. u_n and p_n satisfy the canonical commutation relation

$$[u_n, p_n] = i\hbar.$$

In the ground state, the polymer chain is dimerized,[6] and the ground-state expectation values $\bar{u}_n$ of the lattice displacements u_n are not zero. In order to cast this Hamiltonian into a more standard "electron plus phonon plus interaction" form, we rewrite H_{SSH} in terms of v_n, the shifts of the lattice positions u_n around their ground-state expectation values $\bar{u}_n$. After substituting the equation $u_n \equiv \bar{u}_n + v_n$ into H_{SSH}, the Hamiltonian can be divided into three parts:

$$H_{SSH} = H_e + H_{el} + H_l, \quad (3)$$

with

$$H_e = -\sum_{n,s} [t_0 - t_1(-1)^n - \alpha(\bar{u}_{n+1}-\bar{u}_n)]$$
$$\times (C_{n+1,s}^\dagger C_{n,s} + C_{n,s}^\dagger C_{n+1,s}),$$

$$H_{el} = \alpha\sum_{n,s} (v_{n+1}-v_n)(C_{n+1,s}^\dagger C_{n,s} + C_{n,s}^\dagger C_{n+1,s}),$$

$$H_l = \frac{K}{2}\sum_n [(\bar{u}_{n+1}-\bar{u}_n)^2 + 2(\bar{u}_{n+1}-\bar{u}_n)(v_{n+1}-v_n)$$
$$+ (v_{n+1}-v_n)^2].$$

Note that v_n's are operators while $\bar{u}_n$'s are c numbers. Due to dimerization, terms linear in the lattice fluctuations v_n appear in both H_{el} and H_l. This linear dependence is only formal, and will soon disappear when we project our problem to the subspace of one conduction electron below.

It is well known that, if the lattice positions u_n are treated as c-number configuration parameters without dynamics, the ground-state lattice configuration is a perfectly dimerized chain. The configuration can be shown to be of the form $u_n^c = w + (-1)^n u$,[9] where w and u can be explicitly calculated. The superscript "c" indicates classical. In a full quantum theory where u_n, together with p_n, are operators, the ground-state expectation value $\bar{u}_n$ is not simply equal to u_n^c in general.[10] In fact, there is no way to calculate u_n exactly beforehand, and then proceed our development afterwards. Therefore, we need to determine $\bar{u}_n$ self-consistently by the requirement that, after making the projection into the subspace of one conduction electron, no linear terms in v_n are left in the lattice part of the effective Hamiltonian. We remark that the $\bar{u}_n$ thus determined is not the exact bond position, but a part of our approximations. The expansion of v_n in terms the usual phonon operators makes sense only if this requirement is fulfilled. It turns out that the correct choice of $\bar{u}_n$ is exactly equal to u_n^c in such a self-consistency scheme:

$$\bar{u}_n = w + (-1)^n u. \quad (4)$$

Therefore, the electronic part of the Hamiltonian H_e becomes

$$H_e = -\sum_{n,s} [(t_0 - \alpha w) - (t_1 - \alpha u)(-1)^n]$$
$$\times (C_{n+1,s}^\dagger C_{n,s} + C_{n,s}^\dagger C_{n+1,s})$$
$$= \sum_{k,s} \varepsilon_{ck} c_{ks,c}^\dagger c_{ks,c} + \varepsilon_{vk} c_{ks,v}^\dagger c_{ks,v}. \quad (5)$$

Here $\varepsilon_{c,vk}$ are the dispersion of the conduction and valence bands, respectively. $c_{ks,c}$ and $c_{ks,v}$ are the annihilation operators of the conduction and valence electrons, respectively. The energy dispersions of the bands are[11]

$$\varepsilon_{ck} = -\varepsilon_{vk} = |z_k|, \quad (6)$$

with

$$z_k = t + \delta t + (t - \delta t)e^{2ika}, \quad t \equiv t_0 - \alpha w, \quad \delta \equiv t_1 - \alpha u. \quad (7)$$

a is the lattice constant before dimerization. For later use, we also define another quantity, $\zeta_k \equiv (z_k/2|z_k|)^{1/2}$.

In order to make a tractable theory, we truncate the electronic sector of the Hilbert space by keeping only the low-lying states. The error introduced is believed to be very

small, as explained below. We choose the basis as the eigenstates of the electronic Hamiltonian H_e without interaction with the lattice. Then we compute the matrix elements of the interaction Hamiltonian H_{el} among these eigenstates. Without interaction, the electron part of the Hamiltonian is that of a perfect rigid chain with two bands. In the polaron problem, we are concerned with the one extra conduction electron injected from outside. In other words, the total number of electrons is equal to the total number of carbon atoms plus one. Equivalently, the number of electrons in the conduction band is one more than the number of holes in the valence band. Therefore, the eigenstates of H_e fall into groups: one (conduction) electron, no hole group, two electrons, one hole group, and three electrons, two holes group, etc. These groups all together form a complete set of the system, and no approximation is made so far. We truncate the Hilbert space by keeping only the first group. This is expected to be a very good approximation since we are interested in the ground state (zero momentum) and lowest excited states (small momentum). The states in the other groups are higher in energy than the first group by a multiple of the band gap, and are, therefore, not likely to contribute significantly to the exact low-energy spectrum. This truncated Hilbert space is spanned by the basis vectors $|k,s\rangle \equiv c_{ks,c}^{\dagger}|0\rangle$, where the ground state of H_e is denoted by $|0\rangle$, in which all the valence-band states are filled, and all the conduction-band states are empty. In the following, we derive the representation of the total Hamiltonian in this subspace by calculating the matrix elements $\langle k's'|H_{SSH}|ks\rangle$, which can be simply written in the form $\langle k'|H_{SSH}|k\rangle \delta_{s's}$. The spin part is omitted in the following.

The representation of the electronic part of the Hamiltonian is

$$\langle k|H_e|k'\rangle = \varepsilon_{ck}\delta_{k',k}. \qquad (8)$$

In order to calculate the matrix elements of H_{el}, we need the matrix elements of $C_{n+1,s}^{\dagger}C_{n,s}+C_{n,s}^{\dagger}C_{n+1,s}$, which turn out to be

$$\langle k'|C_{n+1,s}^{\dagger}C_{n,s}+C_{n,s}^{\dagger}C_{n+1,s}|k\rangle$$
$$= \langle 0|C_{n+1,s}^{\dagger}C_{n,s}+C_{n,s}^{\dagger}C_{n+1,s}|0\rangle + \gamma_n^{k'k}, \qquad (9)$$

where

$$\gamma_n^{k'k} \equiv \begin{cases} (2/N)e^{i(k'-k)na}(\zeta_{k'}^*\zeta_k^*+\zeta_{k'}\zeta_k), & n \text{ even} \\ (2/N)e^{i(k'-k)na}(e^{-i(k'+k)a}\zeta_{k'}^*\zeta_k^*+e^{i(k'+k)a}\zeta_{k'}\zeta_k), & n \text{ odd.} \end{cases} \qquad (10)$$

N is the total number carbon atoms in the chain. Using the relation[12]

$$\alpha\langle 0|C_{n+1,s}^{\dagger}C_{n,s}+C_{n,s}^{\dagger}C_{n+1,s}|0\rangle + K(\bar{u}_{n+1}-\bar{u}_n)=0, \qquad (11)$$

the terms linear in $v_{n+1}-v_n$ in H_l and H_{el} are all canceled with each other as expected. In fact, the above relation is exactly the condition that the total energy is minimized by the (classical) lattice configuration $\bar{u}_n$.[12] Collecting everything together, the representation of the total Hamiltonian becomes

$$\bar{H}^{k'k} \equiv \langle k'|H_{SSH}|k\rangle = \varepsilon_{ck}\delta_{k'k} + \frac{K}{2}\sum_n (v_{n+1}-v_n)^2 + \sum_n \frac{p_n^2}{2M}$$
$$- \alpha\sum_n (v_{n+1}-v_n)\gamma_n^{k'k}. \qquad (12)$$

The three lines on the right-hand side of Eq. (12) are referred to as $\bar{H}_e^{k'k}$, $\bar{H}_p^{k'k}$, and $\bar{H}_{ep}^{k'k}$, respectively. e and p denote electron and phonon, respectively. The next step is to expand v_n and p_n in terms of the standard phonon creation and annihilation operators:

$$v_m^i = \sqrt{\frac{2}{N}}\sum_{k\lambda} \sqrt{\frac{\hbar}{2M\omega_\lambda(k)}}(a_{k\lambda}+a_{-k\lambda}^{\dagger})\epsilon_\lambda^i(k)e^{ik2am},$$

$$p_m^i = -i\sqrt{\frac{2}{N}}\sum_{k\lambda} \sqrt{\frac{\hbar M\omega_\lambda(k)}{2}}(a_{k\lambda}-a_{-k\lambda}^{\dagger})\epsilon_\lambda^i(k)e^{ik2am},$$

and rewrite the Hamiltonian in the standard ''electron plus phonon plus interaction'' form. Here the integer m is the index for unit cells, which now contain two carbon atoms due to dimerization. $i=1,2$ is the index for the two atoms within a unit cell. More explicitly, $v_m^1=v_{2m}, v_m^2=v_{2m+1}$. $\lambda=1,2$ corresponds to acoustic and optical phonons, respectively. $\epsilon_\lambda^i(k)$ is the phonon polarization vectors. $a_{k\lambda}$ and $a_{k\lambda}^{\dagger}$ are the phonon annihilation and creation operators. $\omega_{1,2}(k)$ is equal to $\sqrt{2K/M}[1\pm|\cos(ka)|]^{1/2}$, respectively. In terms of $a_{k\lambda}$ and $a_{k\lambda}^{\dagger}$, we find that the interaction part of Eq. (12) becomes

$$\bar{H}_{ep}^{k'k} = -\alpha\sum_{\lambda=1}^{2} \sqrt{\frac{\hbar}{NM\omega_\lambda(k-k')}}[\beta_{kk'\lambda}^{(1)}+\beta_{kk'\lambda}^{(2)}]$$
$$\times(a_{k-k',\lambda}+a_{k'-k,\lambda}^{\dagger}), \qquad (13)$$

with

$$\beta_{kk'\lambda}^{(1)} \equiv [\epsilon_\lambda^2(k-k')-\epsilon_\lambda^1(k-k')](\zeta_k\zeta_{k'}+\text{c.c.}),$$

$$\beta_{kk'\lambda}^{(2)} \equiv [\epsilon_\lambda^1(k-k')e^{i2(k-k')a}-\epsilon_\lambda^2(k-k')]$$
$$\times e^{i(k'-k)a}[e^{i(k'+k)a}\zeta_k\zeta_{k'}+\text{c.c.}].$$

For small k and k', the above electron-phonon interaction part of the Hamiltonian reduces to a simple form:

$$\bar{H}_{ep}^{k'k} = -A\left[\frac{3}{4}|(k'-k)a|^{1/2}(a_{k-k',1}+a_{k'-k,1}^{\dagger})\right.$$
$$\left.+\left(\frac{1}{2}\right)^{1/4}i\frac{k'-k}{|k'-k|}(a_{k-k',2}+a_{k'-k,2}^{\dagger})\right],$$

with

$$A \equiv \alpha\frac{2\sqrt{2}}{\sqrt{N}}\left(\frac{\hbar}{\sqrt{KM}}\right)^{1/2}. \quad (14)$$

Finally, in the representation of the position operator x and momentum operator p of the conduction electron, the effective total Hamiltonian becomes

$$\bar{H} = \frac{p^2}{2m_B} + \sum_q \hbar\omega_1(q)a_{q,1}^{\dagger}a_{q,1} + \hbar\omega_2(q)a_{q,2}^{\dagger}a_{q,2}$$
$$+\sum_q V_q e^{iqx}(a_{q,1}+a_{-q,1}^{\dagger}) + U_q e^{iqx}(a_{q,2}+a_{-q,2}^{\dagger}),$$
$$(15)$$

with

$$V_q \equiv -A\frac{3}{4}|qa|^{1/2}, \quad U_q \equiv -A\left(\frac{1}{2}\right)^{1/4}i\frac{qa}{|qa|}, \quad (16)$$

and

$$m_B = \frac{\hbar^2}{(2at_0)^2}\Delta, \quad \Delta = 4t_0 e^{-\pi t_0 K/\alpha^2}. \quad (17)$$

Here Δ is the Peierls half band gap.[12] $m_B = \hbar^2\Delta/(2at_0)^2$ is the conduction-band effective mass. x and p satisfy the canonical commutation relation $[x,p]=i\hbar$. Note that the q dependence of the optical phonon coupling constant U_q is quite different from the one in the Fröhlich Hamiltonian, in which $U_q \sim 1/|q|$. This is anticipated because, as stressed in the Introduction, the origin of the electron-phonon coupling in a conjugated polymer is of deformation origin, instead of the polar origin as in the Fröhlich Hamiltonian. Even though the acoustic coupling constant V_q vanishes as the momentum transfer q goes to zero, there is no reason for us to ignore the acoustic coupling altogether, since finite q's contribute to the polaron state as well. In fact, we find in the following calculations that the contribution from the acoustic phonons to the polaron effective mass is about the same order as the optical phonons in some cases. Note that A, V_q, and U_q all go to zero as the monomer mass M goes to infinity. Electrons and phonons are then decoupled, as claimed in the Introduction.

III. POLARON ENERGY SPECTRUM, EFFECTIVE MASS

We make the Lee-Low-Pines unitary transformation[1] on our effective Hamiltonian $\bar{H}$:

$$\bar{H} \rightarrow S^{-1}\bar{H}S \equiv H,$$

$$S \equiv \exp\left\{i\left[P/\hbar - \sum_k (a_{k,1}^{\dagger}a_{k,1}+a_{k,2}^{\dagger}a_{k,2})k\right]x\right\}. \quad (18)$$

P is the total crystal momentum of the polaron. The transformed Hamiltonian H becomes

$$H = \sum_k \hbar\omega_1(k)a_{k,1}^{\dagger}a_{k,1} + \hbar\omega_2(k)a_{k,2}^{\dagger}a_{k,2}$$
$$+\sum_k V_k(a_{k,1}+a_{-k,1}^{\dagger}) + U_k(a_{k,2}+a_{-k,2}^{\dagger})$$
$$+\frac{1}{2m_B}\left[P-\sum_k \hbar k(a_{k,1}^{\dagger}a_{k,1}+a_{k,2}^{\dagger}a_{k,2})\right]^2. \quad (19)$$

The polaron energy spectrum $E(P)$ is the ground-state energy of H for given P. In the following, we make a variational calculation of the ground-state energy based on coherent phonon wave functions

$$|\Psi\rangle = \exp\left[\sum_k a_{k,1}^{\dagger}f(k) + a_{k,2}^{\dagger}g(k) + \text{H.c.}\right]|\Psi_0\rangle, \quad (20)$$

where $|\Psi_0\rangle$ is the state without any phonon. $f(k)$ and $g(k)$ are adjusted such that the energy expectation value $\langle\Psi|H|\Psi\rangle$ is minimized. In terms of the trial functions $f(k)$ and $g(k)$, the ground-state energy expectation value $\langle\Psi|H|\Psi\rangle$ is given by

$$\langle\Psi|H|\Psi\rangle = \frac{P^2}{2m^*} + \sum_k V_k[f(k)+f^*(-k)]$$
$$+ U_k[g(k)+g^*(-k)]$$
$$+\sum_k |f(k)|^2\left[\hbar\omega_1(k) - \frac{P\hbar k}{m^*} + \frac{\hbar^2k^2}{2m^*}\right]$$
$$+\sum_k |g(k)|^2\left[\hbar\omega_2(k) - \frac{P\hbar k}{m^*} + \frac{\hbar^2k^2}{2m^*}\right]$$
$$+\frac{1}{2m^*}\left\{\sum_k \hbar k[|f(k)|^2+|g(k)|^2]\right\}^2. \quad (21)$$

Performing the variation

$$\frac{\delta\langle\Psi|H|\Psi\rangle}{\delta f(k)} = \frac{\delta\langle\Psi|H|\Psi\rangle}{\delta g(k)} = 0,$$

we obtain both $f(k)$ and $g(k)$, and the variational ground-state energy $E(P)$. The result is

$$E(P) = \frac{P^2}{2m_B}(1-\eta^2) - \sum_k \left[\frac{|V_k|^2}{D_f(k)} + \frac{|U_k|^2}{D_g(k)}\right], \quad (22)$$

where

$$D_f(k) \equiv \hbar \omega_1(k) - \frac{1-\eta}{m_B} P \hbar k + \frac{\hbar^2 k^2}{2 m_B},$$

$$D_g(k) \equiv \hbar \omega_2(k) - \frac{1-\eta}{m_B} P \hbar k + \frac{\hbar^2 k^2}{2 m_B}.$$

The parameter η is determined by the implicit equation

$$\eta P = \sum_k \hbar k [|f(k)|^2 + |g(k)|^2], \qquad (23)$$

with

$$f(k) = -\frac{V_k^*}{D_f(k)}, \quad g(k) = -\frac{U_k^*}{D_g(k)}. \qquad (24)$$

After some algebra, we obtain

$$E(P) = E_0 + \frac{P^2}{2 m^*} + \cdots. \qquad (25)$$

m^* is, by definition, the effective mass of the polarons. We express our final results in terms of two dimensionless quantities τ and μ, defined as

$$\tau \equiv \frac{\alpha^2}{\hbar K} \sqrt{\frac{M}{K}}, \quad \mu \equiv \frac{a^2 m_B}{\hbar} \sqrt{\frac{K}{M}}. \qquad (26)$$

The constant part of the energy is given by

$$\frac{E_0}{\hbar \omega_2(0)} = \frac{E_0}{\hbar \sqrt{2K/M}} = -\tau \left[\frac{1}{2 \pi^2} F(\mu) + \frac{2 \sqrt{2}}{\pi} \mu \right]. \qquad (27)$$

Note that the denominator $\hbar \sqrt{2K/M}$ on the left-hand side of Eq. (25) is the optical phonon energy at zero wave number. The function $F(\mu)$ is defined by the integral[13]

$$F(\mu) = \int_{-\infty}^{\infty} dx \frac{2\{1 + \cos^2(x) - [1/2|\cos(x/2)|][1 + \cos(x) + \cos(2x) + \cos(3x)]\}}{|x|\{[1 - |\cos(x)|]^{1/2} + (1/2\sqrt{2}\mu)x^2\}}.$$

Finally, the polaron effective mass m^* is given by

$$\frac{m^*}{m_B} = \frac{1}{1 - \eta_0^2 - (1 - \eta_0)^2 \tau [8/\pi^2 + (1/\pi) 2^{5/4} \mu^{1/2}]}, \qquad (28)$$

where m_B is the band mass for a rigid lattice and η_0 is the limit of $\eta(P)$ as P goes to zero, which is equal to

$$\eta_0 = \frac{(9/\pi)\tau[1 + (\pi/9)2^{13/4}\mu^{1/2}]}{1 + (9/\pi)\tau[1 + (\pi/9)2^{13/4}\mu^{1/2}]}. \qquad (29)$$

The numerical values of the dimensionless quantities τ and μ depend on the parameters a, t_0, t_1, α, K, and M suitable for the particular conjugated polymers under considerations. For small τ, we plot the behavior of the ratios m^*/m_B and $E_0/\hbar \omega_2$. In Fig. 1(a), the effect of the coupling constant α is shown. As α increases, $\tau \sim \alpha^2$, while μ remains constant. m^*/m_B are therefore plotted as a function of τ for various fixed μ's. In Fig. 1(b), we examine the effect of the monomer mass M. As M increases, $\tau \sim \sqrt{M}$, while $\tau\mu$ remains fixed. The behavior of the two ratios for various values of $\tau\mu$ are plotted as a function of $\tau^2 (\sim M)$. When $\mu \ll 1$ and $\tau \gg 1$, the expression for m^*/m_B can be further simplified to

$$\frac{m^*}{m_B} \simeq \frac{81}{18\pi - 8} \tau. \qquad (30)$$

For polyacetylene, we use the following values of the parameters: $a = 1.22$ Å, $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, and $K = 21$ eV/Å^2.[8] For such values, $\Delta = 0.86$ eV and $m_B = 0.18 m_e$. The

carbon atom mass is used for M. The results are $\tau = 30.7$ and $\mu = 9.53 \times 10^{-3}$. After substituting τ and μ into Eqs. (27) and (28), we obtain $m^*/m_B = 66.7$, and $E_0/\hbar \omega_2(0) = -1.65$. The absolute magnitudes of the effective mass m^* and the constant E_0 are $m^* = 11.7 m_e$, and $E_0 = 0.45$ eV. m_e is the free-electron mass. m^* is about four times larger than the classical mass obtained by Campbell and co-workers.[8] Note that we use the renormalized value of the force constant K (21 eV/Å^2), instead of the bare value (46 eV/Å^2),[12] because we did not explicitly consider the Coulomb interactions. However, m^* turns out to be an exponentially decreasing function of K, and is very sensitive to the degree of renormalization by the Coulomb interaction. A comment on the $M \to \infty$ limit seems appropriate at this point. From Eqs. (14), (15), and (16), we can easily see that there should be no mass renormalizaion at such a limit. In fact, we find that if P is held constant when M goes to infinity, $E(P,M)$ in Eq. (22) approaches $P^2/2m_B$ exactly. However, the resulting m^*/m_B in Eq. (28) does not approach one. It turns out that this is only a rather subtle artifact. More detailed analysis shows that the series expansion of $E(P,M)$ in Eq. (25) is convergent only when P is smaller than a critical value $P_c(M)$. For $P > P_c(M)$ there is a range of P where Lee-Low-Pines variational scheme seems to break down since there is no solution for the self-consistency equation (23). For even greater P, $E(P,M)$ quickly recovers to $P^2/2m_B$. Most importantly, $P_c(M)$ approaches zero as $M \to \infty$. We expect that $E(P,M)$ crosses over from $P^2/2m^*$ to $P^2/2m_B$ around $P_c(M)$, if the calculation could be carried out exactly. In such a case, as long as the momentum of the electron is much larger than $P_c(M)$ (which is always true for $M \to \infty$), the mass is the same as if it were
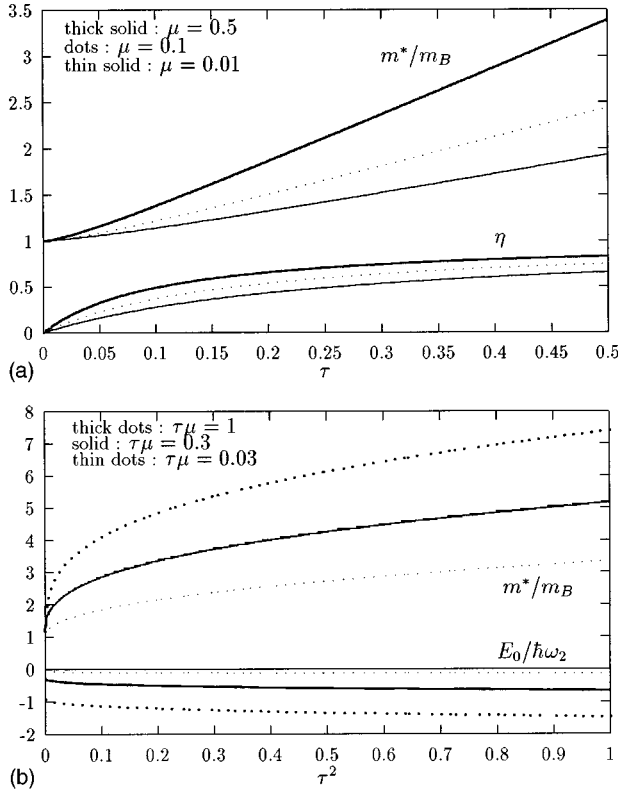
FIG. 1. (a) The effects of the increase of the coupling constant on the polaron mass (upper three curves) are shown in (a). The ground-state energy is not shown because it is simply proportional to τ. The auxiliary parameter η is shown instead (lower three curves). (b) The effects of the increase of the monomer mass on the polaron mass (upper three curves) and ground-state energy renormalization (lower three curves) are shown [see Eqs. (27) and (28)].

equal to m_B. However, in the above formula, the mass is defined by small P for which the expansion in Eq. (25) is valid.

IV. SUMMARY AND DISCUSSIONS

Starting from the SSH Hamiltonian with fully quantized electron and lattice degrees of freedom, we derive an effective Hamiltonian for the electron-phonon coupling in the one-conduction-electron subspace. Unlike the Fröhlich Hamiltonian for polar crystals, coupling to both acoustic and optical phonons is present for conjugated polymers. We perform the Lee-Low-Pines transformation and make a variational calculation on the polaron energy spectrum. Analytical results are obtained for the polaron effective mass m^*. For polyacetylene, the ratio between m^* and the electron band mass turns out to be quite large. In other words, the phonon cloud accompanying the conduction electron overwhelms the effective mass of the electron itself. However, the absolute value of m^* is only slightly larger than the effective mass of conduction electrons in conventional inorganic semiconductors such as GaAs. Such effective mass implies that the polarons are quite mobile in polymer samples with high quality and reasonable mean free time. For polymers other than polyacetylene, we can easily get the approximate values of

their polaron effective mass by the relation $m^*/m_B \sim \tau \sim \alpha^2 M^{1/2} K^{-3/2}$, which is true for $\mu \ll 1$. In words, the polaron mass becomes larger for stronger coupling constant α, heavier ion mass M, or softer spring constant K, as expected physically. The condition on μ is true for the physical range of the parameters. Even though some measurements on the polaron mobility do exist,[14] our assertion on the magnitude of the effective mass is difficult to judge experimentally at this moment, since the bulk mobility is strongly influenced by the interchain hopping which is not considered in our model for an ideal infinite chain. Moreover, to our knowledge, no reliable data on the carrier mean free time exist due to poor material quality.

The question of whether our quantum-mechanical mass or the classical mass obtained by Campbell and co-workers[7,8] is more relevant to the mobility still remains. We think that as long as the translational symmetry is not broken, our result is more reliable. However, when the symmetry is broken and the electron becomes localized, the classical picture seems closer to the real situation. Translational symmetry breaking can be caused by any form of disorder. Even for ideal systems without disorder, for strong α, "self-trapping" accompanied by a spontaneous breaking of translational invariance cannot be ruled out for infinite systems.[15] Such symmetry breaking would imply the divergence of m^*, as mentioned in the Introduction. The variational calculation based on coherent states is not expected to be applicable near the regime of "self-trapping."

The Coulomb interaction among electrons is only partially included by using the renormalized parameters, and not explicitly considered. This is justified because there is no hole in the valence band. The Coulomb interaction should be important in the case of the "exciton polaron," where one electron-hole pair is interacting with the phonons.

We conclude with a brief remark on the validity of the Lee-Low-Pines variational scheme (LLP). We confess that, without data from more reliable variational calculations, any quantitative estimate of the validity of LLP in our model is very difficult. However, some estimates on the LLP validity for the rather similar Holstein model do exist.[15] The only major difference between these two models is the type of electron-lattice coupling. We can only rely on the analogy and make identifications of the parameters between our model and the Holstein model, and hope that their result provides a reasonable guide for us. Two dimensionless parameters are used by Magna *et al.*: $\gamma = \hbar\omega/J$, and $\lambda = \chi^2/2\hbar\omega J$, where ω is the optical phonon frequency, J is the electron hopping integral, and χ is the coupling constant. We make the following identifications: $\sqrt{N}A \to \chi$, $t_0 \to J$, $\omega_2(0) \to \omega$. It turns out that for polyacetylene (see above for parameter values), $\gamma = 0.22, \lambda = 0.18$. Fortunately, these values fall well inside the range of validity for LLP in the Holstein model [$\lambda < 0.75$ for $\gamma = 0.22$ (Ref. 15)]. If the coupling type does not cause too much difference on the energy scale, our result should be valid.

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