Quantum dynamics of polaron formation

Li-Chung Ku and S. A. Trugman
Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
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We calculate the real space and time formation of a polaron quasiparticle from a bare electron. The time-dependent Schrödinger equation for the Holstein model of electron-phonon coupling is numerically integrated in a large Hilbert space to obtain the time evolution of the electron and phonon densities and the electron-phonon (el-ph) correlation functions. The quantum dynamical nature of the phonons is preserved. As the el-ph coupling increases, qualitative changes in polaron formation occur when the one-phonon polaron bound state forms. A potential barrier between the quasifree and heavy polaron states exists in dimensions $D \geqslant 2$, consistent with earlier adiabatic theory. We compare to recent experiments.

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The dynamics of quasiparticle formation is fundamental to several branches of physics. In condensed matter, the formation of a polaron quasiparticle determines the electronic and optical properties of materials including manganites[1] and conducting organic polymers.[2] Recent advances in ultrafast time-resolved spectroscopy have made it possible to investigate physical phenomena on the time scale of a molecular vibration or optical phonon in crystals. Important aspects of chemical reaction dynamics have been revealed by observing the motion of oscillating atoms.[3] Observations of the femtosecond dynamics of polaron formation, and the closely related problem of the dressing of excitons by phonons[4] have recently been reported.[5–9] In contrast, theoretical development in this subject lags somewhat behind. The theory of polarons spans over six decades.[10,11] Theoretical studies of the dynamics of polaron formation have found that in dimensions 2 and above, a potential barrier between a delocalized electron and a "self-trapped" polaron substantially increases the polaron formation time.[12–14] Some issues, however, remain unresolved.[15] We take a different approach. We turn the initial wave function loose in an enormous fully quantum many-body Hilbert space of well over a million basis states, and time evolve it essentially without approximation. The resulting dynamics are unconstrained by any *a priori* notion of how polarons should form.

The polaron formation time has been measured in recent experiments.[5–9] The time is found to be less than a picosecond, on the order of a phonon period. Our goal is to provide a theory for the following fundamental questions: (i) How are phonon excitations triggered and how do they evolve into the correlated phonon cloud of the polaron quasiparticle? (ii) How much time does it take to form a polaron? (iii) What is the effect of dimension on the dynamics of polaron formation?

To understand the process of polaron formation, we examine how the bare particle wave function time evolves into a polaron quasiparticle. One approach is to construct a variational many-body Hilbert space including multiple phonon excitations, and to numerically integrate the many-body Schrödinger equation, $i\frac{d\psi}{dt}=H\psi$ in this space.[16] The full many-body wave function can be obtained at early times. The main approximation is the size of the variational space, which can be increased systematically until convergence is achieved. This method includes the full quantum dynamics of electrons and phonons. Alternative treatments, such as the semiclassical approximation,[15,17] can be inaccurate when applied to the present problem. We solve for the dynamics of the Holstein Hamiltonian

$$H = H_{el} + H_{el\text{-}ph} + H_{ph} = -t\sum_{\langle i,j\rangle}(c_i^{\dagger}c_j + \text{H.c.}) - \lambda\sum_j c_j^{\dagger}c_j(a_j + a_j^{\dagger}) + \omega_0\sum_j a_j^{\dagger}a_j, \quad (1)$$

where $c_j^{\dagger}$ creates an electron and $a_j^{\dagger}$ creates a phonon on site j. The parameters are the nearest-neighbor hopping integral t, the el-ph coupling strength λ, and the optical phonon frequency ω_0. Strong coupling is defined as $\alpha > 1$, where $\alpha \equiv \lambda^2/(2Dt\omega_0)$, when a polaron confined to one site has a lower energy than a free electron. D is the spatial dimension. Weak coupling is $\alpha < 1$.

Figure 1 shows snapshots of polaron formation at weak coupling. An initial bare electron wave packet is launched to the right as shown in panel (a). [This initial condition is relevant to the recent experiments,[5–9] and to electron injection from a time-resolved scanning tunnel microscope (STM) tip[18,19]]. In panel (b) the electron is not yet dressed and thus is moving roughly as fast as the free electron (dashed line). In addition, there exists a backscattered current (which later evolves into a left-moving polaron) on the left side of the wave packet (green and black curves). In panel (c) after an elapsed time of one phonon period, the electron density consists of two peaks. The peak on the right (black arrow) is essentially a bare electron. The peak on the left is a polaron wave packet moving more slowly. As time goes on, the bare electron peak decays and the polaron peak grows. Some phonons are left behind (blue line), mainly near the injection point. These phonons are of known phase with displacement shown in red. Some phonon excitations travel with the polaron (magenta). Finally, a coherent polaron wave packet is observed when the polaron separates from the uncorrelated phonon excitations. The velocity operator is defined as $V_j \equiv 2J_{j,j+1}/[e(c_j^{\dagger}c_j + c_{j+1}^{\dagger}c_{j+1})]$, where j is the site index and J is the current operator, $J_{j,j+1} = -iet(c_j^{\dagger}c_{j+1} - \text{H.c.})$. $\langle V_j\rangle$ is shown in green.

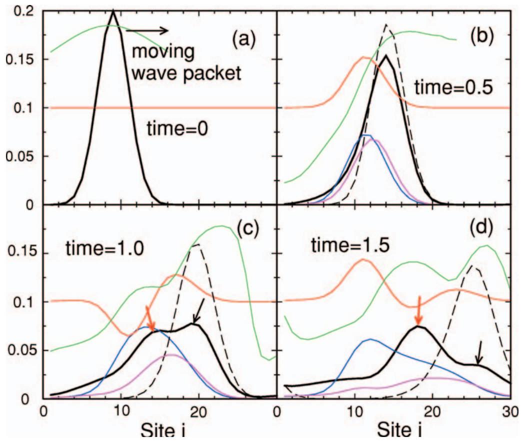

FIG. 1. (Color) Snapshots of the polaron-formation process, for hopping $t=\omega_0=1$, and $\lambda=0.4$. The calculation is performed on a 30-site periodic lattice. Time is measured in phonon periods. Black: electron density $\langle c_j^\dagger c_j\rangle$; Blue: phonon density $\langle a_j^\dagger a_j\rangle$; Red: lattice displacement $\langle X_j\rangle \equiv \langle a_j + a_j^\dagger\rangle$; Green: velocity in units of lattice constant per phonon period; Magenta: el-ph correlation function $\langle c_j^\dagger c_j a_j^\dagger a_j\rangle$; Dashed: free-electron wave packet for reference. For clarity, the origins of the red and green curves are offset by 0.1 and their values are rescaled by a factor of 0.2 and $0.05/(2\pi)$, respectively. The blue curve has been rescaled by a factor of 0.5.

There are regimes where the polaron formation time is a calculable constant of order unity times a phonon period T_0, as seen in some experiments and in Fig. 1, but there are other regimes where the phonon period is not the relevant time scale. The limit hopping $t\to 0$ is instructive.[20,21] After a time $T_0/4$, the expectation of the lattice displacement $\langle X_j\rangle$ on the electron site has the same value as a static polaron. It is tempting (but we would argue incorrect) to identify this as the polaron formation time. At later times, $\langle X_j\rangle$ overshoots by a factor of two, and after time T_0, $\langle X_j\rangle$ and all other correlations are what they were at time zero when the bare electron was injected. The system oscillates forever. In general an electron emits phonons enroute to becoming a polaron, and we propose that the polaron formation time be defined as the time required for the polaron to physically separate from the radiated phonons. The polaron formation time for hopping $t\to 0$ is thus infinite, because the electron is forever stuck on the same site as the radiated phonons.[22]

An electron injected at several times the phonon energy ω_0 above the bottom of the band is another instructive example. The electron radiates successive phonons to reduce its kinetic energy to near the bottom of the band, and then forms a polaron. For very weak el-ph coupling $\alpha \ll 1$, the rate for radiating the first phonon can be computed by Fermi's golden rule, $\tau_{FGR}^{-1}=\lambda^2/[\hbar t\sin(k_f)]$, where k_f is the electron momentum after emitting a phonon. The phonon emission time can be arbitrarily longer than the phonon period T_0 for small λ. For strong coupling, the rate approaches $\tau_{SC}^{-1}=\lambda/\hbar$ because the spectral function smoothly spans numerous narrow bands and its standard deviation is equal to λ. For $\alpha \ll 1$, our numerical results agree with perturbation theory (not shown).

We now consider polaron formation in more detail. After injecting a bare electron at time zero, the wave function at later times τ is

$$|\psi(\tau)\rangle = \sum_{j=1}^{\infty} e^{-iE_j\tau}|\Psi_j\rangle\langle\Psi_j|c_k^\dagger|0\rangle, \tag{2}$$

where $|\Psi_j\rangle$ are a complete set of total momentum k eigenstates of the system of one electron coupled to phonons.[23] There are several distinct types of states contributing to the sum: (A.1) The state $|k\rangle$ of a momentum k polaron, corresponding to the smallest eigenvalue E_j. (A.2) The states $|k-q;q\rangle$ corresponding to a polaron of momentum $k-q$ and an unbound phonon of momentum q. The energy difference between the polaron state $|k-q\rangle$ and the continuum state $|k-q;q\rangle$ is ω_0, since the phonon is unbound. Therefore, the full width of the continuum is the same as the polaron band. Similarly for two unbound phonons, etc. If the electron-phonon coupling is sufficiently strong, there are additional states in the sum: (B.1) A polaron excited state consisting of a polaron and an additional bound phonon of total momentum k, designated $|k^{(I)}\rangle$.[25] This quasiparticle excited state is also split off from the continuum. (B.2) The states $|(k-q)^{(I)};q\rangle$ corresponding to an excited state polaron of momentum $k-q$ and an unbound phonon of momentum q. Similarly for two unbound phonons, etc. For stronger el-ph coupling (larger α), more highly excited polaron states corresponding to bound states of a polaron and two or more additional phonons, $|k^{(II)}\rangle,\ldots$ enter the sum.[26]

From Eq. (2), the amplitude to remain in the initial state after time τ, $\langle\psi(\tau)|c_k^\dagger|0\rangle$, is given by the Fourier transform of the spectral function

$$A(k,\omega) = \sum_{j=1}^{\infty} |\langle\Psi_j|c_k^\dagger|0\rangle|^2\delta(\omega-\omega_j). \tag{3}$$

The numerically determined spectral function at weak coupling is shown in Fig. 2.[27,28] There is an isolated delta function corresponding to state (A.1) above, and a group of states that is approaching an approximately Lorentzian continuum as the number of sites increases, corresponding to (A.2) above. The coupling $\lambda/\omega_0=0.8$ is too weak to form bound quasiparticle excited states $|k^{(I)}\rangle$. If the spectral function were a pure Lorentzian, a measurement would yield an exponential decay of the initial state, with the polaron formation time τ_p the inverse width of the Lorentzian. Since the spectral function has an isolated delta function as well, an experiment would measure the probability $P(\tau)\equiv|\langle\Psi(\tau)|c_k^\dagger|0\rangle|^2$ to remain in the initial bare particle state as follows:

$$P(\tau) = a_1^2 + a_2^2e^{-2b\tau} + 2a_1a_2e^{-b\tau}\cos[(\omega_1-\omega_2)\tau]. \tag{4}$$

This form already shows some complications, with an additive constant, a pure exponential decay, and an exponential decay half as fast multiplied by a cosine oscillating at the energy difference between the delta function and the center of the Lorentzian. Decaying oscillations in polaron formation (actually the formally equivalent problem of an exciton coupled to phonons[4]) have been observed in a pump-probe experiment[6] that measures reflectivity after a bare exciton is created. The observed oscillatory reflectivity was interpreted

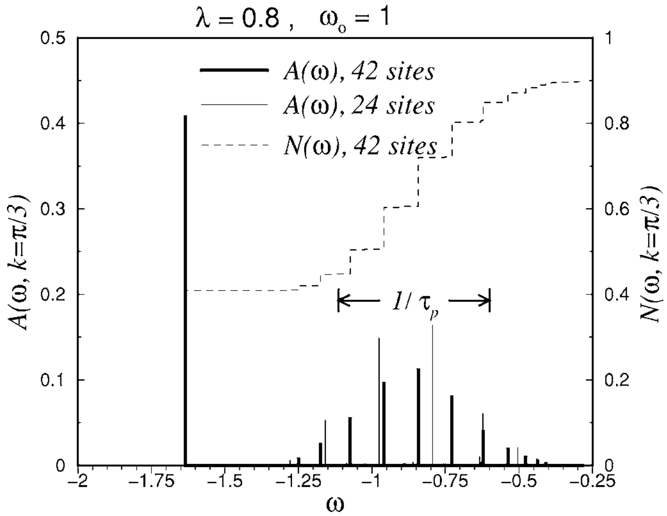

FIG. 2. Spectral function at weak coupling for two system sizes. τ_p is the polaron formation time. About 10% of the total spectral weight is at energies beyond the range plotted. At the present resolution, the quasiparticle peaks at $\omega=-1.63$ of the two calculations are essentially identical.

as the lattice motion in the phonon-dressed (or self-trapped) exciton level. Assuming the modulation in the exciton level goes as $\Delta E=-\lambda c_j^\dagger c_j X_j$, where $X_j=\langle(a_j+a_j^\dagger)\rangle$ is lattice displacement, the model Hamiltonian applies directly to the experiment. We calculate the corresponding el-ph correlation function in Fig. 3. In this regime, the polaron formation time (damping time) increases as the electron-phonon coupling λ increases, and also as the initial electron (exciton) energy approaches the band bottom. We find satisfactory agreement when compared to Fig. 2(b) of Ref. 6. Both show a damped

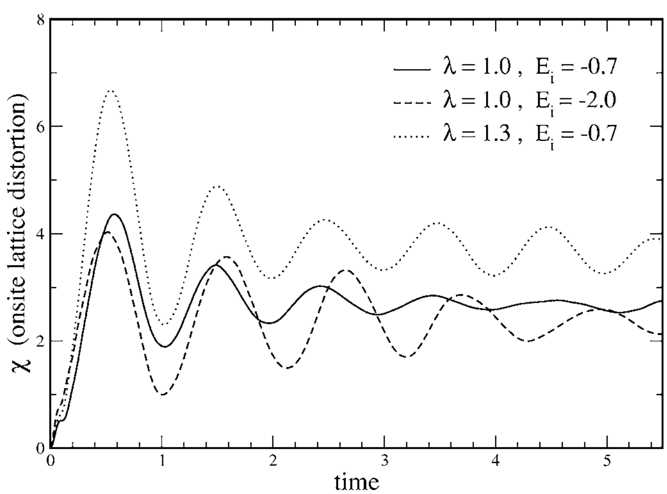

FIG. 3. The on-site electron-phonon correlation function $\chi=\langle c_j^\dagger c_j(a_j+a_j^\dagger)\rangle$ as a function of time measured in phonon periods. For all curves, $\omega_0=0.5$ and hopping $t=1$. The solid line is for a bare electron injected with nonzero initial momentum at energy $E_i=-0.7$, where the bottom of the bare band is at energy -2. The phonon displacement is larger and more weakly damped for larger electron-phonon coupling λ, dotted line. In contrast to a bare electron, an exciton (bound particle-hole pair) is generally created with an initial momentum zero, corresponding to $E_i=-2$, dashed line.

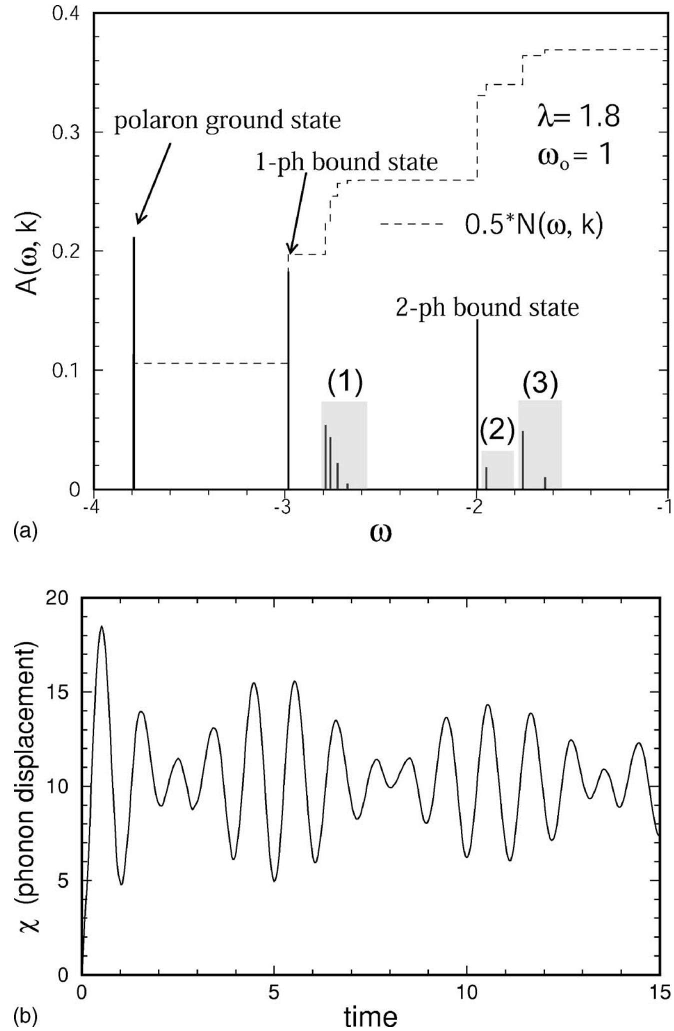

FIG. 4. Panel (a): spectral function at strong coupling. There are three quasiparticle excited states split off from the continua. Shaded areas (1) and (2) correspond to continuum states (A.2) and (B.2), respectively. (b): Quantum beat formed by multiple excited states and continua.

oscillation with a delayed phase. (Numerical calculations in Figs. 3–5 are performed on an extended system, not a finite cluster.)

Figure 4 shows the spectral function at stronger coupling than Fig. 2. Three delta functions are shown, corresponding to polaron ground and excited states, along with three continua containing unbound phonons. There is additional structure at higher energy (not shown). The probability decay $P(\tau)$ for this spectrum is considerably more complicated, and includes oscillating terms that do not decay to zero at zero temperature from the polaron ground and excited states beating against each other. The branching ratios into the various channels are calculated in Ref. 29.

Next we discuss the role of dimensionality. The effect of dimensionality on static properties has been studied previously.[13,24] The eigenvalues of the low-lying states (with zero total momentum) are shown as functions of λ in Fig. 5. The energy spectra in $D>1$ are qualitatively different than in one dimension (1D). The 1D polaron ground state becomes

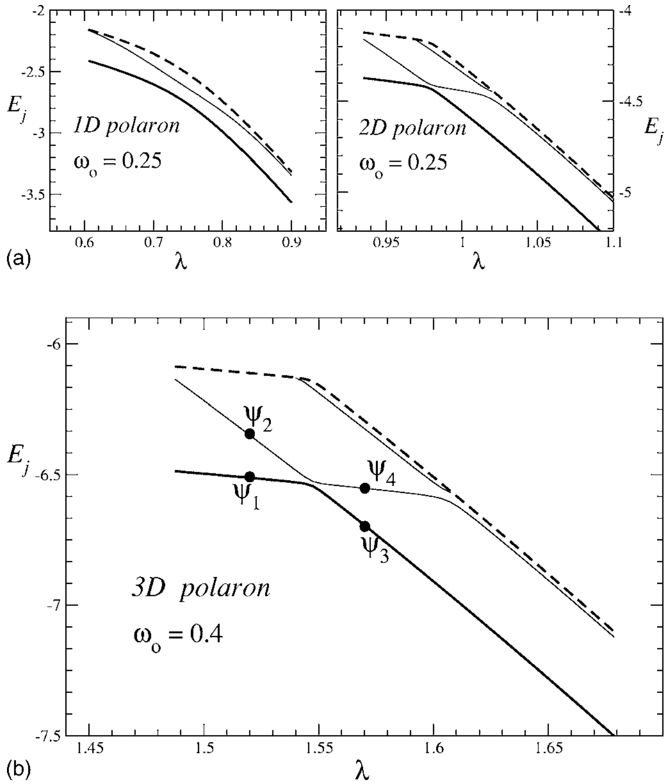

FIG. 5. Eigenvalues of low-lying states as functions of coupling constant in 1D through 3D. Hopping $t=1$ in all panels. In the adiabatic regime in higher dimensions, the ground state (thick solid lines) shows a fairly abrupt change in slope. In the 3D panel, ψ_1 and ψ_4 are a lightly dressed electron state; ψ_2 and ψ_3 are a heavy polaron state. The dashed lines are the beginning of the lowest continua. Levels above the lowest continuum are not shown.

heavy gradually as λ increases. However, in $D \geqslant 2$, the ground state crosses over to a heavy polaron state by a *narrow avoided level crossing*, which is consistent with the existence of a potential barrier.[13] In the lower panel of Fig. 5, ψ_1 and ψ_4 are nearly free electron states; ψ_2 and ψ_3 are heavy polaron states. The inner product $|\langle \psi_1 | \psi_4 \rangle|$ is equal to 0.99. Just right of the crossing region the effective mass (approximately equal to the inverse of the spectral weight) of the first excited state can be smaller than the ground state by 2 or 3 orders of magnitude, while their energies can differ by much less than ω_0. As a result, there is no optical phonon of the correct energy for the light electron to emit and become a heavy polaron, and the polaron formation time at $T=0$ would be infinite unless low energy acoustic modes are included in the model. The narrow avoided crossing description works less well for larger ω_0.

In summary, we have calculated the time evolution of the many-body wave function and find that the bare electron evolves into a polaron quasiparticle by emitting phonons. The excess kinetic energy excites uncorrelated phonons. The question "How long does it take a polaron to form?" may not have a simple answer, given the potentially complicated form of $P(\tau)$: there are multiple time scales in the dynamics. This function has been calculated numerically, and at zero temperature depends on the parameters of the Hamiltonian, the spatial dimension, the initial bare electron momentum, the final polaron momentum, and the possible existence of bound polaron-phonon excited states. A further complication is that decay out of the initial state need not be synonymous with decay into a polaron final state. In addition, we confirm that a tunneling barrier between the quasifree and heavy polaron state exists in both two and three dimensions (when $0 < \omega_0 \leqslant 2Dt$). As a consequence, the tunneling barrier inhibits the formation of a polaron in the crossover regime, in agreement with the conventional description. Our approach can be extended to other types of quasiparticle formation, such as the vibrational exciton[30] and the spin polaron.

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