Localization and the density of states for an electron in a quantized elastic continuum

Sajeev John
Department of Physics, Jadwin Hall, Princeton University, Princeton, New Jersey 08544
and Exxon Corporate Research Science Laboratory, Route 22E, Annandale, New Jersey 08801
(Received 12 March 1987)

A physical picture is presented for the energy spectrum of a quantum particle localized by a deformable nonlinear medium. For a strongly coupled electron-lattice system interacting by a deformation potential, quantum fluctuations of the lattice lead to an exponential band tail at zero temperature in the zero-phonon sector of the lattice Hilbert space which terminates at the polaron ground state. This has an exponentially small overlap with a coexisting free-polaron band.

A longstanding fundamental problem in the theory of an electron interacting with a quantized elastic field is the elucidation of the spectrum of excited states associated with polaron formation. The problem is a specific realization of the general phenomenon of a quantum particle or classical wave propagating in a deformable nonlinear medium which has applications in a variety of areas in physics and engineering. Such nonlinearities lead to bistable response and switching between states of small and large deformation of the underlying medium.

Studies of strongly coupled electron-phonon systems have focused largely on the polaron ground-state energy.[1–9] When the elastic energy associated with deforming the quantized lattice field is less than the quantum-mechanical binding energy of the electron to such a deformation, the electron is said to be self-trapped, this being the lowest-energy state of the many-body system.[3] On the other hand, quantum fluctuations of the unperturbed lattice by themselves provide potential fluctuations in which the electron may be localized. In this Brief Report, I derive from first principles a physical picture of the nature and density of states associated with the transition from the nearly-free-electron continuum states to self-trapped small-polaron states. In particular it is shown that the many-body density of states (DOS) projected onto the phonon vacuum, for sufficiently strong coupling, exhibits an exponential band tail in the absence of disorder which terminates at the polaron ground state. Such a projected DOS may be relevant for optical-absorption processes which are fast compared to the time scale of the lattice distortion required for true self-trapping. On the other hand, electronic transport is determined by the mobility of the fully developed small polaron.[10] The density of states of the polaron band exists in a different sector of the lattice Hilbert space in which the lattice normal coordinates are displaced relative to their vacuum position. For these states, as will be shown, the overlap of the lattice wave function with the phonon vacuum decreases exponentially with the electron-lattice coupling constant (Fig. 1). Such a coexistence of different solutions for a given energy is general characteristic of wave propagation in a nonlinear medium.

The path-integral method introduced by Feynman[2] provides a convenient tool for treating the full quantum-mechanical nature of both the electron and the lattice. It allows a generalization of the one-parameter scaling theory of the polaron ground-state energy with polaron radius developed by Emin and Holstein,[5] which considers a *classical* elastic continuum, to include the self-energy shift of the free-electron continuum as well as a further lowering of the small polaron energy, both arising from the nonadiabaticity of the electron-phonon interaction.[4,11] I present first a simple physical picture of the band-tail density of states and then demonstrate how this picture emerges from a path-integral representation of the electron propagator.

The total Hamiltonian $H=H_e+H_{\rm ac}+H_{e\text{-ac}}$ for an electron coupled to acoustic phonons consists of the electron kinetic energy $H_e=p^2/2m$, the harmonic phonon energy[4]

$$H_{\rm ac}=\frac{M}{2}\sum_{\mathbf{k}}(|\dot{q}_{\mathbf{k}}|^2+\omega_{\mathbf{k}}^2|q_{\mathbf{k}}|^2) \tag{1}$$

and the interaction

$$H_{e\text{-ac}}=\frac{E_d}{u}\sum_{\mathbf{k}}\dot{q}_{\mathbf{k}}\frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{\sqrt{N}}\,. \tag{2}$$

Here, m is the bare-electron band mass and M is the atomic mass. $q_{\mathbf{k}}\equiv\hat{\mathbf{k}}\cdot\mathbf{q}_{\mathbf{k}}$ is the normal coordinate of a longitudinal acoustic phonon of wave vector $\mathbf{k}$ and fre-

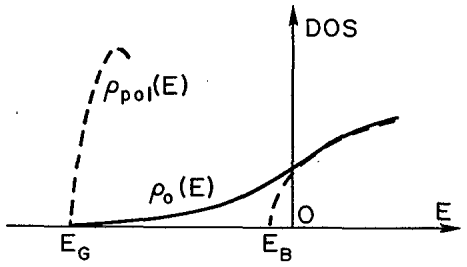

FIG. 1. Many-body density of states ρ_0 projected onto the phonon vacuum depicted as a function of total energy E in strong-coupling limit showing (i) exponential tail which terminates at polaron ground-state energy E_G and (ii) shift E_B of square-root continuum arising from virtual phonons. The small-polaron band $\rho_{\rm pol}$ occurs in a nearly orthogonal sector of the lattice Hilbert space.

quency $\omega_{\mathbf{k}}=uk$. Also E_d is a deformation-potential energy constant and u is the speed of sound. The summation is over all wave vectors $\mathbf{k}$ in the Brillouin zone of a cubic crystal containing N atoms.

A projected density of states may be defined through the matrix element of the evolution operator

$$G_0(x,0\,|\,x,t)\equiv\langle\psi_0;x\,|\,\exp(-iHt/\hbar)\,|\,\psi_0;x\rangle\ ,$$

where x is the electron coordinate and ψ_0 is the ground-state wave function of the lattice:

$$\psi_0\{q_{\mathbf{k}}\}=\prod_{\mathbf{k}}(M\omega_{\mathbf{k}}/\pi\hbar)^{1/4}\exp[-(M\omega_{\mathbf{k}}/2\hbar)\,|\,q_{\mathbf{k}}\,|^2]\ . \tag{3}$$

The projected DOS onto the phonon vacuum then becomes

$$\rho_0(E)\equiv\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\exp(iEt/\hbar)G_0(x,0\,|\,x,t) \tag{4}$$

which is independent of x by translational symmetry. Since the wave function ψ_0 is normalized, it is straightforward to verify by direct integration of ρ_0 with respect to E that the total number of states in this projection is precisely the number of one-electron states in the absence of the electron-phonon interaction. An alternative projection which also satisfies this unitarity property may be obtained by displacing the harmonic-oscillator wave function (3). Defining $\psi_{\rm pol}(q_{\mathbf{k}})\equiv\psi_0(q_{\mathbf{k}}+d_{\mathbf{k}})$, where $d_{\mathbf{k}}$ describes of displacement of the normal coordinate of wave vector $\mathbf{k}$ in the polaron ground state, a polaron density of states $\rho_{\rm pol}$ analogous to (4) may be defined by replacing ψ_0 in G_0 by $\psi_{\rm pol}$. This latter projection describes transport states whereas the former projection might be probed by optical excitation of an electron from the valence to conduction band of a semiconductor. In the presence of static disorder the deformability of the quantized lattice in response to the electron influences the nature of already existing Urbach band tails.[12] Sufficiently strong electron-phonon coupling can, however, lead to a band tail even in the absence of disorder.

The existence of a polaronic band tail in $\rho_0(E)$ may be seen by considering the probability distribution for the lattice in its unperturbed ground state obtained by taking the square modulus of the wave function (3):

$$P\{q_{\mathbf{k}}\}\sim\exp\left[-\sum_{\mathbf{k}}(M\omega_{\mathbf{k}}/\hbar)\,|\,q_{\mathbf{k}}\,|^2\right]\ . \tag{5}$$

In the adiabatic limit, it follows from (2) that the electron sees an essentially static random potential with Fourier components $E_d k q_{\mathbf{k}}/\sqrt{N}$. If the electron can form a localized state in a potential fluctuation on a time scale short compared to the actual oscillation period of the potential well, then the exponential part of the density of states $\rho_0(E)$ is obtained by maximizing (5) with respect to $\{q_{\mathbf{k}}\}$ subject to the constraint that the electron binding energy plus the elastic lattice distortion energy equal E. If the elastic energy can be neglected, the resulting DOS is analogous to that of an electron in a static Gaussian random potential with a spatial correlation length determined by the Brillouin-zone cutoff in the wave-vector summation.[12] The presence of the factor $\omega_{\mathbf{k}}$ in (5) gives greater weight to long-wavelength fluctuations and so the resulting band tail is that of an Urbach tail in one higher spatial dimension, in a sense to be explained below. Very deep in the tail, such a picture breaks down due to the increasing importance of the elastic energy which in fact causes the tail to terminate at the polaron ground state. In the vicinity of the ground state the electron creates a potential well rather than simply stabilizing one which arises from the probability distribution (5).

In the very shallow part of the band tail, the nonadiabaticity of the electron-phonon interaction also leads to a breakdown of the nearly static potential-well picture. If for simplicity one considers an electron which is harmonically bound to a local lattice deformation with a harmonic oscillator frequency ν, then it follows that the size of the potential well $R\sim\sqrt{\hbar/m\nu}$. The dominant oscillation frequency ω_R of such a well is simply that of the associated phonon of wavelength R. In the shallow part of the tail the electron is weakly bound and the frequency $\nu<\omega_R\equiv 2\pi u(m\nu/\hbar)^{1/2}$ as $\nu\to 0$. Consequently the potential well oscillates on time scales shorter than the time required for the electron to localize. In this energy regime, the density of states is influenced by the shift of the continuum-band edge associated with the emission and reabsorption of virtual phonons (Fig. 1).

As discussed in a previous paper[11] a continuum model for electron-phonon interactions may be obtained by replacing the wave-vector sum in (2) by an integral in which points in k space are weighted by $VH_c(k)/(2\pi)^3$. Here V is the volume of the crystal and the choice of the cutoff function $H_c(k)=\exp[-(\pi/4)(k/k_0)^2]$ with $k_0\equiv\pi/a$ preserves the volume of the Brillouin zone of a simple-cubic crystal of lattice constant a. The projected Green's function has a Feynman path-integral representation[13,14] of the form

$$G_0(0,0\,|\,0,t)=\int\mathscr{D}X(\tau)\exp(iS_{\rm eff}/\hbar),\quad X(0)=X(t)=0 \tag{6}$$

where the effective action $S_{\rm eff}$ is obtained by integrating over all phonon coordinates and the remaining integration is over electron paths $X(\tau)$. A trial action $S_{\rm trial}$ is introduced in which the electron is harmonically coupled by a spring constant $K_{\rm trial}$ to a fictitious mass $M_{\rm trial}$, both being variational parameters, and a first-cumulant expansion of the true action $S_{\rm eff}$ is performed about this trial action. This leads to an approximant to the Green's function which has poles along the real-time axis spaced by the period of oscillation $2\pi/\nu$ of the trial harmonic oscillator. The time integral in (4) is interpreted as a contour integral in the lower half complex time plane and may be distorted by writing $t=-iT+t'$ and integrating over all real t'. Choosing $\nu T\gg 1$, the approximant becomes[11]

$$G_0(0,0\,|\,0,t)\simeq(m_T/2\pi i\hbar t)^{3/2}\sin^3(bt/2)\exp[-F(t)]\ , \tag{7a}$$

where $b\equiv(K_{\rm trial}/M_{\rm trial})^{1/2}$, $m_T\equiv m+M_{\rm trial}$, and

$$F(t)=it[(3\nu/4)(2-\mu/m)-E/\hbar]+I_{\rm int}(t)\ , \tag{7b}$$

$$I_{\rm int}(t)=\frac{\pi}{2}S_{\rm ac}\left[\frac{u}{k_0}\right]^2\int_0^t d\tau(t-\tau)\int_0^\infty dk\,k^3\exp\left[-\frac{k^2}{2k_0^2}[\pi-iQ(\tau;t)]-iuk\tau\right]\ . \tag{7c}$$

Here, $\mu\equiv mM_{\rm trial}/(M_{\rm trial}+m)$ is the reduced mass and $S_{\rm ac}$ is a dimensionless coupling constant defined by $\hbar uk_0S_{\rm ac}\equiv E_d^2/(2Mu^2)$. For $\nu T\gg 1$, the kernel

$$-iQ\simeq\hbar k_0^2\left[\frac{\mu}{m^2\nu}-i\frac{(\tau-t)\tau}{tm_T}\right]\ . \tag{8}$$

The second term in (8) expresses the fact that the center of mass (c.m.) of the polaron with total mass m_T can move freely through the solid.

It is readily seen that the function $F(t)$ has a saddle point $-iT_s$ along the negative imaginary time axis for energies $-|E|$ which are above the polaron ground state. If T_s is small compared to the time required for the c.m. of the polaron to translate a lattice spacing, the second term in (8) may be neglected. In this infinite-effective-mass approximation ($m_T=\infty$), the time integral in (7c) may be evaluated to give

$$F(t)=-it[E-E_G(\nu)]/\hbar + [I_1(0)-I_1(\beta)]S_{\rm ac}/[1+(2\varepsilon_B/\pi\hbar\nu)]\ , \tag{9a}$$

where

$$E_G(\nu)\equiv\frac{3\hbar\nu}{4}-\varepsilon_D S_{\rm ac}/[2+4\varepsilon_B/(\pi\hbar\nu)]^{3/2} \tag{9b}$$

is the scaling form of the polaron ground-state energy.[11] Here, $\varepsilon_D\equiv\hbar uk_0$ is the Debye energy and $\varepsilon_B\equiv\hbar^2k_0^2/2m$ is analogous to an electron bandwidth. Also,

$$I_n(\beta)\equiv\int_0^\infty dq\,q^n\exp(-q^2-\beta q) \tag{9c}$$

is a parabolic cylinder function with argument $\beta\equiv iuk_0t(\pi/2+\varepsilon_B/\hbar\nu)^{-1/2}$.

The physical picture of localization by a nearly static potential well follows from solving the saddle-point equation $F'(t)=0$ using the small-time expansion $I_1(0)-I_1(\beta)\sim\sqrt{\pi}\beta/4-\beta^2/4$. This is equivalent to neglecting the factor $iuk\tau$ in $I_{\rm int}(t)$, Eq. (7c), which expresses the retardation of the electron-phonon interaction. In the saddle-point approximation the exponential part of the DOS becomes $\rho_0(E)\sim\exp[-F(-iT_s)]$ where

$$F(-iT_s)=\frac{4}{\pi S_{\rm ac}\varepsilon_D^2}(|E|+\tfrac{3}{4}\hbar\nu)^2\left[\frac{\pi}{2}+\frac{\varepsilon_B}{\hbar\nu}\right]^2\ . \tag{10}$$

Generalizing this result to d spatial dimensions reveals that the factor in large parentheses here is raised to the power $(d+1)/2$. A similar result[12,15] may be obtained for the band tail arising from a static Gaussian random potential in d spatial dimensions with rms fluctuation $\sim\varepsilon_D\sqrt{S_{\rm ac}}$ and spatial correlation length $\sim k_0^{-1}$ in which the corresponding exponent is $d/2$. This is precisely the shift in weight of the phase space resulting from the factor $\omega_{\rm k}$ in the static probability distribution (5).

It may be demonstrated[16] that the approximate DOS (10) is in fact a lower bound to the true density of states for any value of the variational parameters and the greatest lower bound is obtained by choosing $(\hbar\nu)^2=8|E|\varepsilon_B/3\pi$. The resulting DOS is an essentially linear exponential throughout the range of validity of the small-time expansion which can be accurately fitted to the expression

$$\rho_0(E)\sim\exp(-21.1y/S_{\rm ac}\gamma^2)\ , \tag{11}$$

where $y\equiv|E|/\varepsilon_B$ and $\gamma\equiv\varepsilon_D/\varepsilon_B$ is the nonadiabaticity parameter.

The self-consistency of the small-time expansion requires that the value of β at the saddle point with $\hbar\nu$ chosen to maximize the DOS be small compared to unity. This in fact occurs over an intermediate energy range spanning many decades in the DOS provided $S_{\rm ac}\gamma\gtrsim 3.5$. This may be compared to the threshold value $S_{\rm ac}\gamma\simeq 3.0$ for small polaron formation obtained from (9b). The small-time expansion, however, fails to be self-consistent in the limit $E\to 0$. Physically, this is due to the oscillation of the broad, shallow potential wells on the time scale required for the electron itself to oscillate within the well as discussed previously. In the opposite limit of $E\to E_G$, the polaron ground-state energy, the small-β expansion is again inadequate since the electron must now create its own lattice distortion rather than simply finding one and stabilizing it. Such a process may be described by the large-time expansion $I_1(\beta)\sim 1/\beta^2$ in Eq. (9a) which reveals that for energies approaching the polaron ground state, the saddle point T_s diverges as $[E-E_G(\nu)]^{-1/3}$. Here, in fact, the saddle-point approximation itself breaks down and the entire contour integral must be performed. In particular, for $E<E_G(\nu)$, the time contour in (4) may be closed in the lower half-plane, enclosing no singularities, thereby demonstrating the vanishing of the density of states below the polaron ground state. For $E>E_G(\nu)$, the contour cannot be closed. However, sufficiently close to $E_G(\nu)$, the contour passing through $-iT_s$ lies in the range of validity of the large-time expansion of (9a) and the DOS may be approximated by neglecting $I_1(\beta)$:

$$\rho_0(E)\simeq\rho_{\rm pol}(E)\exp[-(\pi S_{\rm ac}/4)(\pi/2+\varepsilon_B/\hbar\nu)^{-1}]\ , \tag{12}$$

where $\rho_{\rm pol}(E)\equiv m_T^{3/2}[E-E_G(\nu)]^{1/2}/\pi^2\hbar^3$ is a free-polaron continuum which vanishes at E_G and has an effective mass m_T. Here both m_T and ν are chosen to minimize the polaron ground-state energy. In obtaining (12) the factor $\sin^3(bt/2)$ appearing in (7a) has been incorporated into the exponential and the complete contour integration has been performed. It is straightforward to verify that the exponential damping factor in (12) is precisely the Franck-Condon overlap integral $|\langle\psi_0|\psi_{\rm pol}\rangle|^2$ of the lattice wave functions in the phonon vacuum and polaron ground state as discussed previously. It followed that the

polaron density of states $\rho_{\rm pol}$ exists in a nearly orthogonal sector of the lattice Hilbert space from the exponential band tail ρ_0, their actual overlap decreasing exponentially with the coupling constant $S_{\rm ac}$. The apparent infinite continuum of polaron states, however, is an artifact of the free particle form of the electron kinetic energy: Although an ultraviolet cutoff k_0 was introduced for the phonon coordinates no such cutoff restricted the electron motion. Real band-structure effects may lead to a *finite* polaron band which coexists with an exponential band tail in their respective sectors of the many-body Hilbert space.

In summary, a physical picture for the spectrum of energy levels for a coupled electron-phonon system exhibiting three distinct regimes has been derived. At high energies, the nonlinearity of the medium gives rise to nearly-free-electron states with a perturbative self-energy correction. This crosses over to self-trapped states near the polaron ground state by means of a finite linear exponential tail. This is analogous to an Urbach tail arising from static short-range disorder only, except in $d+1$ dimensions. In materials for which the electron-phonon coupling is near the threshold for polaron formation, in the absence of disorder such a tail would be pinched between the polaron band edge and the shifted free-electron continuum edge. The presence of static disorder, however, can trigger polaron formation even for weak coupling.[5] For an amorphous semiconductor the resulting interplay between static disorder and electron-phonon interactions may be of considerable importance in describing band tailing and localization. The deformability of the underlying lattice may also play a significant role in determining the nature of a mobility edge separating extended from localized states. In the case of classical waves propagating in a disordered medium, the presence of an analogous self-focusing nonlinearity may also enhance the prospects for experimental observation of localization.

ACKNOWLEDGMENTS

I am grateful to Morrel H. Cohen and E. N. Economou for many stimulating discussions and their constructive criticisms during the course of this work. This work was supported in part by a grant from Exxon Research and Engineering Company. This work received partial support from the National Science Foundation Grant No. DMR 8518163 at Princeton University.

[1]L. Landau, Phys. Z. Sowjetunion **3**, 664 (1933).
[2]R. P. Feynman, Phys. Rev. **97**, 660 (1955).
[3]Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961).
[4]A. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. **55**, 137 (1973).
[5]D. Emin and T. Holstein, Phys. Rev. Lett. **36**, 323 (1976).
[6]G. Whitfield and P. B. Shaw, Phys. Rev. B **14**, 3346 (1980).
[7]S. A. Jackson and P. M. Platzman, Phys. Rev. B **24**, 499 (1981).
[8]H. Shoji and N. Tokuda, J. Phys. C **14**, 1231 (1981).
[9]B. A. Mason and S. Das Sarma, Phys. Rev. B **33**, 1412 (1986).
[10]R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962).
[11]S. John and M. H. Cohen, Phys. Rev. B **34**, 2428 (1986).
[12]S. John, C. M. Soukoulis, M. H. Cohen, and E. N. Economou, Rev. Lett. **57**, 1777 (1986); **57**, 2877(E) (1986).
[13]R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[14]V. Sa'Yakanit, J. Phys. C **7**, 2849 (1974).
[15]W. Sritrakool, V. Sa'Yakanit, and H. R. Glyde, Phys. Rev. B **33**, 1199 (1986).
[16]S. John (unpublished). A general discussion of variational methods for the density of states may be found in P. Lloyd and P. R. Best, J. Phys. C **8**, 3752 (1975).