PHYSICAL REVIEW B VOLUME 40, NUMBER 12 15 OCTOBER 1989-II

Surface polaron: Statics

Th. Martin and R. Bruinsma
Physique de la Matiere Condensee, College de France, 11 place Marcelin-Berthelot, 75231 Paris CEDEX 05, France and Department of Physics–Solid State Science Center, University of California, Los Angeles, Los Angeles, California 90024
(Received 19 September 1988; revised manuscript received 19 December 1988)

This is the first in a series of two papers on the statics and dynamics of surface polarons. In the present paper, we discuss the ground-state wave function by variational methods. Two transitions occur as we switch on the particle-surface phonon interaction: At the first transition, the normal component of the wave function collapses on the surface due to the renormalization of the zero-point energy. At the second transition, there is a rapid increase in the effective mass of the particle for parallel transport. The second transition is essentially triggered by the first one. It is argued that the normal collapse lies at the basis of the singular behavior in the adsorption probability observed in numerical calculations.

I. INTRODUCTION

The interaction between an electron in a polar crystal and the phonon modes of a lattice has long been known to lead to the mass renormalization of the electron—the polaron.[1] For weak coupling, this effect is small and the electron wave function remains extended (large polaron). With increasing coupling, there is a sudden mass increase which can be accompanied by a collapse of the electron wave function (small polaron) leading to "self-trapping."[2] This remains somewhat controversial,[3,4] since there exists no proof of the existence of a critical coupling constant. When the kinetic energy of the lattice can be neglected, a more quantitative description of the transition can be achieved.[4]

A similar mass renormalization also occurs for particles trapped on surfaces.[5] A well-known case concerns electrons on a liquid^4-He film.[6] Other examples are electrons in Si inversion layers and positron surface states in metals.[7] For such "surface polarons," the wave function is of course quite anisotropic. In the conventional description of surface polarons, one assumes that the component of the wave function in the direction normal to the surface is simply the lowest bound state of the potential which restrains the particle to the surface. For instance, for electron on ^{4}He, the bound states have a hydrogenlike spectrum with a Bohr radius of about 50 Å. The collapse of the wave function of surface polarons generally refers to the in-plane component of the wave function, although some work was done including the normal extent of the wave function.[8] Any strong renormalization of the wave function in the normal direction would be very important for dynamical problems such as surface scattering and adsorption. As the scattering states of the renormalized potential have a large amplitude near the surface, the excitation of surface modes will be facilitated, and adsorption will follow. In a recent numerical study of surface adsorption,[9] we found that upon varying the coupling strength, the capture rate increases dramatically beyond a specific value of the coupling constant. In this model, only normal motion was included, and a natural guess would be that beyond this critical value, the normal component of the wave function has collapsed.

This is the first of two papers in which we investigate the statics and dynamics of surface polarons including both the normal and in-plane components of the wave function. In the present paper, we will discuss the statics in the intermediate-coupling regime of adsorbed particles (the transition in the capture rate was observed in this range of coupling strength). We will generalize the Lee, Low, and Pines[1] (LLP) variational method to surface polarons in order to look for a wave-function collapse in the direction perpendicular to the surface. Although it is an important issue, we shall not focus our attention on the nature of the transition, but rather examine which collapse is the first to occur: in-plane collapse or normal collapse. Normal collapse is usually neglected. We find two separate critical values of the coupling strength: one where the normal component of the wave function collapses and one where the in-plane component collapses. The existence and the magnitude of those different coupling strengths are directly related to the range of the inelastic electron-phonon potential. When this range is small compared to the extent of the bound state of the uncoupled system, we predict that normal collapse occurs first. The critical value corresponding to normal collapse is of the same order as the critical coupling constant where we observed previously a dramatic increase in the adsorption rate. Normal collapse thus appears to be a dominant effect for the statics and the dynamics of the problem.

The outline of this paper is as follows. In Sec. II, the wave-function ansatz is presented, and we carry out a unitary transformation on the Hamiltonian of the particle-phonon system. This enables us to derive the equations for the ansatz parameters in the ground state (Sec. III). We then propose approximate solutions for the many-body wave function and discuss the results for the different forms of the inelastic potential. In Sec. IV, we treat the in-plane collapse, and Sec. V contains a summary and discussion of the results.

II. THE VARIATIONAL WAVE FUNCTION

The Hamiltonian of the coupled particle-phonon system reads[10]

$$H=-\frac{\hbar^2\nabla^2}{2m}+V_0(z)+\sum_{\mathbf{q}}\hbar\omega_q a_{\mathbf{q}}^\dagger a_{\mathbf{q}} + \sum_{\mathbf{q}} V_q(z)(a_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{r}_\parallel}+\text{H.c.}) \ . \tag{1}$$

In this expression, $V_0(z)$ is the elastic surface potential which binds the particle to the surface, while $V_q(z)$ is the interaction potential between the particle and a surface excitation of wave vector $\mathbf{q}$. We will assume that $V_0(z)$ is attractive for $z>0$ and $V_0(z)=+\infty$ for $z\leq 0$. If the surface excitations are surface phonons and if $V_q(z)$ is a deformation potential, we should expect that it goes to zero when $qz \ll 1$, since in this case a surface phonon is indistinguishable from a flat, displaced surface. Here, m is the bare mass of the particle and ω_q is the surface-phonon dispersion relation. Finally, $\mathbf{r}_\parallel$ refers to a position on the surface while z is the distance in the direction perpendicular to the surface.

Ideally, we should now solve the corresponding Schrödinger's equation for the many-body wave function ψ which describes the whole system. Formally, ψ can be decomposed as a superposition of zero-, one-, two-, etc., phonon states as follows:

$$\psi=\sum_{n=0}^{\infty}\sum_{\mathbf{q}_1\cdots\mathbf{q}_n}\psi^{(n)}_{\mathbf{q}_1\cdots\mathbf{q}_n}(\mathbf{r})a^\dagger_{\mathbf{q}_1}\cdots a^\dagger_{\mathbf{q}_n}|0\rangle \ , \tag{2}$$

where $|0\rangle$ is the phonon vacuum.

A. Perturbative theory

A general solution for all possible n phonon contributions of the wave function is difficult, and we have to rely on approximate solutions. In the context of perturbation theory, one can systematically obtain the limiting form of the first few wave functions $\psi^{(0)}(\mathbf{r})$, $\psi^{(1)}_{\mathbf{q}}(\mathbf{r})$, $\psi^{(2)}_{\mathbf{q},\mathbf{q}'}(\mathbf{r})$, etc., in the presence of small electron-phonon coupling. It is useful to first discuss lowest-order perturbation theory.

If the surface binding energy E_B of the particle is large enough, we can use the Born-Oppenheimer approximation for the z dependence of ψ:

$$\psi=\phi(\mathbf{r}_\parallel,\ldots)g(z) \tag{3}$$

with $g(z)$ the wave function of the lowest bound state. This eliminates the perpendicular degree of freedom, as we can replace $V_q(z)$ by its expectation value in the ground state. The remaining in-plane wave function ϕ is that of a conventional two-dimensional polaron. When the coupling with surface phonons [Eq. (1)] is present, the ground-state energy of the particle is lowered. Normal collapse will thus occur when the correction of the ground-state energy due to this coupling becomes comparable to the elastic binding energy E_B. Using lowest-order perturbation theory, we estimate the natural dimensionless parameter of the problem to be

$$\beta=\frac{S}{4\pi E_B}\int_0^{q_m} q\,dq\frac{|\langle V_q\rangle|^2}{\hbar^2q^2/2m+\hbar\omega_q} \ , \tag{4}$$

where S is the surface area and q_m is the magnitude of the Debye wave vector.

As far as the in-plane collapse is concerned, we must determine when the parallel effective-mass correction becomes large. The dimensionless parameter is here

$$\alpha\equiv S\frac{\hbar^2}{m}\int_0^{q_m} q^3dq\frac{|\langle V_q\rangle|^2}{(\hbar^2q^2/2m+\hbar\omega_q)^3} \ . \tag{5}$$

This is simply the standard electron-phonon coupling constant of polaron theory.[1] We expect in-plane collapse when α is of order 1 and normal collapse when β is of order 1.

B. Variational method

As explained in the introduction, we are interested in the intermediate coupling range. Our aim is to find a variational wave function which is of the LLP form for the in-plane coordinates including the z dependence in an appropriate manner. We thus use a global ansatz based on the unitary transformation method. First, we note that since both potentials depend only on z, there is translational invariance in the x-y plane so that the total (i.e., electron plus phonon) parallel momentum is a conserved quantity. Following LLP's procedure, we eliminate $\mathbf{r}_\parallel$ from the Hamiltonian (1) via the transformation

$$S=\exp\left[\frac{i}{\hbar}\left[\mathbf{P}-\sum_{\mathbf{q}}\hbar\mathbf{q}a^\dagger_{\mathbf{q}}a_{\mathbf{q}}\right]\cdot\mathbf{r}_\parallel\right] \ . \tag{6}$$

The transformed Hamiltonian $H'=S^{-1}HS$ has the same structure as in the paper of LLP, except for the z dependence of the potentials. The transformed wave function is defined by $\psi'=S^{-1}\psi$. We now choose the following form for ψ':

$$\psi'=\exp\left[\sum_{\mathbf{q}}[f^*_{\mathbf{q}}(z)a_{\mathbf{q}}-\text{H.c.}]\right]g(z)|0\rangle \ , \tag{7}$$

where $f_{\mathbf{q}}$ and g will be determined variationally. g represents the normal component of the particle wave function, while $f_{\mathbf{q}}$, is identified as the z-dependent phonon amplitude for the mode with wave vector $\mathbf{q}$, for reasons that will appear clear later on. To justify this choice of ansatz, we consider the following limits.

(i) $E_B\to\infty$, $\mathbf{P}=0$. In this limit, the Born-Oppenheimer decomposition of Eq. (3) should be valid, and we replace $V_q(z)$ by its average value $\langle V_q\rangle$. For the in-plane component of the wave function, we can then use the LLP variational result in the form of Eq. (7), where

$$f_q=-\frac{\langle V_q\rangle}{\hbar^2q^2/2m+\hbar\omega_q} \ . \tag{8}$$

(ii) $m\to\infty$. Here the particle can be treated as classical. Let z_0 be its equilibrium position, with $\mathbf{r}_\parallel=0$. The phonon wave function is known as

$$\psi=\exp\left[\sum_{\mathbf{q}}\frac{V_q(z_0)}{\hbar\omega_q}(a_q^\dagger-a_q)\right]|0\rangle \tag{9}$$

from which we can deduce the value of the parameter $f_q(z)$ in the classical limit.

(iii) $V_q\rightarrow 0$. First-order perturbation theory can be recovered trivially when expanding the variational ansatz to first order in f_q.

(iv) *Adiabatic limit.* Finally, we consider the limit in which both the elastic and the interaction potential vary very slowly in the normal direction. The z dependence of ψ' is thus also rather weak (in the ground state). Up to an intermediate coupling α, we can build ψ' as the linear superposition of a series of LLP polarons, each one in a slice between z and $z+dz$, having an amplitude $g(z)$. This leads again to the variational wave function of Eq. (7), now with

$$f_{\mathbf{q}}(z)=-\frac{V_q(z)}{\hbar^2q^2/2m-(\hbar/m)\mathbf{P}\cdot\mathbf{q}+\hbar\omega_q} . \tag{10}$$

The variational ansatz thus covers a wide range of limits. Its main defect is that, as in the case of LLP, it neglects correlations between phonons.[11] It thus cannot describe properly the in-plane collapse of the wave function for large α, which involves the construction of a static "dimple" on the surface around the particle. To compute $f_q(z)$ in the general case, we will require that the energy

$$E=\frac{\langle\psi'|H|\psi'\rangle}{\langle\psi'|\psi'\rangle} \tag{11}$$

be a minimum. The calculation of the above expression is similar to that of LLP's paper, apart for the fact that we have introduced some inhomogeneity in the z direction. The new terms arise from the evaluation of $U^{-1}S^{-1}(\hbar^2/2m)(\partial^2/\partial z^2)SU$. In the calculation of the expectation value of Eq. (11), the algebra is simplified if we introduce the two quantities

$$\eta(z)=\sum_{\mathbf{q}}\frac{\hbar\mathbf{q}\cdot\mathbf{P}}{P}|f_{\mathbf{q}}|^2 \tag{12a}$$

and

$$\delta(z)=\frac{1}{2}\sum_{\mathbf{q}}\left[f_{\mathbf{q}}^*\frac{\partial f_{\mathbf{q}}}{\partial z}-f_{\mathbf{q}}\frac{\partial f_{\mathbf{q}}^*}{\partial z}\right] . \tag{12b}$$

Minimizing E with respect to g and $f_{\mathbf{q}}$ yields the following two variational equations:

$$\left\{\frac{P^2}{2m}(1-\eta)^2+\frac{\hbar^2}{2m}\left[\frac{1}{i}\frac{\partial}{\partial z}+i\delta\right]^2+V_0+\sum_{\mathbf{q}}\left[\frac{\hbar}{2m}\left|\frac{\partial f_{\mathbf{q}}}{\partial z}\right|^2+\left[\frac{\hbar^2q^2}{2m}+\hbar\omega_q\right]|f_{\mathbf{q}}|^2+V_q(f_{\mathbf{q}}+f_{\mathbf{q}}^*)\right]\right\}g=Eg , \tag{13}$$

$$\frac{\hbar^2}{2m}\frac{\partial}{\partial z}\left[-|g|^2\frac{\partial f_{\mathbf{q}}}{\partial z}\right]+\left[-g^*\frac{\partial g}{\partial z}+g\frac{\partial g^*}{\partial z}-2\delta|g|^2\right]\frac{\partial f_{\mathbf{q}}}{\partial z}+\left[\frac{\hbar^2q^2}{2m}+\hbar\omega_q-\frac{\hbar\mathbf{q}\cdot\mathbf{P}}{m}(1-\eta)\right]f_{\mathbf{q}}|g|^2=-V_q|g|^2 . \tag{14}$$

Equation (13) is a Schrödinger equation for $g(z)$. The potential $V_0(z)$ is renormalized by the surface modes. In addition, there appears a term which has the form of a scalar potential. The equation for the phonon wave function $f_q(z)$ is inhomogeneous. The particle probability density $|g|^2$ acts as a source term for the phonons. Thus, Eqs. (13) and (14) are of the form encountered in quantum electrodynamics where the particle feels a potential which is renormalized by photons and where it acts in turn as a photon source.

III. GROUND STATE

The variational equations simplify greatly if we only allow real solutions. This forces $\delta=0$ and cancels all the currentlike terms in the previous equations. Choosing a real g is natural for the ground-state wave function of a particle. The assumption of a real f_q is less obvious. However, we note that for all limiting cases examined in Sec. II, f_q is real as long as V_q is real. The latter situation corresponds to the case of surface deformation potentials, which is the situation of physical interest for adsorption problems.

In this section, we are only interested in the ground-state wave function, so that we set $\mathbf{P}=0$. Since g represents the particle wave function, it must vanish at the surface because of the hard core repulsion of the elastic potential. In addition, it should have no nodes and it should decay exponentially at infinity. We thus choose the form

$$g(z)=\frac{2z}{\xi^{3/2}}\exp\left[-\frac{z}{\xi}\right] . \tag{15}$$

Later on, ξ will be chosen so as to minimize the energy. The boundary condition on f_q is less stringent: this function has to be chosen as a solution of Eq. (14) which is sufficiently well behaved so that no divergences appear in the energy functional. With the choice for g as in Eq. (15), the inhomogeneous differential equation for f_q now transforms to

$$-\frac{d^2}{dz^2}f_q-2\left[\frac{1}{z}-\frac{1}{\xi}\right]\frac{d}{dz}f_q+L_q^2f_q+\frac{2m}{\hbar^2}V_q=0 . \tag{16}$$

For simplicity of notation, we have defined $L_q\equiv[q^2+(2m/\hbar)\omega_q]^{1/2}$. We note that one can immediately compute the average of $f_q(z)$ by integrating this equation from 0 to ∞. With this procedure, we find that this expectation value coincides with the Born-Oppenheimer value of Eq. (8). Typically, f_q is a superposition $f_q=\tilde{f}_q+A_qf_q^H$ of a particular solution $\tilde{f}_q$ (chosen so that $\tilde{f}_q=0$ when $V_q=0$) and a homogeneous solution f_q^H. The coefficient A_q determines the number of phonons present in the absence of coupling. We thus expect it to be equal to zero in the ground state. The energy functional is bilinear in A_q; in the Appendix, we show that indeed $A_q=0$ upon minimization. Thus, we are only interested in the inhomogeneous solutions of Eq. (16).

An exact solution of Eq. (16) via Green's-function methods is possible but does not lead to much insight, due to the complexity of the Green's function. A numerical solution is also possible, but would constrain us to choose a specific physical system for calculation purposes. We still adopt a different point of view: one can gain more physical insight in studying which part of the phonon spectrum is responsible for the strong renormalization of the ground-state energy. We will thus employ the relevant approximate forms for the phonon amplitudes. As we will see later on, this approach is justified, as all the quantities we evaluate are dominated by their large wave-number contribution. Moreover, we are able to discuss the results for different forms of inelastic potentials.

We examine the behavior of f_q in the two regimes: $0<z\ll\xi$ and $z\gg\xi$. The resulting developments bear two distinct limiting behaviors depending on the product $q\xi$: for $q\xi\gg1$, the expression for f_q corresponds indeed to the adiabatic limit Eq. (10), which is valid when the range of the wave function is large compared to q^{-1}.

For low-energy phonons a similar analysis can be carried out, taking the limit $q\xi\ll1$. In this limit, V_q only appears as an average due to the zero-point motion.

Our next problem is to compute the particle energy as a function of ξ. In the absence of coupling, the particle energy is

$$E_0=\int_0^\infty dz\left[\frac{\hbar^2}{2m}\left[\frac{dg}{dz}\right]^2+V_0(z)g^2\right] . \tag{17}$$

The first term diverges as $1/\xi^2$ for $\xi\to0$. The second term is attractive and will favor a small ξ. In Fig. 1, we show $E_0(\xi)$ for a Coulomb elastic potential. The minimum of E_0 lies at the Bohr radius $\xi^*=\hbar^2/2m\Lambda_0$. The normal part of the wave function will remain unchanged as long as the total energy has an absolute minimum near ξ^*.

The correction term due to surface phonons is

$$\Delta E(\xi)=\frac{S}{2\pi}\int_0^{q_m}q\,dq\int_0^\infty dz\,g^2(z)V_q(z)f_q(z) . \tag{18}$$

Since f_q is generally proportional to $-V_q$, we have $\Delta E<0$. If we replace f_q by its average value $\langle f_q\rangle$, we recover the result of the Born-Oppenheimer approximation. We will now evaluate $\Delta E(\xi)$ for short- and long-range interaction potentials. We shall only consider two simple limiting cases which are of physical interest.

A. Step potential

We start with the step potential of Gadzuk and Metiu:[12]

$$V_q(z)=\begin{cases}V/N^{1/2}, & z<\lambda\\ 0, & z>\lambda\end{cases} \tag{19}$$

where N is the number of surface atoms and λ is the range of V_q.

For $\xi\ll\lambda$, we expand $g(z)$ for small z. Defining q^* by $\hbar q^{*2}/2m=\omega_{q^*}$, the expression for the ground state gives

$$\Delta E(\xi)\simeq-\frac{m}{\pi\hbar^2}V^2\left[\frac{S}{N}\right]\ln\left[\frac{q_m}{q^*}\right] , \tag{20}$$

the result of the perturbative approach. Here, we have assumed that for short wavelengths, the free electron energy is large compared to the surface-phonon energy.

For $\xi\gg\lambda$, we can assume that $V_q(z)$ is a constant, and we only need to consider that part of the integral for which $L_q\lambda>0$. In this range, Eq. (18) reduces to

$$\Delta E(\xi)\simeq-\frac{m}{\pi\hbar^2}\left[\frac{\lambda}{\xi}\right]^3V^2\left[\frac{S}{N}\right]q_m\lambda . \tag{21}$$

This expression is valid when $\omega_q\simeq q^\gamma$ for large wavelengths, with $\gamma\le2$.

The complete function $\Delta E(\xi)$ thus falls off as $1/\xi^3$ for $\xi\gg\lambda$, while it approaches the perturbative limit for $\xi\ll\lambda$. Near $\lambda=\xi$, $|\Delta E(\xi)|$ is larger than $|\Delta E(0)|$ by a factor $q_m\lambda$. We thus conclude that $\Delta E(\xi)$ has a minimum around $\xi=\lambda$, the range of the interaction potential. If there is normal collapse, the wave function assumes the extent of the interaction potential. We now consider the complete ground-state energy $E(\xi)=E_0(\xi)+\Delta E(\xi)$ for different values of the coupling constant V (see Fig. 2).

For small V (Fig. 1), there is little effect on the minimum of $E(\xi)$ at ξ, but with increasing V [Fig. 2(a)], a second minimum appears near $\xi=\lambda$. This could suggest that certain excited states have an appreciable nonzero amplitude a distance of the order λ near the surface, while the ground state is still localized around ξ^*. Beyond a critical value V_c, the minimum at $\xi=\lambda$ becomes the absolute minimum [Fig. 2(b)] and the ground

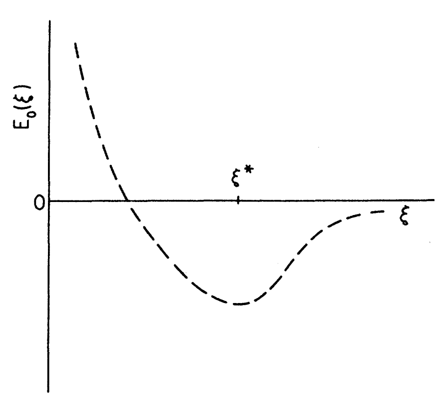

FIG. 1. Energy as a function of the normal extension ξ of the particle wave function in the absence of interaction with surface exitations.

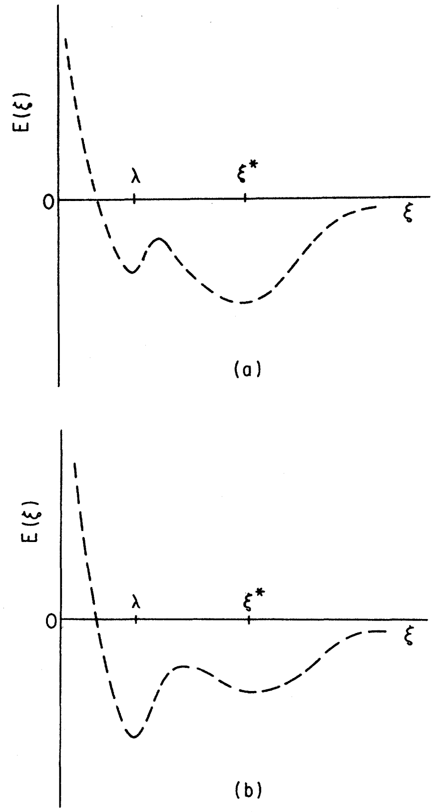

FIG. 2. Energy as a function of the normal extension ξ of the particle wave function in the presence of inelastic coupling with surface phonons. The case represented here corresponds to the step potential of Gadzuk and Metiu which has a range λ, in the case $\lambda \ll \xi^*$. (a) For small coupling, $V \ll V_c$, the minimum at ξ represents the ground state. (b) For large coupling, $V \gg V_c$, the minimum at λ takes over and the particle collapses on the surface.

state collapses. If $\lambda \ll \xi$, then at the critical value of V, $|\Delta E(\xi=\lambda)|$ is comparable to the zero-point energy $\hbar^2/2m\lambda^2$, which tries to prevent the collapse. From Eq. (21), we thus come to the conclusion that

$$V_{c_\perp} \simeq \frac{\hbar^2}{m\lambda^2}(\lambda q_m)^{1/2} \; . \tag{22}$$

To derive this expression, we have assumed that $(S/N)^{1/2} \sim q_m^{-1}$. Apparently, the most important contribution to the wave-function renormalization comes from large wave-number phonons.

This result should be compared with the prediction of the naive perturbative calculation [see Eq. (4)]. The predicted critical coupling is then $\beta=1$, which corresponds to

$$V_{c_\perp} = \frac{\hbar^2 q_m}{m\xi} \tag{23}$$

which is wrong. Our value for the critical coupling has been reduced by a factor $(\lambda q_m)^{1/2}\lambda/\xi$ compared to the latter value. Thus, the criterion $\beta=1$ is unreliable for estimating the point of normal collapse when $\lambda q_m \simeq 1$.

B. Long-range potential

For a long-range interaction potential (e.g., charged particles on a ^{4}He film or neutral atoms subject to the van der Waals attraction of the surface), the situation could be quite different. Generally, the potential behaves like a power law at large distances, while it depends strongly on the ripplon wave number at short distances. We make the following choice:

$$V_q(z) = \begin{cases} U_q/N^{1/2}z_c^{\zeta}, & z_c > \max(q^{-1}, z) \\ U_q q^{\zeta}/N^{1/2}, & q^{-1} > \max(z_c, z) \\ U_q/N^{1/2}z^{\zeta}, & z > \max(q^{-1}, z_c) \end{cases} \tag{24}$$

with $\zeta > 2$ ($\zeta=2$ for electrons on ^{4}He and $\zeta=4$ for nonretarded van der Waals forces[13]). Here, z_c is a cutoff which is comparable to q_m^{-1}, and has to be introduced as the power-law behavior becomes invalid at distances which are comparable to the surface interatom spacing. Furthermore, for long-wavelength phonons, V_q has to vanish since, as mentioned, the surface at distances $qz \ll 1$ is indistinguishable from a flat surface. Since $V_q(z)$ is a decreasing function of z, for large coupling, the dominant contribution in ΔE is expected to come from the behavior of the integrant where $z \simeq \xi$. For large ξ, we can truncate the integral over position in Eq. (18) at $z=\xi$ and then expand the result in powers of $1/\xi$. After extracting the dominant contribution of the phonon sum, we reach the following expression for ΔE:

$$\Delta E(\xi) \simeq \frac{4m}{\hbar^2}\frac{S}{N}\int_0^{q_m} q\,dq U_q^2 \left[\frac{\gamma L_q^{2\zeta-5}}{\xi^3} + \frac{1}{\xi^{2\zeta}L_q^2}\right] , \tag{25}$$

where γ is a numerical constant. The large-ξ behavior of $\Delta E(\xi)$ would only be significantly affected by the power-law nature of $V_q(z)$ if $\zeta < \frac{3}{2}$, which is outside the range of physical interest.

For $\xi \to 0$, the wave function is sharply peaked at $z=\xi$, and we can use a similar argument as in the case of the step potential:

$$\Delta E(\xi) = -\frac{m}{\pi\hbar^2}\frac{S}{N}\int_0^{q_m} q\,dq \frac{U_q^2}{z_c^{\zeta}}\frac{q^{\zeta}}{L_q^2} \tag{26}$$

which is again independent of ξ. The qualitative ξ dependence of ΔE is very similar to the case of short-range potentials, as long as $\zeta > \frac{3}{2}$. We can now estimate the location of the minimum of ΔE. The correction term proportional to $1/\xi^{2\zeta}$ becomes comparable to the $1/\xi^3$ term at distances of the order

$$\xi_{\min} = \left[\left[\int_0^{q_m} q\,dq \frac{U_q^2}{L_q^2} \right] \Big/ \left[\int_0^{q_m} q\,dq U_q^2 L_q^{2\zeta-5} \right] \right]^{1/(2\zeta-3)} . \tag{27}$$

Looking at the denominator, we see that it is always dominated by large wave numbers when $\zeta \geq 2$, and the position of the minimum is proportional to q_m^{-1}.

Therefore, following the argumentation of the previous section, the ground state will collapse when

$$\int_0^{q_m} q\,dq \frac{U_q^2}{L_q^{5-2\zeta}} \geq \left[\frac{\hbar^2}{m}\right]^2 q_m \; . \tag{28}$$

IV. PARALLEL MASS

After normal collapse, there is a considerable increase in the amplitude of the wave function for small z. This leads to an increase in the effective electron-phonon coupling constant. The simplest way to see this is by first considering the Born-Oppenheimer approximation for the in-plane mass enhancement coefficient m^*/m, as was done in Sec. II. For the step potential of the previous section, we should expect that α depends on ξ as

$$\alpha(\xi)=\alpha(0)(\lambda/\xi)^6 . \tag{29}$$

A reduction in ξ by a factor 2 would imply an increase in α by 2 orders of magnitude.

In this section we include the z dependence of the phonon amplitudes in the calculation of the effective mass. To go beyond the perturbative result, we use again the variational method, this time allowing for a finite parallel momentum $\mathbf{P}$. The energy is now written as

$$E=E_0+\int_0^\infty dz\left[\frac{P^2}{2m}(1-\eta)^2+\sum_{\mathbf{q}} V_q f_{\mathbf{q}}\right]g^2 , \tag{30}$$

where E_0 is defined as in Eq. (17).

Here, however, $f_{\mathbf{q}}$ is a solution of the equation

$$-\frac{d}{dz}g^2\frac{d}{dz}f_{\mathbf{q}}+\left[L_q^2-2\frac{\mathbf{P}\cdot\mathbf{q}}{\hbar}(1-\eta)\right]g^2 f_{\mathbf{q}}+\frac{2m}{\hbar^2}V_q g^2=0 . \tag{31}$$

Since we are interested in the computation of the parallel mass, we expand the energy in powers of the parallel momentum $\mathbf{P}$:

$$E=E(\mathbf{P}=0)+\frac{P^2}{2}\frac{\partial^2 E}{\partial P^2}\bigg|_{\mathbf{P}=0} . \tag{32}$$

Equation (40) suggests that second-order contributions to the energy will come from the zero-order contribution of η and from the second-order contribution of $f_{\mathbf{q}}$. Defining $G_q(z,z')$ as the Green's function associated with Eq. (31), the perturbative expansion of $f_{\mathbf{q}}$ in powers of $\mathbf{P}$ can be written as

$$f_{\mathbf{q}}=f_q^{(0)}+f_{\mathbf{q}}^{(1)}+f_{\mathbf{q}}^{(2)}+\cdots \tag{33}$$

with

$$f_q^{(0)}(z)=\int_0^\infty dz' G_q(z,z')\left[-\frac{2m}{\hbar}\right]V_q(z')g^2(z') \tag{34a}$$

and

$$f_{\mathbf{q}}^{(n)}(z)=\int_0^\infty dz' G_q(z,z')\frac{2\mathbf{P}\cdot\mathbf{q}}{\hbar}[1-\eta(z')] \times g^2(z')f_{\mathbf{q}}^{(n-1)}(z') . \tag{34b}$$

In the latter expression, $f_{\mathbf{q}}^{(n)}$ is defined as the nth-order contribution of the phonon amplitude, for $n>1$. Inserting the last equation in the expression for the energy and using the symmetry of the Green's function, we can now write the second-order contribution as

$$\frac{\partial E}{\partial P^2}\bigg|_{\mathbf{P}=0}=\frac{1}{m}(1-\langle\eta\rangle) \tag{35}$$

which has exactly the form of the perturbative result of Sec. I. To calculate $\langle\eta\rangle$, we first extract the zero-order contribution of η using the earlier definition, Eq. (5). For $0<z,z'\ll\xi$, we know the limiting form of the Green's function defined above, and we obtain the following integral equation for η:

$$\eta(z)=\int_0^{q_m}\frac{Sq^3dq}{2\pi}\int_0^\infty\frac{dz'}{L_q}f_q^{(0)}(z')f_q^{(0)}(z)[1-\eta(z')] \times\frac{z'}{z}(e^{-L_q|z-z'|}-e^{-L_q(z+z')}) . \tag{36}$$

For small η, we can compute its expectation value, which appears in the expression for the effective mass, Eq. (45). To do this, we split the integration range over momentum into two parts, giving rise to the contributions $\langle\eta^+\rangle$ for $q\xi\gg1$ and $\langle\eta^-\rangle$ for $q\xi\ll1$. In the former case, the kernel in Eq. (36) is sharply peaked at $z=z'$; for the step potential with λ, $q_m^{-1}\ll\xi$, this leads to

$$\langle\eta^+\rangle\simeq\frac{1}{2\pi}\left[\frac{S}{N}\right]\left[\frac{2m}{\hbar^2}\right]^2 V^2\left[\frac{\lambda^3}{\xi}\right] . \tag{37}$$

Since $L_q\simeq q$ for $q\gg q^*$, the integral over momentum in $\langle\eta^-\rangle$ is dominated by the regime $q\simeq\xi^{-1}$. Short-wavelength phonons do not contribute to the in-plane mass enhancement. Our final expression is

$$\langle\eta^-\rangle\simeq\frac{S}{N}V^2\frac{1}{6\pi}\left[\frac{2m}{\hbar}\right]^2\frac{\lambda^4}{\xi^2} . \tag{38}$$

For $\xi^*\gg\lambda$, $\langle\eta^-\rangle\simeq(\lambda/\xi)\langle\eta^+\rangle$ and it is thus small compared to $\langle\eta^+\rangle$. However, for the collapsed state, $\langle\eta^+\rangle$ and $\langle\eta^-\rangle$ are of similar magnitude. We must conclude that the perturbative result greatly overestimated the true mass-enhancement factor. A collapse of the normal part of the wave function from ξ to λ leads to an increase in the in-plane coupling constant only by a factor (ξ/λ). We can now estimate the point of in-plane collapse by using Eq. (35). As $\langle\eta\rangle$ approaches 1, the in-plane effective mass becomes large. The divergence at $\langle\eta\rangle=1$ only indicates that our ansatz is invalid for $\langle\eta\rangle\geq1$. We should then be in the small-polaron regime, by analogy with bulk polarons. In the literature, the existence of a transition from small to large polarons is still being questioned. This controversy does not affect us here since we are only trying to locate at which value of the coupling strength the extended surface-state scheme breaks down. The fact is that a transition of the perpendicular component of the wave function is unavoidable here, as the surface potential is peaked near the surface. The main purpose of the present section is to support the validity of the result of the previous section.

Setting $\langle\eta^+\rangle=1$, we find the estimated critical coupling constant for the parallel transition to be

$$V_{c_\parallel}=\frac{\hbar^2}{2m\lambda^2}(\lambda q_m)^{1/2}(\xi q_m)^{1/2} . \tag{39}$$

On the other hand, normal collapse occurred at $V=V_{c_\perp}$ defined by Eq. (22). Thus, we must conclude that normal collapse is expected before in-plane collapse, at least if $\xi^* q_m > 1$. After the collapse, ξ is reduced to λ. This increases the effective electron-phonon coupling constant and thus reduces the critical value V_c by $(\lambda/\xi)^{1/2}$. Further increases in V will thus possibly produce an in-plane collapse of the wave function when $V \simeq V_c(\lambda q_m)^{1/2}$. For clarity, a schematic diagram of the transition is drawn in Fig. 3, showing the different regimes which can be expected in the (λ, V) configuration space, for $q_m^{-1} < \lambda < \xi^*$.

V. CONCLUSION

We have studied the ground state of a particle interacting with the excitations of the surface on which it is trapped. To represent the many-body wave function of this system, we used a variational ansatz which is a generalization of the LLP wave function. The specific choice for the wave function was justified by the fact that we can recover many of the known limiting behaviors: the weak-coupling limit, where perturbation theory holds; the large-binding-energy limit, where the wave function can be factored into a particle and a phonon contribution; the classical limit; and finally the adiabatic limit where the interaction potential is a smooth function of z. The parameters of the ansatz were then determined upon minimization of the energy functional of the global system. From this, we obtained a set of $N+1$ coupled equations, where N is the number of phonon modes. Each mode amplitude is the solution of an inhomogeneous second-order differential equation whose coefficients depend on both the spatial variation of the particle wave function and the interaction potential. For phonon wave numbers which are sufficiently large or sufficiently small compared to the extent of the uncoupled system, it is possible to obtain a closed expression for the phonon amplitudes. Due to momentum conservation along the surface, in our formulas, the phonon dispersion relation only appears together with the free particle dispersion. The latter always dominates at high energies, and as a result the ground-state energy depends mostly on the contribution of short-wavelength phonons.

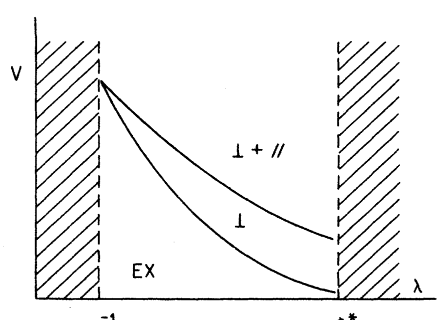

FIG. 3. Schematic diagram of the instability, in the (λ, V) plane. λ is the range of the inelastic potential, while V is the coupling strength. Equations (22) and (39) define the boundaries between the different regimes: the extended (EX) regime, the normal collapsed regime ($\perp$), and the regime where the wave function has collapsed in all directions ($\perp + \|$). We only consider the range $q_m^{-1} < \lambda < \xi^*$.

We found little difference between short-range interaction potentials and the power law potentials relevant for image-charge and van der Waals potentials.

With increasing coupling constant, we found a collapse in the normal part of the ground-state wave function at a critical coupling constant. The transition is rather different from the controversial in-plane collapse, since it is driven by the renormalization of the zero-point energy by short-wavelength phonons. Surprisingly, if the typical height ξ^* of the bound state above the surface exceeds the range λ of the particle-phonon interaction potential, the normal collapse will take place before a possible change in the parallel extend of the wave function, such as in-plane collapse. The normal collapse enhances the electron-phonon coupling constant and triggers in-plane collapse for a slightly larger coupling constant.

This result is disturbing because it would imply that previous treatments of surface polarons could be qualitatively in error as they only allowed in-plane collapse. Our result suggests that the parallel mass enhancement is basically slaved to the zero-point energy renormalization. We thus reexamine some of the important assumptions we made. The above result is valid when the range of the inelastic potential is smaller than the normal extent of the wave function in the absence of coupling. For electrons on ^{4}He, we know that $\xi^* \gg \lambda$, but for electrons trapped on solid surfaces, ξ may be comparable to λ. At the same time, since E is found to be sensitive to the short-wavelength cutoff, our conclusions could be affected if we have overestimated q_m. If q_m was comparable to q^*, for instance, a much larger coupling constant would be needed for normal collapse. For typical surface-phonon and ripplon dispersions, this is not the case.

A number of significant questions still remain to be settled. First, the nature of the transitions.

We would expect the normal collapse to be similar to a first-order phase transition, since upon varying the coupling strength, the ground-state energy acquires a metastable state which becomes the true energy minimum at the critical coupling $V_{c_\perp}$. Whether or not the in-plane collapse is a transition is, as in the case of bulk polarons, a delicate question. Our variational method is certainly not appropriate to study this aspect of the problem. As was pointed out by Peeters and Devreese[3] in the case of the bulk polaron, critical behavior may be a mere artifact of the method of approximation.

Secondly, and related to the first point, we have not mentioned finite-temperature effects. We shall briefly discuss their importance here. In a path-integral approach, Jackson and Platzman[14] showed that the inclusion of temperature will smooth out the transition (in the effective-mass enhancement, for example). Moreover, Peeters and Jackson[15] showed that dynamical quantities, such as the frequency-dependent mobility, could still exhibit visible rapid crossover behavior at finite temperatures. In our case, it is possible to generalize the variational method introducing a ground-state energy which is thermally averaged over all phonon configurations, as was done by Davidov[16] in his description of the propagation of electronic exitations along DNA chains. Upon inspection of this new functional, we find that the interaction potential will be effectively reduced at finite temperatures, therefore suggesting that the collapse of the wave function will be less abrupt in this case.

We will end this discussion with the example of electrons on ^{4}He. For this system, the interaction potential is well understood. For electron parameters, the criterion of Eq. (28) is violated, which indicates that we are far into the weak-coupling regime. This is indeed seen in the experimental situation, as the electrons trapped upon a thick helium film seem to lie in the hydrogenlike levels of the elastic image-charge potential. For Eq. (28) to hold, we would need the mass of a heavy ion. At this point, it is tempting to draw a parallel between the surface-polaron behavior and the adsorption probability of a particle incident on a surface. In a numerical experiment,[9] we measured the sticking probability of an electron, solving the time-dependent Schrödinger equation for the particle wave function in the time-dependent Hartree (TDH) approximation. We observed a transition in the adsorption as the coupling strength was increased. One way to increase the coupling strength is to use heavier masses than that of the electron. We observed that significant adsorption only occurred for masses comparable to the mass of a fluoride ion, which roughly corresponds to the criterion of Eq. (28). We thus believe that the transition in the adsorption behavior is a mere consequence of a singular feature of the static system. Above the critical coupling constant for normal collapse, the particle potential is strongly renormalized by the interaction with surface phonons, which yields the transition from an extended to a collapsed state. As a parallel between the static and dynamic situation seems justified, we believe that an extension of the present formalism to time-dependent systems should be investigated. This will be the subject of the next publication.[17]

ACKNOWLEDGMENTS

We thank Dr. P. M. Platzman for useful discussions and Professor P. G. DeGennes for his hospitality at the College de France. One of us (Th.M) would like to thank Professor R. Vinh Mau for his hospitality at Université de Paris–VI. This work was supported by National Science Foundation Grant No. DMR-8603217. The Physique de la Matiere Condensee is a "unité associee au Centre National de la Recherche Scientifique, No. 792."

APPENDIX: DETERMINATION OF A_q

$$\Delta E\{f_q\}=\sum_q \int_0^\infty dz\, g^2 \left[\frac{\hbar^2}{2m}L_q^2 f_q^2+\frac{\hbar^2}{2m}\left[\frac{\partial f_q}{\partial z}\right] +2V_q f_q\right], \tag{A1}$$

where $f_q=\tilde{f}_q+A_q f_q^H$.

Inserting this expression in (A1) and minimizing the energy with respect to A_q yields

$$A_q=\frac{N_q}{D_q}, \tag{A2}$$

with

$$N_q=-\int_0^\infty dz\left[L_q^2 f_q^H \tilde{f}_q+\frac{\partial}{\partial z}f_q^H\frac{\partial}{\partial z}\tilde{f}_q+\frac{2m}{\hbar^2}V_q f_q^H\right]g^2, \tag{A3a}$$

$$D_q=\int dz\left[L_q^2 f_q^{H^2}+\left[\frac{\partial}{\partial z}f_q^H\right]^2\right]. \tag{A3b}$$

The denominator D_q is positive definite.

According to Eq. (12), f_q^H is a solution of the equation

$$-\frac{\partial^2}{\partial z^2}f_q^H-2\left[\frac{1}{z}-\frac{1}{\xi}\right]\frac{\partial}{\partial z}f_q^H+L_q^2 f_q^H=0. \tag{A4}$$

For large z, we get the two limiting behaviors

$$f_{qH}^{\pm}(z)=e^{K_\pm z} \text{ with } K_\pm=\frac{1}{\xi}\pm\left[\frac{1}{\xi^2}+L_q^2\right]^{1/2}. \tag{A5}$$

The + subscript solution grows at infinity faster than $e^{2z/\xi}$. This suggests that one look for solutions of Eq. (A4) in the form

$$f_{qH}^{\pm}=e^{K_\pm z}u_\pm\left[\mp 2\left[\frac{1}{\xi^2}+L_q^2\right]^{1/2}z\right], \tag{A6}$$

where $u_\pm$ satisfies the equation

$$\frac{d^2u_\pm}{dx^2}+(2-x)\frac{du_\pm}{dx}-\gamma_\pm=0, \tag{A7}$$

with $\gamma_\pm=\mp[1\pm(1+L_q^2\xi^2)^{-1/2}]$.

Equation (A7) is known as Kummer's equation.

Let us look at the small-z behavior of the solution of Eq. (A5) which is regular at infinity (f_{qH}^-). With the subscript −, Eq. (A7) has two solutions:[8] $M(\gamma_-,2,x)$ and $U(\gamma_-,2,x)$. The latter solution is regular at $x=0$, but blows up exponentially for large x. On the other hand, for large x,

$$U(\gamma_-,2,x)=x^{-\gamma_-}[1+O(x^{-1})], \tag{A8}$$

which means that f_{q-}^H must be connected to this solution.

For small x,

$$U(\gamma_-,2,x)=\frac{1}{\Gamma(\gamma_-)x}\frac{1}{x}. \tag{A9}$$

Therefore, f_{qH}^- has a $1/z$ singularity at $z=0$, which will lead to a divergence of the denominator D_q. At the same time the exponential behavior of f_{qH}^+ also leads to a divergence in D_q. We thus conclude that $D_q=\infty$. On the other hand, since $\tilde{f}_q$ is a well-behaved function, the factor g^2 in the integrant of N_q will not allow for any divergences of this integral. Therefore,

$$A_q=0. \tag{A10}$$

[1]T. D. Lee, F. Low, and D. Pines, Phys. Rev. B **90**, 297 (1953).
[2]Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961); Y. Toyozawa and Y. Shinozuka, J. Phys. Soc. Jpn. **48**, 472 (1980).
[3]F. M. Peeters and J. T. Devreese, Phys. Status Solidi B **112**, 219 (1982).
[4]S. Das Sarma, Solid State Commun. **54**, 1067 (1985); B. A. Mason and S. Das Sarma, Phys. Rev. B **33**, 1412 (1986).
[5]G. A. Farias, N. Studart, and O. Hipólito, Solid State Commun. **43**, 95 (1982); G. Barton, J. Phys. C **14**, 3975 (1981); G. Barton and M. Babiker, *ibid.* **16**, 4951 (1981).
[6]S. A. Jackson and P. M. Platzman, Phys. Rev. B **24**, 499 (1981); N. Tokuda and H. Kato, J. Phys. C **16**, 1573 (1983).
[7]R. M. Nieminen and C. H. Hodges, Phys. Rev. B **18**, 2568 (1977); N. Barberan and P. M. Echenique, *ibid.* **19**, 5431 (1979); M. Rona and A. Ercelebi, *Physics of Semiconductors* (IOP, London, 1979).
[8]E. Evans and D. L. Mills, Solid State Commun. **11**, 1903 (1972); Phys. Rev. B **8**, 4004 (1973); E. L. de Bodas and O. Hipólito, *ibid.* **27**, 6111 (1983).
[9]Th. Martin, R. Bruinsma, and P. M. Platzman, Phys. Rev. B **39**, 12411 (1989).
[10]V. B. Shikin and Y. Monarkha, J. Low Temp. Phys. **16**, 193 (1974); P. M. Platzman and G. Beni, Phys. Rev. Lett. **36**, 626 (1976); D. S. Fisher, B. I. Halperin, and P. M. Platzman, *ibid.* **42**, 798 (1979).
[11]S. Tomonaga, Prog. Theor. Phys. **2**, 6 (1947).
[12]J. W. Gadzuk and H. Metiu, Phys. Rev. B **22**, 2603 (1980).
[13]D. O. Edwards *et al.*, Phys. Rev. Lett. **24**, 1153 (1975).
[14]S. A. Jackson and P. M. Platzman, Phys. Rev. B **25**, 4886 (1982).
[15]F. M. Peeters and S. A. Jackson, Phys. Rev. B **34**, 1539 (1986).
[16]A. S. Davydov, Zh. Eksp. Teor. Fiz. **78**, 789 (1980) [Sov. Phys.—JETP **51**, 397 (1982)].
[17]Th. Martin and R. Bruinsma (unpublished).
[18]H. Abramovitz and A. Stegun, *Handbook of Mathematical Functions,* Natl. Bur. Stand. (U.S.) Appl. Math. Ser. No. 55 (U.S. GPO, Washington, D.C., 1964).