Polarons Bound in a Coulomb Potential. I. Ground State*

DAVID M. LARSEN
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173
(Received 29 May 1969)

We introduce a trial function for the ground state of a polaron bound in a Coulomb field which yields, in the experimentally important ranges of Coulomb binding and polaron coupling constant α lower energies than have previously been reported. In distinction from earlier calculations, our ansatz gives, additionally, the correct polaron mass renormalization in the weak-binding–weak-coupling limit. For the very weakly bound polaron, our trial function is not continuous in α; a discontinuity occurs at $6.25<\alpha<6.5$. We speculate that this discontinuity is associated with a long conjectured breakdown of perturbation theory for the free-polaron ground state near $\alpha=6$. Methods for evaluating the perturbed bound-polaron ground-state energy for weak coupling are discussed.

INTRODUCTION

An electron bound to a hydrogenic impurity center in a polar lattice will experience, in the effective-mass approximation, not only the screened central Coulomb attraction of the impurity but also additional forces due to the lattice polarization charge induced by the electron. Such bound systems are customarily treated by invoking the Born-Oppenheimer approximation, in which one assumes that the electron-lattice wave functions have the product form

$$\psi_e(\mathbf{r})\Phi_L, \tag{1}$$

where ψ_e depends only upon the electron coordinate $\mathbf{r}$, and Φ_L, the lattice-wave function, is independent of $\mathbf{r}$.

We know, however, that a free slowly propagating electron in a polar lattice carries lattice polarization along with it, and that the mean value of the induced lattice polarization at some point $\mathbf{r}_L$ is a function of $\mathbf{r}_L-\mathbf{r}$.[1] Wave functions of the form (1) clearly could not describe such a situation. We expect, therefore, that (1) will not accurately describe cases in which the electron is only weakly bound to the impurity center (either because the binding potential is weak or because the electron is in an excited state of large radius). In such cases the electron barely knows that a potential is present and should carry along lattice distortion as it traverses its orbit, much as a slow freely propagating polaron does.

A major purpose of the present paper is to investigate the accuracy of the adiabatic approximation (1) for describing the ground state of the Fröhlich Hamiltonian with a Coulomb potential added. Taking $\psi_e(r)$ to be the Coulomb $1S$ state with Bohr radius optimized variationally, we vary Φ_L to produce minimum energy. We expect the energy so obtained, E_{PA}, to lie only slightly higher than the lowest energy attainable from the product ansatz (Born-Oppenheimer) wave function (1) when the Coulomb Rydberg divided by the LO phonon energy is not much smaller than the electron-phonon coupling constant α. Various wave functions are introduced to compete with (1), the most general of which has enough parameters so that it not only can assume the form (1) but also can describe accurately the motion of an almost-free slow polaron in a $1S$ orbit.

Using this wave function we have made a numerical study of the self-trapping of a polaron in a fixed, extremely weak Coulomb field. We find that for small α the radius of the ground-state wave function is proportional to $(\mathrm{Ry})^{-1/2}$ as in the hydrogen atom and is therefore very large. However, when α exceeds a certain critical value (~ 6), the wave function *abruptly* shrinks (self-traps) to an orbit radius which is determined essentially by α and not by Ry. We are clearly observing in the language of polaron theory a sudden transition from the weak coupling to the strong coupling form of the polaron wave function.

Results of Buimistrov and Pekar (BP)[2] and Platzman,[3] the two previously published variational calculations, are discussed and compared to our best energies; the BP ansatz turns out to be a special case of the wave function used here.

We begin by discussing briefly two approaches for evaluating the simplest perturbative expression for the ground-state energy of an electron bound in a Coulomb field and interacting only weakly with the LO phonons. Although unable to obtain an energy expression valid for all Ry even in this limit, we suggest that Platzman's lowest-order result for small Ry is correct and indicate a calculational procedure which might be useful for large Ry.

PERTURBATION THEORY

The Fröhlich Hamiltonian for an electron in the conduction band of an ionic crystal acted on by an attractive Coulomb center can be written in dimensionless form [energy in units of the optical-phonon energy $\hbar\omega$,

* Work sponsored by the U. S. Air Force.

[1] See, for example, Frölich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950). The result obtained on p. 232 there is essentially correct well beyond the weak-coupling regime $\alpha\ll 1$, but is probably not valid for $\alpha\gtrsim 6$.

[2] V. M. Buimistrov and S. I. Pekar, Zh. Eksperim. i Teor. Fiz. **32**, 1193 (1957) [English transl.: Soviet Phys.—JETP **5**, 970 (1957)].

[3] P. M. Platzman, Phys. Rev. **125**, 1961 (1962).

length in units of $r_0=(\hbar/2m\omega)^{1/2}$ where m=band mass],

$$\begin{aligned} H&=H_0+H_1,\\ H_0&=\hat{p}^2-\beta/r+\sum n_{\mathbf{k}},\\ H_1&=\sum v_k(e^{-i\mathbf{k}\cdot\mathbf{r}}b_{\mathbf{k}}^{\dagger}+e^{i\mathbf{k}\cdot\mathbf{r}}b_{\mathbf{k}}), \end{aligned} \tag{2}$$

where, using notation slightly different from Platzman's,

$$\beta^2/4=R=\text{Ry/optical-phonon energy}=me^4/2\epsilon_0^2\hbar^3\omega,$$
$$v_k=(4\pi\alpha r_0^3/\Omega)^{1/2}1/k,\quad n_{\mathbf{k}}=b_{\mathbf{k}}^{\dagger}b_{\mathbf{k}},$$

and $b_{\mathbf{k}}^{\dagger}$ is the creation operator for a LO phonon of wave vector $\mathbf{k}$.

From (2) it is clear that the eigenvalues of H can be regarded as functions of the two dimensionless parameters R and α. In order to gain some insight into the R dependence of the ground-state energy, E_{GS}, for small α, we might try to calculate E_{GS} from second-order Rayleigh-Schrödinger perturbation theory using H_1 as a perturbation on the eigenfunctions of H_0. This procedure, found successful in obtaining an accurate ground-state energy in the free-polaron case ($R=0$) for $\alpha\lesssim 1$, would be expected to be quite accurate for $R\neq 0$ in the same range of α. Denoting the unperturbed levels of an electron in a Coulomb field by E_n, we obtain for the lowest-order shift in the ground-state energy

$$\begin{aligned} E_{GS}&=E_0+\Delta E_2,\\ \Delta E_2&=-\sum_{\mathbf{k}}\sum_{n}\frac{|M_{n0}(\mathbf{k})|^2}{E_n-E_0+1}, \end{aligned} \tag{3}$$

where

$$\begin{aligned} M_{n0}(\mathbf{k})&=v_k\langle\phi_n|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_0\rangle,\\ E_0&=-R,\ (\hat{p}^2-\beta/r)|\phi_n\rangle=E_n|\phi_n\rangle \end{aligned}$$

and the sum is over both discrete and continuum intermediate states.

Unfortunately (3) appears to be extremely difficult to evaluate exactly. Platzman attempted an approximate evaluation by replacing the energy denominator in (3) by an expression obtained by iterating the identity

$$\frac{1}{E_n-E_0+a}=\frac{1}{k^2+a}-\frac{E_n-E_0-k^2}{k^2+a}\left(\frac{1}{E_n-E_0+a}\right) \tag{4}$$

and then truncating to remove the term containing the factor $1/(E_n-E_0+a)$. (The constant a in our case equals 1.)

Following this procedure, one can establish the inequality[4]

$$-\Delta E_2>W\equiv\alpha(1+\tfrac{1}{6}R-\tfrac{1}{3}R^2), \tag{5}$$

where ΔE_2 is the exact correction to the unperturbed ground-state energy, $-R$, in second-order Rayleigh-Schrödinger perturbation theory. Platzman has conjectured that

$$\lim_{R\to 0}(-\Delta E_2)=W+O(R^3). \tag{6}$$

Comparison of W with the variational results to be described suggests that W is not a particularly accurate approximation to $-\Delta E_2$ even for R as small as 0.1. A much better approximation to the variational ground-state energy for $\alpha<1$ and $R\lesssim 4$ is

$$-\alpha-(1+\tfrac{1}{6}\alpha)R, \tag{7}$$

which is just the simple weak-coupling effective-mass result.

Finally, we note that the expansion (4) leads to the upper bound

$$-\Delta E_2<\alpha(1+\tfrac{2}{3}R) \tag{8}$$

first derived by Platzman. As might be expected (5) and (8) do not bracket $-\Delta E_2$ very closely for $R\gtrsim 1$.

A second method for evaluating (3) is based on the procedure adopted by Dalgarno[5] and co-workers for calculating the perturbation of hydrogenic levels by a weak external potential. The idea of the method as applied to evaluating (3) is to find a function $f(\mathbf{r})$ such that for all intermediate states $|\phi_n\rangle\neq|\phi_0\rangle$

$$\frac{\langle\phi_n|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_0\rangle}{E_n-E_0+a}=\langle\phi_n|f(\mathbf{r})|\phi_0\rangle. \tag{9}$$

Once $f(\mathbf{r})$ is found, (3) is evaluated immediately using completeness; we obtain

$$\begin{aligned} \Delta E_2=&-\langle\phi_0|e^{-i\mathbf{k}\cdot\mathbf{r}}f(\mathbf{r})|\phi_0\rangle+\langle\phi_0|f(\mathbf{r})|\phi_0\rangle\langle\phi_0|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_0\rangle\\ &-|\langle\phi_0|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_0\rangle|^2/a. \end{aligned} \tag{10}$$

The partial-differential equation satisfied by $f(\mathbf{r})$ is obtained by observing that for $n\neq 0$

$$\begin{aligned} (E_n-E_0)\langle\phi_n|f(\mathbf{r})|\phi_0\rangle&=\langle\phi_n|[(H_0-\textstyle\sum n_{\mathbf{k}}),\ f(\mathbf{r})]|\phi_0\rangle\\ &=\langle\phi_n|(-\nabla^2 f(\mathbf{r})-2\nabla f(\mathbf{r})\cdot\nabla)|\phi_0\rangle, \end{aligned}$$

so that multiplying (9) by E_n-E_0+a and using the fact that $|\phi_0\rangle=\text{const}\times e^{-\beta r/2}$, we obtain

$$\langle\phi_n|\left[-\nabla^2 f(\mathbf{r})+\beta\frac{\partial f(\mathbf{r})}{\partial r}+af(\mathbf{r})\right]|\phi_0\rangle=\langle\phi_n|e^{-i\mathbf{k}\cdot\mathbf{r}}|\phi_0\rangle.$$

This equation is satisfied for all n if

$$-\nabla^2 f(\mathbf{r})+\beta\frac{\partial f(\mathbf{r})}{\partial r}+af(\mathbf{r})=e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{11}$$

Thus, in the Dalgarno approach we substitute the problem of solving (11) for the problem of summing (3). Unfortunately, (11) itself appears to be difficult to solve exactly, although one can hope that replacing

[4] The expression for W given by Platzman has the wrong sign for the R^2 term.

[5] A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **233**, 70 (1955).

$e^{-i\mathbf{k}\cdot\mathbf{r}}$ by the first few terms in its partial-wave expansion might suffice for large R.

Bajaj and Clark[6] have suggested an approximation for small R.

Having pointed out the computational difficulties presented by even a lowest-order perturbative calculation of the ground-state energy of H, we turn now to variational methods.

VARIATIONAL CALCULATION

It has been known for a long time that a trial function of the form (1) can give an excellent free-polaron ground-state energy for $\alpha\gg1$. One expects that even for small α, (1) would also be excellent if $R\gg1$. The argument is that for $R\gg1$, the electron is tightly bound and moves very rapidly in the Coulomb well—too rapidly for the lattice to follow the instantaneous position of the electron. In that case it would seem sensible to take $\psi_e(\mathbf{r})$ in (1) to be the normalized Coulomb ground-state wave function

$$\psi_e(\mathbf{r})=(\beta_S^3/8\pi)^{1/2}e^{-\beta_S r/2}. \tag{12}$$

Making this substitution in (1), and minimizing the expectation value of H with respect to both the lattice wave function Φ_L and the variational parameter β_S after having integrated over $\mathbf{r}$ in the expectation value gives

$$\begin{aligned}\psi_{\mathrm{PA}}&=(\beta_S^3/8\pi)^{1/2}e^{-\beta_S r/2}\Phi_L,\\ E_{\mathrm{PA}}&=-R-5\alpha/16(2R^{1/2}+\tfrac{5}{16}\alpha),\end{aligned} \tag{13}$$

where

$$\Phi_L=U_{\mathrm{LS}}(F_k)\,|0\rangle,\quad F_k=-\nu_k/(1+k^2/\beta_S^2)^2,$$

$U_{\mathrm{LS}}(F_k)$ is the linear shift transformation

$$\exp[\Sigma F_k(b_k^\dagger-b_k)],$$

and

$$\beta_S=\beta+\tfrac{5}{8}\alpha. \tag{14}$$

We remark that for $\alpha\gg R$ a better trial function of the form (1) could be obtained by replacing the right-hand side of (12) by a function which cuts off more rapidly at large r (a Gaussian, for example).

For small R and α, we note that (13) does not approach the weak-coupling–weak-binding result (7), conjectured by Platzman. This is not surprising in view of our earlier intuitive discussion of the validity of (1).

We have shown previously[7] that a polaron bound in a weak slowly varying potential, $U(r)$, can be well described by the wave function

$$\exp(-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}})\phi(\hat{\mathbf{p}})\chi_n(\mathbf{r}), \tag{15a}$$

where $\hat{\mathbf{p}}$ is the electron momentum operator with eigenvalue $\hat{\mathbf{p}}$ and

$$\exp(-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}})\phi(\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{r}} \tag{15b}$$

is the exact free-polaron wave function expanded in powers of p to order p^2 ($e^{i\mathbf{p}\cdot\mathbf{r}}$ is not expanded). $\chi_n(\mathbf{r})$ satisfies

$$\left[\frac{m\hat{p}^2}{m^*}+U(r)\right]\chi_n(\mathbf{r})=E_n\chi_n(\mathbf{r}), \tag{16}$$

with m^*/m being the ratio of the polaron mass to the band mass. Physically, (15a) represents a weakly bound polaron moving in the orbit prescribed by (16).

Although, even a weak Coulomb potential ($R\ll1$) is not slowly varying near the Coulomb center, the perturbation results (5) and (6) suggest that, exercising some caution, we might usefully attempt a trial function of the form (15a).

Our choice of $\phi(\hat{\mathbf{p}})$ is the form first introduced by Haga[8]:

$$\phi_H(\hat{\mathbf{p}})=U_{\mathrm{LS}}(f_k)[1+\Sigma d_{\mathbf{k}}(\hat{\mathbf{p}})b_{\mathbf{k}}^\dagger]\,|0\rangle, \tag{17}$$

where $f_k=-\nu_k/1+k^2$. While (17) does not produce an exact free-polaron wave function when $\phi_H(\hat{\mathbf{p}})$ with $d_{\mathbf{k}}(\hat{\mathbf{p}})$ optimized variationally is inserted for $\phi(\hat{\mathbf{p}})$ in (15b), we have shown that the resulting wave function

$$e^{-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}}}\phi_H(\hat{\mathbf{p}})e^{i\mathbf{p}\cdot\mathbf{r}} \tag{18}$$

yields a ground-state energy of $-\alpha$, an effective mass, $m_H^*/m=(1+\frac{1}{12}\alpha)/(1-\frac{1}{12}\alpha)$ and a realistic energy-momentum relationship for the polaron.[9] In these latter two respects the Haga wave function is superior to the better known ansatz of Lee, Low, and Pines.[10]

Although our prescription calls for expanding $\phi_H(\hat{\mathbf{p}})$, and therefore $d_{\mathbf{k}}(\hat{\mathbf{p}})$ to order $\hat{p}^2$, it turns out to be sufficient to expand $d_{\mathbf{k}}(\hat{\mathbf{p}})$ only to order $\hat{p}$ to obtain from (18) the variational energy $E_H(p)$ given by

$$E_H(p)=-\alpha+mp^2/m_H^*. \tag{19}$$

The trial function leading to (19) for the free polaron is obtained by replacing $\phi_H(\hat{\mathbf{p}})$ in (18) by

$$U_{\mathrm{LS}}(f_k)(1+\Sigma D(k)(\mathbf{k}\cdot\hat{\mathbf{p}})b_{\mathbf{k}}^\dagger)\,|0\rangle.$$

Thus we would expect that a good trial function for the Coulomb ground state when R is not too large would be

$$\begin{aligned}\psi_H=(\beta_S^3/8\pi)^{1/2}&e^{-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}}}U_{\mathrm{LS}}(f_k)\\ &\times(1+\Sigma h(k)\mathbf{k}\cdot\hat{\mathbf{p}}b_{\mathbf{k}}^\dagger)\,|0\rangle e^{-\beta_S r/2},\end{aligned} \tag{20}$$

where the spherically symmetric function $h(k)$ and the constant β_S are to be determined variationally.

Observe that setting $h(k)=0$ and $\beta_S=\beta$ in (20) produces a product of the LLP ground-state wave function and the Coulomb $1S$ wave function, giving a

[6] K. K. Bajaj and T. D. Clark, Bull. Am. Phys. Soc. **14**, 377 (1969).

[7] D. M. Larsen, Phys. Rev. **180**, 919 (1969). Although no explicit assumptions are made on size of the coupling constant in the reference, it is suggested there that the argument leading to (15a) could break down for large enough α.

[8] E. Haga, Progr. Theoret. Phys. (Kyoto) **13**, 555 (1955).

[9] D. M. Larsen, Phys. Rev. **144**, 697 (1966).

[10] T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. **90**, 297 (1953).

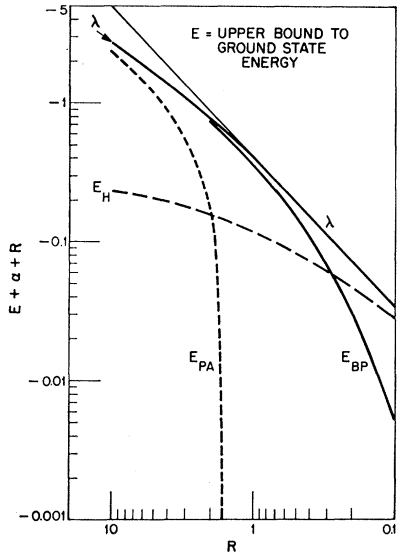

FIG. 1. Lowest ground-state energies obtainable at $\alpha=2$ from (13), (19), (23), and (30), denoted, respectively, $E_{\rm PA}$, E_H, λ, and $E_{\rm BP}$. The straight-line asymptote to $\lambda+\alpha+R$ is $E_{\rm SL}+\alpha+R$, where $E_{\rm SL}$ is the effective-mass energy given by (22).

ground-state energy of

$$-\alpha-R; \tag{21}$$

this energy is lower than (13) when

$$\alpha<(32/5)[(8/5)-R^{1/2}].$$

More generally, a product of the exact polaron ground state and the $1S$ Coulomb wave function gives the upper bound $E_{\rm GS}(\alpha)-R$ to the ground state of H, where $E_{\rm GS}(\alpha)$ is the exact free-polaron ground-state energy when the total momentum of the electron-phonon system is zero.

Comparison of the energy of (20) and (13) is made in Fig. 1 for $\alpha=2$. It is not difficult to show that in the limit $R\to 0$ the ground-state energy obtained from ψ_H is (for $\alpha<12$)

$$-\alpha-(1+\tfrac{1}{12}\alpha)/(1-\tfrac{1}{12}\alpha)R, \tag{22}$$

in agreement with (7) for small α.

In order to interpolate between the weak-binding result of (22) and the strong-binding result (13), we introduce as our final and most general trial wave function

$$\begin{aligned}\psi_{\rm BPH}&=U_{\rm LS}(F_k)\psi_H\\&=(\beta_S^3/8\pi)^{1/2}U_{\rm LS}(F_k)\exp(-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}})U_{\rm LS}(g_k)\\&\quad\times[1+\Sigma h(k)\mathbf{k}\cdot\hat{\mathbf{p}}b_{\mathbf{k}}^{\dagger}]|0\rangle e^{-\beta_S r/2},\end{aligned} \tag{23}$$

where all three spherically symmetric functions F_k, g_k, and $h(k)$ and the parameter β_S are to be varied. By inspection, if $F_k=0$, $g_k=-\nu_k/(1+k^2)$, we have $\psi_{\rm BPH}=\psi_H$; while, if $g_k=h(k)=0$, we have $\psi_{\rm BPH}=\psi_{\rm PA}$. Thus, we can expect (23) to provide a reasonable interpolation between the small R and large R limits.

Turning now to the optimization of ψ, we note that $\langle\psi|\psi\rangle$ is a functional of $h(k)$ so that $\delta\langle\psi|\psi\rangle/\delta h(k)\neq 0$. We seek to render $\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle$ stationary with respect to variations of F_k, g_k, and $h(k)$ at fixed β_S. Denoting the stationary value of this ratio by $\lambda(\beta_S)$ we require

$$\begin{aligned}&\delta(\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle)\\&\quad=\frac{1}{\langle\psi|\psi\rangle}\left(\delta\langle\psi|H|\psi\rangle-\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\delta\langle\psi|\psi\rangle\right)=0,\end{aligned}$$

hence,

$$\delta\langle\psi|H-\lambda(\beta_S)|\psi\rangle=0. \tag{24}$$

Thus, solving (24) gives us an optimized wave function and energy $\lambda(\beta_S)$ for each β_S. The variational ground-state energy λ is found by choosing β_S to minimize $\lambda(\beta_S)$.

Evaluating the expectation values in (24) is straightforward but tedious. Noting from (23) that we can introduce a unitary operator U such that

$$\psi=U|\theta\rangle,$$

where

$$\begin{aligned}U&=U_{\rm LS}(F_k)\exp(-i\mathbf{r}\cdot\Sigma\mathbf{k}n_{\mathbf{k}})U_{\rm LS}(g_k),\\|\theta\rangle&=[1+\textstyle\sum h(k)\mathbf{k}\cdot\hat{\mathbf{p}}b_{\mathbf{k}}^{\dagger}|0\rangle](\beta_S^3/8\pi)^{1/2}e^{-\beta_S r/2},\end{aligned}$$

we compute $U^{-1}HU=\mathfrak{IC}$. We drop terms in $\mathfrak{IC}$ which do not contribute to $\langle\theta|\mathfrak{IC}|\theta\rangle$, thereby producing $\tilde{\mathfrak{IC}}$, satisfying

$$\langle\theta|\tilde{\mathfrak{IC}}|\theta\rangle=\langle\theta|\mathfrak{IC}|\theta\rangle,$$

where

$$\begin{aligned}\tilde{\mathfrak{IC}}=&E_0+\hat{p}^2+(\textstyle\sum\mathbf{k}n_{\mathbf{k}})^2+\sum n_{\mathbf{k}}-\beta/r\\&+\textstyle\sum[\nu_k+(1+k^2)g_k](b_{\mathbf{k}}^{\dagger}+b_{\mathbf{k}})\\&+\textstyle\sum F_k(e^{i\mathbf{k}\cdot\mathbf{r}}b_{\mathbf{k}}^{\dagger}+e^{-i\mathbf{k}\cdot\mathbf{r}}b_{\mathbf{k}})+2\sum(\nu_k+g_k)F_k\cos\mathbf{k}\cdot\mathbf{r}\\&-2\hat{\mathbf{p}}\cdot\textstyle\sum\mathbf{k}g_k(b_{\mathbf{k}}^{\dagger}+b_{\mathbf{k}})+2\sum\mathbf{k}\cdot\mathbf{l}g_kg_lb_{\mathbf{k}}^{\dagger}b_1,\end{aligned} \tag{25a}$$

$$E_0=\textstyle\sum[f_k^2+(1+k^2)g_k^2+2\nu_kg_k]. \tag{25b}$$

The expectation values are

$$\begin{aligned}\langle\theta|\tilde{\mathfrak{IC}}|\theta\rangle=&\langle(1+2\xi)\hat{p}^2-\beta/r\rangle+E_0-\zeta\\&+\tfrac{1}{3}\textstyle\sum k^2h^2(k)(1+k^2+M-\lambda+E_0-\zeta)\langle\hat{p}^2\rangle\\&+\tfrac{1}{3}\lambda\textstyle\sum k^2h^2(k)\langle\hat{p}^2\rangle+2\xi(1+\xi)\langle\hat{p}^2\rangle\\&+\textstyle\sum k^2F_kh(k)V_k,\end{aligned} \tag{26a}$$

$$\langle\theta|\theta\rangle=1+\tfrac{1}{3}\textstyle\sum k^2h^2(k)\langle\hat{p}^2\rangle, \tag{26b}$$

where if A is an operator, $\langle A\rangle$ denotes $(\beta_S^3/8\pi)\int d\mathbf{r}\times e^{-\beta_S r/2}Ae^{-\beta_S r/2}$ and

$$\begin{aligned}&\xi=-\tfrac{1}{3}\textstyle\sum k^2g_kh(k),\\&\zeta=-2\textstyle\sum(\nu_k+g_k)F_kV_k,\quad V_k=\langle\cos\mathbf{k}\cdot\mathbf{r}\rangle,\\&M=\langle\mathbf{k}\cdot\hat{\mathbf{p}}(\hat{p}^2-\beta/r)\mathbf{k}\cdot\hat{\mathbf{p}}\rangle/(\tfrac{1}{3}k^2\langle\hat{p}^2\rangle)=-\tfrac{1}{2}\beta\beta_S+\tfrac{1}{4}5\beta_S^2.\end{aligned} \tag{27}$$

In deriving (26a), we have repeatedly exploited the assumed spherical symmetry of F_k, g_k, and $h(k)$ and, in

addition, have used the relation

$$\sum h^2(k)\langle \mathbf{k}\cdot\hat{\mathbf{p}}(\cos\mathbf{l}\cdot\mathbf{r})\mathbf{k}\cdot\hat{\mathbf{p}}\rangle/\langle\cos\mathbf{l}\cdot\mathbf{r}\rangle=\gamma=\tfrac{1}{3}\sum k^2h^2(k)\langle\hat{p}^2\rangle.$$

Setting

$$\frac{\delta\langle\theta|(\tilde{\mathcal{H}}-\lambda(\beta_S))|\theta\rangle}{\delta F_k}=\frac{\delta\langle\theta|(\tilde{\mathcal{H}}-\lambda(\beta_S))|\theta\rangle}{\delta g_k}=\frac{\delta\langle\theta|(\tilde{\mathcal{H}}-\lambda(\beta_S))|\theta\rangle}{\delta h(k)}=0,$$

gives

$$\begin{aligned}&[1+k^2+E_0+M-\zeta-\lambda(\beta_S)]h(k)\\&\qquad=2(1+\xi)g_k-\tfrac{3}{2}F_kV_k/\langle\hat{p}^2\rangle,\\&F_K=-(\nu_k+g_k)V_k-\tfrac{1}{2}k^2h(k)V_k/(1+\gamma),\\&(1+k^2)g_k=-\nu_k-F_kV_k+\tfrac{2}{3}(1+\xi)k^2h(k)\langle\hat{p}^2\rangle/(1+\gamma).\end{aligned}\tag{28}$$

Using (27) and $\langle\theta|(\tilde{\mathcal{H}}-\lambda(\beta_S))|\theta\rangle=0$, we obtain after some computation

$$\begin{aligned}\lambda(\beta_S)=&(1+2\xi)\tfrac{1}{4}\beta_S^2-\tfrac{1}{2}\beta\beta_S-\tfrac{1}{2}[(1+\xi)\xi/(1+\gamma)]\beta_S^2-\alpha\\&+\sum\nu_k[g_k+\nu_k/(1+k^2)]-\sum\nu_k(g_k+\nu_k)V_k^2\\&-[1/2(1+\gamma)]\sum k^2h(k)(\nu_kV_k^2-\gamma F_kV_k).\end{aligned}\tag{29}$$

Equations (28) are easily solved in terms of the unknown constants E_0, ζ, ξ, γ, and $\lambda(\beta_S)$. These constants are determined in turn from (25b), (27), and (29). For performing the numerical calculations, we convert all sums to integrals, guess an initial set of values for the constants and from the algebraic solution of (28) compute a set of new values. Using this new set of values, we repeat the process until the computed value of $\lambda(\beta_S)$ becomes stable. In practice we find only a few iterations are necessary. Values of $\lambda(\beta_S)$ are computed in this way for a number of values of β_S and the lowest λ obtained is taken as the approximate ground-state energy.

A very interesting special case occurs when we set $h(k)=0$ in (23) but allow F_k and g_k to vary freely. We obtain an energy

$$\begin{aligned}&E_{\mathrm{BP}}(\beta_S)=-\alpha+\tfrac{1}{4}\beta_S^2-\tfrac{1}{2}\beta\beta_S-2\alpha\vartheta(\beta_S)/\pi,\\&\vartheta(\beta_S)=\beta_S^4\int_0^\infty du\frac{V^2u^4}{(1-V^2+\beta_S^2u^2)(1+\beta_S^2u^2)},\end{aligned}\tag{30}$$

where $V^2=1/(1+u^2)^4$.

$E_{\mathrm{BP}}(\beta_S)$ turns out to be precisely the energy expression which BP would have found had they used a $1S$ electronic wave function instead of a Gaussian.[11] Basically, then, the BP ansatz can be considered a special case of our final ansatz (23).

[11] R. C. Brandt and F. C. Brown, Phys. Rev. **181**, 1241 (1969). The expression quoted by these authors is, in our notation,

$$E_{\mathrm{BP}}(\beta_S)=\tfrac{1}{4}\beta_S^2-\tfrac{1}{2}\beta_S\beta-\tfrac{5}{16}\alpha\beta_S-\frac{2\alpha\beta_S}{\pi}\int_0^\infty du\frac{[1-V^2]^2}{1-V^2+\beta_S^2u^2},$$

which is equivalent to (30).

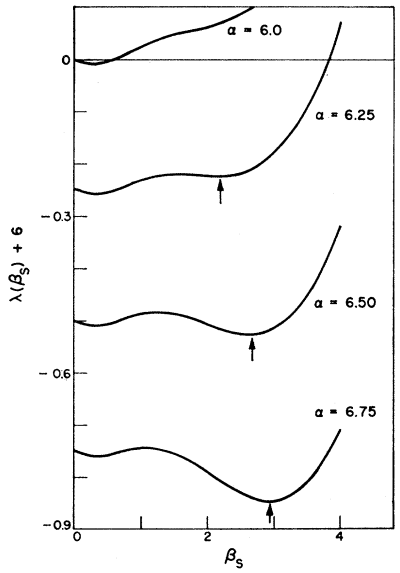

FIG. 2. Dependence of polaron ground-state energy on β_S in the transition region between weak and strong coupling. Arrows indicate relative minima associated with the formation of the small radius (large β_S) strong coupling state. $\lambda(\beta_S)$ is computed from (27), (28), and (29) at fixed β_S and $R=0.0025$.

It is important to note from (30) that because $\lim\vartheta(\beta_S)=0(\beta_S^4)$ as $\beta_S\to 0$ the BP ansatz does not renormalize the bare mass at all. Thus, BP is essentially a strong-field ansatz, although, as is evident from Fig. 1, much better for intermediate values of R than the product ansatz (13).

In Fig. 1 we compare (for $\alpha=2$) E_{PA}, E_{H}, E_{BP} and λ, each energy having been evaluated at its own optimum value of β_S. As expected, λ approaches E_{PA} for $R\gg1$ and E_{H} for $R\ll1$, remaining lower than either of these variational energies over the whole range of R. We observe that, over a remarkably large range of R, λ is given by the effective-mass expression

$$\lambda\cong-\alpha-[(1+\tfrac{1}{12}\alpha)/(1-\tfrac{1}{12}\alpha)]R.\tag{31}$$

To gain some insight into the transition between the weak coupling and strong coupling polaron we investigate the ground-state energy and wave function as a function of α for $R\ll1$. For values of α obeying $6.25\leq\alpha\leq11$, we find that the graph of $\lambda(\beta_S)$ versus β_S shows *two* distinct relative minima for fixed, small R (see Fig. 2). One of the minima, occurring at $\beta_S\cong[(1+\frac{1}{12}\alpha)/(1-\frac{1}{12}\alpha)]\beta$, is given by (31). We call this the weak coupling minimum. Since $R\ll1$, both β and β_S are small and the wave function is spread out. The second minimum invariably occurs at a much larger value of β_S, a value which is relatively insensitive to R. The energy corresponding to this minimum is very different from (31), varying like

$$\lambda\sim-C_0(\alpha)-C_1(\alpha)R^{1/2},\tag{32}$$

where $C_0(\alpha)$ and $C_1(\alpha)$ are positive.

To understand the meaning of (32) consider the ground-state wave function for the free polaron in the strong coupling limit. We assume this can be written in the form[12]

$$\psi_e(|\mathbf{r}-\mathbf{r}_0|)\Phi_L, \tag{33}$$

where ψ_e is a localized electronic wave function centered on $\mathbf{r}_0$. Since the energy of the free polaron in a continuum model is independent of where its wave function is centered, the states (33) with different $\mathbf{r}_0$ are degenerate. If we now turn on a very weak Coulomb potential the degeneracy is broken—the state with $\mathbf{r}_0$ located on the Coulomb center having the lowest energy. Treating the Coulomb term $-\beta/r(=-2R^{1/2}/r)$ as a perturbation, we take its expectation value in (33) with $\mathbf{r}_0=0$ and obtain for the perturbed energy the expression (32) with $-C_0(\alpha)$ the free-polaron ground state and $C_1(\alpha)$ a positive function which increases with α. Thus, we conclude that (32), and therefore the energy of the minimum at larger β_S, is characteristic of a strong coupling wave function.

Examining Fig. 2 we see that as α increases from 6 at fixed small R, a strong coupling relative minimum begins to form, becoming deeper with increasing α until it finally exceeds in depth the weak coupling minimum. At this point the ground-state wave function shifts abruptly from weak coupling to strong coupling form.

This behavior suggests that the transition between the weak and strong coupling free polaron may not be continuous in α. If, as is generally believed, the strong coupling energy of the free-polaron ground state approaches[13] $-A\alpha^2-B$, as $\alpha\rightarrow\infty$, then the perturbation expansion of the polaron ground-state energy in powers of α, $P(\alpha)$, must have a finite radius of convergence. This follows from the fact that if $P(\alpha)$ has an infinite radius of convergence, then $P(z)-Az^2-B$ would be everywhere analytic and therefore everywhere zero. But this would imply $P(\alpha)=-A\alpha^2-B$, which is not so, since we know, for example, that $\lim_{\alpha\rightarrow 0}P(\alpha)=-\alpha$.

In fact it has been conjectured that perturbation theory breaks down near $\alpha=6$. Thus, it is not unreasonable that we should find that the ground-state wave function of the weakly bound polaron is not a continuous function of α in this region. We must emphasize, however, that the discontinuity in our variational trial function does not imply that the true ground-state wave function is likewise discontinuous in α. Our result is only suggestive.

In the limit $\alpha\rightarrow\infty$, $R\rightarrow 0$ Platzman has obtained[3]

$$E=-K_0(\alpha)-K_1(\alpha)R \tag{34}$$

from his adaptation of the Feynman theory to the Coulomb problem. This result resembles (31) and not (32). From the perturbation argument given earlier it seems clear that (32) has the correct field dependence as $\alpha\rightarrow\infty$, $R\rightarrow 0$. Thus, Platzman's theory seems to give a qualitatively incorrect behavior for the energy of the weakly bound strong coupling polaron.

We have compared λ from (29) with Platzman's tabulated results for parameters pertinent to CdS over the range $0.46\leq\alpha\leq 0.7$. In every case we found λ to be somewhat more than 10% lower than the corresponding energy of Platzman. As Platzman has pointed out, a basic defect of the Feynman method for this problem resides in the seemingly unavoidable use of a Gaussian approximation for the Coulomb wave function.

We have argued that if for given α, the free-polaron wave function has the form (33), then, at the same value of α, the weakly bound polaron ($R\rightarrow 0$) likewise can be represented by (33). The fact that (33) does not give the lowest ground-state energy in our calculation for small R and $\alpha<6$, suggests, therefore, that the adiabatic assumption, conjectured for $\alpha<6$ by Kartheuser and co-workers,[14] is incorrect for this range of α. Thus, we would not expect to find peaked free-polaron absorption spectra in materials with $3\lesssim\alpha<6$ as suggested by those authors.

[12] Wave functions of the form (33) give the lowest variational energy yet obtained for the free-polaron ground state in the limit $\alpha\rightarrow\infty$ (see Ref. 13, especially p. 450).

[13] G. R. Allcock, Advan. Phys. **5**, 412 (1956).

[14] E. Kartheuser, R. Evrard, and J. Devreese, Phys. Rev. Letters **22**, 94 (1969).