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Polarons Bound in a Coulomb Potential. II. 2*P*-State Zeeman Effect*

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Approximate polaron effective-mass trial functions are constructed to describe 2*P* hydrogenic polaron levels in weak magnetic fields. Breakdown of the effective-mass description due to level crossing of the 2*P* effective-mass states with 1*S* one-phonon states [denoted (1*S*, 1)] necessitates admixture of (1*S*, 1) states to the initial effective-mass state in order to achieve lowest cariational energy. The effect of mixing in the (1*S*, 1) states is to produce, effectively, a double-values 2*P* energy and to reduce considerably the linear Zeeman splitting near the point of level crossing. Level crossings with (1*S*, *n*) states for $n > 1$ are expected, on the basis of a heuristic argument, to produce similar discontinuities near the respective crossing energies. Perturbation theory is used to find expressions in the weak-coupling limit for the Zeeman splitting in the limit of weak binding, and, for stronger binding, near the (1*S*, 1) level crossing.

I. INTRODUCTION

A slowly moving electron in the conduction band of a polar crystal finds itself surrounded by lattice polarization charge induced by the electron's own Coulomb field. Treating the lattice as a polarizable continuum one can show[1] that in the simple case of a parabolic conduction band the electron-lattice (or more precisely, electron–LO-phonon) coupling strength is characterized by a dimensionless constant α, given by

$$\alpha = \frac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{(r_0 \hbar\omega)}\,, \tag{1}$$

where $r_0 = (\hbar/2m\omega)^{1/2}$. The length r_0 turns out to be essentially the radius of the polarization charge distribution surrounding the slowly moving electron (unless α is very large). This complex of electron plus polarization cloud is the so-called polaron. We have used m for the electron band mass, $\hbar\omega$ for the energy of a long-wavelength LO phonon, and ϵ_∞ and ϵ_0 for the high-frequency and static dielectric constants, respectively, of the lattice.

If α is not too large, the polaron energy, which in the absence of interaction is simply $p^2/2m$, becomes with interaction

$$E(p) = -\alpha\hbar\omega + \frac{p^2}{2m(1+\alpha/6)} - \frac{3\alpha}{160}\frac{p^4}{m^2\hbar\omega} + O\left(\frac{\alpha p^6}{m^3(\hbar\omega)^2}\right)\,. \tag{2}$$

Thus, carriers in a nominally parabolic conduction band will behave as if the band were, in fact, nonparabolic, due to the terms in (2) proportional to p^4, p^6, etc.

Polaron-induced nonparabolicity has been clearly demonstrated by cyclotron-resonance experiments in InSb[2,3] and CdTe.[4] In these experiments, the magnetic analog of $E(p)$ is probed by measuring the $n = 0$ to $n = 1$ Landau-level energy separation as a function of magnetic field.

Perhaps the most striking aspect of polaron nonparabolicity is the pinning phenomenon[5] observed at fields large enough to bring the unperturbed ($\alpha = 0$) cyclotron frequency close to ω. At such fields, the cyclotron resonance appears to split into two branches, one always lying above $\hbar\omega$ in energy, the other always below. The lower-branch energy approaches $\hbar\omega$ with increasing field, while at the same time the upper-branch frequency becomes close to the unperturbed cyclotron frequency.

We describe the lower-branch behavior by saying that the $n=1$ Landau-level energy becomes pinned to the $n=0$ energy plus $\hbar\omega$. Likewise, the upper branch becomes pinned in weak magnetic fields.

The pinning phenomenon just described for polaron Landau levels is expected on theoretical grounds to have an analog for any pair of discrete polaron states which, for $\alpha=0$, are separated by an energy close to $\hbar\omega$. An important special case is the 1*S* and 2*P* states of hydrogenic donors in some of the II-VI semiconductors. We expect to find the 2*P* level split into two components when the hydrogenic Rydberg $\mathcal{R}$ obeys

$$\text{unperturbed } 1S-2P \text{ energy difference} = \tfrac{3}{4}\mathcal{R} \cong \hbar\omega \tag{3}$$

much as the $n=1$ Landau level is split when the unperturbed cyclotron frequency lies close to ω. In addition, the Zeeman splitting in a magnetic field of each of the two components of the LO-phonon-split 2*P* level can be profoundly affected by the electron–LO-phonon interaction. This effect is a major subject of the present investigation.

The experimental motivation for the study of the polaron Zeeman effect is the observation by Brandt[6] and co-workers that the AgBr Zeeman mass, that is, the mass associated with the orbital Zeeman splitting of the strong *S* to *P* transition in AgBr, is ~19% higher than the measured cyclotron mass in this polar insulator. In the parabolic-band picture, the orbital Zeeman mass is equal to the cyclotron mass, as we shall show. Unfortunately, the transition observed by Brandt could not be attributed to a simple hydrogenic donor; the exact nature of the underlying states is not understood at this writing, although the hydrogenic model appears to be qualitatively correct.

The Hamiltonian for an electron in the Coulomb field of a donor impurity ion subjected to a uniform magnetic field in the *z* direction can be written

$$H_{\text{el}} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\epsilon_0 r} + \tfrac{1}{2}\omega_c L_z + \tfrac{1}{8} m\omega_c^2 (x^2+y^2) , \tag{4}$$

where ω_c is the cyclotron frequency $e\mathcal{H}_{\text{mag}}/mc$ in the field $\mathcal{H}_{\text{mag}}$, and L_z is the *z* component of the orbital angular momentum, given by

$$L_z = (x\hat{p}_y - y\hat{p}_x) = \frac{\hbar}{i}\frac{\partial}{\partial\phi} , \tag{5}$$

where ϕ is the polar angle in circular cylindrical coordinates.[7] Since L_z commutes with H_{el}, we can take the eigenfunctions of H_{el} to be simultaneously eigenfunctions of L_z. These eigenfunctions have the form

$$\chi_{n,M}(\vec{r}) = e^{iM\phi}\psi_n(\rho, z) ,$$

where $\rho = (x^2+y^2)^{1/2}$. Writing $\hat{p}^2$ in the form

$$\hat{p}^2 = -\left(\frac{\partial}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial z^2}\right) ,$$

we see by inspection that if $\chi_{n,M}(\vec{r})$ is an eigenfunction of H_{el} with eigenvalue $E_{n,M}$, then $\chi_{n,-M}(\vec{r}) = e^{-iM\phi} \times \psi_n(\rho, z)$ is likewise an eigenfunction but with eigenvalue $-M\hbar\omega_c + E_{n,M}$. Thus, for example, the frequency separation between the $M=\pm 1$ components of the hydrogenic 2*P* state in a magnetic field is just the cyclotron frequency.

This result, derived for the simple parabolic-band case, does not hold for nonparabolic bands. In particular, when polaron nonparabolicity is important, one expects to observe a shift of the Zeeman splitting from the cyclotron splitting at the same field. In fact, different *P* levels will have different Zeeman splittings. Conventionally, m_c, the cyclotron mass at the bottom of the band, is defined by

$$\frac{1}{m_c} \equiv \lim_{\mathcal{H}_{\text{mag}}\to 0} \frac{[\mathcal{E}_{\text{Lnd}}(1) - \mathcal{E}_{\text{Lnd}}(0)]c}{\hbar e \mathcal{H}_{\text{mag}}} , \tag{6}$$

where $\mathcal{E}_{\text{Lnd}}(N)$ is the energy at the bottom of the *N*th Landau band. Likewise, the "Zeeman mass" m_z for the 2*P* state can be defined as

$$\frac{1}{m_z} = \lim_{\mathcal{H}_{\text{mag}}\to 0} \frac{(\mathcal{E}_{+1} - \mathcal{E}_{-1})c}{\hbar e \mathcal{H}_{\text{mag}}} , \tag{7}$$

where $\mathcal{E}_M$ is the energy of the 2*P* state[8] with $M=\pm 1$.

In this paper, we attempt to calculate the energies $\mathcal{E}_M$, and thereby, the linear Zeeman splitting of the 2*P* state of a polaron bound to a fixed Coulomb center in a weak magnetic field.

Because the essential qualitative features of the bound-polaron problem for moderate electron–LO-phonon coupling strengths can be understood by treating this coupling as a small perturbation, we first explore polaron corrections to the 2*P* levels in second-order perturbation theory. Expressions for the perturbed energy are obtained for weak binding and for binding strong enough to produce level crossing. Arguing that the 2*P* states can be well described by polaron effective-mass wave functions (when the binding is not very strong) except near the level-crossing region, we construct approximate polaron 2*P* effective-mass trial functions and study the variational energies obtained. Next, we discuss the level-crossing phenomenon from a general point of view and finally produce 2*P* polaron trial functions which take account of the effect of level crossing on the 2*P* effective-mass energies. The Zeeman splitting is calculated as a function of binding from these wave functions and compared to the AgBr measurements of Brandt.

We treat this problem in the single-impurity approximation (SIA), that is, we assume that the energy levels of each impurity can be calculated as if no other impurities were present in the crystal. In the absence of electron-phonon interactions, this approximation can be justified if the wave functions of electrons bound to nearest-neighbor impurity centers have, on the average, very small overlap. However, with electron–LO-phonon interaction present, it is not clear how dilute the impurities have to be before the SIA is valid, because several additional physical effects are possible at nonzero impurity density. These include (a) renormalization and broadening of the phonon levels themselves (the latter effect due to elastic scattering of phonons from impurity electrons), (b) broadening of impurity levels in processes involving the transfer of excitation from one site to another via virtual emission and absorption of phonons, and (c) shift in impurity-level energies due to forces between nearby impurities arising from the exchange of virtual phonons. One expects that processes (a) and (b) will be strongly enhanced when the unperturbed single-impurity ground state and some discrete excited state (such as the 2P state) are separated by an energy close to $\hbar\omega$.

A number of dimensionless parameters will be introduced in this paper. Some of these are α, dimensionless Fröhlich electron-phonon coupling constant [see (1)]; $\beta = 2(\mathcal{R}/\hbar\omega)^{1/2}$; $\gamma = \frac{1}{2}\hbar\omega_c/\mathcal{R}$; $\lambda^2 = \omega_c/\omega$; M, quantum number for angular momentum along the magnetic field; and $R = \mathcal{R}/\hbar\omega$.

II. PERTURBATION THEORY

A. Weak Coulomb Binding

The Fröhlich Hamiltonian for our problem in the SIA is given in polaron units by

$$\begin{aligned} H &= H_0 + H_1 + H_2 + H_3 \ , \\ H_0 &= -\nabla^2 - 2R^{1/2}/r \ , \\ H_1 &= \sum b_{\vec{k}}^{\dagger} b_{\vec{k}} + \tfrac{1}{2}\lambda^2 L_z \ , \\ H_2 &= \sum \nu_k (e^{-i\vec{k}\cdot\vec{r}} b_{\vec{k}}^{\dagger} + \text{h. c.}) \ , \\ H_3 &= \tfrac{1}{16}\lambda^4 (x^2 + y^2) \ , \end{aligned} \tag{8}$$

where

$$\lambda^2 = \omega_c/\omega,$$

$$R = \frac{\mathcal{R}}{\hbar\omega} = \frac{1}{4}\left(\frac{e^2}{\epsilon_0 r_0}\,\frac{1}{\hbar\omega}\right)^2, \quad \nu_k = \left(\frac{4\pi\alpha}{\Omega/r_0^3}\right)^{1/2}\frac{1}{k} \ ,$$

Ω is the crystal volume, and lengths, energies, and wave vectors are in units of r_0, $\hbar\omega$, and $1/r_0$, respectively. The operator $b_{\vec{k}}^{\dagger}$ creates an LO phonon of wave vector $\vec{k}$.

Unless otherwise indicated, we will neglect H_3, since we are interested only in the linear Zeeman effect. (Terms of order ω_c^2/ω^2 and higher will be consistently neglected.)

Of course, we cannot expect to be able to calculate the eigenvalues of H or even $H - H_3$ exactly. For $\alpha \ll 1$ accurate results can be obtained by treating H_2 as a perturbation on the eigenstates of $H_0 + H_1$ in second-order perturbation theory. We expect that the perturbed energies so calculated will be qualitatively correct even for α as large as 3 or 4.

The eigenstates X_i of $H_0 + H_1$ have the form

$$X_i = \phi_i(\vec{r})\,|\vec{k}_1 \cdots \vec{k}_m\rangle \ , \tag{9}$$

where

$$|\vec{k}_1 \cdots \vec{k}_m\rangle = b_{\vec{k}_1}^{\dagger} \cdots b_{\vec{k}_m}^{\dagger}|0\rangle$$

so that X_i is an m-phonon eigenstate, and $\phi_i(\vec{r})$ is chosen to be simultaneously an eigenfunction of $-\nabla^2 - 2R^{1/2}/r$ with eigenvalue E_i and of L_z with eigenvalue M_i. Thus,

$$(H_0 + H_1)X_i = [E_i + \tfrac{1}{2}\lambda^2 M_i + m]X_i \ , \tag{10}$$

where E_0 will denote the ground-state energy $-R$ and $M_0 = 0$. Let $\phi_1(\vec{r})$ denote any of the three 2P eigenfunctions of H_0 and let

$$L_z\phi_1(\vec{r}) = M\phi_1(\vec{r}) \quad (M = \pm 1, 0) \ .$$

To find the perturbed eigenvalue corresponding to the unperturbed state $\phi_1(\vec{r})|0\rangle$ with unperturbed eigenvalue $E_{\text{RS}}(\lambda^2)$ given by

$$E_{\text{RS}}(\lambda^2) = -\tfrac{1}{4}R + \tfrac{1}{2}\lambda^2 M \ ,$$

we write for the energy correction

$$\Delta E_{\text{RS,WB}}(\lambda^2) = -\sum_{\vec{k}}\sum_{n}\nu_k^2 \times \frac{|\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle|^2}{E_n + \frac{1}{2}\lambda^2(M_n - M) - E_{\text{RS,WB}}(0) - T_{\text{RS,WB}} + 1} \ , \tag{11}$$

where the subscripts RS and WB refer, respectively, to values appropriate to Rayleigh-Schrödinger perturbation theory (RSPT) and Wigner-Brillouin perturbation theory (WB). Thus, $T_{\text{RS}} = 0$ and

$$T_{\text{WB}} = \Delta E_{\text{WB}}(\lambda^2) - \Delta E_{\text{WB}}(0) \ ,$$

which is the field-dependent part of the energy correction in WBPT. From WBPT and (11), one finds that

$$E_{\text{WB}}(\lambda^2) = -\tfrac{1}{4}R + \tfrac{1}{2}\lambda^2 M + \Delta E_{\text{WB}}(\lambda^2) \ . \tag{12}$$

Our neglect of H_3 restricts us to the weak-field range defined by

$$\gamma \equiv \frac{\lambda^2}{2R} \ll 1 \ . \tag{13}$$

We take γ fixed in the following discussion.

When $\frac{1}{4}R \ll \alpha$, we expect ΔE_{RS} to be more accurate than ΔE_{WB}, since it is known that for $R = 0$ (free polaron), ΔE_{WB} for low-lying excited states gives a much too large contribution in order α^2. On the other hand, when $\frac{1}{4}R + \frac{1}{2}\lambda^2 M$ approaches $E_0 + 1$, the energy denominator vanishes in RSPT giving a divergent energy correction. In this situation, WBPT gives a reasonable energy correction, producing the polaron-pinning phenomenon described earlier.

The Zeeman splitting using either form of perturbation theory is calculated by expanding the energy denominator of (11) giving

$$\Delta E_{\mathrm{RS,WB}}(\lambda^2) \equiv \Delta E_{\mathrm{RS,WB}}(0) + \tfrac{1}{2}\lambda^2\,\Delta E_{z,\mathrm{RS,WB}} \,, \quad (14)$$

where

$$\Delta E_{\mathrm{RS,WB}}(0) = -\sum_{\vec{k},n} \nu_k^2 \frac{|\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle|^2}{E_n - E_{\mathrm{RS,WB}}(0)+1} \,, \quad (15a)$$

$$\Delta E_{z\,(\mathrm{RS,WB})} = \sum_{\vec{k},n} \nu_k^2 \frac{|\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle|^2 \langle\phi_n|(L_z - M - (2/\lambda^2)\,T_{\mathrm{WB}})|\phi_n\rangle}{(E_n - E_{\mathrm{RS,WB}}(0)+1)^2} \,. \quad (15b)$$

In (15), $\Delta E_{\mathrm{RS,WB}}$ is simply the correction to the energy of the hydrogenic $2P$ state in the absence of magnetic field, whereas $\frac{1}{2}\lambda^2\,\Delta E_{z(\mathrm{RS,WB})}$ is the part of the correction linear in the magnetic field.

The problem of evaluating (15a) and (15b) exactly remains unsolved. For Coulomb fields sufficiently weak ($R \ll 1$), one might expect that the matrix elements $|\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle|^2$ would tend to be peaked near $E_n + \frac{1}{4}R \sim k^2$ so that (15) could be accurately evaluated by expanding the energy denominators in powers of δ_n, where

$$\delta_n \equiv E_n + \tfrac{1}{4}R - k^2 \,. \quad (16)$$

An expansion of this type was first used in the problem of bound polarons by Platzman[9] who attempted in this way to obtain the perturbed Coulomb ground-state energy as a power series in R. Application of this procedure to (15a) in complete analogy to Platzman's calculation gives in RSPT

$$\Delta E_{\mathrm{RS}}(0) = -\alpha - \tfrac{1}{6}\alpha\tfrac{1}{4}R + O(R^3) \,. \quad (17)$$

The term $-\alpha$ is the ground-state energy of the free polaron and $-\frac{1}{6}\alpha\frac{1}{4}R$ arises simply from the mass renormalization in RSPT. We find no surviving term in order R^2.

The evaluation of (15b) is not quite so straightforward. Details of the calculation are relegated to Appendix A. Here, we merely quote the result derived there for the total perturbed $2P$ energy in the weak-field–weak-binding–weak-coupling approximation:

$$E_{2P(\mathrm{RS})} = -\alpha - \tfrac{1}{4}(1+\tfrac{1}{6}\alpha)R + \tfrac{1}{2}\lambda^2(1-\tfrac{1}{6}\alpha)M - \tfrac{1}{2}\lambda^2\alpha(\tfrac{3}{80}R + \tfrac{5}{288}R^2)M \,. \quad (18)$$

The first three terms on the right-hand side of (18) are easily understood, since $-\alpha$ is the free-polaron ground-state energy in RSPT, and $-\frac{1}{4}(1+\frac{1}{6}\alpha)R$ is the binding energy of a particle of mass $m_{\mathrm{eff}} = (1+\frac{1}{6}\alpha)m$ in the $2P$ hydrogenic state. Likewise $\lambda^2(1-\frac{1}{6}\alpha)$ is the cyclotron energy of a particle of mass m_{eff}, neglecting terms of order α^2 and higher. Thus, for very weak external fields, the $2P$ energy and Zeeman splitting is characteristic of a particle whose mass m_{eff} is just the free-polaron effective mass in the weak-coupling limit.

The lowest-order correction to the simple effective-mass energy is the term $-\frac{1}{2}\lambda^2\alpha(\frac{3}{80}R)$, which can be shown to arise from nonparabolicity in the polaron energy described by the term proportional to p^4 in (2). [In our units, this term of (2) can be written $-\frac{3}{40}\alpha p^4$.] Thus, if we attempt to simplify our problem by replacing H by the effective Hamiltonian $E(\hat{\pi}) - \beta/r$ in the Schrödinger equation,

$$H\psi = E\psi \,,$$

where $\hat{\pi}^2 = -\nabla^2 + \frac{1}{2}\lambda^2 L_z$ in the weak-field case, then the term $-\frac{3}{40}\alpha\hat{\pi}^4$ in $E(\hat{\pi})$ is a small perturbation on $\hat{\pi}^2$, and its contribution to E is

$$-\tfrac{3}{40}\alpha\langle\phi_1(r)|\hat{\pi}^4|\phi_1(r)\rangle = -\tfrac{1}{2}\lambda^2\alpha(\tfrac{3}{80}R) + O(R^2) + O(\lambda^4) \,.$$

Equation (18) is probably not exact to order R^2 since contributions of this order are expected to arise additionally from terms of order δ_n^5, which have been omitted from the present calculation.

From (7) and (18), we obtain for the ratio of the bare mass to the Zeeman mass,

$$m/m_z = [1 - \tfrac{1}{6}\alpha - \tfrac{3}{80}\alpha R + O(\alpha R^2)] \,, \quad (19)$$

which is to be compared to the perturbation-theory result for the cyclotron mass[10] (or polaron mass),

$$m/m_{\mathrm{pol}} = 1 - \tfrac{1}{6}\alpha \,. \quad (20)$$

Thus, for small R, the Zeeman mass will be slightly larger than the weak-field cyclotron mass.

The foregoing calculation can be extended to order λ^4 (quadratic Zeeman effect) by following the general procedure outlined in Appendix A. Of course, the energy denominator in (11) must be modified to include the diagonal part of H_3 and expanded to order λ^4.

B. Level Crossing, Moderate Binding

A second and very important case for which (15a) and (15b) can be evaluated quite accurately occurs when energy denominators in these expressions become very small. This can only happen for the $n=0$ terms, which then become dominant. In that case, (15a) can be rewritten to good approximation in WBPT:

$$E_{\mathrm{WB}}(0) = -\frac{1}{4}R - \sum_{k} \nu_k^2 \frac{|\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_0\rangle|^2}{E_0 - E_{\mathrm{WB}}(0)+1} = -\frac{1}{4}R - \frac{C}{-R+1-E_{\mathrm{WB}}(0)} \,, \quad (21)$$

where $C=\frac{112}{6561}\alpha R^{1/2}$. As described in Ref. 6, the solution of (21), $E_{\text{WB}}(0)$, considered as a function of R, has two branches, one branch remaining always above $-R+1$, the other always below. From (15b), we find, again keeping only the $n=0$ term,

$$\Delta E_{z(\text{WB})}=-(M+\Delta E_{z(\text{WB})})/[-R+1-E_{\text{WB}}(0)]^2 ,$$

hence,

$$\Delta E_{z(\text{WB})}=-MC/\{[-R+1-E_{\text{WB}}(0)]^2+C\} . \qquad (22)$$

Thus, if $E_{\text{WB}}(0)\rightarrow -R+1$, the Zeeman splitting, which is equal to $\frac{1}{2}\lambda^2(M+\Delta E_{z(\text{WB})})$, vanishes (Zeeman mass becomes infinite). In fact, $E_{\text{WB}}(0)$ given implicitly by (21), becomes close to $-R+1$ on the lower branch at large R and on the upper branch as $R\rightarrow 0$. Clearly, the calculation for small R leading to (18) is relevant to the lower branch alone.

To provide an interpolation between the small- and large-R limit for both lower and upper branches and to extend the results to larger values of α, we turn to a variational calculation of the energy of the lowest-lying states of P symmetry belonging to $H_0+H_1+H_2$.

III. VARIATIONAL THEORY

A. Effective-Mass Trial Functions

In the absence of magnetic field ($\lambda^2=0$), the Hamiltonian H, given in (8), is invariant to rotations. Thus, the ground state[11] is spherically symmetric, and triply degenerate excited states of P symmetry can be expected.

A magnetic field in the z direction breaks the P-state degeneracy, producing magnetic eigenstates which transform as $x\pm iy$ (denoted $P_{\pm1}$) and z (denoted P_0) under proper rotations. Trial wave functions transforming as $P_{\pm1,0}$ give variational energies which are necessarily upper bounds to the exact energies of the lowest-lying eigenstates of corresponding symmetry.

To motivate our choice of a variational ansatz for the polaron $2P$ states, we recall from polaron effective-mass theory[12] that if $\theta(p)e^{i\vec{p}\cdot\vec{r}}$ is the exact free-polaron wave function expanded to order p^2, then

$$\theta(-i\vec{\nabla})\chi_n(\vec{r}) \qquad (23)$$

is the effective-mass approximation to the wave function of a polaron bound in the potential $U(r)$, provided $\chi_n(\vec{r})$ satisfies

$$[mp^2/m_{\text{pol}}+U(r)]\chi_n(\vec{r})=[E-E(0)]\chi_n(\vec{r}) , \qquad (24)$$

where m_{pol} and $E(0)$ are, respectively, the free-polaron effective mass and ground-state energy. The effective-mass approximation is good only when $U(r)$ is slowly varying in regions where $|\chi_n(r)|^2$ is not small and when the Fourier transform of $\chi_n(\vec{r})$ is strongly weighted towards low-momentum components.

For given value of R, the $2P$ states more nearly satisfy the above criteria for goodness of the effective-mass approximation than does the $1S$ state. Taking $\chi_n(\vec{r})$ to be a $2P$ state in (24) with $U(r)$ replaced by $-2R^{1/2}/r$, we find that $\chi_n(\vec{r})$ has a mean kinetic energy of only $\frac{1}{4}(m_{\text{pol}}/m)R$ as compared to $(m_{\text{pol}}/m)R$ for the $1S$ solution of (24). In addition, because $2P$ states vanish at $r=0$, where the Coulomb potential is most rapidly varying, the $2P$ state covers, on the average, a region of more slowly varying potential than does the $1S$ state.

It is important to notice, however, that (24) results from the neglect of certain terms[12] which, though they may be small, are presumably capable of connecting the state (23) to one-phonon excited states. If (23) is itself an approximate excited state – for example, if $\chi_n(\vec{r})$ is taken to be a $2P$ state – then for some values of R the terms neglected in deriving (24) may couple (23) to one-phonon states nearly degenerate with (23). In such circumstances, the coupling cannot be neglected and the simple effective-mass picture breaks down. For the moment, however, we ignore this important complication and proceed to construct an approximate version of (23).

Denoting the simple approximation to $\theta(-i\vec{\nabla})$, which has already been employed in I by $\phi(\hat{\vec{p}})$, we have

$$\begin{aligned} \phi(\hat{\vec{p}}) &= U_{LS}(f_k)\,(1+\textstyle\sum h(k)\,(\vec{k}\cdot\hat{\vec{p}})\,b^\dagger_{\vec{k}})\,|0\rangle , \\ U_{LS}(f_k) &= e^{\Sigma(f_k^* b^\dagger_{\vec{k}}-f_k b_{\vec{k}})} , \\ f_k &= -\nu_k/(1+k^2) , \end{aligned} \qquad (25)$$

where $h(k)$ is a real spherically symmetric function to be determined variationally and $\hat{\vec{p}}=-i\vec{\nabla}$.

Since both the splitting of the $2P$ states in a weak magnetic field and the zero-field energy are of interest, we generalize (25) in accordance with the discussion in Ref. 12 to take into account the possible presence of a magnetic field and write for an initial trial function $\psi_H(\vec{r},M)$

$$\begin{aligned} \psi_H(\vec{r},M) &= \phi(\hat{\vec{\pi}})\,\chi_{2P,M}(\vec{r}) , \\ \phi(\hat{\vec{\pi}}) &= e^{-i\vec{r}\circ\Sigma\vec{k}b^\dagger_{\vec{k}}b_{\vec{k}}}\,U_{LS}(f_k)\,[1+\textstyle\sum h(k)\,(\vec{k}\cdot\hat{\vec{\pi}})\,b^\dagger_{\vec{k}}]\,|0\rangle , \\ \hat{\vec{\pi}} &= (\hat{p}_x-\tfrac{1}{4}\lambda^2 y,\ \hat{p}_y+\tfrac{1}{4}\lambda^2 x,\ \hat{p}_z) , \\ \chi_{2P,\pm1}(\vec{r}) &= \tfrac{1}{32}(\beta_P^5/2\pi)^{1/2}(x\pm iy)\,e^{-\beta_P r/4} , \\ \chi_{2P,0}(\vec{r}) &= \tfrac{1}{32}(\beta_P^5/\pi)^{1/2}\,z\,e^{-\beta_P r/4} , \end{aligned} \qquad (26)$$

where both $h(k)$ and β_P are to be determined variationally.

Neglecting H_3 in (8) as before, we find

$$\langle\psi_H|(H_0+H_1+H_2)|\psi_H\rangle$$

$$
\begin{aligned}
&= \langle \hat{p}^2 - \beta/r + \tfrac{1}{2}\lambda^2 L_z - \alpha \rangle \\
&\quad + \sum (1 + k^2 - \alpha + \mathfrak{M}) \langle (\vec{k}\cdot\hat{\vec{\pi}})^2 \rangle h^2(k) \\
&\quad - 4 \sum \langle (\vec{k}\cdot\hat{\vec{\pi}})^2 \rangle h(k) f_k \\
&\quad + 2 \langle \sum_{\vec{k},\vec{l}} (\vec{k}\cdot\hat{\vec{\pi}})(\vec{l}\cdot\hat{\vec{\pi}}) h(k) h(l) f_k f_l \rangle , \qquad (27)
\end{aligned}
$$

where for any operator $\mathcal{O}$,

$$\langle \mathcal{O} \rangle \equiv \langle \chi_{2P,M}(\vec{r}) \, | \mathcal{O} | \chi_{2P,M}(\vec{r}) \rangle ,$$

$$\mathfrak{M} = \sum_{\vec{k}} \left\langle \vec{k}\cdot\hat{\vec{\pi}} \left(\hat{p}^2 - \frac{\beta}{r} + \tfrac{1}{2}\lambda^2 L_z \right) \vec{k}\cdot\hat{\vec{\pi}} \right\rangle h^2(k) \Big/ \sum \langle (\vec{k}\cdot\hat{\vec{\pi}})^2 \rangle h^2(k) ,$$

$\beta = 2R^{1/2}$. Performing the sums on $\vec{k}$, keeping in mind that $h(k)$ is spherically symmetric, we obtain

$$
\begin{aligned}
\mathfrak{M} &= \sum_{i=1}^{3} \frac{\langle \hat{\pi}_i (\hat{p}^2 - \beta/r + \frac{1}{2}\lambda^2 L_z) \hat{\pi}_i \rangle}{\langle \hat{\pi}^2 \rangle} \\
&= \tfrac{1}{24} \beta_P (3.5\beta_P - 5\beta) \left(1 - \frac{8\lambda^2 M}{\beta_P^2} \right) \\
&\quad + \lambda^2 M \left(1 - \frac{\beta}{\beta_P} \right) + O(\lambda^4) . \qquad (28)
\end{aligned}
$$

The most important point to note is that $\mathfrak{M}$ is independent of the form of $h(k)$.

If we take

$$\xi = \tfrac{1}{3} \sum k^2 h(k) f_k , \qquad (29)$$

we obtain, upon performing the $\vec{k}$ and $\vec{l}$ summations,

$$\langle \sum_{\vec{k},\vec{l}} (\vec{k}\cdot\vec{l})(\vec{k}\cdot\hat{\vec{\pi}})(\vec{l}\cdot\hat{\vec{\pi}}) h(k) h(l) f_k f_l \rangle = \xi^2 \langle \hat{\pi}^2 \rangle .$$

Thus, denoting the variational energy by E_H, we have

$$
\begin{aligned}
&\langle \psi_H \, | (H_0 + H_1 + H_2 - E_H) | \psi_H \rangle \\
&\quad = - E_H + \left\langle (1 - 2\xi) \hat{\pi}^2 - \frac{\beta}{r} - \alpha \right\rangle \\
&\qquad + \tfrac{1}{3} \sum (1 + k^2 - \alpha + \mathfrak{M} - E_H) k^2 h_k^2 \langle \hat{\pi}^2 \rangle \\
&\qquad + 2\xi(\xi - 1) \langle \hat{\pi}^2 \rangle . \qquad (30)
\end{aligned}
$$

The variational procedure to be followed is described in I. Minimizing (30) with respect to $h(k)$, treating E_H as a constant, we obtain

$$h(k) = [2(1 - \xi) f_k] / (1 + k^2 - \alpha + \mathfrak{M} - E_H) . \qquad (31)$$

Insertion of (31) into (30) and setting to zero the right-hand side of (30) gives

$$E_H = \langle (1 - 2\xi) \hat{\pi}^2 - \beta/r - \alpha \rangle . \qquad (32)$$

The expression in the expectation value of (32) is an effective-mass Hamiltonian with polaron effective mass given by

$$m_{\mathrm{eff}}/m = (1 - 2\xi)^{-1} . \qquad (33)$$

When $R \ll 1$, we have $- \alpha - E_H + \mathfrak{M} \cong 0$ so that from (31) and (29),

$$\xi = \tfrac{2}{3} \{ \sum [k^2 f_k^2 / (1 + k^2)] \} (1 - \xi) ; \qquad (34)$$

converting the sum to an integral and solving for ξ yields finally

$$
\left.
\begin{aligned}
\xi &= \tfrac{1}{12}\alpha / (1 + \tfrac{1}{12}\alpha) \;\; (\gamma \ll 1) \qquad \text{as } R \to 0 , \\
m_{\mathrm{eff}}/m &= (1 + \tfrac{1}{12}\alpha)/(1 - \tfrac{1}{12}\alpha) \qquad \text{as } R \to 0 .
\end{aligned}
\right\} \qquad (35)
$$

The mass renormalization given in (35) approaches the perturbation theory result discussed earlier as $\alpha \to 0$. Thus, for very weak magnetic and Coulomb fields, our ansatz leads to the picture of a particle with mass equal to the Haga effective mass[13] moving in the external fields. As R increases, we find that m_{eff} slowly decreases.

It is important to realize that result (35) is valid without restriction on the size of γ and, in particular, holds for the case $\gamma \to \infty$ with $\lambda^2 \ll 1$ (cyclotron resonance, no Coulomb binding). To verify this, one need merely replace $\chi_{2P,M}(\vec{r})$ in the expression for ψ_H in (25) by the appropriate eigenfunction of $\hat{\pi}^2 - \beta/r$, take the expectation value of the full Hamiltonian H in ψ_H, and observe that in the limit $R \to 0$, $\mathfrak{M} = O(\lambda^2)$. This means that, from (29) and (31), $\mathfrak{M}$ contributes to the energy in order λ^4. In this way, we obtain the cyclotron resonance effective-mass result

$$E_H = \langle (1 - 2\xi) \hat{\pi}^2 - \alpha \rangle_{\mathrm{CR}} + O(\lambda^4) \;\; (\gamma \to \infty) \quad \text{as } R \to 0 ,$$

where $\langle\,\rangle_{\mathrm{CR}}$ denotes expectation value in a low-lying normalized eigenstate of $\hat{\pi}^2$, and

$$(1 - 2\xi)^{-1} = (1 + \tfrac{1}{12}\alpha)/(1 - \tfrac{1}{12}\alpha)$$

in accordance with (33) and (35).

A more complete account of the cyclotron-resonance problem will be given in a future publication.

Turning back to the problem at hand, we note that the optimum value of β_P in the ansatz (26) is given by

$$\beta_P = \beta/(1 - 2\xi) \qquad (36)$$

and

$$E_H = - \tfrac{1}{4} (1 - 2\xi)^{-1} R + (1 - 2\xi) M \lambda^2 - \alpha + O(\lambda^4) . \qquad (37)$$

Of course, ξ is a function of $\alpha, R,$ and λ^2 in general. Thus, it is possible to ask whether in the limit $\alpha \to 0$, E_H approaches $E_{2P(\mathrm{RS})}$ given in (18). From (31), (37), (36), (29), and (28), we find that

$$\mathfrak{M} = - \tfrac{1}{4} R + \tfrac{1}{2} M \lambda^2 + O(\alpha) ,$$

so that

$$- \alpha + \mathfrak{M} - E_H = O(\alpha) ;$$

hence, (34) is correct to order α regardless of how large R or λ^2 may be. This means that E_H does not contain nonparabolic terms of the form $\alpha R\lambda^2$ or $\alpha R^2\lambda^2$. To produce such terms in the variational theory, it would be necessary, presumably, to improve ψ_H by introducing additional terms into $\phi(\hat{\vec{\pi}})$ [see (26)] involving higher powers of $\vec{k}\cdot\hat{\vec{\pi}}$. Certainly, the inaccurate treatment of nonparabolic effects is one of the weaknesses of our variational approach. Hopefully, these terms are not large for $R < 2$.

Numerical solutions for E_H are easily computed by iteration from initial guesses for E_H and ξ.

It is of some interest to compare E_H with the energy of a trial function closely related to the Buimistrov ansatz[14] for the lowest-lying odd-parity state of $H_0 + H_1 + H_2$ with zero magnetic field.

The Buimistrov-type ansatz we use is

$$U_{LS}(F_{\vec{k}}) \exp - i\vec{r}\cdot\sum \vec{k} n_{\vec{k}} U_{LS}(g_{\vec{k}}) \,|0\rangle \chi_{2P,0}(\vec{r}) \; , \quad (38)$$

where the functions $F_{\vec{k}}$ and $g_{\vec{k}}$ are determined variationally with no restriction as to symmetry; β_P in $\chi_{2P,0}$ is also varied. Buimistrov himself used a normalized function of the form $ze^{-\beta_P r^2}$ instead of $\chi_{2P,0}(r)$. The Gaussian ansatz is, however, inferior to (38) in the range of α and R of interest here. Because optimal $F_{\vec{k}}$ and $g_{\vec{k}}$ for (38) are not spherically symmetric, the wave function (38) producing lowest energy does not have pure P symmetry. Thus, it is not surprising that substituting $\chi_{2P,1}(\vec{r})$ for $\chi_{2P,0}(\vec{r})$ in (38) produces a different (slightly higher) energy minimum.

For $R \leq 10$, $\alpha = 2$, $\lambda^2 = 0$, computer calculations show that E_H is substantially lower than the lowest energy obtainable from (38). This result stands in sharp contrast to a similar comparison made previously for the $1S$ polaron state where, as described in I, the analog of (38) was found superior to the effective-mass wave function for $R \gtrsim 0.3$ at $\alpha = 2$.

B. Level Crossing

Both the Buimistrov and effective-mass approaches leave out a vital feature of the problem of excited states of the bound polaron, namely, the effect of level crossing.

To reduce the level-crossing problem to its barest essentials consider a Hamiltonian which can be written

$$\mathrm{H} = \mathrm{H}_0(\zeta) + \mathrm{H}' \; ,$$

with eigenfunctions ϕ_i satisfying

$$\mathrm{H}_0(\zeta)\phi_i(\zeta) = E_i(\zeta)\phi_i(\zeta) \; ,$$

where ζ is some parameter in the Hamiltonian which controls the eigenvalues (imagine, for definiteness, that ζ is the Rydberg R).

Assume that H_0 has two eigenfunctions $\phi_1(\zeta)$ and $\phi_2(\zeta)$ with respective energies $E_1(\zeta)$ and $E_2(\zeta)$. Suppose now that although $E_1(0) < E_2(0)$, $E_1(\zeta)$ grows more rapidly with ζ than does $E_2(\zeta)$ so that for $\zeta = \zeta_c$ the levels cross $[E_1(\zeta_c) = E_2(\zeta_c)]$. Finally, we assume that the crossing levels are directly coupled by the perturbation H', that is

$$\mathrm{H}'_{12} = \langle \phi_1(\zeta) \,|\, \mathrm{H}' \,|\, \phi_2(\zeta)\rangle \neq 0 . \quad (39)$$

Then taking as a variational trial function the unnormalized function ψ given by

$$\psi = \phi_1(\zeta) + a(\zeta)\phi_2(\zeta) \; , \quad (40)$$

where $a(\zeta)$ is to be varied, it is easy to show that the variational energy E can be determined from the equations

$$E_1 + a(\zeta)\mathrm{H}'_{12} = E \; ,$$

$$(E_2 - E)a(\zeta) = -\mathrm{H}'_{12} \; . \quad (41)$$

These equations can be obtained formally by setting $\mathrm{H}\psi = E\psi$ and neglecting the coupling via H' of ϕ_1 and ϕ_2 to any other unperturbed states. The solution of (41) can be written

$$E(\zeta) = E_1(\zeta) - M_{12}/[E_2(\zeta) - E(\zeta)] \; , \quad (42)$$

where

$$M_{12} = |\mathrm{H}'_{12}|^2 \; .$$

Equation (42) defines a quadratic equation for $E(\zeta)$, the two solutions of which give two branches for $E(\zeta)$ [and therefore for $a(\zeta)$]. The upper- and lower-energy branches lie, respectively, always above and below the energy $E_2(\zeta)$. Following the lower-branch energy as ζ grows from zero, we find that if M_{12} is not too large, $E(\zeta)$, which for small ζ lies near $E_1(\zeta)$, smoothly shifts over to the proximity of $E_2(\zeta)$ for $\zeta > \zeta_c$. This shift in energy behavior with increasing ζ is accompanied by a shift of ψ corresponding to the lower-branch energy from being "ϕ_1-like" to "ϕ_2-like" as ζ exceeds ζ_c. The wave function corresponding to the upper-branch energy is orthogonal to its lower-branch companion and becomes ϕ_1-like as ζ exceeds ζ_c.

The relevance of the general considerations above to the calculation of the energy of the polaron $2P$ state is clear from the single variational calculation outlined in Ref. 6 where ϕ_1 in (40) is taken to be the zero-phonon $2P$ state and $a(\zeta)\phi_2$ corresponds to a superposition of degenerate one-phonon $1S$ states. As expected, the calculation of Ref. 6 is completely equivalent to the approximate WBPT given by (21). In particular, the lower branch of the $2P$ zero-phonon state is found to pin to the $1S$ one-phonon state. Since this is a variational result, it proves that an effective-mass theory cannot be valid for the lower branch when $R \gtrsim \frac{4}{3}$ and suggests that to take into account the breakdown of the effective-mass approximation for the $2P$ states due to level crossing, we must allow for free mixing of $1S$ one-phonon states into the $2P$ wave function.

C. Final Ansatz

A relatively simple choice for the $1S$ 1-phonon polaron wave functions is

$$\phi_{\vec{k}} = U_{LS}(F_k) b_k^\dagger \,|\, 0\rangle \, (\beta_s^3/8\pi)^{1/2} e^{-\beta_s r/2} \;, \tag{43}$$

where

$$\beta_s = \beta + \tfrac{5}{8}\alpha,$$

$$F_k = -\nu_k/(1 + k^2/\beta_s^2)^2 \;.$$

Comparison with Eqs. (13) and (14) of I shows that (43) is essentially a product-ansatz $1S$ polaron wave function with a phonon of wave vector $\vec{k}$ excited. The wave functions $\phi_{\vec{k}}$ have the simplifying properties

$$\langle \phi_{\vec{k}} \,|\, \phi_{\vec{l}} \rangle = \delta_{\vec{k}\vec{l}} \;, \tag{44a}$$

$$\langle \phi_{\vec{k}} \,|\, H \,|\, \phi_{\vec{l}} \rangle = [E_{PA} + 1 + O(\lambda^4)] \delta_{\vec{k}\vec{l}} \;, \tag{44b}$$

where

$$E_{PA} = -R - \tfrac{5}{16}\alpha(2R^{1/2} + \tfrac{5}{16}\alpha) \;.$$

From I, it is clear that polaron $1S$-plus-1 phonon states which are lower in energy than (43) can be constructed, but the price of using such "improved" wave functions for $\phi_{\vec{k}}$ is to complicate the variational calculation by invalidating (44b).

We take for our final variational trial functions

$$\Psi_{\pm 1} = \psi_H(\vec{r}, \pm 1) + 2^{-1/2}\, i \sum (k_x \pm i k_y) S(k) \phi_{\vec{k}} \;, \tag{45a}$$

$$\Psi_0 = \psi_H(\vec{r}, 0) + i \sum k_z S(k) \phi_{\vec{k}} \;, \tag{45b}$$

where $S(k)$ is a spherically symmetric function to be determined variationally.

The variational problem for (45) is slightly complicated by the fact that the $\phi_{\vec{k}}$ are not orthogonal to ψ_H. Nevertheless, the minimization condition is given, as usual, by

$$\frac{\delta}{\delta S(k)} \langle \Psi | (H - E) | \Psi \rangle = 0 \;, \tag{46}$$

with the variational energy E determined by

$$\langle \Psi | H | \Psi \rangle = E \langle \Psi | \Psi \rangle \;.$$

The result is

$$\left\{ \begin{matrix} \dfrac{2^{-1/2}(k_x \pm i k_y)}{k_z} \end{matrix} \right\} S(k) = \frac{C(\vec{k}) - E Z(\vec{k})}{1 + E_s - E} \;,$$

$$E = E_H - \sum_{\vec{k}} \frac{C(\vec{k}) - E Z(\vec{k})}{1 + E_{PA} - E} \tag{47}$$

where

$$\begin{aligned} Z(\vec{k}) &= \mathrm{Re}\, i \langle \psi_H \,|\, \phi_{\vec{k}} \rangle \;, \\ C(\vec{k}) &= \mathrm{Re}\, i \langle \psi_H \,|\, H \,|\, \phi_{\vec{k}} \rangle \;. \end{aligned} \tag{48}$$

Explicit computation of $Z(\vec{k})$ and $C(\vec{k})$ for the ansatz (45) is quite tedious; essential details are relegated to Appendix B.

The two solutions of (47) are approximate eigenvalues of H corresponding to a pair of orthogonal trial functions of P symmetry. Both $h(k)$ and β_P, variational parameters appearing in ψ_H, are determined by minimizing $\langle \psi_H | H | \psi_H \rangle$ (keeping terms of no higher order than λ^2) rather than the full expectation value $\langle \Psi | H | \Psi \rangle$. We find that the lower eigenvalue solution of (47) changes only slightly when β_P is changed to minimize $\langle \Psi | H | \Psi \rangle$, and it is very insensitive to optimizing $h(k)$. The upper eigenvalue, however, is extremely sensitive to β_P: It matters greatly whether β_P is chosen by minimizing $\langle \Psi | H | \Psi \rangle$ in the lower-energy wave function or, alternatively, by using (36). Since we expect, in the spirit of our use of the effective-mass wave functions, that for energies not too close to $E_{PA} + 1$ the corresponding wave functions will be effective-mass-like, we have been willing to sacrifice a slight lowering of the lower-branch energies for a (presumably) more accurate description of the upper-branch energies for the larger values of R.

Based on this approach, our results at $\alpha = 2$ for the energy of the upper and lower branches of the $2P$ state in zero field and the corresponding Zeeman masses as a function of R are given in Figs. 1 and 2, respectively. For small R, the computations indicate $E = E_H + O(R^{5/2})$. Thus E, from ansatz (45), goes to the effective-mass limit for small R. For large R, E on the lower branch pins to $1 + E_S$ (E_S approaches the exact polaron ground-state energy as $R \to \infty$).

We have recalculated m_g/m_{pol} for the case of AgBr studied in Ref. 6, correcting an error in the program used for calculations reported there and refraining from complete optimization of $h(k)$ as

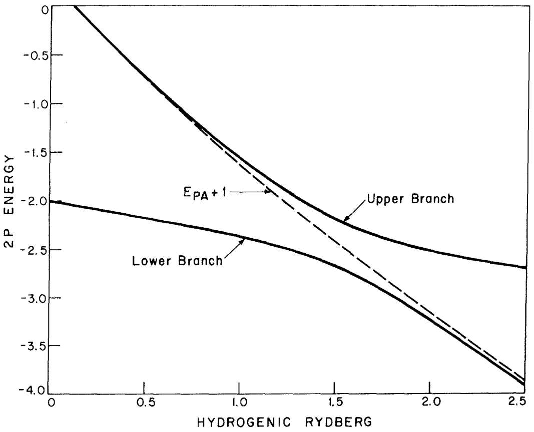

FIG. 1. Energy of polaron $2P$ level with no magnetic field present as a function of the hydrogenic Rydberg using the trial functions of (45) and $\alpha = 2$. The dotted line is the energy of the polaron product-ansatz ground state plus one LO phonon [wave function given by (43)].

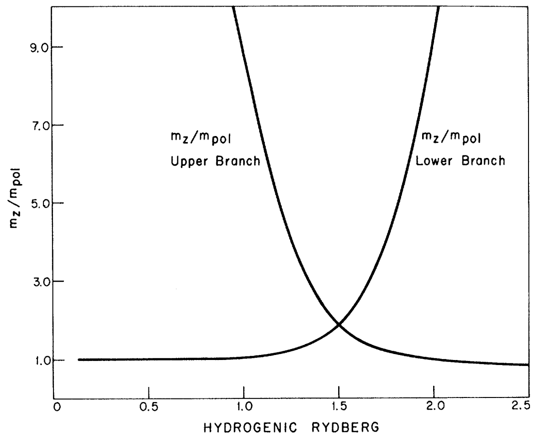

FIG. 2. Ratio of Zeeman mass to polaron mass at $\alpha = 2$ for polaron $2P$ level in a weak magnetic field as a function of the hydrogenic Rydberg. Results are calculated from the ansatz of (45a).

described above. The bare-mass value adopted in computing m_z/m_{pol} was determined by requiring the calculated $1S$-$2P$ separation to agree with the experimental value (167.6 cm^{-1}). As explained in Ref. 6 the bare mass calculated in this way ($m_{\text{bare}} = 0.22 m_{el}$) cannot be expected to agree well with the same quantity determined from cyclotron-resonance experiments. Taking $\hbar\omega_{LO} = 124\ \text{cm}^{-1}$, we obtain $m_z/m_{pol} = 1.27$ as compared to the experimental value of 1.19. In view of theoretical and experimental uncertainties, particularly the extreme sensitivity of our result to the value of $\hbar\omega_{LO}$ chosen (for $\hbar\omega_{LO} = 120\ \text{cm}^{-1}$, calculated $m_z/m_{pol} \cong 1.20$), we consider agreement between theory and experiment to be satisfactory at present.

Toyozawa and Hermanson[15] (TH) have studied the lower branch of the polaron $2S$ excited state of the hydrogenic impurity (infinite-mass exciton). Their trial function is

$$\psi_{2S} + \sum S(k) \phi_{\vec{k}} ,$$

where ψ_{2S} is a polaron $2S$-like state of the product-ansatz form

$$\psi_{2S} = U_{LS}(F_k) | 0 \rangle [3 - \tfrac{1}{2}(\beta_S + \tfrac{1}{2}\beta_{2S}) r] e^{-\beta_{2S} r/4}$$

and the $\phi_{\vec{k}}$ functions are defined in (43). The constant β_{2S} and the function $S(k)$ are determined by energy minimization. Although TH found pinning of the lower branch at large R, this variational result does not guarantee that the exact first excited S state of the bound polaron will, in fact, pin, since the energy calculated is not automatically an upper bound on the exact excited-state energy. There is, however, no reason to doubt that the exact state does in fact pin, as concluded by TH.

A more serious objection to the TH ansatz from the point of view of the present calculation is that the choice of a product-ansatz $2S$ polaron wave function is not good in a variational sense. We know from I that the effective-mass wave function is superior to the product ansatz for $R < 2$ and $\alpha = 2$ for the polaron $1S$ state. The $2S$ state should be much more nearly effective-mass-like than the $1S$ state, so that we expect that the product ansatz would not be well suited for an accurate variational calculation unless R or α is very large. In particular, as $R \to 0$ the product ansatz used gives no mass renormalization for the polaron.

Pinned states of the kind discussed here and by TH always occur in pairs, exhibiting qualitatively the behavior indicated in Fig. 1. Lower-branch pinning shown in Fig. 1 would be described by TH (who ignored the upper branch) as binding of a phonon to the impurity. Since one would hardly describe the upper branch as representing, in any region, an impurity-phonon bound state, such terminology lends itself to an asymmetrical description of a symmetrical phenomenon. For this reason, we prefer not to speak of bound-phonon states.

Rodriguez and Schultz[16] (RS) have studied the problem of the strain-induced splitting of impurity excited states interacting with optical phonons having some dispersion. They considered not only pinning but also line-broadening effects arising from the nonzero-phonon dispersion. However, the RS calculation is intended only for weak electron-phonon coupling and, unlike ours, neglects dressing effects due to this coupling. The greatest qualitative difference between our results and those of RS is the possible appearance of *three* absorption peaks for a given impurity level rather than two, as found here. The extra peak is a consequence of a local minimum in $\Gamma_{RS}(E)$, the imaginary part of the RS excited-state self-energy. In our model, the corresponding quantity is zero for all E. RS do not discuss directly the shift in the strain splitting (although such shifts are given implicitly in their calculation). We would expect that the strain splitting would be reduced due to electron-phonon interaction, much as the Zeeman splitting discussed here is diminished by this interaction.

From the fact that H_2 in (8) is linear in phonon creation and annihilation operators, it is clear that the Fröhlich Hamiltonian does not couple directly the zero-phonon $2P$ eigenstates of $H_0 + H_1$ with two-phonon $1S$ states of the form $\chi_S(r) b_{\vec{k}}^\dagger b_{\vec{l}}^\dagger | 0 \rangle$. However two-phonon states can be coupled to the zero-phonon state via a one-phonon intermediate state. This raises the general question as to what kind of level-crossing effect occurs when two levels cross which interact only through an intermediate state.

To investigate this problem we augment the ansatz of (40) by introducing the function ϕ_3 whose eigenvalue satisfies

$$E_3(\zeta) > E_2(\zeta) \text{ for all } \zeta,$$

but, like $E_2(\zeta)$, $E_3(\zeta)$ grows less rapidly than $E_1(\zeta)$ with increasing ζ so that for some $\zeta = \zeta_c'$,

$$E_1(\zeta_c') = E_3(\zeta_c').$$

Assume further that ϕ_3 is only indirectly connected to ϕ_1 in the sense that

$$\mathrm{H}_{13}' = 0 \text{ but } \mathrm{H}_{23}' \neq 0.$$

Then taking

$$\psi = \phi_1(\zeta) + a(\zeta)\phi_2(\zeta) + b(\zeta)\phi_3(\zeta),$$

we obtain

$$E(\zeta) = E_1(\zeta) - \frac{M_{12}}{E_2 - E(\zeta) - M_{23}/[E_3 - E(\zeta)]}. \tag{49}$$

The roots of the denominator of (49) are obtained from the quadratic formula

$$2r_\pm = E_2 + E_3 \pm [(E_3 - E_2)^2 + 4M_{23}]^{1/2}, \tag{50}$$

and (49) can be rewritten

$$E(\zeta) = E_1(\zeta) + M_{12}[E(\zeta) - E_3]/[E(\zeta) - r_+][E(\zeta) - r_-]. \tag{51}$$

Comparing (51) and (42), we see that the main effect of introducing ϕ_3 into the wave function is to produce a second pinning of the upper branch of E in (42) to the energy r_+, which lies only slightly above E_3 if M_{23} is small. The energy spectrum $E(\zeta)$ described by (51) has three branches, the middle branch pinning at low ζ to r_- and at high ζ to r_+. (It remains to be seen whether, in a rigorous calculation, E_3 actually is different from r_+.)

Thus, on the basis of (51), we can expect an additional breakdown of the polaron effective-mass theory for excited states with energies lying near two LO-phonon energies above the ground state. Presumably, the argument can be extended to states lying $n\hbar\omega$ above the ground state. Obviously, we have omitted such states for $n > 1$ in our variational ansatz (45). This omission should be serious, however, only for cases in which the $2P$ state lies close to the $1S$ energy plus $n\hbar\omega$ with $n > 1$.

Up to this point, we have considered only the case of weak magnetic field so that terms of order λ^4 and γ^2 $(= \lambda^4/4R^2)$ could be neglected. There is, however, no reason why trial functions of the structure (45) should not suffice for calculations to order γ^2.

For stronger fields, it becomes necessary to take into account distortion of the hydrogenic wave functions by the magnetic field.

While exact eigenfunctions for a hydrogenic atom in a magnetic field are not known, variational trial functions are available[17] for the distorted $1S$ and $2P\pm1$ states, which appear to give excellent energies.[18] These distorted wave functions could replace the $1S$ and $2P$ wave functions used in (43) and (26), respectively. Both F_k and $h(k)$ could then be recomputed along with $C(\vec{k})$ and $Z(\vec{k})$ in (47). Such computations, though feasible, are considerably involved.

IV. SUMMARY

We have pointed out that when two bound electronic states have an energy separation close to $\hbar\omega$ they become strongly coupled by electron–LO-phonon interaction. The orbital magnetic moment of each of the resulting coupled states is, of course, a linear combination of the magnetic moments of the uncoupled states with coefficients determined by the respective uncoupled-state amplitudes in the coupled wave function considered.

In the particular level crossing considered here, $2P$ states with z angular momentum are strongly coupled to states of zero angular momentum. Orbital magnetic moment is fed from the lower- to the upper-branch coupled state as the unperturbed energy difference $(\frac{3}{4}R)$ between the $1S$ and $2P$ states is increased. This occurs because, with increasing R, the lower-branch wave function becomes more strongly $1S$-like and the upper branch more strongly $2P$-like. (The sum of the magnetic moments of upper- and lower-branch states is nearly constant as a function of R in our ansatz.)

Measurement of the orbital magnetic moment (Zeeman splitting) of strongly coupled states offers a highly sensitive way of studying the electron–LO-phonon interaction.

APPENDIX A

In this section, we evaluate (15b) for $\Delta E_{z(\mathrm{RS})}$ approximately, by expanding the energy denominator there in powers of δ_n defined in (16).

Using the fact that the $|\phi_n\rangle$ are eigenfunctions of L_z, we can write

$$\begin{aligned}\langle\phi_n|(L_z - M)|\phi_n\rangle\langle\phi_n|e^{-i\vec{k}\cdot\vec{r}}|\phi_n\rangle &= \langle\phi_n|(L_z - M)e^{-i\vec{k}\cdot\vec{r}}|\phi_1\rangle \\ &= \langle\phi_n|[(L_z - M), e^{-i\vec{k}\cdot\vec{r}}]|\phi_1\rangle + \langle\phi_n|e^{-i\vec{k}\cdot\vec{r}}(L_z - M)|\phi_1\rangle \\ &= \langle\phi_n|(xk_y - yk_x)e^{-i\vec{k}\cdot\vec{r}}|\phi_1\rangle .\end{aligned}$$

Then

$$\Delta E_{z(\mathrm{RS})} = \sum_{\vec{k},n} \nu_k^2 \frac{\langle\phi_1|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle\langle\phi_n|e^{-i\vec{k}\cdot\vec{r}}(xk_y - yk_x)|\phi_1\rangle}{(E_n - E_1 + 1)^2}. \tag{A1}$$

Expanding the energy denominator in powers of δ_n gives

$$\frac{1}{(E_n - E_1 + 1)^2} = \frac{1}{(1 + k^2 + \delta_n)^2}$$

$$= \frac{1}{1+k^2}\left(1-\frac{2\delta_n}{1+k^2}+\frac{3\delta_n^2}{(1+k^2)^2}-\frac{4\delta_n^3}{(1+k^2)^2(1+k^2+\delta_n)}\right). \tag{A2}$$

Inserting (A2) into (A1) after setting $\delta_n = 0$ in the denominator of the coefficient of the δ_n^3 term, we can evaluate the resulting sums on n using (16) and the identity

$$\sum_n (E_n-E_i)^m \langle\phi_i|e^{i\vec{k}\cdot\vec{r}}|\phi_n\rangle\langle\phi_n|e^{-i\vec{k}\cdot\vec{r}}(xk_y-yk_x)|\phi_i\rangle$$
$$=\langle\phi_i|[\;]_m e^{-i\vec{k}\cdot\vec{r}}(xk_y-yk_x)|\phi_i\rangle , \tag{A3}$$

where $[\;]_m$ stands for the repeated commutator defined by

$$[\;]_m=[[\;]_{m-1}, H_0], \quad m>1$$
$$[\;]_1=[e^{i\vec{k}\cdot\vec{r}}, H_0] .$$

Since we have truncated the expansion (A2) to exclude powers of δ_n higher than the third, we need only evaluate the commutators up to $[\;]_3$. These can be written, defining $\beta = 2R^{1/2}$,

$$[\;]_1 e^{-i\vec{k}\cdot\vec{r}} = -2\vec{p}\cdot\vec{k}+k^2 ,$$
$$[\;]_2 e^{-i\vec{k}\cdot\vec{r}} = (2\vec{p}\cdot\vec{k}+k^2)^2-(2/i)\vec{k}\cdot\vec{\nabla}(-\beta/r) ,$$
$$[\;]_3 e^{-i\vec{k}\cdot\vec{r}} = (-2\vec{p}\cdot\vec{k}+k^2)^3+[(-2\vec{p}\cdot\vec{k}+k^2)^2, -\beta/r]$$
$$-(2/i)[\vec{k}\cdot\vec{\nabla}(-\beta/r)](-2\vec{p}\cdot\vec{k}+k^2)$$
$$-(2/i)[\vec{k}\cdot\vec{\nabla}(-\beta/r), \hat{p}^2] . \tag{A4}$$

Since (A3) is a diagonal matrix element only the even part (in electron coordinates) of $[\;]_m e^{-i\vec{k}\cdot\vec{r}} \times (xk_y-yk_x)$ contributes. Thus, we need consider only the odd parts of $[\;]_3 e^{-i\vec{k}\cdot\vec{r}}$ in (A4), the factor (xk_y-yk_x) being odd in the electron coordinates.

Performing the sum on n in (A1) with (A2) inserted, we find that terms proportional to δ_n^0 and δ_n^2 give zero contribution. In the limit of infinite crystal volume, we convert the sum on $\vec{k}$ to an integral and obtain finally

$$\Delta E_{z\,(\mathrm{RS})} = -\frac{\alpha}{\pi^2}\Bigg[\int\frac{d^3k}{k^2(1+k^2)^3}$$
$$\times\langle\phi_1|(2\vec{k}\cdot\hat{\vec{p}})(xk_y-yk_x)|\phi_1\rangle$$
$$+2\int\frac{d^3k}{k^2(1+k^2)^5}\left\langle\phi_1\left|\Big((2\vec{k}\cdot\vec{p})^3\right.\right.$$
$$\left.\left.+\frac{4\beta}{r^3}(\vec{k}\cdot\vec{p})\;(xk_y-yk_x)\Big)\right|\phi_1\right\rangle\Bigg]$$
$$=-M(\tfrac{1}{6}\alpha+\tfrac{3}{80}\alpha R+\tfrac{5}{288}\alpha R^2) . \tag{A5}$$

Thus, the total perturbed $2P$-state energy given by the present calculation up to terms linear in the magnetic field is, for $R \ll 1$,

$$E_{2P(\mathrm{RS})} = -\alpha-(1+\tfrac{1}{6}\alpha)\tfrac{1}{4}R+\tfrac{1}{2}\lambda^2(1-\tfrac{1}{6}\alpha)M$$
$$-\tfrac{1}{2}\lambda^2\alpha(\tfrac{3}{80}R+\tfrac{5}{288}R^2)M . \tag{A6}$$

APPENDIX B

We indicate here how to evaluate the matrix elements

$$Z(\vec{k}) = \mathrm{Re}\, i\langle\psi_H|\phi_{\vec{k}}\rangle , \tag{B1}$$
$$C(\vec{k}) = \mathrm{Re}\, i\langle\psi_H|H|\phi_{\vec{k}}\rangle , \tag{B2}$$

where

$$|\psi_H\rangle = \exp(-i\vec{r}\cdot\sum\vec{k}n_{\vec{k}})U_{LS}(f_{\vec{k}})$$
$$\times[1+\sum h(\vec{k})\vec{k}\cdot\hat{\pi}\, b_{\vec{k}}^\dagger]|0\rangle\,\chi_{2P,M}(r),$$
$$|\phi_{\vec{k}}\rangle = U_{LS}(F_k)b_{\vec{k}}^\dagger|0\rangle ,$$
$$n_{\vec{k}} = b_{\vec{k}}^\dagger b_{\vec{k}} .$$

In $Z(\vec{k})$, we encounter phonon matrix elements of the form

$$\langle 0|U_{LS}^\dagger(f_k)\exp(i\vec{r}\cdot\sum\vec{k}n_{\vec{k}})U_{LS}(F_k)\,|\,\vec{k}\rangle , \tag{B3a}$$

$$\langle\vec{1}|U_{LS}^\dagger(f_k)\exp(i\vec{r}\cdot\sum\vec{k}\,n_{\vec{k}})U_{LS}(F_k)\,|\,\vec{k}\rangle . \tag{B3b}$$

Using the definition of U_{LS} given in (25) and the fact that

$$\exp(i\vec{r}\cdot\sum\vec{k}\,n_{\vec{k}})b_{\vec{k}}^\dagger\exp(-i\vec{r}\cdot\sum\vec{k}) = e^{i\vec{k}\cdot\vec{r}}b_{\vec{k}}^\dagger ,$$

we can write (B3a) as

$$\langle 0|U_{LS}^\dagger(f_k)U_{LS}(e^{-i\vec{k}\cdot \mathrm{r}}F_k)|\vec{k}\rangle e^{i\vec{k}\cdot\vec{r}} . \tag{B4}$$

Using the identity

$$e^Ae^B = e^{A+B}e^{[A,B]/2} \tag{B5}$$

and the substitutions

$$A=-\sum f_k(b_{\vec{k}}^\dagger-b_{\vec{k}}) ,$$
$$B=\sum(e^{i\vec{k}\cdot\vec{r}}F_kb_{\vec{k}}^\dagger-e^{-i\vec{k}\cdot\vec{r}}F_kb_{\vec{k}})$$

we obtain for (B4) the expression

$$\langle 0|U_{LS}(\mathcal{G}_{\vec{k}}(\vec{r}))|\vec{k}\rangle e^{i\vec{k}\cdot\vec{r}} , \tag{B6}$$

where

$$\mathcal{G}_{\vec{k}}(\vec{r}) = -f_k+e^{-i\vec{k}\cdot\vec{r}}F_k .$$

Again using (B5), this time substituting according to

$$A=\mathcal{G}_{\vec{k}}^*(\vec{r})b_{\vec{k}}^\dagger , \; B=-\mathcal{G}_{\vec{k}}(\vec{r})b_{\vec{k}} ,$$

we can rewrite (B6) in the form

$$\langle 0|\exp[\sum\mathcal{G}_{\vec{k}}^*(\vec{r})b_{\vec{k}}^\dagger]\exp[-\sum\mathcal{G}_{\vec{k}}(\vec{r})b_{\vec{k}}]|\vec{k}\rangle$$
$$\times\exp[-\tfrac{1}{2}\sum|\mathcal{G}_{\vec{k}}(\vec{r})|^2]e^{i\vec{k}\cdot\vec{r}} . \tag{B7}$$

The inner product in (B7) is now easily taken by expanding the exponentials. The final result for (B3a) is

$$-\mathcal{G}_{\vec{k}}(\vec{r})\exp[-\tfrac{1}{2}\sum|\mathcal{G}_{\vec{k}}(\vec{r})|^2]e^{i\vec{k}\cdot\vec{r}} . \tag{B8}$$

In exactly the same way, we find for (B3) the result

$$[\delta_{\vec{k}\,\vec{l}} - \mathcal{J}^{*}_{\vec{l}}(\vec{r})\,\mathcal{J}_{\vec{k}}(\vec{r})]\exp[-\tfrac{1}{2}\textstyle\sum|\mathcal{J}_{\vec{k}}(\vec{r})|^{2}]\,e^{i\vec{k}\cdot\vec{r}}\ . \qquad \text{(B9)}$$

In this way, we obtain

$$Z(\vec{k}) = \text{Re}\,i\,[f_k\langle\chi_P|(1+\textstyle\sum_{\vec{l}}\vec{l}\cdot\hat{\vec{\pi}}e^{i\vec{l}\cdot\vec{r}}h_l f_l)\,e^{-A(r)}\,e^{i\vec{k}\cdot\vec{r}}|\chi_S\rangle$$
$$+h(k)\langle\chi_P|(\vec{k}\cdot\hat{\vec{\pi}})\,e^{i\vec{k}\cdot\vec{r}}e^{-A(r)}|\chi_S\rangle]\ , \qquad \text{(B10)}$$

where

$$A(r)=\tfrac{1}{2}\textstyle\sum|\mathcal{J}_{\vec{k}}(\vec{r})|^{2}\ .$$

Angular integrals involved in evaluating (B10) can be performed analytically by partial-wave expansion of the plane-wave factors appearing in the integrands. The remaining evaluation amounts to a double integral evaluated at each value of k of interest. This is easily performed by computer.

Much the same kind of calculation applies in the calculation of $C(\vec{k})$. Here it is convenient to employ the relation

$$U^{\dagger}_{LS}(f_k)\exp(i\vec{r}\cdot\textstyle\sum\vec{k}n_{\vec{k}})HU_{LS}(f_k)$$
$$=U^{\dagger}_{LS}(f_k)\exp(i\vec{r}\cdot\textstyle\sum\vec{k}n_{\vec{k}})\,U_{LS}(F_k)\,(\hat{\vec{\pi}}^{2}-\beta/r)$$
$$+[\textstyle\sum n_{\vec{k}}-\sum k^{2}f_k(b^{\dagger}_{\vec{k}}+b_{\vec{k}})-\tfrac{3}{2}\alpha]$$
$$\times U^{\dagger}_{LS}(f_k)\exp(i\vec{r}\cdot\textstyle\sum\vec{k}n_{\vec{k}})\,U_{LS}(F_k)\ , \qquad \text{(B11)}$$

where we have used

$$f_k+\nu_k=-k^{2}f_k \ \text{ and } \textstyle\sum(f_k^{2}+2\nu_k f_k)=-\tfrac{3}{2}\alpha\ .$$

Examination of (B11) indicates that in addition to (B3a) and (B3b) the phonon matrix element

$$\langle\vec{l}\,\vec{m}|U^{\dagger}_{LS}(f_k)\exp(i\vec{r}\cdot\textstyle\sum\vec{k}n_{\vec{k}})\,U_{LS}(F_k)|\vec{k}\rangle$$

is required. By the previous arguments, we can show that this matrix element is given by

$$[\delta_{\vec{l}\vec{k}}\mathcal{J}^{*}_{\vec{m}}(\vec{r})+\delta_{\vec{m}\vec{k}}\mathcal{J}^{*}_{\vec{l}}(\vec{r})-\mathcal{J}_{\vec{k}}(\vec{r})\mathcal{J}^{*}_{\vec{l}}(\vec{r})\mathcal{J}^{*}_{\vec{m}}(\vec{r})]\,e^{-A(r)}\,e^{i\vec{k}\cdot\vec{r}}$$

and that

$$C(\vec{k})=(-\tfrac{1}{4}\beta_s^{2}-\alpha+1)\,Z(\vec{k})$$
$$+\text{Re}\,i\,\langle\psi_H|(\beta_s-\beta)/r+\zeta(r)|\phi_{\vec{k}}\rangle \qquad \text{(B12)}$$
$$-f_k\,\text{Re}\,i\,\langle\chi_S|e^{i\vec{k}\cdot\vec{r}}e^{-A(r)}\{1+k^{2}[1+\eta(r)]\}|\chi_P\rangle\ ,$$

where

$$\zeta(r)=-\textstyle\sum k^{2}f_kF_ke^{i\vec{k}\cdot\vec{r}}\ ,$$

$$\eta(r)=\left(-\frac{\beta_p}{4}+\frac{1}{r}\right)\frac{\partial}{\partial r}\,[\textstyle\sum e^{i\vec{l}\cdot\vec{r}}h(l)F_l]\ .$$

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[8] Because of the term $\frac{1}{8}m\omega_c^{2}\rho^{2}$ in (4), the total orbital angular momentum L is not a good quantum number of H_{el}. When we speak of a $2P$ state in a magnetic field, we mean a state which, as the magnetic field vanishes, goes smoothly into a hydrogenic $2P$ state.

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