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Polaron Bound in a Coulomb Potential*

M. H. Engineer and N. Tzoar

The City College of the City University of New York, New York, New York 10031

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We have calculated the shift in ground-state energy of an electron bound in a Coulomb potential in a crystal, to second order in the electron-phonon coupling and for arbitrary values of the electron-impurity coupling.

The problem of an electron, in semiconductors, bound in a Coulomb center and weakly interacting with optic phonons, has been of considerable interest.¹⁻⁷ The first term in the perturbative expansion of the ground-state energy in terms of the electron-phonon coupling constant is a function of the electron-impurity coupling. We have calculated this term exactly. Our result, for the ground-state energy, is in amazingly good agreement with the energy shift obtained using lowest-order effective-mass theory.² In this theory, the energy shift is calculated by replacing the conduction-band effective mass at the bottom of the band by the free-polaron mass at zero momentum. Another approach (Platzman-Sak^{1,3}) is to develop the exact

expression of second-order perturbation theory in the electron-phonon coupling as a power series in the electron-impurity coupling β . The first term in this series is identical to that obtained using effective-mass theory. The next term ($\sim \beta^4$) has also been calculated. Our exact result is, on the other hand, almost identical to the effective-mass-theory result, for values of the unperturbed ground-state energy E_B , lying between zero and the energy of one optic phonon.

The ground-state energy shift has been calculated, numerically, for arbitrary values of the electron-impurity potential strength. It is compared with the approximate calculations for ΔE . These are (i) a power series in the strength of the impurity

potential which has been reported,¹⁻³ (ii) approximate calculations for ΔE , appropriate for large electron radius or small impurity potential, which have been recently published,^{4,5} and (iii) effective-mass theory.

The Hamiltonian of our system, which describes an impurity atom in the presence of optical lattice fluctuations is given, in dimensionless units, by

$$H = H_e + H_p + H_{int}, \quad (1)$$

where

$$H_e = p^2 - \beta/r, \quad H_p = \sum_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}}, \quad (2)$$

and

$$H_{int} = \sum_{\vec{k}} v_{\vec{k}} (a_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} + \text{H. c.}). \quad (3)$$

The natural units of length and energy in our problem, are given, respectively, by $(\hbar/2m\omega)^{1/2}$ and $\hbar\omega$. Here m is the effective mass at the bottom of the conduction band, assumed to be a scalar for simplicity, and ω is the dispersionless optical-phonon frequency. The normalized binding energy R is given by $R = \frac{1}{4}\beta^2 = me^4/(2\epsilon_0\hbar^3\omega)$, where ϵ_0 is the low-frequency dielectric constant of the crystal and $v_{\vec{k}} = (4\pi a/\hbar^2 V)^{1/2}$ represents the electron-phonon interaction. The operators $a_{\vec{k}}$ and $a_{\vec{k}}^\dagger$ are, respectively, the destruction and creation operators of the LO phonons having wave vector \vec{k} .

The energy of the ground state consisting of a 1s electron and no phonons, to second order in the electron-phonon interaction, is given by

$$E = E_0 + \Delta E, \quad (4)$$

where

$$\Delta E = \sum_{n, \vec{k}} v_{\vec{k}}^2 \frac{\langle 0 | e^{-i\vec{k}\cdot\vec{r}} | n \rangle \langle n | e^{i\vec{k}\cdot\vec{r}} | 0 \rangle}{E_0 - E_n - 1}. \quad (5)$$

Here, the sum is over all eigenstates of the Coulomb Hamiltonian, given by $(p^2 - \beta/r) | n \rangle = E_n | n \rangle$ with $E_0 = -R$. The change in energy, as given in Eq. (5), is due to the virtual emission and absorption of a phonon.

The main difficulty in the evaluation of ΔE lies in the sum over the infinite number of negative energy states. To date no calculation which overcomes this difficulty has been presented. Our solution to this problem lies in the observation that by carrying out first the sum over n , ΔE is reduced to an integral over the unperturbed Coulomb Green's function. Integrating next over all wave vectors \vec{k} in Eq. (5), we obtain

$$\frac{\Delta E}{\alpha} = \int d\vec{r} d\vec{r}' \phi_0(r) \frac{G(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \phi_0(r'), \quad (6)$$

where

$$\phi_0(r) = (\beta^3/8\pi)^{1/2} e^{-\beta r/2} \quad (7)$$

is the 1s-wave unperturbed ground state. Here

$G(\vec{r}, \vec{r}')$ is the Coulomb Green's function which, following Hostler,⁶ is given by

$$G(\vec{r}, \vec{r}') = \frac{\Gamma(1 - \beta/2a)}{4\pi a |\vec{r} - \vec{r}'|} \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) W_{\beta/2a, 1/2}(ax) \times M_{\beta/2a, 1/2}(ay), \quad (8)$$

where

$$a = (1 + R)^{1/2}, \quad x = r + r' + |\vec{r} - \vec{r}'|, \quad y = r + r' - |\vec{r} - \vec{r}'|. \quad (9)$$

In Eq. (8), Γ represents the γ function, and W and M are the Whittaker functions.⁹ To cast our result in its final form we make a series of transformations. First, we go to center-of-mass coordinates $\vec{\eta} = \frac{1}{2}(\vec{r} + \vec{r}')$, $\vec{\rho} = \vec{r} - \vec{r}'$ and carry out the three trivial angular integrations to get

$$\frac{\Delta E}{\alpha} = \frac{-2\beta^3}{a} \Gamma(1 - \beta/2a) \int \eta^2 d\eta d\rho dZ \times \exp\left[-\frac{1}{2}\beta\left(|\vec{\eta} + \frac{1}{2}\vec{\rho}| + |\vec{\eta} - \frac{1}{2}\vec{\rho}|\right)\right] \left(\frac{\partial}{\partial x} - \frac{\partial}{\partial y}\right) \times W_{\beta/2a, 1/2}(ax) M_{\beta/2a, 1/2}(ay), \quad (10)$$

where $Z = \hat{\eta} \cdot \hat{\rho}$. Next we change, at fixed ρ , from (η, Z) to (X, Y) , where $X = |\vec{\eta} + \frac{1}{2}\vec{\rho}| + |\vec{\eta} - \frac{1}{2}\vec{\rho}|$, $Y = |\vec{\eta} + \frac{1}{2}\vec{\rho}| - |\vec{\eta} - \frac{1}{2}\vec{\rho}|$. The integral over Y is now trivial and after a little algebra we obtain our final result:

$$\Delta E/\alpha = -C(I - J), \quad (11)$$

where

$$C = \beta^3 \Gamma(1 - \beta/2a)/16a^4, \quad (12)$$

$$I = + \int_0^\infty dx x^2 e^{-\beta x/2a} M_{\beta/2a, 1/2}(x) W_{\beta/2a, 1/2}(x) \quad (13)$$

and

$$J = \frac{1}{6} \int_0^\infty dx e^{-\beta x/2a} M_{\beta/2a, 1/2}(x) \int_0^\infty \rho d\rho e^{-\beta\rho/4a} \times W_{\beta/2a, 1/2}(x + \rho). \quad (14)$$

We have thus replaced the integration over the wave vector \vec{k} and the sum over all states n in Eq. (5) with a double integration over the Whittaker functions, which are well known. The dependence of the ΔE on β was obtained numerically using an IBM 360/50 computer (see Table I and Fig. 1), and represents the exact change in the bound-electron ground-state energy resulting from weak electron-phonon interaction (i. e., to order α).

At this point we would like to compare our calculation with other known results. Platzman,¹ starting with Eq. (5), developed a power series expansion in R . Using his expansion procedure, Sak³ was able to show that up to the order of R^2 one obtains

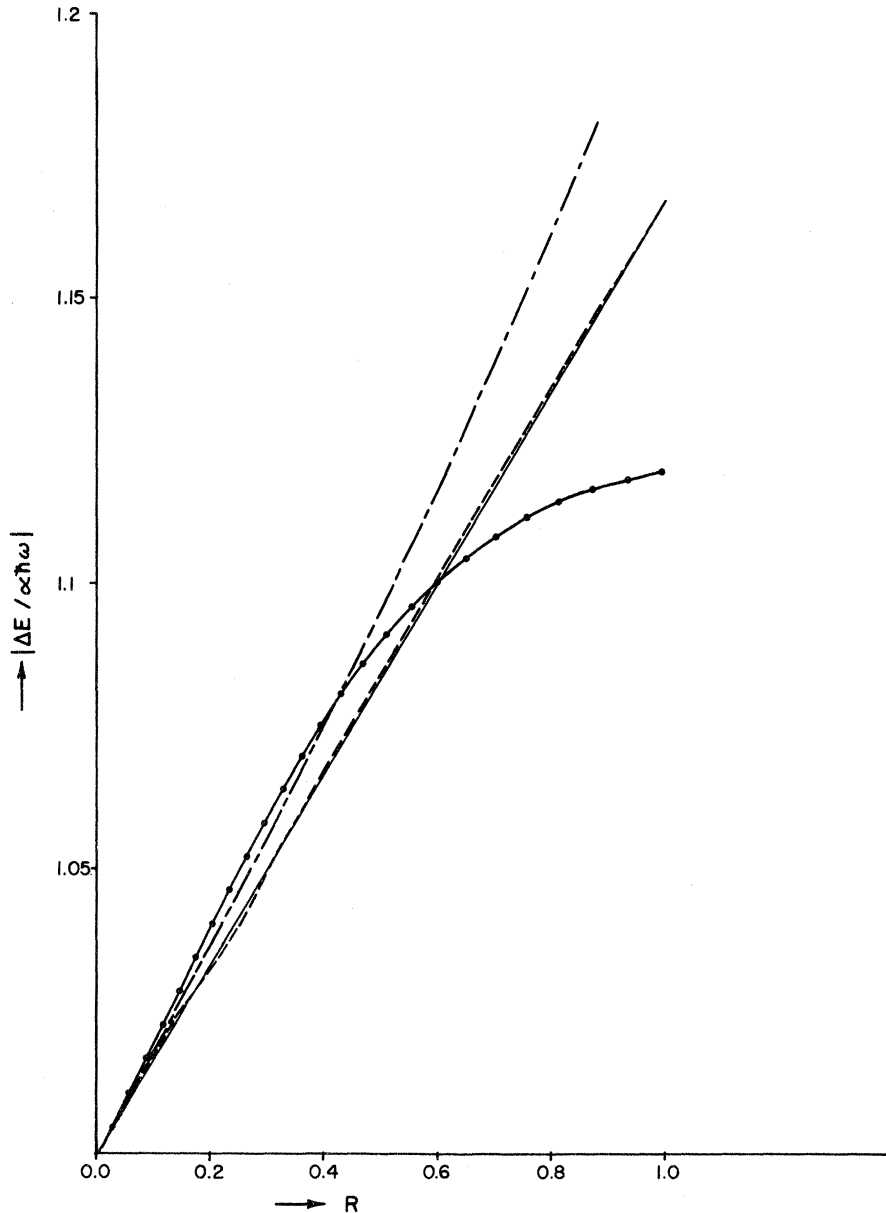


FIG. 1. Graphical presentation of the theoretical calculations of $|\Delta E/\alpha|$: dashed line, numerical; solid line, effective mass; dots and dashes, Platzman-Sak; connected dots, Stoneham-Bajaj.

$$-(\Delta E/\alpha) = 1 + \frac{1}{6}R + \frac{1}{24}R^2. \quad (15)$$

No higher-order terms can be obtained using the Platzman procedure, because of divergent integrals. A different approach is to begin with the quantized Hamiltonian of the free polaron and add to it the Coulomb potential. Here

$$H_{\text{eff}} = \frac{1}{2}p^2(1 - \frac{1}{6}\alpha) - \beta/\gamma + \frac{3}{180}\alpha p^4 + \frac{1}{12}\pi\alpha\beta\delta(\vec{r}),$$

as was considered by Sak.³ His calculations, using the last two terms as a perturbation indicate $\Delta E/\alpha$ to be identical to the result obtained using the Platzman procedure as given by Eq. (15). Again, because of divergent integrals, one cannot obtain in

a straightforward way any higher-order terms in R . A very different approach was taken by Stoneham⁴ and similarly by Bajaj.⁵ They write for the energy shift

$$\Delta E = \sum_{\vec{k}, \vec{q}} \nu_k^2 \frac{|\langle 0 | \vec{q} \rangle|^2}{2\vec{k} \cdot \vec{q} - 1 - k^2}. \quad (16)$$

Within this approximation one sums over all plane waves \vec{q} the values of ΔE_q , the energy shift of the free polaron having momentum \vec{q} , weighting each value by the probability $|\langle 0 | \vec{q} \rangle|^2$ of finding the particular plane wave in the unperturbed ground-state wave function. One thus neglects quantum-mechan-

TABLE I. Numerically evaluated, effective-mass theory, Platzman-Sak, Stoneham-Bajaj, and large- R values of $\Delta E/\alpha$ (in units of $\hbar\omega$).

Rydberg $=R$	Numerically evaluated	Effective mass	Platzman- Sak	Stoneham	$-\frac{5}{8}R^{1/2}$
0.2	-1.0317	-1.03333	-1.0350	-0.0396	
0.5	-1.084097	-1.08333	-1.0933	-1.0887	
0.8	-1.1340	-1.13333	-1.1609	-1.1135	
1.0	-1.166581	-1.16667	-1.2071	-1.1195	
10.0	-2.2015	-2.66667			-1.9764
100.0	-6.3242	-17.66667			-6.25
400.0	-12.5372				-12.5

ical interference of plane waves, which should be a good approximation for large Bohr radii or small values of β . The integrals in Eq. (16) can be analytically performed, and we obtain¹⁰

$$-\Delta E/\alpha = (1+R)^{-1/2} + \frac{2}{3}R(1+R)^{-3/2} + R^2(1+R)^{-5/2}. \quad (17)$$

We finally want to compare the various approximation with our exact calculations for ΔE . All these approximate calculations are good at small R and, in fact, to first order in R , are identical. It is their behavior at intermediate R which is of interest.

In Table I¹¹ and in Fig. 1 we show our numerical results in comparison with the leading terms of the effective-mass theory, the power series solution¹ and the Stoneham-Bajaj approximation.^{4,5} Our "exact" results for ΔE shows an excellent numerical agreement with the energy shift calculated using lowest-order effective-mass theory. From our solution, given by Eqs. (11)–(14), it follows that the power series around $\beta=0$ will contain all powers of R . However, the terms have coefficients that are small and alternate in sign such that, up to about $R=1$, the solution for ΔE is practically linear in the Rydberg with slope $-d(\Delta E)/dR = \frac{1}{6}\alpha$. To lend support to our numerical integrations, we point out that we obtain the correct result for small R and also, as given in Table I, have checked the validity of our calculation for large R . Here, using Eq. (5), in the limit of $R \rightarrow \infty$, $\Delta E/\alpha$ must

approach $-\frac{5}{8}R^{1/2}$.¹² Indeed, our numerical results does so. Interestingly enough, even for $R=10$, the percentage difference between the numerical and effective-mass values is only 20%. It is important to mention that in order to calculate the ionization energy one should subtract the lowering in energy of the lowest continuum state. This is taken to be -1.0 , the value of the free-polaron self-energy, as is customary. For R small this is undoubtedly a good approximation, but for larger R one will have to use the Coulomb continuum eigenstates instead of plane waves.

The ionization energy as given by Platzman-Sak is $\frac{1}{6}R(1 + \frac{1}{4}R)$. This leads one to assume a radius of convergence of $R \sim 4$ for their power series. However, our results indicate that the real radius of convergence is much smaller. Indeed, the actual discrepancy is already greater than 10% for $R=0.2$.

In conclusion, polaron effective-mass theory works extremely well for the ground-state energy of the Coulomb Hamiltonian for $0 < R \leq 1$. Whether the same can be said for the excited states remains to be investigated. Furthermore, lowest-order effective-mass theory predicts that the Lamb shift, i. e., energy difference between the $2p$ and $2s$ state, is zero. The method used here can check the validity of this prediction. One can also, finally, get some insight close to the regions where perturbation theory itself breaks down, i. e., where some pair of Coulomb eigenstates differ in energy by about one optical phonon.

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¹¹The numerical integrations were done using 60 points for each one-dimensional integral. A glance at Table I and Fig. 1 shows that the agreement with the exact asymp-

otic ($R \rightarrow 0$, $R \rightarrow \infty$) values is excellent. However, for $R=0.5$ it was found necessary to improve the accuracy of the numerical calculations, since the other theories give values for the *ionization* energy not too different from the calculated one. The numerical integrations were, therefore, carried out using 120 and 250 points. The values obtained for $\Delta E/a$ were -1.084102 and -1.084097 , re-

spectively. Additionally, for $R=1.0$ the integrations were done with 60 and 120 points. The values obtained were -1.66513 and -1.66581 , respectively.

¹²It follows from this and the low- R behavior that the power series for $\Delta E/\alpha$ must have a finite radius of convergence.

Stress-Modulated Magnetorefectivity of Gallium Antimonide and Gallium Arsenide[†]

M. Reine,^{*‡} R. L. Aggarwal, and B. Lax[‡]

*Francis Bitter National Magnet Laboratory, § Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

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We have employed the differential technique for stress modulation in an extensive study of low-temperature (30 K), interband magnetorefectivity at the fundamental edge of GaSb and of GaAs. The data for GaSb were compared to the coupled-band theory of Pidgeon and Brown by means of an iterative "parameter-optimization" computer program. The following self-consistent set of band parameters was determined: $(m_c/m) = 0.042 \pm 0.001$; $(m_{1h}/m) = 0.042 \pm 0.002$; $(m_{hh}/m)_{100} = 0.29 \pm 0.09$; $(m_{hh}/m)_{110} = 0.36 \pm 0.13$; $(m_{hh}/m)_{111} = 0.40 \pm 0.16$; $\gamma_1^L = 13.3 \pm 0.4$; $\gamma_2^L = 5.7 \pm 0.2$; $\gamma_3^L - \gamma_2^L = 1.3 \pm 0.2$; $\kappa^L = 3.5 \pm 0.6$; $g_c = -7.8 \pm 0.8$; $E_p = (25 \pm 2)$ eV; and $F = -(1.5 \pm 0.5)\hbar^2/m$. Here m is the free-electron mass, m_c is the conduction-band effective mass, m_{1h} and m_{hh} are the light-hole and heavy-hole valence-band effective masses, γ_1^L , γ_2^L , γ_3^L , and κ^L are the Luttinger valence-band parameters, g_c is the conduction-band effective g factor, E_p is the interaction energy introduced by Kane, and F represents the interaction of the conduction band with higher-lying bands.

I. INTRODUCTION

We have employed the differential technique of stress modulation^{1,2} in an extensive study of interband magnetorefectivity at the fundamental edge of gallium antimonide and of gallium arsenide. The greatly enhanced sensitivity afforded by this technique has enabled us to obtain magnetooptical spectra of considerably greater detail and resolution than have previously been reported.³⁻⁵ For example, for GaSb at 30 K transitions involving Landau levels as high as the 18th conduction-band level were observed over the spectral region from 0.8 to 1.25 eV.

The spectra for GaSb were quantitatively compared to the coupled-band theory of Pidgeon and Brown⁶ by means of an iterative computer program based on a generalized least-squares method. The best fit of this theory to the experimental data yielded a self-consistent set of band parameters for the conduction band, the light-hole and the heavy-hole valence bands, and the spin-orbit split-off valence band.

This paper is organized as follows. The experimental details are contained in Sec. II. The theoretical results necessary for the analysis of the experimental spectra are summarized in Sec. III. The experimental results and their analysis for GaSb are presented in Sec. IV. The zero-field spectra

for GaSb are discussed in Sec. IV A and the magnetooptical spectra are discussed in Sec. IV B. A preliminary analysis of the main features of the data based on the parabolic band theory of Roth *et al.*⁷ is given in Sec. IV C. The detailed analysis of the data in terms of the coupled-band theory is described in Sec. IV D, and the set of band parameters thus obtained is compared with previous results in Sec. IV E. Finally, the experimental data for GaAs are presented and discussed in Sec. V.

II. EXPERIMENTAL DETAILS

The stress-modulation technique used in this work is essentially the same as that developed by Engeler *et al.*¹ and adapted for low-temperature experiments by Aggarwal.² This technique and the associated apparatus have previously been described.^{2,8} Briefly, this consists of a thin sample bonded to a piezoelectric transducer with vacuum grease. The transducer is driven by an ac voltage at an audio frequency and the resulting modulation in the reflectivity is detected by a phase-sensitive technique.

Data were taken in both the Faraday and the Voigt configurations. For the Voigt configuration, linearly polarized light was obtained by means of Polaroid-type HN32 or HR sheet polarizers. For the Faraday configuration, circularly polarized light was obtained