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Polaron bound to a massive hole: Binding energy of a bound piezoelectric polaron*

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A method for calculating the energy and wave function of a lattice polaron bound to a massive hole applicable to both the band- and the non-band-mass theories for arbitrary binding and coupling strength is developed. This is accomplished by a second-order perturbation theory on a basis different from the usual perturbation theory, in which the electron-phonon interaction can be reduced to a small perturbation even for the strong coupling. This method is applied to calculate the binding energy of a bound piezoelectric polaron for a wide range of electron-phonon coupling and electron–massive-hole binding. Then, the applicability of the usual second-order perturbation theory and that of the strong-coupling polaron theory to the treatment of the interaction of a bound electron with the acoustic phonons in a piezoelectric crystal is examined.

I. INTRODUCTION

An electron bound to a massive hole plus its associated ionic polarization cloud is known as a bound lattice polaron. In order to study the ionic-polarization-field (IPF) effect on the electronic states, a number of methods[1–11] have been developed to calculate the quantum states of such a polaron both within the band-mass approximation and the non-band-mass theory. Within the band-mass approximation, in which the electron-hole binding (will be referred to simply as binding henceforth) is assumed to be a pure Coulomb-type potential, such methods include the path-integral method,[2–4] the variational method,[1,5] and the usual second-order perturbation method, in which the entire electron-IPF interaction is taken as a perturbation.[6–9] Both the path-integral and the variational methods are able to give satisfactory ground-state energies for arbitrary binding and electron-IPF coupling (will be referred to simply as coupling henceforth). However, only the variational method can give the corresponding wave function, which is needed in some practical applications. For the usual second-order perturbation method, the application is limited to weak-coupling cases only. The non-band-mass theory with electron-hole binding deviated from a pure Coulomb field was considered in Refs. 10 and 11. However, success of the methods proposed in Refs 10 and 11 is limited to cases where the wave function of the electron under consideration is rather strongly localized.

Thus, in this work we first formulate a perturbation method on a basis different from the usual second-order perturbation theory for calculating the energy levels and wave functions of a bound lattice polaron applicable to both the band- and the non-band-mass theories for arbitrary binding and coupling strength. Then, in order to find an appropriate approach for the treatment of the interaction of a bound electron with the acoustic phonons in a real piezoelectric crystal and the corresponding electronic binding energy, we apply the method formulated to calculate the binding energy of a bound lattice polaron in a piezoelectric material for a wide range of binding and coupling. The formulation of the perturbation method is described in Sec. II. The application is given in Sec. III. A summary is then made in Sec. IV, the last section.

II. METHOD

A. Formulation

The Hamiltonian for an electron bound to a massive hole in the IPF may be written

$$H=\frac{p^2}{2m}+V(\vec{r})+\sum_{\vec{k}} A^\dagger_{\vec{k}}A_{\vec{k}}\epsilon_{\vec{k}}+\sum_{\vec{k}}(V_{\vec{k}}A_{\vec{k}}e^{i\vec{k}\cdot\vec{r}}+\text{c. c.})\ , \qquad (2.1)$$

after a canonical transformation which eliminates the explicit phonon–massive-hole interaction.[9,11] In Eq. (2.1) the first term is the electronic kinetic energy and $V(\vec{r})$ denotes the electronic potential modified by the IPF. The third and the last terms of Eq. (2.1) are, respectively, the Hamiltonian of the phonons and the interaction of these phonons with the electron at the position $\vec{r}$, written in terms of creation and annihilation operators $A^\dagger_{\vec{k}}$ and $A_{\vec{k}}$ for phonons of wave vector $\vec{k}$. $V_{\vec{k}}$, characterizing the coupling strength between the electron and phonons, and $\epsilon_{\vec{k}}$ in Eq. (2.1) depend on the particular case under consideration. For example, in the case of a lattice polaron in a piezoelectric crystal they are given by[12]

$$V_{\vec{k}}=\left(\frac{4\pi\langle e^2_{ijk}\rangle e^2\hbar s}{2\epsilon_s^2 ckV}\right)^{1/2}\ , \quad \epsilon_{\vec{k}}=\hbar sk\ . \qquad (2.2)$$

Here ϵ_s is the static dielectric constant, V is the volume of the crystal, c is the average elastic constant, $\langle e_{ijk}\rangle$ is an average of the piezoelectric tensor components, e is the electronic charge, and s is the velocity of sound in the crystal considered.

In the usual perturbation theory, the last term in Eq. (2.1) is taken as a perturbation. However, in the case where the coupling between the electron and the phonons is strong, this perturbation becomes too big to be handled by a low-order perturbation theory. In order to reduce the strength of this perturbation, we transform the Hamiltonian H given by Eq. (2.1) to

$$H = H_e + \sum_{\vec{k}} \alpha_{\vec{k}}^{\dagger} \alpha_{\vec{k}} \epsilon_{\vec{k}} + \sum_{\vec{k}} [V_{\vec{k}} \alpha_{\vec{k}} X(\vec{r}) + \text{c.c.}] \tag{2.3}$$

by a simple canonical transformation in which the operator $A_{\vec{k}}$ transforms to

$$\alpha_{\vec{k}} = A_{\vec{k}} + V_{\vec{k}}^{*} \sigma_{\vec{k}}^{*} / \epsilon_{\vec{k}} \tag{2.4}$$

and the operator $A_{\vec{k}}^{\dagger}$ to $\alpha_{\vec{k}}^{\dagger}$. Here the dimensionless quantity $\sigma_{\vec{k}}$ is a completely arbitrary function of $\vec{k}$. The operators $\alpha_{\vec{k}}$ and $\alpha_{\vec{k}}^{\dagger}$ thus defined are boson annihilation and creation operators, respectively. Then this $\sigma_{\vec{k}}$ can be chosen so that the transformed "electron-phonon interaction" as characterized by $X(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \sigma_{\vec{k}}$ in the third term of Eq. (2.3) can be handled by a low-order perturbation theory. H_e in Eq. (2.3) is given by

$$H_e = \frac{p^2}{2m} + V(\vec{r}) + \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{\epsilon_{\vec{k}}} [|\sigma_{\vec{k}}|^2 - (\sigma_{\vec{k}}^{*} e^{i\vec{k}\cdot\vec{r}} + \text{c.c.})] . \tag{2.5}$$

It should be noted that the canonical transformation of (2.4) is more general than in the adiabatic perturbation theory[11,13] since $\sigma_{\vec{k}}$ here is allowed to take a more general form than in that theory (see Sec. II B).

Taking the last term in Eq. (2.3) as a perturbation and $|n\rangle |0\rangle$, in which there is a bound electron in the state $|n\rangle$ and no phonons are present, as the initial state of the unperturbed Hamiltonian given by the sum of the first two terms in Eq. (2.3), we obtain the energy correction due to the present perturbation to be $\Delta E_n = \Delta E_n^{(2)} + \Delta E_n^{(4)} + \cdots$, where all the odd-order perturbation corrections vanish. In the following, we shall be only concerned with a low-order perturbation theory in which the energy correction is just the second-order correction $\Delta E_n^{(2)}$ given by

$$\Delta E_n^{(2)} = \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle n | X(\vec{r}) | m \rangle|^2}{\epsilon_n^0 - \epsilon_m^0 - \epsilon_{\vec{k}}} . \tag{2.6}$$

Then, the energy of a polaron bound to a massive hole is given by

$$E_n = \epsilon_n^0 + \Delta E_n^{(2)} = \langle n | \left(\frac{p^2}{2m} + V(\vec{r}) \right) | n \rangle + \sum_{m,\vec{k}} \frac{|V_{\vec{k}}|^2 |\langle n | e^{i\vec{k}\cdot\vec{r}} | m \rangle|^2}{\epsilon_n^0 - \epsilon_m^0 - \epsilon_{\vec{k}}} \tag{2.7}$$

and the corresponding wave function is

$$|\psi_n\rangle = |n\rangle \left(1 + \sum_{\vec{k}} \frac{V_{\vec{k}}^{*} \sigma_{\vec{k}}}{\epsilon_{\vec{k}}} \alpha_k^{\dagger} |0\rangle \right) + \sum_{m,\vec{k}} \frac{V_{\vec{k}}^{*} \langle m | e^{i\vec{k}\cdot\vec{r}} | n \rangle}{\epsilon_n^0 - \epsilon_m^0 - \epsilon_{\vec{k}}} |m\rangle \alpha_k^{\dagger} |0\rangle . \tag{2.8}$$

Here $|0\rangle$ is the phonon vacuum state. $|m\rangle$ is an eigenfunction of H_e in Eq. (2.5) and ϵ_m^0 is the corresponding eigenvalue given by

$$\epsilon_m^0 \equiv \langle m | H_e | m \rangle = \langle m | \left(\frac{p^2}{2m} + V(\vec{r}) \right) | m \rangle + \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{\epsilon_{\vec{k}}} [|\sigma_{\vec{k}}|^2 - (\sigma_{\vec{k}}^{*} \rho_{\vec{k},m} + \text{c.c.})] , \tag{2.9}$$

where $\rho_{\vec{k},m} = \langle m | e^{i\vec{k}\cdot\vec{r}} | m \rangle$. It is interesting to note that the form of the energy expression given by Eq. (2.7) is the same as the corresponding one in the usual perturbation theory, though the present perturbation theory and the usual perturbation theory start from different basis. However, this is no longer true if we include higher-order perturbation corrections as can be seen from a comparison of the present fourth-order correction $\Delta E_n^{(4)}$ with that of the usual perturbation theory.

B. Choice of $\sigma_{\vec{k}}$ and effective potentials

If we choose $\sigma_{\vec{k}}$ to be zero, then the present unperturbed Hamiltonian H_e given by Eq. (2.5) and hence the results derived above such as Eqs. (2.7) and (2.8) become the same as those of the usual second-order perturbation theory. On the other hand, if we choose $\sigma_{\vec{k}}$ to be $\rho_{\vec{k},n}$, then the results given by Eqs. (2.7) and (2.8) are nothing but those of the adiabatic perturbation theory.[11,13] This is because for $\sigma_{\vec{k}} = \rho_{\vec{k},n}$ the present unperturbed Hamiltonain H_e becomes the Hamiltonian in the adiabatic or Hartree-type approximation, which assumes that the electron moves so fast that the ionic polarization cannot follow the electronic motion and responds only to the electronic charge cloud or the mean position of that same electron.[13]

In general, however, we can choose $\sigma_{\vec{k}}$ to be

$$\sigma_{\vec{k}} = \frac{\epsilon_{\vec{k}}}{2V |V_{\vec{k}}|^2} \int e^{i\vec{k}\cdot\vec{r}} [V(\vec{r}) - U_{\text{eff}}(\vec{r})] d\vec{r} , \tag{2.10}$$

where V is the volume of the crystal and write the present unperturbed Hamiltonian in the form

$$H_e = p^2/2m + U_{\text{eff}}(\vec{r}) , \tag{2.11}$$

in which the constant energy $\sum_{\vec{k}} |V_{\vec{k}}|^2 |\sigma_{\vec{k}}|^2 / \epsilon_{\vec{k}}$ is dropped. Here $U_{\text{eff}}(\vec{r})$ is an effective potential, which is an arbitrary function of $\vec{r}$ such that the integral on the right-hand side of Eq. (2.10) exists. We note that a result similar to Eq. (2.7) with $|m\rangle$

and ϵ_m^0, respectively, the eigenfunctions and eigenvalues of Eq. (2.11) can also be obtained for the ground state by the path-integral approach of Haken[3] as done in Ref. 4. However, a similar result for the excited states may not be directly obtained from the same approach. In reality, as can be seen from the present perturbation formulation, the result in Eq. (2.7) is explicitly true for both the ground and the excited states.

An immediate consequence of Eq. (2.11) is that, by suitably choosing $\sigma_{\vec{k}}$, $U_{\text{eff}}(\vec{r})$ can be obtained as a close approximation to the "effective" potential felt by the electron due to the total effect of the massive hole and the IPF. This would result in a weakened residual interaction which can be treated by a low-order perturbation theory with sufficient accuracy. Furthermore, by suitably choosing the form of $\sigma_{\vec{k}}$, the unperturbed problem $H_e|m\rangle = \epsilon_m^0|m\rangle$ can always be cast into such a form that simple analytic solutions exist. This makes the evaluation of second- and higher-order perturbation corrections to both the wave function and energy of any state a less formidable task. In the following, we discuss how both purposes can be achieved.

Let us consider a choice of $\sigma_{\vec{k}}$ giving rise to the simple effective potential

$$U_{\text{eff}}(\vec{r}) = -\gamma/r \quad , \tag{2.12}$$

where γ is a parameter to be determined. For this case, the unperturbed eigenfunctions and eigenenergies in Eq. (2.7) are just those in the hydrogen problem with an effective charge γ. The unperturbed ground-state function, for example, is given by $e^{-m\gamma r/\hbar^2}$. Then the last term in Eq. (2.7) can be numerically evaluated as in the usual second-order perturbation theory using the Coulomb Green's function.[14] It should be noted that it is not necessary to replace $p^2/2m + V(\vec{r})$ in Eq. (2.7) by a hydrogenic Hamiltonian in the present theory even if the chosen effective potential is Coulombic.

Now, we come to the choice of the parameter γ. Theoretically, this γ is arbitrary. However, from the perturbation expansion point of view it would be advantageous to choose it in such a manner that the present perturbation characterized by the last term in Eq. (2.3) is effectively small so that the perturbation expansion converges fast. This can be easily accomplished in the ground-state case. For the ground state it can be shown straightforwardly by using the path-integral approach of Haken[3,4] that the energy given by Eq. (2.7) cannot be lower than the true ground-state energy of the system for any choice of the effective potential $U_{\text{eff}}(\vec{r})$. Thus, for the ground state the γ can be chosen to give the lowest value of the ground-state energy $E_g^{(2)}$ from Eq. (2.7). This can be accomplished by varying the $E_g^{(2)}$ with respect to γ. The ground-state energy thus obtained must be below E_g^{USP} calculated by the usual second-order perturbation theory unless E_g^{USP} is the true ground-state energy. This is because the perturbation calculation here is numerically equivalent to the variation of the ground-state energy of the usual second-order perturbation theory with respect to the hydrogenic 1*s* wave function.

The effective potential given by Eq. (2.12) has the Coulombic asymptotic behavior which is an essential feature for most potentials binding a polaron to a massive hole. However, its form near the massive hole cannot usually conform with the actual potential in a realistic case. In general, this effective potential may be unable to give a ground-state energy close enough to the true one to make the higher-order perturbation corrections negligible. This is indeed the case when the electron-hole binding or the electron-phonon coupling becomes large. For this case a more flexible effective potential may have to be chosen. For example, we choose $U_{\text{eff}}(\vec{r}) = -\gamma/r + \delta/r^2$,[15] for which the last term in Eq. (2.7) may be numerically evaluated using the corresponding Green's function[14] and the parameters γ and δ can be determined in a manner similar to the determination of γ in Eq. (2.12).

III. BINDING ENERGY OF A PIEZOELECTRIC POLARON BOUND IN A COULOMB POTENTIAL

There have been three calculations[12,16,17] on the ground-state energy of a piezoelectric polaron bound in a Coulomb potential (will be referred to simply as a bound piezoelectric polaron henceforth). All three calculations are done within the usual second-order perturbation theory for small binding strengths. In the following, we apply the results obtained in the preceding section to the calculation of the binding energy of a bound piezoelectric polaron in the ground state for a wide range of binding and coupling strengths. Then we examine the applicability of both the usual second-order perturbation theory and the strong-coupling theory to the treatment of a bound electron with acoustic phonons in a piezoelectric crystal.

The binding energy in question is given as the difference in energy between the ground state and the state corresponding to $n = \infty$ (i.e., the highest bound state). In the limit of $n = \infty$, where $|n\rangle$ is completely diffused, the first term on the right-hand side of Eq. (2.7) vanishes and its second term can always be calculated by using the method in Ref. 9 as

$$\Delta E_\infty = -\sum_{\vec{k}} \frac{|V_{\vec{k}}|^2}{\epsilon_{\vec{k}} + \hbar^2 k^2/2m} \quad . \tag{3.1}$$

Note that ΔE_∞ does not depend on the particular choice of $\sigma_{\vec{k}}$ and is nothing but the electron self-energy due to the lattice polarization under consideration within the second-order perturbation theory. Therefore, in the present type second-order perturbation theory the energy of the electron in the state with $n=\infty$, E_∞ say, is just that given by Eq. (3.1) for any coupling strength. In the following, as in Refs. 16 and 17, we use the dielectric-continuum approximation for the crystal and the system of units in which $2m_b s^2 = 1$ for energy and $\hbar/2m_b s = 1$ for length.[18] Then, E_∞ can be written

$$E_\infty = -(2\alpha/\pi)\ln\left|1+k_m\right| \quad , \tag{3.2}$$

which is obtained from Eq. (3.1) after substituting Eq. (2.2) into Eq. (3.1) and replacing the summation over $\vec{k}$ in the first Brillouin zone by the $\vec{k}$ integral with the upper limit $\vec{k}_m$. Here, α is the coupling constant given by $e^2\langle e_{ijk}^2\rangle/2c\hbar s\epsilon_s^2$ and k_m is the maximum value of wave vector $\vec{k}$. Note that a result corresponding to that given by Eq. (3.2) for any coupling strength cannot be derived entirely within Haken's path-integral approach.[3,4]

Now, we come to the calculation of the ground-state energy. This energy from Eq. (2.7) is

$$E_g = \langle g|p^2 - \beta/r|g\rangle + \Delta E_g \quad , \tag{3.3}$$

with ΔE_g given by

$$\Delta E_g = \frac{4\pi\alpha}{V}\sum_{m,\vec{k}} \frac{|\langle g|e^{i\vec{k}\cdot\vec{r}}|m\rangle|^2}{k(\epsilon_g^0 - \epsilon_m^0 - k)} \quad , \tag{3.3a}$$

where $\beta = e^2/\epsilon_p\hbar s$ being the strength of the Coulomb potential and $|m\rangle$ and ϵ_m^0 are, respectively, the mth unperturbed state and the mth unperturbed energy depending on an effective potential that we shall choose. Now, let us choose the Coulombic potential as the effective potential so that $|m\rangle$ and ϵ_m^0 are, respectively, the mth eigenfunction and the mth eigenenergy of $H_e = p^2 - \gamma/r$, where γ is a parameter to be determined by minimizing E_g given by Eq. (3.3) (see Sec. II B). Then, ΔE_g given by Eq. (3.3a) can be numerically evaluated by using the Coulomb Green's function and $|g\rangle = (\gamma^3/8\pi)^{1/2}\times e^{-\gamma r/2}$ as[17]

$$\begin{aligned}\Delta E_g = -\frac{\alpha}{6\pi}\int_0^{k_m} dk\,\frac{\Gamma(1-\nu)}{\kappa}\int_0^\infty du\, e^{-u} M_{\nu,0.5}\left(\frac{2\kappa}{\beta}u\right) \\ \times\int_0^\infty dv\, e^{-v}\left[-4v\sin\left(\frac{2k}{\beta}v\right) + \frac{2k}{\beta}(4v^2 + 12vu + 6u^2)\right. \\ \left.\times\cos\left(\frac{2k}{\beta}v\right)\right] W_{\nu,0.5}\left(\frac{2\kappa}{\beta}(u+2v)\right) \quad .\end{aligned} \tag{3.4}$$

Here $\kappa = (k + \frac{1}{4}\gamma^2)^{1/2}$, $\nu = \beta/2\kappa$, $\Gamma(x)$ represents the gamma function, and W and M are the Whittaker functions.[19] Accordingly, the ground-state energy of interest can be numerically calculated by minimizing the above E_g with ΔE_g given by Eq. (3.4) with respect to the parameter γ for given β and α.

In addition, we describe how to get from E_g given by Eq. (3.3) the corresponding result by the usual second-order perturbation theory and that by the strong-coupling polaron theory (i.e., the adiabatic or Hartree self-consistent-field–type approximation). The unperturbed Hamiltonian H_e given above becomes that of the usual second-order perturbation theory, i.e., $p^2 - \beta/r$, if the γ above is set equal to β [which amounts to setting $\sigma_{\vec{k}}$ equal to zero in Eq. (2.3)]. Hence the corresponding result by the usual second-order perturbation theory can be obtained from Eq. (3.3) by simply putting $\gamma=\beta$. However, within the strong-coupling theory, the corresponding result is, from Eq. (2.9) with $\sigma_{\vec{k}} = \rho_{\vec{k},g}$ (see Sec. II B),

$$E_g = \langle g|p^2 - \frac{\beta}{\gamma}|g\rangle - \frac{4\pi\alpha}{V}\sum_{\vec{k}}\frac{|\langle g|e^{i\vec{k}\cdot\vec{r}}|g\rangle|^2}{k^2} \quad , \tag{3.5}$$

where $|g\rangle$ is a variational function. This E_g is the same as that obtained from Eq. (3.3) by keeping only $m=g$ in the sum over m. Thus, the corresponding result by the strong-coupling theory can be calculated from the variation of Eq. (3.3) excluding $m \neq g$ terms with respect to γ for given β and α. Then, the sum of the contributions from all the terms excluded is a correction to the result of the strong-coupling theory. This correction, in general, becomes small as the binding $R = \frac{1}{4}\beta^2$ or the coupling α increases, because the energy denominator for $m \neq g$ is very large for large R or α.

The binding energy of a bound piezoelectric polaron can now be calculated as $|E_g - E_\infty|$, where E_∞ is given in Eq. (3.2). The calculations as presented above have been performed for $\alpha = 1, 3, 10, 30$ and $R = 100, 500, 1000, 1500, 2000$ using the IBM 360/75 at the University of Waterloo. The results obtained are summarized in Table I. In this table the results by the present second-order perturbation theory, the usual second-order perturbation theory and by the strong-coupling theory are, respectively, denoted by E_B^{PSP}, E_B^{USP}, and E_B^{SC}. Here we note that the maximum value of the wave vector $\vec{k}$ used is $k_m = 1000\ (\hbar/2m_b s)^{-1}$.[18] We also note that the corresponding binding energy is almost independent of k_m despite the rather strong k_m dependence of both the ground-state and highest-bound-state energies.

Now, we can make some conclusive remarks on the applicability of the usual second-order perturbation theory and on that of the strong-coupling polaron theory to the problem considered in this section. Firstly, as is shown by comparing E_B^{USP} with E_B^{PSP} in Table I, the usual second-order perturbation theory is valid for any R as long as $\alpha < 10$. Secondly, as expected, the strong-coupling polaron theory becomes better when increasing R or α or both and works better than the usual second-order perturbation theory only in the region where $\alpha \gtrsim 30$. However, this is far from the experimental region. For the piezoelectric materials such as ZnS and CdS, the coupling constant α is of the order of unity and the binding $R = \frac{1}{4}\beta^2$ is of the order of 1.6×10^3.[20] Therefore, experimentally we are in the region where the usual second-order perturbation theory

TABLE I. Binding energies of a bound piezoelectric polaron for $\alpha = 1, 3, 10, 30$ and $R = 100, 500, 1000, 1500, 2000$. E_B^{USP}, E_B^{SC}, and E_B^{PSP} denote the results calculated by the usual second-order perturbation theory, the strong-coupling theory, and the present second-order perturbation method with the hydrogenic effective potential, respectively (see text for details). All energies are in units of $2ms^2 = 1$.

	$\alpha = 1$			$\alpha = 3$			$\alpha = 10$			$\alpha = 30$		
R	E_B^{USP}	E_B^{SC}	E_B^{PSP}	E_B^{USP}	E_B^{SC}	E_B^{PSP}	E_B^{USP}	E_B^{SC}	E_B^{PSP}	E_B^{USP}	E_B^{SC}	E_B^{PSP}
100	104.7	101.9	104.7	114.0	106.4	114.5	146.8	128.3	154.3	240.5	243.4	311.7
500	511.7	509.7	511.8	535.1	529.6	535.8	616.9	605.5	625.4	850.7	875.2	927.9
1000	1017.1	1015.5	1017.2	1051.3	1047.1	1052.0	1171.0	1163.4	1179.7	1513.0	1548.9	1592.3
1500	1521.3	1519.9	1521.4	1563.9	1560.3	1564.7	1713.1	1707.8	1722.1	2139.3	2182.1	2221.6
2000	2024.9	2023.7	2025.1	2074.8	2071.5	2075.6	2249.2	2245.3	2258.4	2747.6	2794.5	2831.6

works well, implying the interaction between a bound electron and the acoustic phonons in a real piezoelectric crystal is weak.

The computer work for the above exact calculation by the Green's function is very much time consuming. Consequently, we develop an approximate method as described in the Appendix to evaluate the last term in Eq. (2.7) for practical cases. We have used Eq. (A1) without S_{n3} and S_{n4} to evaluate Eq. (3.3a), which is the ground-state energy shift, for $\gamma = \beta$. The result so obtained is compared with the exact result obtained from Eq. (3.4) for $\gamma = \beta$ in Table II. Note that the ground-state energy shift is actually given as $-(\Delta E_g - E_\infty)/\alpha$, which is almost independent of k_m, in Table II. It can be seen from this table that the approximate method commits a small error in the region of $R \gtrsim 1000$, i.e., in the experimental region. Moreover, the computer time required is very much less for the approximate method than for the exact calculation by the Green's function (at least 1/100). Therefore, the approximate method suggested in the Appendix is practically appropriate if a few percent error can be tolerated. In addition, we remark that for the present problem the effective-mass method and the method in Ref. 12 do not work at all in the region of $R > 1$ (e.g., for $R = 1500$, $-(\Delta E_g - E_\infty)/\alpha$ is 636.6 by the effective-mass method and -1.92 by the method in Ref. 12).

IV. SUMMARY

By means of a canonical transformation, we separate the interaction of the electron with the phonons of the IPF into two parts. One part is included in an effective potential which is chosen to approximate the total potential effectively felt by the electron in the combined field of the massive hole and the IPF. The other part is treated as a perturbation resulting in a perturbation method, which is more general than the usual and adiabatic perturbation methods for calculating the bound-polaron states. By choosing an effective potential to be close enough to that actually felt by the electron, the perturbation can be much reduced so that it can be tackled within the second-order perturbation theory even for large coupling. In the ground-state case, such a choice corresponds to choosing a trial function by the variation method and hence the energy calculation by the perturbation theory developed in this paper is *numerically* equivalent to a good variational calculation. Further, the present results may overlap to a certain extent with that derived from Haken's path-integral approach for the ground state case. However, a similar result for the excited state may not be obtainable directly from Haken's approach, as is done in the present work.

The method developed is applied to calculate the binding energy of a bound piezoelectric polaron for a wide range of the coupling and binding. From the comparison of the calculated results with those of the usual second-order perturbation and the strong-coupling polaron theories, it is seen that a weak-coupling theory such as the usual second-order perturbation theory is more applicable than the strong-coupling theory for bound polarons in real piezoelectric crystals. Thus, we may conclude that the interaction of a bound electron with the acoustic phonons in a real piezoelectric crystal is essentially weak and can be treated by the usual second-order perturbation theory very accurately.

APPENDIX: AN APPROXIMATE EVALUATION OF THE SECOND-ORDER ENERGY CORRECTION

The second-order energy correction like the last term in Eq. (2.7) can be written

TABLE II. Comparison of results of the numerical evaluation and approximate calculation for the ground-state energy shift $-(\Delta E_g - E_\infty)/\alpha$ (in units of $2ms^2 = 1$).

R	Numerical evaluated	Approximate method
100	4.68	5.04
500	11.7	12.3
1000	17.1	17.8
1500	21.3	22.1
2000	24.9	25.8
2500	28.1	29.0
3000	31.1	31.9

TABLE III. Comparison of the second-order energy shifts of the ground state of an electron, bound in a Coulomb field $-\beta/r$ and interacting with optical phonons, Δ_{gC} and Δ_{gF} calculated from the last term of Eq. (2.7), respectively, using the Coulomb Green's function in Ref. 8 and Eq. (A1) neglecting $S_{n3}+S_{n4}$. R is a usual parameter that measures the binding strength. All energies are in units of a phonon energy.

$R(=\frac{1}{4}\beta^2)$	$-\Delta_{gF}/\alpha$	$-\Delta_{gC}/\alpha$	$(S_{n3}+S_{n4})/\alpha$
0.1	1.015	1.017	−0.002
0.5	1.082	1.085	−0.003
1.0	1.195	1.167	0.028
1.5	1.302	1.245	0.057
2.0	1.397	1.319	0.078
4.0	1.696	1.585	0.111
6.0	1.930	1.813	0.117
8.0	2.132	2.017	0.115
10.0	2.313	2.201	0.112
20.0	3.052	2.958	0.094
30.0	3.640	3.557	0.083
40.0	4.144	4.069	0.075
60.0	5.002	4.937	0.065
100.0	6.379	6.324	0.055

$$\Delta_n = S_n - \sum_{\vec{k}} \frac{|V_{\vec{k}}|^2 |\rho_{\vec{k},n}|^2}{\epsilon_{\vec{k}}} , \qquad (A1)$$

with S_n, which can be calculated as

$$S_n = \sum_{\vec{k}} |V_{\vec{k}}|^2 \sum_{\vec{q},\vec{q}',\vec{q}''} \langle n|\vec{q}\rangle\langle\vec{q}|X_{\vec{k}}|\vec{q}'\rangle \times \langle\vec{q}'|F_{\vec{k}}|\vec{q}''\rangle\langle\vec{q}''|n\rangle \qquad (A2)$$

following a procedure similar to that in Refs. 7 and 12. The matrix element of $F_{\vec{k}}$ for plane waves $|\vec{q}'\rangle$ and $|\vec{q}''\rangle$ is given by

$$\langle\vec{q}'|F_{\vec{k}}|\vec{q}''\rangle = \frac{2m}{\hbar^2}\left(\frac{\langle\vec{q}'|X_{\vec{k}}^*|\vec{q}''\rangle}{q''^2 - q'^2 - \chi^2} - \frac{\langle\vec{q}'|[F_{\vec{k}}, U_{\text{eff}}]|\vec{q}''\rangle}{q''^2 - q'^2 - \chi^2}\right), \qquad (A3)$$

with $\chi^2 = 2m\epsilon_{\vec{k}}/\hbar^2$, obtained from the equation $([F_{\vec{k}}, H_e] - \epsilon_{\vec{k}}F_{\vec{k}} - X_{\vec{k}}^*)|n\rangle = 0$ defining $F_{\vec{k}}$. Equation (A3) can be solved iteratively. Substituting (A3) and $\langle\vec{q}|X_{\vec{k}}|\vec{q}'\rangle = \delta_{\vec{q},\vec{q}'+\vec{k}} - \rho_{\vec{k},n}\delta_{\vec{q},\vec{q}'}$ into Eq. (A2) yields

$$S_n = S_{n1} + S_{n2} + S_{n3} + S_{n4} , \qquad (A4)$$

with

$$S_{n1} = \frac{2m}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 |\langle n|\vec{q}\rangle|^2}{q^2 - |\vec{q}-\vec{k}|^2 - \chi^2} , \qquad (A4a)$$

$$S_{n2} = -\frac{2m}{\hbar^2} \sum_{\vec{k},\vec{q}} \frac{|V_{\vec{k}}|^2 \rho_{\vec{k},n} \langle n|\vec{q}\rangle\langle\vec{q}+\vec{k}|n\rangle}{|\vec{q}+\vec{k}|^2 - q^2 - \chi^2} , \qquad (A4b)$$

$$S_{n3} = \frac{2m}{\hbar^2} \sum_{\vec{k}} \sum_{\vec{q},\vec{q}'} \frac{|V_{\vec{k}}|^2 R_{\vec{q}-\vec{k},\vec{q}'} \langle n|\vec{q}\rangle\langle\vec{q}'|n\rangle}{q'^2 - |\vec{q}-\vec{k}|^2 - \chi^2} , \qquad (A4c)$$

S_{n4} is given by Eq. (A4c) with $\langle n|\vec{q}\rangle$ replaced by $-\rho_{\vec{k},n}\langle n|\vec{q}-\vec{k}\rangle$. Here $R_{\vec{q}-\vec{k},\vec{q}'}$ is $-\langle\vec{q}-\vec{k}|[F_{\vec{k}}, U_{\text{eff}}]|\vec{q}'\rangle$. S_{n1} and S_{n2} can be evaluated exactly by replacing the summation over $\vec{k}$ and $\vec{q}$ by the corresponding integrals. However, S_{n3} and S_{n4} can only be evaluated by using $\langle\vec{q}'|F_{\vec{k}}|\vec{q}''\rangle$ obtained iteratively from Eq. (A3). This needs a lot of computing efforts.

In reality, S_{n3} and S_{n4} vanish in the weak-binding limit where the effective potential U_{eff} is effectively zero, because in such a limit $R_{\vec{q}-\vec{k},\vec{q}'}$ becomes zero. In going from the weak-binding limit to the strong-binding limit, the quantity which characterizes the sum of S_{n3} and S_{n4}, i.e., $\langle n|\vec{q}\rangle - \rho_{\vec{k},n}\langle n|\vec{q}-\vec{k}\rangle$, tends to zero ($\langle n|\vec{q}\rangle$ and $\langle n|\vec{q}-\vec{k}\rangle$ approach each other and $\rho_{\vec{k}}$ tends to unity) and S_{n3} and S_{n4} cancel exactly in the strong-binding limit. It is then expected that a lot of cancellation between S_{n3} and S_{n4} may occur even in the intermediate region of binding. In order to check this conjecture, we use the formalism developed above to calculate the energy shift given by Eq. (A1) with $S_n = S_{n1} + S_{n2}$ for an optical polaron bound in a Coulomb potential $-\beta/r$ in the usual second-order perturbation theory. For this calculation $|g\rangle = (\lambda^3/\pi)^{1/2}e^{-\lambda r}$, with $\lambda = \frac{1}{2}\beta$. The results thus calculated for the energy shift are compared in Table III with the numerically exact calculation by means of a Coulomb Green's function in Ref. 8. From this comparison, we estimate the value of $S_{n3}+S_{n4}$ for different binding R. As expected, S_{n3} and S_{n4} cancel rather well and $S_{n3}+S_{n4}$ is small compared to the total energy shift Δg particularly in the region where the binding R is less than 2 or greater than 10. Accordingly, S_{n3} and S_{n4} may be omitted in some practical case where a few percent error can be tolerated.

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[1] V. M. Buimistrov and S. T. Pekar, Zh. Eksp. Teor. Fiz. 32, 1193 (1957) [Sov. Phys.-JETP 5, 970 (1957)]; V. M. Buimistrov, Fiz. Tverd. Tela 5, 3264 (1963) [Sov. Phys.-Solid State 5, 2387 (1964)].

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

[3] H. Haken, Z. Phys. 147, 323 (1957).

[4] M. Matsuura, Can. J. Phys. 52, 1 (1974).

[5] D. M. Larsen, Phys. Rev. 187, 1147 (1969).

[6] J. Sak, Phys. Rev. B 3, 3356 (1971).

[7] K. K. Bajaj and T. D. Clark, Solid State Commun. 8, 1419 (1970).

[8] M. H. Engineer and N. Tzoar, Phys. Rev. B 5, 3029 (1972).

[9] S. Wang, H. L. Arora, and M. Matsuura, Phys. Rev. B 4, 3685 (1971). Note: The criticism made on this reference by P. K. Dubey, V. V. Paranjape, and M. M. L. Anand [Phys. Rev. B 7, 1718 (1973)] cannot be applied to the general formulation given there, because the electronic potential considered there is not Coulombic for arbitrary electron-hole separations.

[10] S. Wang, Phys. Rev. 153, 939 (1967); 132, 573 (1963).

[11] S. Wang, M. Matsuura, C. C. Wong, and M. Inoue,

Phys. Rev. B 7, 1695 (1973).

[12] K. K. Bajaj, M. J. Goovaerts, and J. T. Devreese, Solid State Commun. 12, 1197 (1973).

[13] G. Whitfield and P. M. Platzman, Phys. Rev. B 6, 3987 (1972).

[14] L. Hostler, J. Math. Phys. 5, 591 (1964).

[15] C. H. Woo and S. Wang, Phys. Rev. B 7, 2810 (1973).

[16] M. Engineer, Solid State Commun. 14, 123 (1974).

[17] M. Matsuura and S. Wang, Solid State Commun. 15, 613 (1974).

[18] Using $m_b \simeq 0.2 m_e$, where m_e is the free-electron mass, and $s \simeq 3\times 10^5$ cm sec^{-1} for piezoelectric materials such as ZnS and CdS, we obtain $2m_b s^2 \simeq 2\times 10^{-2}$ meV and $\hbar/2m_b s \simeq 10^{-5}$ cm. Then the maximum value of the wave vector $\vec{k}$ is $k_m \simeq 10^3(\hbar/2m_b s)^{-1} \simeq 10^8$ cm^{-1}.

[19] *Handbook of Mathematical Functions*, edited by M. Abramovitz and I. Stegun (Dover, New York, 1965).

[20] For piezoelectric materials such as ZnS and CdS, $c \simeq 5\times 10^{11}$ dyn/cm^2, $\langle e_{ijk}^2\rangle \simeq (10^5$ statcoulomb/cm$^2)^2$, $\epsilon_s \simeq 10$ [G. D. Mahan, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. T. Devreese (North-Holland, Amsterdam, London, 1972)], and so $\langle e_{ijk}^2\rangle / c\epsilon_s \simeq 2\times 10^{-3}$. Thus, $\epsilon_p \simeq \epsilon_s$ and $\beta = e^2/\epsilon_p \hbar s \simeq 0.8\times 10^2$ for $s \simeq 3\times 10^5$ cm sec^{-1}. Accordingly, $R = \frac{1}{4}\beta^2 \simeq 1.6\times 10^3$ and $\alpha \lesssim 1$.