

theoretically. The difference of 0.5 eV in the theoretical indirect gap of Ge-Si and the experimental indirect gap of the  $\text{Ge}_{0.5}\text{Si}_{0.5}$  alloy may be in part

due to a difference between the alloy and the pure crystal but probably is due to a defect in the model or in the exchange approximation used in the model.

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## Perturbation Theory for a Bound Polaron\*

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The binding energy of a polaron in a Coulomb potential is determined by the second-order perturbation theory to be  $E_B^{(2)} = E_B + \alpha \hbar \omega_0 (\frac{1}{6} \beta^2 + \frac{1}{24} \beta^4)$ , where  $\alpha$  is the Fröhlich coupling constant and  $\beta^2 = E_B / \hbar \omega_0$ . It is supposed that  $\alpha \ll 1$  and  $\beta \ll 1$ . This improves the earlier calculation of Platzman and brings the perturbation theory to agreement with the result reached previously by the application of field-theoretic methods to the problem of a bound polaron.

### I. INTRODUCTION

We will calculate, approximately, the energy of the ground state of an electron bound in a Coulomb

potential in a weakly polar semiconductor. The problem is described by the following Hamiltonian<sup>1</sup>:

$$\frac{\vec{p}^2}{2m} - \frac{e^2}{\epsilon_s r} + \omega_0 \sum_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}}$$

$$+ \frac{ie}{\sqrt{\Omega}} \left[ 2\pi\omega_0 \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \right]^{1/2} \\ \times \sum_{\mathbf{q}} (e^{-i\mathbf{q} \cdot \mathbf{r}} a_{\mathbf{q}}^\dagger - e^{i\mathbf{q} \cdot \mathbf{r}} a_{\mathbf{q}}) = H_0 + H_{ph} + V. \quad (1)$$

$H_0$  contains the first two terms,  $\mathbf{p}$  and  $\mathbf{r}$  are the momentum and position vectors of the electron,  $\omega_0$  is the optical-phonon frequency,  $a_{\mathbf{q}}^\dagger$  and  $a_{\mathbf{q}}$  are the creation and annihilation operators of optical phonons,  $\Omega$  is the normalization volume, and  $\epsilon_s$  and  $\epsilon_\infty$  are static and optical dielectric constants, respectively;  $\hbar = 1$ .

The region of validity of the theory presented here is delimited by three conditions: (a) The radius of the polaron is large in comparison to the lattice constant;  $d \ll (m\omega_0)^{-1/2}$ . This condition makes it possible to use the continuum approximation and the Fröhlich Hamiltonian (1). (b) The electron-phonon coupling constant is small,

$$\alpha = e^2 \left( \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s} \right) \left( \frac{m}{2\omega_0} \right)^{1/2} \ll 1.$$

This condition will allow us to use perturbation theory. (c) We assume  $\beta \ll 1$ , where  $\beta^2 = E_B/\omega_0$ ,  $E_B$  being the binding energy of the ground state as given by the hydrogenlike Hamiltonian  $H_0$ , since without another small parameter it is very difficult to evaluate the perturbation-theory formulas.

In his paper<sup>2</sup> Platzman used the second-order perturbation-theory formula

$$\Delta E_2 = - \frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}, n} \frac{1}{q^2} \frac{|\langle 0 | e^{-i\mathbf{q} \cdot \mathbf{r}} | n \rangle|^2}{E_n - E_0 + \omega_0}, \quad (2)$$

where  $|0\rangle$  and  $E_0$  are the state vector and energy of the ground state, and the index  $n$  runs over the whole spectrum of  $H_0$ . We use here the shorthand notation  $\epsilon^{-1} = \epsilon_\infty^{-1} - \epsilon_s^{-1}$ . Platzman's result for the binding energy is<sup>3</sup>

$$\omega_0 \left( \beta^2 + \frac{1}{6} \beta^2 - \frac{1}{3} \beta^4 \right), \quad \beta^2 = E_B/\omega_0. \quad (3)$$

Larsen<sup>4</sup> compared his variational calculations with Eq. (3) and found, surprisingly, that the first two terms give a better approximation than the presumably more accurate expression (3) containing a correction of higher order.

In a previous work<sup>5</sup> we have used another approach to the problem defined by the Hamiltonian (1) and the conditions (a)–(c). The starting point is the homogeneous Dyson equation for the electron Green's function near the energy of the bound state. The free-electron (free from external field) Green's function and the vertex part are calculated to include terms of the orders  $\alpha$ ,  $\alpha\beta^2$ , and  $\alpha\beta^4$ . The Dyson equation can be reduced to an effective-mass equation containing correction terms. It has the form

$$\left[ -\alpha\omega_0 + \left( 1 - \frac{\alpha}{6} \right) \frac{p^2}{2m} - \frac{3\alpha p^4}{160m^2\omega_0} \right. \\ \left. - \frac{e^2}{\epsilon_s r} + \frac{\pi\alpha e^2}{12m\omega_0\epsilon_s} \delta(\mathbf{r}) \right] \psi = E\psi. \quad (4)$$

Treating the third and fifth terms in the effective Hamiltonian of Eq. (4) as a perturbation, we find the binding energy of the ground state as

$$\omega_0 \left( \beta^2 + \frac{1}{6} \alpha\beta^2 + \frac{1}{24} \alpha\beta^4 \right). \quad (5)$$

This formula gives a smaller effect in the order  $\alpha\beta^4$  by the factor of 8 and it also has a different sign when compared to Platzman's formula (3). The source of this discrepancy will be found in Sec. II.

## II. SECOND-ORDER PERTURBATION THEORY

The method of calculation is the same as in Platzman's paper. The first stages of the procedure reproduce the results of Ref. 2. We start with Eq. (2) and write the energy denominator as a sum of two terms

$$\frac{1}{E_n - E_0 + \omega_0} = \frac{1}{\omega_0 + q^2/2m} - \frac{E_n - E_0 - q^2/2m}{(\omega_0 + q^2/2m)(E_n - E_0 + \omega_0)}. \quad (6)$$

Correspondingly, the correction to the energy of the ground state is written as a sum of two terms

$$\Delta E_2 = \epsilon_1 + \epsilon_2. \quad (7)$$

The first term shifts the ground state by  $\epsilon_1 = -\alpha\omega_0$ . Since the bottom of the continuum is shifted by the same amount, this term is of no consequence for the binding energy. We are left with the second term

$$\epsilon_2 = \frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} \sum_n |\langle 0 | e^{-i\mathbf{q} \cdot \mathbf{r}} | n \rangle|^2 \\ \times \frac{E_n - E_0 - q^2/2m}{(\omega_0 + q^2/2m)(E_n - E_0 + \omega_0)}. \quad (8)$$

Using Eq. (6) again,  $\epsilon_2$  is split into two terms;

$$\epsilon_2 = \epsilon_3 + \epsilon_4. \quad (9)$$

It turns out that  $\epsilon_3 = 0$ . The expression for  $\epsilon_4$  reads

$$\epsilon_4 = - \frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} \sum_n |\langle 0 | e^{-i\mathbf{q} \cdot \mathbf{r}} | n \rangle|^2 \\ \times \frac{(E_n - E_0 - q^2/2m)^2}{(\omega_0 + q^2/2m)^2 (E_n - E_0 + \omega_0)}. \quad (10)$$

Iterating the denominator,  $\epsilon_4$  divides into two parts

$$\epsilon_4 = \epsilon_5 + \epsilon_6. \quad (11)$$

We are still following Platzman's procedure. He

shows that

$$\epsilon_5 = -\frac{1}{6} \alpha \beta^2 \omega_0. \quad (12)$$

Thus we get the term arising from the renormalization of the electron mass. We proceed further to estimate  $\epsilon_6$ :

$$\begin{aligned} \epsilon_6 &= \frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} \\ &\times \sum_n |\langle 0 | e^{-i\mathbf{q} \cdot \mathbf{r}} | n \rangle|^2 \frac{(E_n - E_0 - q^2/2m)^3}{(\omega_0 + q^2/2m)^3 (E_n - E_0 + \omega_0)} \\ &= \epsilon_7 + \epsilon_8, \end{aligned} \quad (13)$$

where again Eq. (6) has been used to divide  $\epsilon_6$  into  $\epsilon_7$  and  $\epsilon_8$ . Calculating  $\epsilon_7$  we get

$$\epsilon_7 = \frac{1}{3} \alpha \beta^4 \omega_0. \quad (14)$$

Platzman stopped at this point. Gathering the results obtained so far he got the expression (3) for the binding energy.<sup>3</sup>

However, we shall see that  $\epsilon_8$  *does contribute to the order*  $\alpha \beta^4 \omega_0$  and therefore we have to go one step further and find it. By means of one more iteration according to Eq. (6)

$$\epsilon_8 = \epsilon_9 + \epsilon_{10},$$

where

$$\begin{aligned} \epsilon_9 &= -\frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} \\ &\times \sum_n |\langle 0 | e^{-i\mathbf{q} \cdot \mathbf{r}} | n \rangle|^2 \frac{(E_n - E_0 - q^2/2m)^4}{(\omega_0 + q^2/2m)^5}. \end{aligned} \quad (15)$$

Using the operator identity

$$e^{-i\mathbf{q} \cdot \mathbf{r}} \mathbf{p} e^{i\mathbf{q} \cdot \mathbf{r}} = \mathbf{p} + \mathbf{q}, \quad (16)$$

$\epsilon_9$  can be rewritten as

$$\epsilon_9 = -\frac{2\pi e^2 \omega_0}{\epsilon} \frac{1}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} \frac{\langle 0 | [(H_0 - E_0) + \mathbf{p} \cdot \mathbf{q}/m]^4 | 0 \rangle}{(\omega_0 + q^2/2m)^5}. \quad (17)$$

From the sixteen terms arising by expanding the fourth power of the sandwiched operator only two are different from zero,

$$\langle 0 | (\mathbf{p} \cdot \mathbf{q}/m)(H_0 - E_0)^2(\mathbf{p} \cdot \mathbf{q}/m) | 0 \rangle \quad (18)$$

and

$$\langle 0 | (\mathbf{p} \cdot \mathbf{q}/m)^4 | 0 \rangle. \quad (19)$$

The quantity (19) is clearly of the order  $q^4(\omega_0^2/m^2)\beta^4$  and must be taken into account in our approximation, but before evaluating it let us discuss the contribution (18). Formally it is of the order  $(q^2/m)\omega_0^3\beta^6$  but a closer examination shows that it is divergent:

$$\left\langle 0 \left| \frac{\mathbf{p} \cdot \mathbf{q}}{m} (H_0 - E_0)^2 \frac{\mathbf{p} \cdot \mathbf{q}}{m} \right| 0 \right\rangle = \frac{e^4}{m^2 \epsilon_s^2} \left\langle 0 \left| \frac{(\mathbf{q} \cdot \mathbf{r})^2}{r^6} \right| 0 \right\rangle. \quad (20)$$

The divergent expectation values arising in this and subsequent steps of the iterative process correspond to corrections to the Coulomb potential which for large distances have the form  $r^{-n}$ ,  $n > 1$ . For instance, it is likely that there will be a correction of the form  $r^{-4}$ , which corresponds to the force of the vander Waals type.<sup>5</sup> There is, however, a short-distance cutoff for these potentials, and it must be of the order of the polaron radius,  $(m\omega_0)^{-1/2}$ . This fact allows us to estimate the order of the energy shift caused by these corrections. Excluding the volume of the polaron from the integration in (20) we get an estimate

$$\frac{e^4}{m^2 \epsilon_s^2} \left\langle 0 \left| \frac{(\mathbf{q} \cdot \mathbf{r})^2}{r^6} \right| 0 \right\rangle \sim \frac{q^2}{m} \omega_0^3 \beta^5,$$

so that this term is proportional to  $\beta^5$  rather than  $\beta^6$  but still is outside the range of our approximation. Similar analysis can be carried out for  $\epsilon_{10}$  and it shows that  $\epsilon_{10}$  can be neglected in our approximation. The divergent integrals indicate that we are entering a "danger zone" at this stage of calculation and that Platzman's method used here cannot be extended to improve the accuracy beyond the order  $\beta^4$ .

Now we return to the term (19). Using the unperturbed ground-state wave function and binding energy

$$\varphi_{1s}(k) = \left( \frac{\kappa}{2\pi^2} \right)^{1/2} \left( \frac{2\kappa}{k^2 + \kappa^2} \right)^2, \quad E_B = \frac{\kappa^2}{2m} \quad (21)$$

it can be shown that

$$\langle 0 | (\mathbf{p} \cdot \mathbf{q})^4 | 0 \rangle = \kappa^4 q^4. \quad (22)$$

Also useful is the integral

$$\int d^3\mathbf{q} \frac{q^2}{(\omega_0 + q^2/2m)^5} = \frac{3\pi^2}{64} \frac{(2m)^{5/2}}{\omega_0^{5/2}}. \quad (23)$$

With the aid of (22) and (23) it is easy to get the resulting additional shift to the energy of the ground state

$$\epsilon_9 = -\frac{3}{8} \alpha \beta^4 \omega_0. \quad (24)$$

Adding this to the previously calculated terms we get for the binding energy

$$\omega_0 \left( \beta^2 + \frac{1}{6} \alpha \beta^2 + \frac{1}{24} \alpha \beta^4 \right) \quad (25)$$

in agreement with the result provided by the effective-mass equation with corrections, Eq. (5).

### III. CONCLUSION

The energy of the ground state of a weak-coupling

polaron ( $\alpha \ll 1$ ) in a Coulomb field was calculated for the case  $\beta = (E_B/\omega_0)^{1/2} \ll 1$  by the method of Platzman. The disagreement between the correction to the binding energy as determined by Platzman and the result of an effective-mass equation with corrections to the orders  $\alpha\beta^2\omega_0$  and  $\alpha\beta^4\omega_0$  is removed if Platzman's procedure is improved by adding one step in his iterative process. The binding energy is given by the expression (25).

The method of expanding the energy in powers of  $\beta$  cannot be extended in a simple way to include corrections of the orders beyond  $\beta^4$ .

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## Energy-Gap Anomaly in the Semiconductor Sequence PbS, PbSe, and PbTe

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The  $f$ -sum rule has been examined at the conduction- and valence-band edges of PbS, PbSe, and PbTe. Experimental values of electron and hole effective masses, and of energy gaps were used. For both two-band and six-band models, it was found that PbTe *does not* follow the same  $f$ -sum rule as do PbS and PbSe. However, it was also found that, for the III-V and II-VI semiconductor sequences (InSb, InAs, InP), (GaSb, GaAs), and [CdSe, CdS (hexagonal)], the members of each sequence *do* follow the same  $f$ -sum rule. It is concluded that the well-known anomaly in the values of the energy gap  $E_G$  of the PbX sequence [ $E_G(\text{PbS}) > E_G(\text{PbTe}) > E_G(\text{PbSe})$ ] is due to an irregular value of  $E_G$  for PbTe. It appears likely that this anomalous value of the energy gap of PbTe reflects, through the  $L_6^-$  conduction-band edge, an irregular value of the 5s electron energy of the tellurium atom. It is proposed that the  $L_6^-$  conduction-band edge states in PbTe differ from the equivalent states in PbS and PbSe. This difference results in PbTe having an  $f$ -sum matrix element different from that for PbS and PbSe; this is the reason that PbTe does not follow the same  $f$ -sum rule as do PbS and PbSe. The  $f$ -sum-rule plots of the experimental data for these semiconductors have been used to calculate matrix element values.

### I. INTRODUCTION

The energy gap  $E_G$  of a compound semiconductor  $MX$  is generally observed to decrease as the atomic number of the atom  $X$  increases. Examples of this well-known "rule" may be observed by considering the energy-gap values given in Table I for several series of semiconductors. The values shown are optically determined values of  $E_G$  for two III-V series and two II-VI series, including both zinc-blende and wurtzite structures. For each series, the energy gap of  $MX$  decreases monotonically as the atomic number of atom  $X$  increases. The data shown, covering different crystal structures and a range of energy gap of more than a factor of 10, demonstrate that this rule is well established experimentally.

However, the energy gaps of PbS, PbSe, and PbTe *do not* exhibit this monotonic decrease. The ex-

perimental values<sup>1,2</sup> of  $E_G$  between 4 and 373 °K for these semiconductors are such that  $E_G(\text{PbS}) > E_G(\text{PbTe}) > E_G(\text{PbSe})$ . Precise values<sup>1</sup> of these energy gaps at 4 °K are: for PbS,  $E_G = (0.286 \pm 0.003)$  eV; for PbTe,  $E_G = (0.190 \pm 0.002)$  eV; for PbSe,  $E_G = (0.165 \pm 0.005)$  eV. The fact that the sequence of energy-gap values for the PbS group is anomalous in that  $E_G(\text{PbSe}) < E_G(\text{PbTe})$  has been noted by a number of authors<sup>3-6</sup> as far back as 1959. However, there appears to have been little explicit discussion of which member or members of the sequence exhibit an irregular value of the energy gap, and thus even less discussion of possible reasons for the existence of this irregularity.

This paper is a theoretical study, previously reported<sup>7</sup> in preliminary form as a letter, whose aims were: (a) a determination of the irregular member(s) of the PbS sequence; (b) obtaining information concerning the reasons for the existence