

## Energy spectrum of the bound polaron

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An eigenvalue problem for an electron interacting with a Coulomb center and a field of LO phonons is solved by a method of optimized canonical transformation. This method can be applied to arbitrary values of the electron-phonon coupling constant  $\alpha$ . The energy eigenvalues for the  $1s$  through  $4f$  states have been calculated as function of  $\alpha$  and of the ratio  $R$  of the donor rydberg  $m_e e^4 / 2\hbar^2 \epsilon_0^2$  to the LO-phonon energy  $\hbar\omega$ . These values are the upper bounds to the energy  $E_{1s}$  of the ground state as well to all the energy levels of the excited states lying below  $E_{1s} + \hbar\omega$ . In a broad range of  $\alpha$  and  $R$ , the present upper bounds are lower than previous variational results for the states  $1s$ ,  $2s$ , and  $2p$ . The energy levels for the  $3s$ – $4f$  states have been calculated for the first time by variational means. The calculated energy eigenvalues  $E_{nl}$  lie always below the corresponding hydrogenlike levels, i.e.,  $E_{nl}/\hbar\omega \leq -\alpha - R/n^2$ , where  $n$  and  $l$  are the principal and angular momentum quantum numbers, respectively. For all values of  $\alpha$  and  $R$ , the following sequence of the energy levels for a given  $n$  has been obtained:  $E_{nl} \leq E_{n'l'}$  if  $l > l'$ . In particular, it leads to the positive Lamb shift  $E_{2s} - E_{2p}$ . The model of the bound polaron has been applied to the description of shallow donor spectra. The calculated values agree rather well with the measured  $1s$ – $2p$  transition energies for CdTe and ZnSe, and  $1s$ – $2s$  transition energies for CdS. For AgBr, AgCl, and CdF<sub>2</sub> the upper bounds for the  $1s$  level are too low, but the  $2p$ – $3p$  energy differences agree well with the experimental data. It means that the short-range donor potential neglected in the polaron model is repulsive for the considered impurities in the ionic crystals.

### I. INTRODUCTION

The bound polaron is a system composed of an electron bound to a positively charged infinitely heavy center and interacting with a lattice polarization field of a crystal. The theory of this system describes the electron in the effective-mass approximation, its interaction with the positive center is assumed in the Coulomb form, and its coupling with the lattice is described with the help of the Fröhlich Hamiltonian. The bound polaron is an example of a fermion coupled to two boson fields: the Coulomb field and the field of LO phonons, which are the quanta of the lattice polarization field. Besides its meaning in field theory the bound polaron provides a simple model for a donor impurity in polar crystals.

The eigenvalue problem for the bound polaron was treated with the help of the path integral method,<sup>1,2</sup> variational method,<sup>3–9</sup> second-order perturbation theory,<sup>10–13</sup> trial Hamiltonian method,<sup>14,15</sup> and local-density approximation.<sup>16</sup> Most of these papers analyzed the ground-state properties, some of them<sup>4–7,9,11,13</sup> considered the first low-lying excited states  $2s$  and  $2p$  as well. Calculations of the energy levels  $3s$ ,  $3p$ , and  $3d$  were performed in the second-order perturbation theory.<sup>17</sup> However, this method does not provide definite bounds to the energy eigenvalues and cannot be applied to the electron-phonon coupling  $\alpha \geq 1$ . It can be expected that the high-energy levels ( $n \geq 3$ ) are hydrogenlike, at least for small  $\alpha$ , but deviations from this behavior are not excluded.<sup>18</sup>

The purpose of the present work is the calculation of energy levels of the bound polaron with the help of a method, which can be applied for both the ground state

and excited states, and which provides satisfactory results for arbitrary electron-phonon coupling. This approach,<sup>19</sup> called the method of optimized canonical transformation, is presented in Sec. II. It is an extension to strong coupling of a similar approach to an exciton problem given by Bednarek.<sup>20</sup> The results and their discussion are contained in Sec. III, where we investigate moreover to what extent the model of the bound polaron is useful in a description of shallow donor spectra in polar semiconductors and ionic crystals.

### II. METHOD OF OPTIMIZED CANONICAL TRANSFORMATION

The starting Hamiltonian for the bound polaron is given by<sup>1</sup>

$$H = -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{e^2}{\epsilon_0 r} + \hbar\omega \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \hbar\omega \sum_{\mathbf{k}} (v_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \text{H.c.}), \quad (1)$$

where  $\mathbf{r}$  is the position of the electron with respect to the Coulomb center;  $m_e$ , the electron-band mass;  $a_{\mathbf{k}}$  ( $a_{\mathbf{k}}^\dagger$ ), the annihilation (creation) operator of the LO phonon with the frequency  $\omega$  and the wave vector  $\mathbf{k}$ ,

$$v_{\mathbf{k}} = -(i/k)(2\pi e^2/\epsilon\hbar\omega\Omega)^{1/2},$$

$1/\epsilon = 1/\epsilon_\infty - 1/\epsilon_0$ ,  $\epsilon_\infty$  ( $\epsilon_0$ ) is the optical (static) dielectric constant, and  $\Omega$ , the quantization volume. It is convenient to deal with Hamiltonian (1) transformed with the help of a canonical transformation.<sup>21,22</sup> The present ap-

proach is based on the transformation

$$U = \exp \left[ \sum_{\mathbf{k}} [F_{\mathbf{k}}^*(\mathbf{r})a_{\mathbf{k}} - F_{\mathbf{k}}(\mathbf{r})a_{\mathbf{k}}^\dagger] \right], \quad (2)$$

which yields

$$\mathcal{H} = U^{-1}HU = H_0 + H_1 + H_2. \quad (3)$$

Here,

$$H_0 = -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{e^2}{\epsilon_0 r} + \sum_{\mathbf{k}} \left[ \frac{\hbar^2}{2m_e} |\nabla F_{\mathbf{k}}|^2 + \hbar\omega |F_{\mathbf{k}}|^2 - \hbar\omega (v_{\mathbf{k}} F_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \text{c.c.}) \right] \quad (4)$$

does not depend on the phonon operators,

$$H_1 = \sum_{\mathbf{k}} \left[ \left[ -\frac{\hbar^2}{2m_e} (\nabla^2 F_{\mathbf{k}}^* + 2\nabla F_{\mathbf{k}}^* \cdot \nabla) a_{\mathbf{k}} + \text{H.c.} \right] + [\hbar\omega (v_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} - F_{\mathbf{k}}^*) a_{\mathbf{k}} + \text{H.c.}] \right] \quad (5)$$

is a linear function of the phonon operators, and

$$H_2 = \hbar\omega \sum_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \frac{\hbar^2}{2m_e} \sum_{\mathbf{k}, \mathbf{k}'} [2\nabla F_{\mathbf{k}} \cdot \nabla F_{\mathbf{k}'}^* a_{\mathbf{k}}^\dagger a_{\mathbf{k}'} - (\nabla F_{\mathbf{k}}^* \cdot \nabla F_{\mathbf{k}'}^* a_{\mathbf{k}} a_{\mathbf{k}'} + \text{H.c.})] \quad (6)$$

is a bilinear function of them. Equations (4)–(6) are obtained under assumption  $F_{\mathbf{k}}^*(\mathbf{r}) = -F_{-\mathbf{k}}(\mathbf{r})$ . The effective Hamiltonian is defined as

$$H_{\text{eff}} = \langle 0 | \mathcal{H} | 0 \rangle, \quad (7)$$

where  $|0\rangle$  is the phonon vacuum state, i.e.,  $a_{\mathbf{k}}|0\rangle = 0$  and  $\langle 0|0\rangle = 1$ . It leads to the relation

$$H_{\text{eff}} = H_0, \quad (8)$$

which allows us to eliminate phonon coordinates from the problem. The effective Hamiltonian is an auxiliary quantity in the present treatment; it operates only on the electron coordinates, which considerably simplifies further calculations. In order to determine its form one needs to know the displacement amplitudes  $F_{\mathbf{k}}(\mathbf{r})$ . These can be found by one of the following two methods.

(a) A minimization of the expectation value  $\langle \psi_{nl} | H_{\text{eff}} | \psi_{nl} \rangle$  for a given electronic state  $|\psi_{nl}\rangle$  with respect to  $F_{\mathbf{k}}(\mathbf{r})$  yields both the values of  $F_{\mathbf{k}}(\mathbf{r})$  and the energy eigenvalues of the effective Hamiltonian. This method was used for the exciton in polar semiconductors by Pollmann and Büttner,<sup>23</sup> and extended by Kane<sup>24</sup> and Matsuura and Büttner.<sup>25</sup>

(b) In this method<sup>20,26</sup> we assume an explicit form of the displacement amplitudes:  $F_{\mathbf{k}}(\mathbf{r}) = F_{\mathbf{k}}(\mathbf{r}; \xi)$ , where  $\xi$  is a set of variational parameters, which allow to a flexibility

of the canonical transformation (2). Effective Hamiltonian (7) depends on  $\xi$  also. Its eigenvalues obtained by minimizing  $\langle \psi_{nl} | H_{\text{eff}}(\xi) | \psi_{nl} \rangle$  with respect to  $\xi$  and to the variational parameters of the electronic wave function  $\psi_{nl}$  provide estimates to the energy eigenvalues of the starting Hamiltonian  $H$  (see Appendix).

Method (a) leads to numerical complications for the excited states, since the expectation values of  $H_{\text{eff}}$  are biquadratic functionals of  $\psi_{nl}$ . Thus, in this paper method (b) will be applied. I propose displacement amplitudes of the form

$$F_{\mathbf{k}}(\mathbf{r}) = v_{\mathbf{k}} [f_{\mathbf{k}}^{(1)} e^{-i\tau_1 \mathbf{k}\cdot\mathbf{r}} + f_{\mathbf{k}}^{(2)} e^{-i\tau_2 \mathbf{k}\cdot\mathbf{r}}], \quad (9)$$

where the phonon amplitudes are given by

$$f_{\mathbf{k}}^{(1)} = \frac{\lambda_1}{\rho_1^2 a_p^2 k^2 + 1} \quad (9a)$$

and

$$f_{\mathbf{k}}^{(2)} = \frac{\lambda_2}{(\rho_2^2 a_p^2 k^2 + 1)^2}. \quad (9b)$$

In Eqs. (9)  $\tau_j$ ,  $\lambda_j$ , and  $\rho_j$  ( $j=1,2$ ) are the variational parameters, and  $a_p = (\hbar/2m_e\omega)^{1/2}$  is the free polaron radius. The ansatz (9) resembles that applied previously to the exciton,<sup>20,26</sup> but there are two differences. Here I have introduced the parameters  $\tau_j$  according to similar propositions for the free polaron<sup>27,22</sup> and the exciton,<sup>25</sup> and the phonon amplitude  $f_{\mathbf{k}}^{(2)}$ , which describes well the strong-coupling case. For  $\tau_1 = \lambda_1 = \rho_1 = 1$  and  $\lambda_2 = 0$  transformation (2) goes over into the Lee-Low-Pines transformation<sup>21</sup> which provides a solution for weak electron-phonon coupling. On the other hand, for  $\lambda_1 = \tau_2 = 0$  and  $\lambda_2 = 1$ , we obtain a modified Pekar transformation<sup>28,27,22</sup> which describes well the strong-coupling case. Therefore, the proposed canonical transformation [Eq. (2)] with the displacement amplitudes given by Eqs. (9) is a product of weak- and strong-coupling variational solutions.

The same effective Hamiltonian as that given by Eq. (8) can be obtained when applying a product of the two transformations

$$U_1 = \exp \left[ -i(\tau_1 + \tau_2) \sum_{\mathbf{k}} \mathbf{k} \cdot \mathbf{r} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \right] \quad (10)$$

and

$$U_2 = \exp \left[ \sum_{\mathbf{k}} (\tilde{f}_{\mathbf{k}}^* a_{\mathbf{k}} - \tilde{f}_{\mathbf{k}} a_{\mathbf{k}}^\dagger) \right], \quad (11)$$

where  $\tilde{f}_{\mathbf{k}} = f_{\mathbf{k}}^{(1)} + f_{\mathbf{k}}^{(2)}$ . Then,

$$H_{\text{eff}} = \langle 0 | U_2^{-1} U_1^{-1} H U_1 U_2 | 0 \rangle = H_0. \quad (12)$$

In Eq. (10) one can recognize a recoil momentum of the phonon field; the parameters  $\tau_1$  and  $\tau_2$  moderate its influence. Moreover, we see that these parameters are not independent. I used  $\tau_1 = 1$  throughout this paper to obtain a direct correspondence to the Lee-Low-Pines transformation when using only the first term in Eq. (9). Therefore, transformation (2) depends on the set  $\xi$  of the five variational parameters:

$$\xi = (\lambda_1, \lambda_2, \rho_1, \rho_2, \tau = \tau_2).$$

Transformation (10) was proposed for the bound polaron by Huybrechts<sup>29</sup> who next applied the method (a) to find the phonon amplitudes.

The effective Hamiltonian calculated according to Eqs. (4) and (8) with the function  $F_k(\mathbf{r})$  given by Eqs. (9) has a form

$$H_{\text{eff}} = -\nabla^2 + \frac{A}{r} + \frac{B_1}{r} e^{-c_1 r} + \frac{B_2}{r} e^{-c_2 r} + D e^{-c_2 r} + \Sigma, \quad (13)$$

where the polaron units of energy and length ( $\hbar\omega$  and  $a_p$ , respectively) have been used, and

$$A = -2R^{1/2} - \frac{2\alpha\lambda_2}{|1-\tau|} (1-\lambda_1), \quad (13a)$$

$$B_1 = \frac{2\alpha\lambda_1\lambda_2\rho_1^2(\tau-\rho_1^2)}{|1-\tau|(\rho_1^2-\rho_2^2)^2}, \quad (13b)$$

$$B_2 = \frac{2\alpha\lambda_2}{|1-\tau|} \left[ 1 + \frac{\lambda_1}{\rho_1^2-\rho_2^2} \left[ \rho_2^2 - \rho_1^2 \frac{\tau-\rho_2^2}{\rho_1^2-\rho_2^2} \right] \right], \quad (13c)$$

$$C_j = \frac{|1-\tau|}{\rho_j}, \quad (j=1,2), \quad (13d)$$

$$D = \frac{\alpha\lambda_2}{\rho_2} \left[ 1 - \lambda_1 \frac{\tau-\rho_2^2}{\rho_1^2-\rho_2^2} \right], \quad (13e)$$

$$\Sigma = \alpha \left[ \frac{\lambda_1^2}{2\rho_1} \left[ 1 + \frac{1}{\rho_1^2} \right] + \frac{\lambda_2^2}{16\rho_2} \left[ 5 + \frac{\tau^2}{\rho_2^2} \right] - \frac{2\lambda_1}{\rho_1} \right]. \quad (13f)$$

Formulas (13) are valid if  $\tau \neq 1$ ,  $\rho_1 \neq \rho_2$ , and  $\rho_1$  and  $\rho_2 > 0$ . The effective Hamiltonian depends on the following material parameters: the electron-phonon coupling constant  $\alpha = (\epsilon_0/\epsilon_\infty - 1)R^{1/2}$  and the ratio of the donor rydberg to the LO-phonon energy  $R = m_e e^4 / 2\hbar^3 \omega \epsilon_0^2$ .

The Schrödinger equation for Hamiltonian (13)

$$(H_{\text{eff}} - \bar{E}_{nl})\psi_{nl}(\mathbf{r}) = 0 \quad (14)$$

yields the upper bounds  $\bar{E}_{nl}$  to all the energy levels  $E_{nl}$  of the bound polaron lying below the lowest one-phonon level  $E_{1s}+1$  (see Appendix). Equation (14) can be solved with the use of the variational wave function  $\psi_{nl}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi)$ , where  $Y_{lm}(\theta, \varphi)$  are the spherical harmonics,  $n$ ,  $l$ , and  $m$  are the principal, angular-momentum and magnetic quantum numbers, respectively. The radial wave function  $R_{nl}(r)$  has been chosen<sup>30</sup> as a normalized linear combination of ten exponential functions  $\exp(-j\gamma r)$  with one nonlinear variational parameter  $\gamma$  and ten linear parameters  $c_j$  ( $j=1,2,\dots,10$ ). The energy eigenvalues  $\bar{E}_{nl}$  which are degenerate with respect to  $m$  but not with respect to  $l$  are found by minimizing the expectation values  $\langle \psi_{nl} | H_{\text{eff}} | \psi_{nl} \rangle$  over the variational parameters of the canonical transformation ( $\tau, \lambda_1, \lambda_2, \rho_1, \rho_2$ ) and those of the electronic wave function ( $\gamma, c_j$ ).

The present approach is a generalization of the Lee-Low-Pines method,<sup>21</sup> that yields for the bound polaron the hydrogenlike spectrum

$$E_n^{\text{LLP}} = -\alpha - \frac{R}{n^2} \quad (15)$$

in energy units  $\hbar\omega$ . Equation (15) provides as well the upper bounds for the energy levels:  $E_{nl} \leq E_n^{\text{LLP}}$  if  $E_{nl} < E_{1s}+1$ . The present estimates are always lower than  $E_n^{\text{LLP}}$ .

### III. RESULTS

Table I shows the present results for the ground-state energy compared with the best variational estimates of other authors. The present upper bounds are close to those of Matsuura<sup>2</sup> for  $\alpha \leq 2$ , but are lower than those for large  $\alpha$  and  $R$ . They agree within 1% with the results of Kane,<sup>24</sup> which, however, are not variational for strong electron-phonon coupling. Figure 1 shows the calculated  $2s$  and  $2p$  energy levels as functions of  $\alpha$  and  $R$ . The difference between these levels and the hydrogenlike level  $E_2^{\text{LLP}}$  [Eq. (15)] increases with increasing  $\alpha$  and  $R$ . For the ground-state energy this difference becomes very large for large  $\alpha$  and  $R$  (see Table I). Table II shows the calculated energy eigenvalues  $1s$  through  $4f$  for several values of  $\alpha$  and  $R$ . The values for  $R=0.5$  are the upper bounds for all consecutive energy levels of the bound polaron. For  $R=1$  and  $2$  the one- and two-phonon levels with energies approximately equal to  $E_{1s}+1$  and  $E_{1s}+2$  are placed between the levels listed in Table II. The results of Tables I and II, and Fig. 1 give the estimates for the energy levels  $E_{nl}$  measured with respect to the bare conduction band. The experimentally accessible dissociation energy  $D_{nl}$  of the bound polaron is the difference between the ground-state energy of the free polaron  $E_{\text{pol}}^0$  and the energy  $E_{nl}$ :  $D_{nl} = E_{\text{pol}}^0 - E_{nl}$ . The best variational results<sup>31</sup> for  $E_{\text{pol}}^0$  are also listed in Table II. We see that the estimates of the  $3s$ - $4f$  levels for  $\alpha=2$  and  $R=0.5$  as well

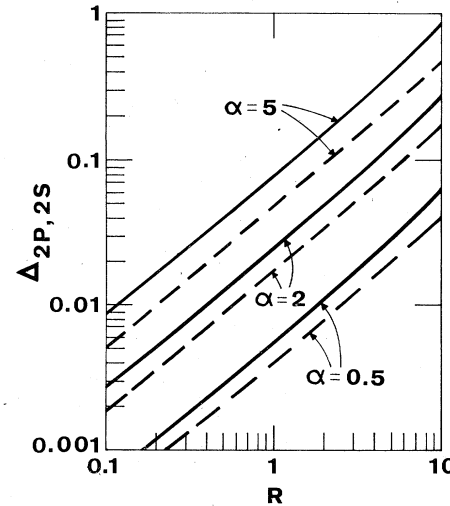


FIG. 1. Estimated energies  $\bar{E}_{2p}$  and  $\bar{E}_{2s}$  of the  $2p$  and  $2s$  states of the bound polaron as functions of  $R$  and  $\alpha$ . Solid curve shows  $\Delta_{2p} = -\bar{E}_{2p} - \alpha - R/4$ , dashed curve  $\Delta_{2s} = -\bar{E}_{2s} - \alpha - R/4$ . Energy is expressed in units of the LO-phonon energy.

TABLE I. Variational estimates of the ground-state energy of the bound polaron calculated by Platzman (Ref. 1), Larsen (Ref. 3), Matsuura (Ref. 2), and Devreese *et al.* (DEKB) (Ref. 9), compared with the present results for several values of  $\alpha$  (electron-phonon coupling constant) and  $R$  (ratio of the donor rydberg to the LO-phonon energy  $\hbar\omega$ ). All energies are expressed in units of  $\hbar\omega$ .

$\alpha$	2			5		
$R$	1	5	10	1	5	10
Platzman	-3.31	-7.85	-13.08	-7.93	-14.56	-21.39
Larsen	-3.41	-8.64	-14.69	-7.86	-15.30	-23.02
Matsuura	-3.47	-8.69	-14.73	-7.99	-15.39	-23.10
DEKB		-8.60	-14.66		-15.21	-23.00
Present results	-3.42	-8.66	-14.72	-8.03	-15.53	-23.28

$\alpha$	7			11		
$R$	1	5	10	1	5	10
Platzman	-11.89	-20.00	-27.90	-22.17	-33.26	-43.42
Larsen	-11.62	-20.61	-29.47	-21.34	-33.45	-44.59
Matsuura	-11.78	-20.74	-29.59	-21.54	-33.63	-44.79
DEKB		-20.52	-29.41		-33.40	-44.60
Present results	-12.02	-21.09	-30.00	-22.47	-34.71	-45.95

as those of the  $4s-4d$  levels for  $\alpha=2$  and  $R=1$  are not satisfactory since they lie above  $E_{\text{pol}}^0$ .

The present estimates for the  $2p$  levels lie below those of Devreese *et al.*,<sup>9</sup> which were obtained with the use of the variational wave function including one-phonon states. If  $E_{2p} < E_{1s} + 1$  then both methods yield the upper bounds to the true energy eigenvalues. Therefore, the lower value is closer to the true one, e.g., for  $\alpha=1$  and  $R=1$ ,  $\bar{E}_{1s} = -2.165$  and  $\bar{E}_{2p} = -1.262$  (see Table II), whereas the estimate for  $E_{2p}$  given in Ref. 9 is  $-1.113$ .

It follows from Fig. 1 that  $\bar{E}_{2s} - \bar{E}_{2p} > 0$  for all values of  $\alpha$  and  $R$ , i.e., the Lamb shift is positive similarly as in the hydrogen atom.<sup>32,33</sup> The results given in Table II allow us to extend this property up to  $4f$  states:  $\bar{E}_{nl} - \bar{E}_{n'l'} \geq 0$  if  $l < l'$ . The equality holds for small  $\alpha$  and/or large  $n$ . This is a general property<sup>30</sup> of the potential being the superposition of the attractive Coulomb and the repulsive Yukawa potentials. The effective potential

in Eq. (13) includes two Yukawa potentials and the exponential potential, but their net contribution to the total energy is always positive and the repulsive Yukawa potential dominates in the correction to the Coulomb potential. This result is interesting due to a formal analogy<sup>34</sup> between the theory of the bound polaron and the hydrogen atom.<sup>33</sup> Moreover, there exists another system having the energy eigenvalues, which increase with decreasing  $l$  for a given  $n$ . It is a quarkonium<sup>35</sup> being a bound state of two heavy quarks, whose interaction is described in a simple model<sup>36</sup> as a superposition of an attractive Coulomb potential and a confinement potential.

The arrangement of the bound-polaron energy levels is mainly a quantitative result, because it was obtained by variational means. The effective Hamiltonian given by Eq. (13) possesses a variational character also. The calculations with the use of the second-order perturbation theory yield the negative Lamb shift<sup>12,13,37</sup> for small  $\alpha$

TABLE II. Calculated energy levels  $1s$  through  $4f$  of the bound polaron as functions of the electron-phonon coupling constant  $\alpha$  and  $R = m_e e^4 / 2\hbar^2 \omega \epsilon_0^2$ .  $E_{\text{pol}}^0$  is the ground-state energy of the free polaron calculated by Larsen (Ref. 31). The unit of energy is  $\hbar\omega$  (LO-phonon energy).

$\alpha =$	0.5			1			2		
$E_{\text{pol}}^0 =$		-0.5040			-1.0160			-2.0640	
$R =$	0.5	1	2	0.5	1	2	0.5	1	2
$1s$	-1.034 54	-1.574 33	-2.653 70	-1.576 95	-2.165 39	-3.335 06	-2.698 58	-3.415 83	-4.795 85
$2s$	-0.627 11	-0.754 15	-1.008 15	-1.129 29	-1.258 43	-1.516 51	-2.133 87	-2.267 39	-2.534 11
$2p$	-0.627 99	-0.755 90	-1.011 69	-1.131 19	-1.262 18	-1.523 91	-2.138 20	-2.275 89	-2.551 12
$3s$	-0.555 96	-0.611 96	-0.723 91	-1.056 40	-1.112 81	-1.225 61	-2.057 32	-2.114 51	-2.229 08
$3p$	-0.556 03	-0.612 08	-0.724 16	-1.056 53	-1.113 07	-1.226 14	-2.057 53	-2.115 10	-2.230 19
$3d$	-0.556 26	-0.612 51	-0.725 01	-1.056 98	-1.113 97	-1.227 88	-2.058 57	-2.117 01	-2.233 91
$4s$	-0.531 35	-0.562 76	-0.625 41	-1.031 47	-1.063 03	-1.125 94	-2.031 77	-2.063 56	-2.127 00
$4p$	-0.531 37	-0.562 79	-0.625 49	-1.031 53	-1.063 08	-1.126 07	-2.031 87	-2.063 67	-2.127 24
$4d$	-0.531 41	-0.562 85	-0.625 70	-1.031 59	-1.063 20	-1.126 40	-2.031 91	-2.063 86	-2.127 76
$4f$	-0.531 50	-0.562 98	-0.625 96	-1.031 73	-1.063 48	-1.126 96	-2.032 21	-2.064 51	-2.128 99

and  $R$ , although the change of the sign is not excluded<sup>13,38,39</sup> for large values of  $\alpha$  and  $R$ . For strong electron-phonon coupling the estimates for the energy levels can be obtained in an analytical form

$$\tilde{E}_{1s} = -R - 0.625\alpha R^{1/2} - 0.097656\alpha^2, \quad (16a)$$

$$\tilde{E}_{2s} = -0.25R - 0.147645\alpha R^{1/2} - 0.021799\alpha^2, \quad (16b)$$

$$\tilde{E}_{2p} = -0.25R - 0.180028\alpha R^{1/2} - 0.032410\alpha^2. \quad (16c)$$

Formulas (16) have been derived using the strong-coupling canonical transformation, i.e., solving the eigenvalue problem for effective Hamiltonian (13) with  $\lambda_1 = \tau = 0$  and  $\lambda_2 = 1$ . It can be done straightforward with the help of the hydrogenlike wave functions of the states  $1s$ ,  $2s$ , and  $2p$ . The result for the  $1s$  state [Eq. (16a)] was already given in Refs. 3, 9, 14, and 23; Eq. (16c) leads to higher upper limit for  $E_{2p}$  than that obtained by Devreese *et al.*<sup>9</sup>

Equations (16) give the analytical expressions for the energy levels, but they are not the best upper bounds obtained by the present method. For example, for  $\alpha = 100$  and  $R = 1$  the minimization over all the variational parameters in Eq. (13) yields  $\tilde{E}_{1s} = -1142.7\hbar\omega$ , whereas Eq. (16a) yields  $\tilde{E}_{1s} = -1040.1\hbar\omega$ . Although the upper bound  $\tilde{E}_{2p}$  lies above the corresponding asymptotic expression,<sup>9</sup> and also above the numerical estimate for  $E_{2p}$  obtained by the present method, it gives a reasonable approximate formula for this energy level. For large  $\alpha$  Eqs. (16) provide estimates mainly of qualitative character. They show that the Lamb shift is positive and increases like  $\alpha^2$  for the strong coupling. It remains an open question if the Lamb shift changes the sign for small  $\alpha$  and  $R$ .

One can attempt to describe a shallow donor in a polar crystal as a bound polaron. In the polaron model of the donor one assumes the effective-mass approximation and neglects, e.g., an anisotropy and a short-range part of the

TABLE III. Transition energies measured for donors (Expt.) and calculated in the bound polaron model (Theor.). The material data used in the calculations: electron-band mass  $m_e$ , static ( $\epsilon_0$ ) and optical ( $\epsilon_\infty$ ) dielectric constants, and LO-phonon energy  $\hbar\omega$ , are also quoted. All energies are in meV.

Crystal	$m_e/m_{e0}$	$\epsilon_0$	$\epsilon_\infty$	$\hbar\omega$	Transition	Expt.	Theor.
CdTe	0.096 <sup>a</sup>	9.6 <sup>a</sup>	7.21 <sup>b</sup>	21.1 <sup>a</sup>	$1s-2p$	10.8 <sup>a</sup>	11.1
CdS (A)	0.155 <sup>c</sup>	8.42 <sup>c</sup>	5.27 <sup>c</sup>	38.0 <sup>d</sup>	$1s-2s$	23.4–25.7 <sup>e</sup>	24.5
CdS (B)	0.155 <sup>c</sup>	8.78 <sup>f</sup>	5.27 <sup>c</sup>	37.8 <sup>g</sup>	$1s-2s$		22.7
ZnSe (A)	0.16 <sup>h</sup>	8.66 <sup>i</sup>	5.9 <sup>j</sup>	31.4 <sup>d</sup>	$1s-2p$	19.1–22.3 <sup>j</sup>	23.5
ZnSe (B)	0.15 <sup>k</sup>	9.14 <sup>j</sup>	6.3 <sup>l</sup>	31.9 <sup>m</sup>	$1s-2p$		19.6
AgBr	0.215 <sup>n</sup>	10.6 <sup>c</sup>	4.8 <sup>o</sup>	17.2 <sup>p</sup>	$1s-2p$	20.8 <sup>p</sup>	25.9
					$1s-3p$	23.8 <sup>p</sup>	29.9
					$2p-3p$	3.0 <sup>p</sup>	4.0
AgCl	0.302 <sup>n</sup>	9.5 <sup>c</sup>	4.04 <sup>q</sup>	24.4 <sup>p</sup>	$1s-2p$	33.5 <sup>r</sup>	49.5
					$1s-3p$	40.6 <sup>r</sup>	56.7
					$2p-3p$	7.1 <sup>r</sup>	7.2
CdF <sub>2</sub>	0.283 <sup>s</sup>	7.78 <sup>t</sup>	2.4 <sup>t</sup>	50.0 <sup>t</sup>	$1s-2p$	65.0 <sup>s</sup>	82.9
					$1s-3p$	75.6 <sup>s</sup>	93.6
					$2p-3p$	10.6 <sup>s</sup>	10.7

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<sup>c</sup>E. Kartheuser, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. Devreese (North-Holland, Amsterdam, 1972), p. 717.

<sup>d</sup>R. E. Halsted, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 385.

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donor potential. The transition energies calculated by the present method and those measured for the donors are listed in Table III. I have chosen those values of material parameters from many literature data, which led to the best agreement with the experiment. The results for CdS and ZnSe labeled as (A) and (B) show the dependence on these parameters. The agreement between the theory and experiment is quite good for the polar semiconductors CdTe, CdS, and ZnSe. For the ionic crystals AgBr (Ref. 40), AgCl (Refs. 41 and 42), and CdF<sub>2</sub> (Ref. 43) the calculated transition energies  $1s-2p$  and  $1s-3p$  are too large for all values of the material parameters found in the literature. Nevertheless, the  $2p-3p$  energy differences agree well with the experiment. Therefore, the upper bounds obtained for the  $1s$  level lie too low. Since the short-range potential neglected in the polaron model of the donor affects mostly the ground state, it means that this potential is repulsive for the ionic crystals and donors considered in this paper. The short-range potential is due to the difference of atomic properties of the donor and the host lattice,<sup>44</sup> the local lattice distortion (especially in CdF<sub>2</sub>, Ref. 45), and the acoustic phonons. The excited states of the donor are rather insensitive to the short-range effects and can be well described by the polaron model.

Unfortunately, this model does not reproduce properly the splittings  $2s-2p$  and  $3s-3p$ , which, although very small, were measured with a high accuracy in CdS (Ref. 46) and ZnSe (Ref. 47). As stated previously the present approach yields positive-energy differences  $\bar{E}_{2s}-\bar{E}_{2p}$  and  $\bar{E}_{3s}-\bar{E}_{3p}$ , whereas the experiments<sup>46,47</sup> yield the negative values for these splittings. In CdS this effect is probably due to the anisotropy of the electron band mass and the dielectric constant. In both the crystals the properties of individual donor atoms affect the spectra which results in the observed chemical shifts.<sup>46-48</sup>

The energy levels  $1s$ ,  $2s$ , and  $2p$  of shallow donors in ionic crystals were previously calculated by Bajaj and Clark<sup>11,17</sup> with the use of the second-order perturbation theory. Despite the fact that the perturbation theory can hardly be used for  $\alpha \geq 1$  the authors<sup>17</sup> calculated the transition energies for AgBr, AgCl, and CdF<sub>2</sub> and claimed a good agreement with the experiment. These calculations were next extended to the  $3s$ ,  $3p$ , and  $3d$ , states.<sup>49</sup> This approach takes advantage of the Dalgarno-Lewis<sup>50</sup> method of summation of the second-order perturbation series. In this method an auxiliary operator  $F$  [defined by Eq. (8) of Ref. 11] is of great importance. Bajaj and Clark<sup>17</sup> assume that  $F$  is a function of only space coordinates:  $F=F(\mathbf{r})$ . Next, they try to find the matrix elements  $\langle \mathbf{k}' | F | \mathbf{k}'' \rangle$  in the plane-wave basis  $|\mathbf{k}\rangle$ . The matrix elements  $\langle \mathbf{k}' | F(\mathbf{r}) | \mathbf{k}'' \rangle$  depend only on  $\mathbf{k}' - \mathbf{k}''$ , as the Fourier transforms of a function, which depends only on  $\mathbf{r}$ . Instead of solving the infinite set of linear equations for  $\langle \mathbf{k}' | F | \mathbf{k}'' \rangle$  [Eq. (14), Ref. 11] the authors propose a special solution [Eq. (15), Ref. 11]. However, the solution proposed for the matrix elements depends explicitly on  $(\mathbf{k}'')^2 - (\mathbf{k}')^2$ , which is in contradiction to the assumption made by the authors<sup>11,17</sup> that the operator  $F$  is only a function of  $\mathbf{r}$ . The proposed form of the matrix elements does not fulfill the set of equations for them [Eq. (14), Ref. 11]. Therefore, an analytical summation of the

second-order perturbation series has not been achieved, and the results of Refs. 11, 17, and 49 cannot be helpful in a description of the donor spectra.

#### IV. CONCLUSIONS

The present method provides variational upper bounds for all the energy levels of the bound polaron, which lie below the lowest one-phonon level  $E_{1s} + \hbar\omega$ . These upper bounds are lower than most of the previously obtained variational results. The high-energy levels have been calculated for the first time. I have shown here only the results up to the  $4f$  level. Calculations for higher excited states can be performed with the same computational effort. The present approach is fairly simple, all expressions are given in the analytical form, which enables us to apply them to the high-energy levels and arbitrary electron phonon coupling. The estimates for the levels lying above  $E_{1s} + \hbar\omega$  are variational solutions only for the zero-phonon Hamiltonian  $H_0$ . The  $N$ -phonon states with  $N \geq 1$  are to be treated by other methods.<sup>4</sup> Nevertheless, the present results can be helpful even for these states as a basis for further studies.<sup>4</sup>

The properties of the obtained spectra can be summarized as follows.

(i) The energy levels lie always below the corresponding hydrogenlike levels given by Eq. (15), i.e.,  $\bar{E}_{nl} \leq E_n^{\text{LLP}}$ .

(ii) For small electron-phonon coupling  $\alpha$  the estimates  $\bar{E}_{nl}$  go over into  $E_n^{\text{LLP}}$ .

(iii) For large  $\alpha$  the energy eigenvalues of the  $1s$ ,  $2s$ , and  $2p$  states can be approximated by the analytical expressions [Eqs. (16)], showing that the  $2s-2p$  splitting is positive and proportional to  $\alpha^2$ .

(iv) For arbitrary  $\alpha$  and  $R$ ,  $\bar{E}_{nl} \geq \bar{E}_{n'l'}$  if  $l < l'$  (at least for the states  $1s-4f$ ).

Property (ii) means that for very small  $\alpha$  the present approach does not lead to any change of the electron-band mass into the polaron mass. This can be improved by using the canonical transformation, which depends explicitly on the momentum operator of the electron.<sup>39</sup> However, the corrections should be very small.

The polaron model of the donor impurity in polar crystals, which includes the long-range screening through the LO phonons, leads to the substantial increase of the dissociation energies in comparison to those obtained from the hydrogenlike model with the Coulomb potential screened by  $\epsilon_0$ . The results agree rather well with the observed donor spectra for excited states. The results for the ground state permit us to describe the character of the short-range part of the donor potential, which is repulsive in the ionic crystals AgBr, AgCl, and CdF<sub>2</sub>.

*Note added.* After submission of the present paper, a paper by Y. Lépine, Solid State Commun. 52, 427 (1984), has been brought to my attention. The author calculated upper bounds for the  $2p$  excited-state energy of the bound polaron and obtained results, which for  $\alpha < 11$  lie above the present upper bounds.

*Note added in proof.* In a recent paper on the bound polaron by M. Matsuura, J. Phys. Soc. Jpn. 53, 284 (1984), the author calculated the second-order perturbation corrections to the  $1s$ ,  $2s$ , and  $2p$  energy levels and ob-

tained the positive (negative) Lamb shift for  $R > \frac{4}{3}$  ( $R < \frac{4}{3}$ ). The calculated  $1s-2p$  transition energies for silver halides are larger than the experimental values, which agrees with the results of the present paper.

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#### APPENDIX

The present method is based on the unitary transformation  $U$  [Eq. (2)]. The starting Hamiltonian  $H$  [Eq. (1)] is transformed to the new Hamiltonian

$$\mathcal{H} = U^\dagger H U = H_0 + H_1 + H_2, \quad (\text{A1})$$

[cf. Eqs. (3)–(6)], which has the same spectrum as  $H$ . In this paper the energy is determined with respect to the bottom of the conduction band. The ground-state energy  $E_{\text{pol}}^0$  of the free polaron which is therefore negative separates two parts of the spectrum of  $\mathcal{H}$ : above  $E_{\text{pol}}^0$  the spectrum is continuous, below  $E_{\text{pol}}^0$  only discrete energy levels exist. Due to the infinite mass of the positive center no real phonon recoil effects disturb the spectrum below  $E_{\text{pol}}^0$ , which remains discrete on the contrary to the free polaron and the exciton. The exciton can possess both discrete and resonant states in an energy gap.

The eigenstates of  $\mathcal{H}$  satisfying the equation

$$\mathcal{H} |u_i\rangle = E_i |u_i\rangle \quad (\text{A2})$$

can be expanded in the basis

$$|N, i\rangle = |N\rangle |\psi_i\rangle, \quad (\text{A3})$$

where  $|N\rangle$  is the  $N$ -phonon state and  $|\psi_i\rangle$  is the electronic state. The basis states with  $N=0$  are the eigenstates of the Hamiltonian  $H_0$ , that is independent of the phonon operators. I will denote them by

$$|\bar{u}_i\rangle = |0\rangle |\psi_i\rangle \quad (\text{A4})$$

and call them zero-phonon states. The energies of the states with  $N \geq 1$  are determined by  $H_0$  as well as by  $H_1$  and  $H_2$  [the one- and two-phonon operators given by Eqs. (5) and (6)]. If the zero-phonon state has the energy  $E_i$ , then the corresponding states with  $N \geq 1$  possess the energies approximately equal to  $E_i + \hbar\omega$ ,  $E_i + 2\hbar\omega$ , etc., provided that the coupling between the states  $|0, i\rangle$  and  $|N \geq 1, i\rangle$  is not large.

Our purpose is to prove that the method of optimized canonical transformation yields upper bounds both for the ground-state energy  $E_0$  and for the excited states with the energies below  $E_0 + \hbar\omega$ . The proof which relies on the work of Löwdin<sup>51</sup> will be done in two steps.

(a) Let us consider the case when the variational parameters  $\xi$  in the canonical transformation  $U$  are fixed. The transformation  $U$  can have, for example, the form of the

Lee-Low-Pines<sup>21</sup> transformation. The introduction of the effective Hamiltonian [Eqs. (7) and (13)] is equivalent to the outer projection<sup>51</sup>

$$\bar{\mathcal{H}} = P \mathcal{H} P \quad (\text{A5})$$

of the operator  $\mathcal{H}$  with respect to the subspace defined by the operator  $P = |0\rangle\langle 0|$ , where  $|0\rangle$  is the phonon vacuum state. The eigenvalue problem for

$$\bar{\mathcal{H}} |\bar{u}_i\rangle = \bar{E}_i |\bar{u}_i\rangle \quad (\text{A6})$$

is equivalent to Eq. (14) for the effective Hamiltonian, since

$$\bar{\mathcal{H}} = |0\rangle\langle 0| H_0 |0\rangle\langle 0| = |0\rangle H_{\text{eff}} \langle 0|.$$

Equation (A6) is solved with the help of the orthonormalized electronic wave functions  $\psi_{nl}(\mathbf{r}) = \langle \mathbf{r} | \psi_i \rangle$ , where  $i = (nl)$  and

$$\langle \bar{u}_i | \bar{u}_{i'} \rangle = \langle \psi_i | \psi_{i'} \rangle = \delta_{ii'}. \quad (\text{A7})$$

I will further proceed as if I had the exact solutions of Eq. (A6), because  $\bar{\mathcal{H}}$  is spherically symmetric and therefore Eq. (A6) [cf. Eqs. (13) and (14)] is reduced to the one-dimensional eigenvalue problem, which can be solved numerically with an arbitrary precision. Moreover, the use of upper bounds for  $\bar{E}_i$  instead of  $E_i$  themselves does not change further considerations provided that the variational wave functions for different states are mutually orthogonal.

If  $E_i < E_0 + \hbar\omega$ , where  $E_0 = E_{1s}$  is the ground-state energy of the bound polaron, then the eigenvalues  $\bar{E}_i$  of  $\bar{\mathcal{H}}$  provide the upper bounds to the eigenvalues  $E_i$  of  $\mathcal{H}$  in order:<sup>51</sup>  $E_i \leq \bar{E}_i$ . If  $E_i \geq E_0 + \hbar\omega$ , then the  $N$ -phonon states ( $N = 1, 2, \dots$ ) with the energies approximately equal to  $\bar{E}_{1s} + \hbar\omega$ ,  $\bar{E}_{1s} + 2\hbar\omega$ , ..., are to be taken into account. In this case  $\bar{E}_i$  are the upper bounds only for the energy eigenvalues of the zero-phonon Hamiltonian  $H_0$ . In order to construct upper bounds to all consecutive energy levels of  $\mathcal{H}$  one should apply the projection operator including the corresponding  $N$ -phonon states.

(b) For the optimized canonical transformation the proof<sup>20</sup> is similar as in case (a), although now the variational parameters  $\xi$  take on different values for each state and all the quantities in Eq. (A6) depend on  $\xi$ . Now, Eq. (A6) is solved by minimizing the expectation values

$$\bar{E}_i(\xi) = \langle \bar{u}_i(\xi) | \bar{\mathcal{H}}(\xi) | \bar{u}_i(\xi) \rangle \quad (\text{A8})$$

with respect to  $\xi$ , which yields the optimal values of  $\xi = \xi_i$ . The energy eigenvalue of the state  $i$  is  $E_i = \bar{E}_i(\xi_i)$ . The eigenvalue  $\bar{E}_0 = \bar{E}_0(\xi_0)$  found in this way for the ground state  $|\bar{u}_0(\xi_0)\rangle$  is obviously the upper bound to the ground-state energy:  $E_0 \leq \bar{E}_0$ . The minimization for the first excited state yields the values  $\xi_1$  and  $\bar{E}_1 = \bar{E}_1(\xi_1)$  as well the orthogonal eigenstates

$$\langle \bar{u}_0(\xi_1) | \bar{u}_1(\xi_1) \rangle = 0. \quad (\text{A9})$$

The eigenvalue  $\bar{E}_0(\xi_1)$  corresponding to the eigenstate  $|\bar{u}_0(\xi_1)\rangle$  is an upper bound to the ground-state energy also, although worse than the previously obtained  $\bar{E}_0(\xi_0)$ :  $\bar{E}_0(\xi_0) \leq \bar{E}_0(\xi_1)$ , and has not been given in the present pa-

per. Moreover, it fulfills the inequality  $\bar{E}_0(\xi_1) < \bar{E}_1(\xi_1)$ , which together with Eq. (A9) leads to the conclusion<sup>51</sup> that  $E_1 \leq \bar{E}_1$ . The same procedure can next be repeated for each excited state, which gives  $E_i \leq \bar{E}_i$  for all the energy levels lying below  $E_0 + \hbar\omega$  as in case (a).

I would like to comment on the approximation made in the present method. The use of the states [Eq. (A4)] does not mean that the zero-phonon approximation has been applied. The total variational wave function has the form

$$U|0\rangle\psi_{nl}(\mathbf{r}). \quad (\text{A10})$$

Its phonon part is the coherent state  $U|0\rangle$  being the Hartree ansatz for bosons.<sup>18,21</sup> This approximation does not include phonon-phonon correlation.<sup>3,18</sup> The states  $|N \geq 1, i\rangle$  can provide corrections to the energy levels in the vicinity of the level crossing,<sup>4</sup> but outside of this region the corrections should be negligible.

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