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Effective electron-hole interaction potentials and the binding energies of exciton–ionized-donor complexes

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Several recently proposed effective potentials for the electron-hole interaction in a polarizable medium are tested in the calculation of the binding energies of Wannier-exciton–ionized-donor complexes for CdS and ZnO crystals. The recent contention concerning unsuitability of the Haken potential for this problem is confirmed. None of the potentials investigated was found to be successful in both crystals. For CdS the potential proposed recently by Aldrich and Bajaj is able to yield good agreement with experiment. For ZnO the potential proposed by Pollmann and Büttner is found to be the best but the agreement with experiment is in general worse than for CdS. The possible causes of the discrepancies are pointed out, and treatments to account for these effects are suggested.

I. INTRODUCTION

Since the early papers on this topic, there has been an increasing interest in calculating the binding energies of various complexes of Wannier excitons[1] in polar crystals, with special stress on the exciton–ionized-donor. Calculations with neglect of the polarizable phonon field have been performed[2] using a sophisticated variational ansatz, and satisfactory agreement with experiment has been attained.

The Coulomb interaction between the charges is, however, known to be screened in polar crystals due to the polarization of the lattice, or stated another way, due to the interaction with the phonon field.[3] In effect, the dielectric constant turns out to depend on the distance between the particles.

Calculations based on the assumed Haken (H) interaction potential[3] have been started by Elkomoss,[4] who has developed an elaborate computational technique involving averaging of the dielectric constant over the wave function of the system in a self-consistent manner. He has found his results to be in good agreement with experiment.

The Elkomoss treatment has been criticized by Schröder,[1] who pointed out that the Haken potential cannot be used for the interactions with the defect because of the very large mass of the latter. Since the coupling constant α depends on the square root of the mass, it turns out to be very large as well. As a result, the intermediate-coupling treatment which results in the Haken effective-interaction potential is not valid. In fact, one can check by direct calculation that the coupling constant for the defect–phonon-field interaction is at least of the order of 50, whereas the intermediate-coupling approach is known to be reliable up to $\alpha \approx 3$.[5] In addition, it seems that the Elkomoss treatment suffers from some minor inconsistencies in treating particle masses, the polaron mass being assumed equal to the band mass. Reliability of the procedure based on extensive averaging also seems to be worth independent verification.

Mahler and Schröder[6] have proposed a competitive approach involving exact treatment of the donor interactions. They have found the dependence of the effective masses of the particles on their distance to be an important factor in reproducing the experimental results. The complex binding energies calculated relative to the exciton binding energy were found to compare favorably with the experimental data, although the absolute values of both energies were substantially overestimated. Comparison with the neutral-donor binding energies has not, to the best of our knowledge, been published so far.

On the other hand, Gorzkowski in his recent paper[7] reports that the Haken potential significantly overestimates the complex binding energy, calculated with respect to the neutral-donor binding energy. He finds this situation to be a rule rather than an exception in polar crystals. He suggests a possible solution by rescaling the polaron radius to fit the free-exciton energy, while still retaining the algebraic form of the Haken potential, or, alternatively, utilization of a different form of the potential.

In fact, one should rather wonder why the Haken potential would be successful in interpreting the binding energies of exciton complexes, were it successful indeed. Although the Haken potential is recognized as an efficient qualitative means for studying electron-hole interactions in polar crystals, it has been found to fail in interpreting quantitatively the exciton binding energies in some crystals.[8,9] Consequently, new effective potentials have been developed.[10-12]

Barentzen[10] has generalized the Haken theory to cover larger values of the coupling constant. His approximation scheme yields the interaction potential as a series in powers of the coupling constant α, and is capable of systematically (with increasing powers of α) improving the intermediate-coupling results for stronger coupling.

Pollmann and Büttner[11] and recently Aldrich and Bajaj[12] have taken the correlation between electron and hole polarons into account, and have also obtained some corrections to the Haken potential.

The aim of the present paper is to investigate the possibilities of utilizing the above-mentioned potentials in calculating the binding energy of the Wannier-exciton–ionized-donor complex. The explicit forms of the potentials considered in our study are summarized in Sec. II. In Sec. III we describe briefly our computational method. The numerical results are presented in Sec. IV, and are discussed in some detail in Sec. V.

II. INTERACTION POTENTIALS

(i) As a reference potential, we re-examine the Haken potential in the form[3]

$$V_H = -(e^2/r)\{1/\epsilon_\infty - 1/\epsilon^* [1 - \tfrac{1}{2}(e^{-\kappa_1 r} + e^{-\kappa_2 r})]\}, \qquad (1)$$

where $1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_0$; ϵ_0 and ϵ_∞ are the static and optical dielectric constants, respectively; $\kappa_i = (2m_i\omega/\hbar)^{1/2}$; ω is the frequency of longitudinal-optical (LO) phonons; m_i is the band mass of the ith particle, $i=1$ corresponds to an electron and $i=2$ corresponds to a hole; r is the electron-hole distance; and $1/\kappa_i$ is the corresponding polaron radius.

The masses m_i^* of the particles which enter into the kinetic-energy operator are the polaron masses, renormalized due to the interaction with phonons:

$$m_i^* = m_i(1 + \tfrac{1}{6}\alpha_i), \qquad (2)$$

with

$$\alpha_i = (e^2/\hbar\epsilon^*)(m_i/2\hbar\omega)^{1/2}. \qquad (3)$$

(ii) Next, we are going to study the Barentzen[10] (B) potential

$$V_B = V_H + \hbar\omega[(\tfrac{1}{10}\alpha_1)^2 \xi_1 e^{-\kappa_1 r} + (\tfrac{1}{10}\alpha_2)^2 \xi_2 e^{-\kappa_2 r}], \qquad (4)$$

with

$$\xi_i = 1.26(1 + \kappa_i r) + 0.84\kappa_i^2 r^2. \qquad (5)$$

The masses in the kinetic-energy operator are the polaron masses m_i^* defined according to Tulub[13]

$$m_i^* = m_i[1 + \tfrac{1}{6}\alpha_i + 2.24(\tfrac{1}{10}\alpha_i)^2] \qquad (6)$$

(iii) The potential proposed recently by Aldrich and Bajaj[12] (AB) has the form

$$V_{\mathrm{AB}} = V_H + \frac{e^2}{2\epsilon^*}\left(\frac{\kappa_1}{\tau_1} e^{-\kappa_1 r} + \frac{\kappa_2}{\tau_2} e^{-\kappa_2 r}\right), \qquad (7)$$

where

$$\tau_i = \{1 + \alpha_i/[4(1 + \tfrac{1}{12}\alpha_i)^2]\}(1 + \tfrac{1}{12}\alpha_i). \qquad (8)$$

The polaron masses enter again into the kinetic energy operator but this time they are calculated from the Haga relation[12,14]:

$$\overline{m}_i^* = m_i(1 + \tfrac{1}{12}\alpha_i)/(1 - \tfrac{1}{12}\alpha_i). \qquad (9)$$

(iv) Finally, we will study the potential proposed by Pollmann and Büttner[11] (PB)

$$V_{\mathrm{PB}} = V_H + (e^2/2\epsilon^*)(M/\Delta m)(1/r)(e^{-\kappa_1 r} - e^{-\kappa_2 r}), \qquad (10)$$

where

$$M = m_2 + m_1 \quad \text{and} \quad \Delta m = m_2 - m_1,$$

m_i being the corresponding band masses. According to their original paper,[11] the band masses m_i enter also into the kinetic-energy operator, and are identified with those observed experimentally. Strictly speaking, the PB potential is a good approximation to the actual interaction merely in the limit of very large exciton radii relative to the polaron radius. This is usually not the case in the crystals we are going to study. It may, however, turn out to be more appropriate than the Haken potential.

(v) In addition, we will investigate the Haken potential (1) with the polaron radii rescaled to fit the free-exciton energy, according to Gorzkowski's suggestion.[7] We will assume the vibrational frequency ω to be scaled, but not the band masses. Such an approach might perhaps be justified by taking into account the other polarization channels, not just one phonon branch as in the original Haken treatment. These might include other vibrations or even polarization of atomic cores. The frequency ω would then be an "effective" frequency averaged over all contributing modes.

(vi) For comparison, we will consider the phenomenological potential proposed by Bajaj[15]

$$V_{\mathrm{phen}} = -\frac{e^2}{\epsilon_0 r} - \frac{e^2}{2\epsilon^* r}\left(\frac{\epsilon_\infty}{\epsilon_0}\right)^\gamma \left(e^{-\kappa_1 r} + e^{-\kappa_2 r}\right), \qquad (11)$$

where the phenomenological scaling constant γ is set equal to $\frac{3}{5}$, according to the prescription in the original paper. The masses in the kinetic-energy operator are calculated from (2). When γ is set equal to zero in Eq. (11), the Haken potential V_H is recovered.

Following Schröder,[1] the interaction with the donor will in this paper be assumed to be renornormalized in the exact way by means of the transformation given by Platzmann,[16] and has the form

$$U(r_i)=ee_i/\epsilon_0 r_i\,, \tag{12}$$

regardless of the form of the interaction potential between an electron and a hole. In this equation, r_i is the distance of the ith particle from the donor and e_i is the charge of the ith particle ($e_1=-e$ and $e_2=+e$).

III. COMPUTATIONAL METHOD

The generator-coordinate method (GCM) was originally introduced by Wheeler *et al.*[17] in nuclear physics studies. Next, it was adapted and generalized by Somorjai[18] with the name integral transform method for use in atomic and molecular problems,[19] and recently was further developed by Thakker and Smith to generate compact wave functions for two-electron ions.[20,21]

In the present paper we will take advantage of the formal similarity between a two-electron atom and an ionized-donor–Wannier-exciton complex,[4] and will therefore adopt a similar procedure. We have only to make allowances for (i) change of the charge of one of the mobile particles (a hole instead of an electron), (ii) different effective masses of the mobile particles, and (iii) the potential, screened according to the appropriate formulas of Sec. II instead of the Coulomb potential for the interaction between the mobile charges. The static dielectric constant ϵ_0 is included in the definition of our energy ($m_1^* e^4/\epsilon_0^2\hbar^2$) and length ($\epsilon_0\hbar^2/m_1^* e^2$) atomic units.[4] In these atomic units $m_1^*=\hbar=e^2/\epsilon_0=1$ (Ref. 4) and the neutral-donor binding energy is $\frac{1}{2}$ a.u. The Hamiltonian for the complex reads

$$H=-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\sigma\Delta_2-1/r_1+1/r_2+V(r_{12})\,, \tag{13}$$

where $\sigma=m_1^*/m_2^*$; r_1, r_2, r_{12} denote the donor-electron, donor-hole, and electron-hole distances, respectively; and $V(r_{12})$ is approximated by one of the potentials described in Sec. II expressed in our atomic units. The donor is assumed to be static.

Hamiltonian (13) was first derived by Mahler and Schröder.[6] They started from the Fröhlich-type Hamiltonian involving explicitly the phonon-field operators. The donor-phonon coupling was removed in the exact way by means of the transformation proposed by Platzmann.[16] Next, the phonon-field operators were approximately eliminated by means of the intermediate-coupling variational treatment, as originally developed by Haken.[3] (For more details see Refs. 1 and 6).

Given the problem of finding the eigenfunctions of an N-particle system with Hamiltonian H, the basic idea of the GCM or integral-transform method is to systematically generate trial functions by the prescription

$$\begin{aligned}\Psi(x_1,x_2,\ldots,x_N)&=\Psi(\vec{\mathrm{x}}_N)\\&=\int_{D_M} S(\vec{\mathrm{t}}_M)\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}_M)\,d\vec{\mathrm{t}}_M\,,\end{aligned} \tag{14}$$

where D_M is an M-dimensional integration domain for the parameter space ($\vec{\mathrm{t}}$ space), Φ is some known function (and can be thought of as an exact eigenfunction for some model Hamiltonian), and the weight or shape function $S(\vec{\mathrm{t}}_M)$ is to be determined. We shall assume that Ψ, Φ, and S are real.

Insertion of the ansatz (14) into the variational principle yields

$$\begin{aligned}E\int d\vec{\mathrm{t}}_M\int d\vec{\mathrm{t}}'_M\, I(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)S(\vec{\mathrm{t}}_M)S(\vec{\mathrm{t}}'_M)\\=\int d\vec{\mathrm{t}}_M\int d\vec{\mathrm{t}}'_M\, K(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)S(\vec{\mathrm{t}}_M)S(\vec{\mathrm{t}}'_M)\,,\end{aligned} \tag{15}$$

where

$$\begin{aligned}I(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)&=\int d\vec{\mathrm{x}}_N\,[\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}_M)\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}'_M)]_{\mathrm{sym}}\,,\\K(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)&=\int d\vec{\mathrm{x}}_N\,[\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}_M)H\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}'_M)]_{\mathrm{sym}}\,,\end{aligned} \tag{17}$$

$(f\hat{O}g)_{\mathrm{sym}}=f\hat{O}g+g\hat{O}f$, and hence the Hamiltonian kernel K and the overlap kernel I are Hermitian.

By varying Eq. (15) with respect to $S(\vec{\mathrm{t}}_M)$, one obtains the Fredholm-type integral equation

$$E\int d\vec{\mathrm{t}}_M\, I(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)S(\vec{\mathrm{t}}_M)=\int d\vec{\mathrm{t}}_M\, K(\vec{\mathrm{t}}_M;\vec{\mathrm{t}}'_M)S(\vec{\mathrm{t}}_M)\,, \tag{18}$$

for the unknown $S(\vec{\mathrm{t}}_M)$. Equation (18) may now be solved by approximate numerical integration. This produces the familiar secular equations

$$\sum_{i=1}^{L} W_i S(\vec{\mathrm{t}}_i)[K(\vec{\mathrm{t}}_i;\vec{\mathrm{t}}'_j)-EI(\vec{\mathrm{t}}_i;\vec{\mathrm{t}}'_j)]=0\,, \tag{19}$$

for $j=1,2,\ldots,L$. The W_i and t_i are weights and abscissas, respectively, for the numerical integration. If the sets $\{t_i\}$ and $\{t'_i\}$ are chosen to coincide, one obtains a convergent sequence of upper bounds to the true energy.[20] This is the procedure that we will follow in the present paper.

In order to apply this method to a specific problem, one must choose (i) a functional form for $\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}_M)$ in Eq. (14), (ii) an appropriate integration domain in Eq. (14), and (iii) a quadrature scheme.

As we are interested in the ground state of the ionized-donor–Wannier-exciton complex, we chose $\Phi(\vec{\mathrm{x}}_N;\vec{\mathrm{t}}_M)$ to be

$$\Phi(r_1, r_2, r_{12}; \alpha, \beta, \gamma) = (4\pi)^{-1} \exp(-\alpha r_1 - \beta r_2 - \gamma r_{12}), \quad (20)$$

where r_1, r_2, and r_{12} are the donor-electron, donor-hole, and electron-hole distances, respectively.

This choice of Φ corresponds to the variational ansatz

$$\Psi(r_1, r_2, r_{12}) = (4\pi)^{-1} \sum_{k=1}^{L} C_k \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}). \quad (21)$$

In effect, the nonlinear parameters are chosen to be the lattice points of a three-dimensional quadrature formula, and the linear coefficients are found by solving the secular equation.

Note that for the ansatz of Eq. (21) all integrals required for the calculation of the energy and various other expectation values, probability density functions, and lower bounds can be done analytically.[22-25] This ansatz is also particularly well suited for handling the Haken-type potentials containing exponential factors such as those described in Sec. II. No averaging of the dielectric constant is necessary as in the Elkomoss procedure.[4] Evaluation of the corresponding integrals is simply done by renormalizing the coefficients in the exponents, and then following exactly the same procedure as for the familiar integrals for the Coulomb interaction. Except for the potential proposed by Barentzen,[10] the additional integrals to be evaluated are of the same type as those needed for the generation of the Hamiltonian matrix in the case of the Coulomb potential. For the Barentzen potential, the only "new" integrals are the same ones that are required for the calculation of $\langle r_{12}\rangle$ and $\langle r_{12}^2\rangle$. They are also easily evaluated according to the well-known scheme.[22-25]

Next, the integration domain must be chosen. It is evident that we may restrict our attention to finite values of α_k, β_k, and γ_k, and so D_3 can be chosen to be a parallelotope in three-space. Thus, we may write

$$\alpha_k \in [A_1, A_2], \quad \beta_k \in [B_1, B_2], \quad \gamma_k \in [G_1, G_2] \quad (22)$$

for $k = 1, 2, \ldots, L$. The paralleloptope is not completely arbitrary. Since we are considering bound states we must have

$$\min \alpha_k > 0, \quad \min \gamma_k > 0 \quad (23)$$

where the minimum is to be taken over all $k \in \{1, 2, \ldots, L\}$. We allow β_k's to take on negative values.[26,27] However, in order to ensure that all of the integrals required for the computation of the energy and other properties exist, we impose the following constraints:

$$\begin{aligned} &\min(\alpha_k + \alpha_l + \gamma_k + \gamma_l) > 0, \\ &\min(\beta_k + \beta_l + \gamma_k + \gamma_l) > 0, \\ &\min(\alpha_k + \beta_l + \gamma_k + \gamma_l) > 0, \end{aligned} \quad (24)$$

where the minimum in all of the above cases is to be taken over all $k \in \{1, 2, \ldots, L\}$ and all $l \in \times \{1, 2, \ldots, L\}$.

Thus, D_3 is chosen to be a parallelotope defined by Eq. (22), with A_1, A_2, B_1, B_2, G_1, and G_2, being variational parameters subject to the constraints of Eqs. (23) and (24).

Finally, it is necessary to choose a quadrature scheme.[26] Monte Carlo methods[28,29] seem to be most appropriate because the number of quadrature points required for satisfactory accuracy is smaller than in traditional methods. We use one particular method[30] that is found to be quite successful.[20,21] In this method the quadrature points are pseudorandom numbers in the unit cube which may be mapped into the required parallelotope by an affine transformation. In this scheme the $3L$ nonlinear parameters are generated by the following equations:

$$\begin{aligned} \alpha_k &= (A_2 - A_1)\langle \tfrac{1}{2}k(k+1)\sqrt{2}\rangle + A_1, \\ \beta_k &= (B_2 - B_1)\langle \tfrac{1}{2}k(k+1)\sqrt{3}\rangle + B_1, \\ \gamma_k &= (G_2 - G_1)\langle \tfrac{1}{2}k(k+1)\sqrt{5}\rangle + G_1, \end{aligned} \quad (25)$$

for all $k = 1, 2, \ldots, L$. In the above $\langle x\rangle$ is defined to be the fractional part of x. A_1, A_2, B_1, B_2, G_1, and G_2 are the variational parameters that define the parallelotope of Eq. (22).

In our calculations all overlap and energy integrals were computed with the recursion relations given by Sack *et al.*[20,23] The optimization of the variational parameters A_1, A_2, B_1, B_2, G_1, and G_2 [cf. Eqs. (22) and (25)] was carried out using Powell's algorithm[31] modified by the inclusion of a barrier function to handle the constraints given by Eqs. (23) and (24). All of the algorithms used for the solution of the secular equation were taken from Wilkinson and Reinsch.[32] The sequential combination of *reduce*1, *tred*1, and *ratqr* was used. The calculations were carried out on a Burroughs B6700 computer using a 78-bit (~23 significant figures) mantissa.

IV. RESULTS

We have studied the binding energies of the exciton-ionized-donor complex in crystals of cadmium sulfide and zinc oxide. Our input data are collected in Table I. There is relatively good agreement between the sets proposed for CdS by different authors. We decided to use the one

TABLE I. Input parameters.

	m_e^{*} [a]	m_h^{*} [a]	ϵ_0	ϵ_∞	$\hbar\omega$ (meV)	References
CdS	0.18	0.7	9.83	5.24	38	1, 4, 11, 12, 34–36
ZnO I	0.27	0.58	7.88	4.59	73	1, 11, 36, 37
ZnO II	0.271	0.95	8.15	4.0	72	12, 38

[a] In the case of PB potential (Ref. 11) we use $m_i^{*} = m_i$.

quoted by Schröder.[1] For ZnO on the other hand, the variance between the different sets proposed in the literature is considerable, especially regarding the hole mass.[11,12] For this reason, we performed the calculations for ZnO with two alternative data sets.[1,12]

For cadmium sulfide, the calculations have been carried out in the basis of $L = 20$ functions for the complex and $L = 15$ functions for the bare exciton. As follows from the convergence test,[32] this ensured the accuracy of the binding energies to be of the order of four significant digits for E/E^{ex}. For zinc oxide, where the input parameters as well as the experimental data concerning the binding energies seem to be less well established, we confined ourselves to $L = 15$ for the complex and $L = 6$ for the bare exciton. As we have found convergence in this case to be better than for CdS, the resulting accuracy in this case is of the order of three significant digits for ΔE^{ex} and ΔE^{D}, and is certainly good enough to allow comparison with experiment.

The results are presented in Table II–IV. They essentially confirm Gorzkowski's observation[7] that the Haken potential gives overestimated complex binding energies with respect to the binding energy of the bare neutral donor. On the other hand, the binding energies with respect to the exciton binding energy tend to be underestimated. This effect is most clearly manifested for the CdS crystal.

It is perhaps most striking that the Haken potential fails to reproduce the proper sequence of binding energies. The experimental sequence is $E^{ex} < E^{D} \lesssim E$, whereas that obtained for the Haken potential is $E^{D} < E^{ex} \lesssim E$. It is therefore in error even in accounting for some qualitative features of the system under consideration.

In CdS, the AB potential is the only one to reproduce properly the sequence of binding energies. It also turns out to be quite successful in providing the quantitative estimates of the "relative" quantities $\Delta E^{D}/E^{D}$ and $\Delta E^{ex}/E^{ex}$. The complex binding energy with respect to the neutral-donor binding energy is still slightly overestimated (as compared to Refs. 39 and 40), but already not by an order of magnitude as in the case of the Haken potential. The absolute values of all energies are slightly underestimated, not surprisingly, however, since the difficulties in accounting properly for the absolute values are a well known nuisance in many problems.

The PB potential turns out to yield reasonable results, but slightly worse than the AB potential. In particular, it fails to reproduce the experimental sequence of the binding energies. Just as for the AB potential, all energies are slightly underestimated. These discrepancies were to be expected, since the form of the potential is in principle valid only for excitons of very large radius with respect to the polaron radius, and this is not the case in cadmium sulfide.

TABLE II. Binding energies (in meV) for various potentials (see text) compared with experimental data for CdS. $\Delta E^{D} = E - E^{D}$, $\Delta E^{ex} = E - E^{ex}$.

Method	E^{D}	E^{ex}	E	ΔE^{D}	$\Delta E^{D}/E^{D}$ (%)	ΔE^{ex}	$\Delta E^{ex}/E^{ex}$ (%)	E/E^{ex}
H	25.36	34.83	35.44	10.09	39.79	0.61	1.75	1.0175
AB	25.36	24.23	26.97	1.62	6.39	2.75	11.34	1.1134
PB	25.36	25.54	27.91	2.55	10.06	2.36	9.25	1.0925
B	25.36	33.72	34.40	9.04	35.63	0.68	2.02	1.0202
H-scaled [a]	25.36	28.84	30.38	5.02	19.81	1.54	5.33	1.0533
phen	25.36	28.85	30.45	5.09	20.08	1.60	5.55	1.0555
Expt. 1 [b]	32 ± 2	29	32.8	0.8	2.5	3.8	13.10	1.131
Expt. 2 [c]	32.1 ± 0.4	29.8	35.6	3.45	10.75	5.75 ± 0.02	19.30	1.1930

[a] Scaled for $E^{ex} = 29$ meV.

[b] References 39 and 40.

[c] References 41–44.

TABLE III. Binding energies (in meV) for various potentials (see text) compared with experimental data for ZnO I. $\Delta E^D = E - E^D$, $\Delta E^{ex} = E - E^{ex}$.

Method	E^D	E^{ex}	E	ΔE^D	$\Delta E^D/E^D$ (%)	ΔE^{ex}	$\Delta E^{ex}/E^{ex}$ (%)	E/E^{ex}
H	59.38	64.03	68.37	9.00	15.2	4.34	6.8	1.068
AB	59.38	46.27	59.34	−0.03	−0.05	13.07	28.3	1.283
PB	59.38	50.86	60.43	1.05	1.8	9.56	18.8	1.188
B	59.38	63.70	68.10	8.72	14.7	4.40	6.9	1.069
H-scaled[a]	59.38	58.98	65.31	5.93	10	6.33	10.7	1.107
phen	59.38	55.67	63.33	3.95	6.7	7.66	13.8	1.138
Expt. 1[b]		59	70.5			11.5	16.3	1.163
Expt. 2[c]	52	42	57	5	9.6	15	35.7	1.357

[a] Scaled for $E^{ex} = 59$ meV.
[b] References 45–49.
[c] References 50–52.

The Barentzen potential[10] is only slightly better than the Haken one. This is again consistent with the expectations,[10] since this potential was intended to provide generalization for strong electron-phonon coupling, and in the case of CdS (weak coupling) it should yield only some minor corrections.

The phenomenological procedure of rescaling the polaron radius does not seem to be very successful either. Moreover, it requires very serious rescaling of the phonon effective frequency (from 38 to 88 meV), that does not look reasonable from the physical viewpoint.

The phenomenological potential proposed by Bajaj[15] yields results close to those obtained for the Haken potential with the scaled polaron radius.

The comparison with experiment seems, however, to be difficult in the case of ZnO, due to the incompleteness and controversies in interpreting the existing data.[45–50] Provided that set "Expt. 1" is correct, and that the neutral-donor binding energy exceeds the exciton binding energy as is believed to be usually the case,[4] the Haken potential with the rescaled polaron radius seems to be relatively successful. Also, the scaling of the vibrational frequency is not so serious in this case (from 73 to 110.5 meV), and may perhaps be physically acceptable.

The scaling of the coefficient of the exponential part in the Haken potential (phenomenological), as proposed by Bajaj,[15] yields slightly worse results, although the proper sequence of binding energies is still preserved.

Among the potentials involving no adjustable parameters, the Pollmann-Büttner potential[11] turns out to be the best in this case. It is the only one to interpret the proper sequence of the binding energies. It should be noted, however, that if Hutson's result[53] for the neutral-donor binding energy is accepted, the binding energy of the donor is then smaller than the exciton binding energy. Such sequence of binding energies would be uncommon but not impossible.[4] In that case, the Haken and Barentzen potentials would turn out to be the best of a poor lot. It should be also noted that the AB potential fails in this case to yield any binding at all. For reasons that are not clear to us, this potential seems to be strikingly inap-

TABLE IV. Binding energies (in meV) for various potentials (see text) compared with experimental data for ZnO II. $\Delta E^D = E - E^D$, $\Delta E^{ex} = E - E^{ex}$.

Method	E^D	E^{ex}	E	ΔE^{ex}	$\Delta E^D/E^D$ (%)	ΔE^{ex}	$\Delta E^{ex}/E^{ex}$ (%)	E/E^{ex}
H	55.51	87.99	88.23	32.72	59	0.24	0.3	1.003
AB	55.51	58.63	62.15	6.64	12	3.52	6	1.06
PB	55.51	60.51	63.82	8.31	15	3.31	5.5	1.055
B	55.51	86.45	86.75	31.24	56.3	0.30	0.4	1.004
H-scaled[a]	55.51	59.05	63.08	7.57	13.6	4.03	6.8	1.068
phen	55.51	67.42	70.11	14.6	26.3	2.69	4	1.04
Expt. 1[b]		59	70.5			11.5	16.3	1.163
Expt. 2[c]	52	42	57	5	9.6	15	35.7	1.357

[a] Scaled for $E^{ex} = 59$ meV.
[b] References 45–49.
[c] References 50–52.

propriate for this system, as might already have been gathered from the enormous error in the bare exciton energy.

Since the results for all the potentials are generally in rather bad agreement with experiment for ZnO II, we conclude that this data set is inappropriate. However, it does fit the bare exciton energy if the potential of Aldrich and Bajaj[12] is used.

V. DISCUSSION

Our calculations confirm Gorzkowski's result[7] that the Haken potential is not sufficient to account properly for the experimental binding energies of the exciton–ionized-donor complex. Unfortunately, no one of the other effective electron-hole interaction potentials proposed so far in the literature[10-12,15] is generally successful. The Aldrich-Bajaj potential[12] seems superior to the others although it tends to overestimate the electron-hole effective repulsion, just opposite to the Haken potential, which disregards it.

The AB potential yields reasonable agreement with experiment for CdS, but completely fails in the case of ZnO. The reason for this breakdown is not clear to us. It might perhaps be conjectured that in this case the corrections to the Haken potential due to the coupling to degrees of freedom other than the LO phonons, are more important than those due to the electron-hole polaron correlation. This conjecture is supported by the relative success of the method based on the use of the Haken potential with rescaled polaron radius. To test this hypothesis, one should investigate in some detail the effects of the interaction between the charges in motion and the other vibrations,[54] and estimate the possible contribution of the polarization of atomic cores. For this interpretation to be accepted, the effects mentioned above should be demonstrated to contribute much more in ZnO than in CdS.

It is, however, interesting to note that the binding energies obtained for the scaled Haken potential do not critically depend on whether the exponents or the coefficient in front of the exponentials (phenomenological) are scaled. Scaling of the vibrational frequency seems to be a bit easier to rationalize in physical terms. On the other hand, the advantage of the Bajaj[15] phenomenological potential is its universality, since the same value of the parameter γ is maintained for all crystals, while the vibrational frequency has to be readjusted for each crystal separately.

Leaving for a moment the complex binding energy aside, it should also be established why the neutral-donor binding energy, calculated in the electrostatic model in CdS (25.4 meV for our set of material parameters), differs so much from the experimental value (32 meV).[40,41] This discrepancy may be due to the additional stabilization gained because of the interaction with the local or resonant modes,[55] and to the local strain[56] caused by the donor misfitting to the host crystal lattice. Both effects have already been suggested to influence optical spectra of the defect.[55,56]

Provided the above interactions do contribute to the stabilization energy of the neutral donor, they should also have some effect on the binding energy of the exciton–ionized-donor complex. Perhaps this is the reason that the complex binding energy with respect to the donor is substantially overestimated in CdS, and that the dramatic discrepancies with experiment arise in the case of ZnO.

The difference between the approaches proposed by Elkomoss[4] and Schröder[1] seems to be relevant in this connection. Schröder is treating properly the donor–mobile-charge interactions, but the price to be paid is that he is forced to assume the donor to be static. However, it does oscillate with respect to the lattice, since one can hardly imagine an impurity atom that might be considered infinitely heavy with respect to Cd or S atoms. Elkomoss,[4] on the other hand, treats the donor center, the electron, and the hole on equal footing, but fails to include correctly their interaction via the polarization field, since it is no more tractable within the intermediate coupling theory. Inclusion of the donor vibrations should result in some changes in the lattice phonon field, and sometimes in the appearance of localized or resonant modes that have to be included in the treatment. It seems, therefore, that the future theory should be in a sense intermediate between the two approaches. The other effect to be included is the local static lattice deformation due to the donor ion.

It should be noted that the comparison of our results as well as the previous ones[1,4] with experiment is by no means straightforward. The chemical shift and central cell corrections are known to affect the binding energies of the complex.[41] For CdS we refer our results to the I donor where the corrections are minimized. Based on the experimental energy difference between the S and P states of the neutral donor, the corrections are expected to contribute to the energy of the order of 0.5 meV, and hence are not likely to affect our conclusions very much. For the ZnO crystal, however, where the corrections are known to be substantial, the comparison is less reliable.

The computational method presented in this paper can yield the binding energies up to any desired accuracy for the exponential-type potentials. No averaging is necessary and all integrals are calculated exactly. Final accuracy is therefore limited merely by the energy-minimization procedure and by the length of the basis set. The wave functions are compact,[20,21] and we get about the same accuracy in E/E^{ex} with $L=20$ as Elkomoss does by diagonalizing 50×50 matrices.[4] This reduces the time of the calculations, and also seems promising in future analysis of the wave functions by reducing the computational effort in calculating the expectation values. It should also be noted that the method is capable of optimizing for any chosen root of the secular equation, not just the lowest one, and is therefore well suited for the study of the excited states.

However, before any more extensive calculations are started, the experimental evidence regarding the input data and binding energies should be thoroughly reinvestigated. Considerable variance in the experimental data[41-44] regarding the binding energies of the complex in CdS makes the situation difficult. The variance in experimental results for ZnO is even more striking.[45-50] The accurate masses from cyclotron resonance experiments would be of great assistance in both cases. We suggest, therefore, that some model systems be ultimately reinvestigated with maximum available experimental accuracy.

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