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Mass-ratio dependence and critical binding of exciton-ionized donor complex in polar crystals

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The dependence of the binding energy of an exciton-ionized donor complex on the electron-to-hole mass ratio is investigated. Recently published forms of the electron-hole interaction potential including the interaction via the phonon field are used. The calculations are performed for a few typical sets of parameters characterizing the coupling of the charges with the phonon field. The results indicate that the highly accurate estimates of the critical mass ratio obtained for the Coulomb form of the electron-hole interaction potential are inapplicable for most typical crystals, suffering from an inherent error due to the neglect of the exponential screening due to polarization. For crystals where the electron-phonon interaction is strong, the mass-ratio dependence of the binding energy is found to differ from the Coulomb-like behavior even in the most general qualitative features.

INTRODUCTION

It is well known that the binding energy of the Wannier exciton-ionized donor complex strongly depends on the ratio σ of the electron mass to the hole mass.[1] The binding energy is supposed to decrease monotonicly with increasing mass ratio, such that at some cirtical value σ_c the complex becomes unbound. Such an expectation is based on the use of the Hellmann-Feymman theorem[1]:

$$\frac{d\Delta(\sigma)}{d\sigma}=-\frac{dH}{d\sigma}=-\frac{1}{2}\langle p_h^2\rangle\leq 0, \tag{1}$$

where $\Delta=E_D-E$, E is the complex ground-state energy, E_D is the neutral-donor ground-state energy, H is the Hamiltonian of the complex, p_h is the hole momentum operator, and the average is taken with respect to the true ground-state wave function. However, Eq. (1) is valid as long as the only σ-dependent term in the Hamiltonian is the hole kinetic energy, i.e., when the potential energy does not depend on particle masses. This holds true for the Coulomb interaction potentials, where the best calculated value of σ_c is $\sigma_c=0.454$ (Refs. 1 and 2) (obtained by extrapolation). Actually, the interaction potentials in polar crystals differ from the Coulomb potential. This is due to the indirect interaction via the phonon field. The charges are accompanied by clouds of virtual phonons (lattice distortion) and can interact via the clouds.

There are a few alternative approximate expressions for the effective interaction potentials. In test calculations of the exciton-ionized donor complex in a few crystals none of them appeared to be generally superior to the others,[3-5] but all of them are similar in containing some exponential terms which depend on particle masses, invalidating the argument based on Eq. (1). The deviations from the Coulomb-like behavior may be particularly important for crystals where the electron-phonon coupling is strong.[1] In such cases the analysis based on the results obtained for the Coulomb potential may be seriously in error.

The objective of this paper is to present the results of calculations of the binding energy of exciton-ionized donor complex, depending on the mass ratio σ. We use the best available electron-hole interaction potentials derived recently with inclusion of the screening by the phonon field. These are the Pollmann-Büttner[6] (PB) and Aldrich-Bajaj[7] (AB) potentials. Both of these potentials are very successful in reproducing the complex binding energies, and it depends on the specific crystal under consideration, as to which potential is better. This suggests, in principle, that the calculations should be performed for both forms of the potential. However, we will focus our attention on the Pollmann-Büttner potential.[6]

In the case of purely Coulomb interactions, the eigenvalue problem is fully defined (in terms of the dimensionless Hamiltonian denoted in atomic units) by the mass ratio σ. In other words, σ is the only relevant material constant. When the interaction via the phonon field is included, some additional (dimensionless) material constants characterizing the coupling with phonons have to be considered in order that the eigenvalue problem be properly defined. For the PB potential, there are only two additional parameters necessary, while the AB potential requires three independent parameters (Sec. 2). Since the results depend on these additional parameters, the increased number of parameters would require more cases to be investigated, resulting in excessive computational effort as well as exceedingly voluminous results of, as will be argued in the discussion, questionable usefulness. This makes the PB potential more suitable for a detailed study than the AB potential.

We have also performed some sample calculations for the AB potential. Fortunately, it turned out that the general conclusions are similar for both potentials, and that the quantitative differences between the corresponding results are of only secondary physical interest. This statement will be substantiated in the discussion (Sec. 5). Consequently, we confined the results explicitly presented in this paper to those obtained for the PB potential, which is more transparent and, at the same time, does not deprive the reader of any physically significant material.

The paper is organized as follows. In Sec. 2 we present the Hamiltonian and, in particular, the interaction potentials to be considered. In Sec. 3 a brief outline of our computational method is given, while in Secs. 4 and 5, the results are presented and discussed.

THE HAMILTONIAN

In the effective mass approximation, the Hamiltonian of the exciton-ionized donor complex reads

$$H = -\tfrac{1}{2}(\Delta_1 + \zeta\,\Delta_2) - \frac{1}{r_1} + \frac{1}{r_2} + V(r)\,, \tag{2}$$

where r_1, r_2 and r denote the donor-electron, donor-hole and electron-hole distances, respectively. $\zeta = m_e^*/m_h^*$ is the ratio of (observed) polaron masses of the electron and the hole. The Hamiltonian (2) is expressed in energy $(m_e^* e^4/\epsilon_0^2\hbar^2)$ and length $(\epsilon_0\hbar^2/m_e^* e^2)$ atomic units, where ϵ_0 is the static dielectric constant and m_e^* is the electron effective mass (polaron mass).

Of the forms proposed for the effective electron-hole interaction, we found in our previous works the following two potentials to be particularly successful in reproducing the complex binding energy.

1. The Pollmann and Buttner potential[6]

$$V_{PB} = V_H + \frac{K}{2r}\,\frac{1+\sigma}{1-\sigma}\,(e^{-\kappa_1 r} - e^{-\kappa_2 r})\,, \tag{3}$$

where

$$V_H = -\frac{1}{r} - \frac{K}{2r}(e^{-\kappa_1 r} + e^{-\kappa_2 r})\,, \tag{4}$$

$$\sigma = \frac{m_e}{m_h}\,, \tag{5}$$

$$K = \epsilon_0(1/\epsilon_\infty - 1/\epsilon_0)\,, \tag{6}$$

$$K_1 = \frac{\epsilon_0\hbar^{3/2}}{e^2 m_e^*}(2m_e\,\omega)^{1/2}\,, \tag{7}$$

$$K_2 = K_1\sigma^{-1/2}\,. \tag{8}$$

ω is the frequency of longitudinal optical (LO) phonons, ϵ_∞ is the optical dielectric constant, and m_e and m_h are the band (in distinction to polaron) masses of the electron and the hole. For the PB potential the polaron masses are set equal to the band masses[6] and identified with those observed experimentally, so that in Eq. (2), $\zeta = \sigma$. $1/\kappa_1$ is the electron-polaron radius and $1/\kappa_2$ is the hole-polaron radius, expressed in atomic units.

2. The Aldrich-Bajaj potential[7]

$$V_{AB} = V_H + \frac{K}{2}\left(\frac{K_1}{\tau_1}e^{-\kappa_1 r} + \frac{K_2}{\tau_2}e^{-\kappa_2 r}\right)\,, \tag{9}$$

where

$$\tau_i = \{1 + \alpha_i/[4(1+\alpha_i/12)^2]\}(1+\alpha_i/12)\,, \tag{10}$$

$$\alpha_i = \frac{K}{2\Omega}\,\kappa_i\,, \tag{11}$$

and

$$\Omega = \frac{\epsilon_0^2\hbar^3\omega}{m_e^* e^4}\,. \tag{12}$$

Ω is the LO phonon vibrational frequency expressed in atomic units. For the AB potential the polaron masses are calculated from the Haga formula[8]

$$m_i^* = m_i(1+\alpha_i/12)/(1-\alpha_i/12)\,. \tag{13}$$

Therefore, for the AB potential, $\zeta \neq \sigma$ and ζ has to be calculated from the polaron masses of Eq. (13).

The Hamiltonian (2) was derived by Mahler and Schröder[1,9] for the Haken potential $V_H(r)$. They started from the Fröhlich-type Hamiltonian involving explicitly the phonon-field operators. The phonon-donor coupling was removed in the exact way by means of the transformation proposed by Platzmann.[10] Next, the phonon-field operators were approximately eliminated by means of the intermediate coupling variational treatment, as originally developed by Haken.[11]

A derivation entirely analogous to that presented by Mahler and Schröder is possible also for the AB potential. For the PB potential where the variational ansatz is not based on free-polaron wave functions, Eq. (2) may be derived by means of the treatment used for the biexciton.[12] The Hamiltonian (2) is recovered from the biexciton Hamiltonian by setting the appropriate coupling constants equal to zero, and performing the

Platzmann[10] transformation prior to the variational procedure.

The PB potential is fully characterized by three dimensionless parameters: electron-polaron radius κ_1, effective dielectric constant K, and mass ratio σ. The AB potential is fully defined by four parameters: electron-polaron radius κ_1, effective dielectric constant K, band mass ratio σ, and vibrational frequency Ω. The AB potential would therefore require a much larger computational effort to cover the same range of physically possible cases. Since neither potential is remarkably superior to the other, the PB potential is therefore much better suited for our purposes. Hence, we will investigate in some detail the PB potential and only occasionally refer to our results for the AB potential. It should be noted, however, that the general qualitative conclusions are for both potentials similar.

3. Computational method

As in our previous papers,[3-5] we use the integral transform (generator coordinate) method which in our particular formulation is equivalent to a variational treatment with the ansatz

$$\psi(r_e, r_h, r) = \sum_{k=1}^{L} C_k \phi_k(\alpha_k, \beta_k, \gamma_k;\ r_e, r_h, r), \tag{14}$$

$$\phi_k = (4\pi)^{-1} \exp(-\alpha_k r_e - \beta_k r_h - \gamma_k r), \tag{15}$$

for the complex, and

$$\phi_k = (4\pi)^{-1} \exp(-\gamma_k r) \tag{16}$$

for the free-exciton. (The calculations for the exciton are performed in the exciton center-of-mass reference frame.) We choose $L = 20$ for the complex and $L = 6$ for the exciton. The linear parameters C_k are found by solving the secular equation while α_k, β_k, and γ_k are nonlinear parameters chosen to be the lattice points of a three- (one-) dimensional quadrature formula. They are subject to some constraints so that the theory be physically acceptable and all necessary integrals exist.[13] The actual values of the nonlinear parameters are pseudorandom numbers generated according to the formulas

$$\alpha_k = [(A_2 - A_1)\langle \tfrac{1}{2}k(k+1)\sqrt{2}\,\rangle + A_1], \tag{17}$$

$$\beta_k = [(B_2 - B_1)\langle \tfrac{1}{2}k(k+1)\sqrt{3}\,\rangle + B_1], \tag{18}$$

$$\gamma_k = [(G_2 - G_1)\langle \tfrac{1}{2}k(k+1)\sqrt{5}\,\rangle + G_1], \tag{19}$$

where $\langle x \rangle$ denotes the fractional part of x.

The true variational nonlinear parameters of the method of A_1, A_2, B_1, B_2, G_1, and G_2, which define the boundaries of a parallelotope in the space of the parameters α, β, γ. Further details of the method can be found elsewhere (Refs. 3 and 13).

4. Results

The dependence of the complex- and free-exciton ground-state energies on the electron-to-hole mass ratio σ is shown in Figs. 1 and 2. The exciton energy (dash-dot lines) is included only in the cases where it exceeds the neutral-donor ground-state energy (0.5 a.u.), i.e., when the actual complex binding energy should be referred to the exciton rather than to the donor.

The plot in Fig. 1, obtained for $K = 0.6546$, $\kappa = 1.08$, represents a typical situation for a CdS-type crystal ($\epsilon_0 = 8.67$, $\epsilon_\infty = 5.24$[4]). The other plots of Fig. 1 show the dependence on polaron radius. For $\kappa = 3.24$ the exponential part of the potential has a very short range such that the potential is practically Coulombic. The value of σ_c is in agreement with the estimate of Skettrup *et al.*[14] for the Coulomb potential, i.e., $\sigma_c = 0.426$. (The value of Ref. 14 was obtained directly from the calculation of the binding energy, and not by extrapolation as was done in Ref. 2. As we do not use any extrapolation either, the estimate of Ref. 14 is the most natural reference point for our calculations and it is not surprising that the results agree.) When the coupling with phonons is stronger and the range of the exponential term in the potential is longer, the critical value increases, and for $\kappa = 2.16$, σ_c is close to 0.46, but the overall appearance of the plot remains similar. For $\kappa = 1.08$, the critical value is $\sigma_c = 0.618$, which differs remarkably from the Coulombic value. The shape of the curve changes too. However, the most striking change is observed in the exciton binding energy which, for

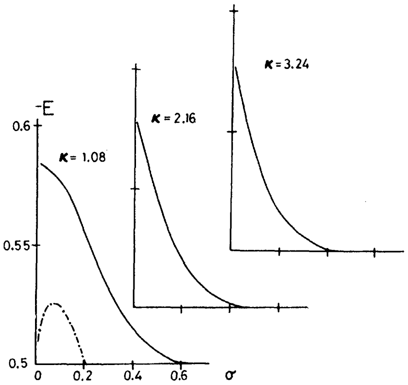

FIG. 1. Dependence of the complex and exciton ($-E > 0.5$ a.u.) ground-state energy on electron-to-hole mass ratio σ for $K = 0.6546$ and different values of κ. All energies are expressed in a.u.

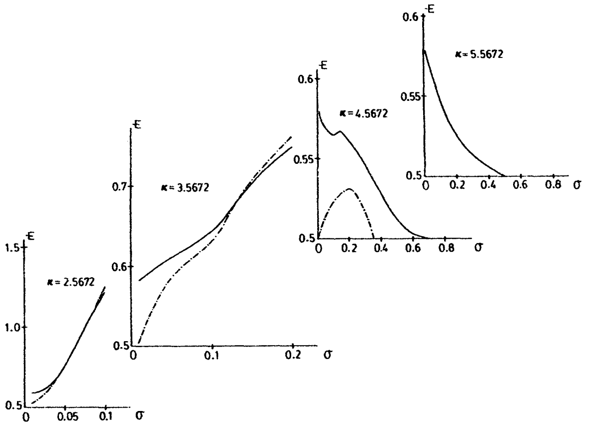

FIG. 2. Dependence of the complex and exciton ($-E > 0.5$ a.u.) ground-state energy on electron-to-hole mass ratio σ for $K = 6.3725$ and different values of κ. All energies are expressed in a.u.

some range of σ values, exceeds the donor ground-state binding energy. The result is that in this range the complex is more likely (in terms of required energy) to decay into the free-exciton and ionized donor than into the ionized donor and free-hole. Consequently, the true complex binding energy should be calculated with respect to the exciton, not to the neutral donor. This behavior is drastically different from the case of the Coulomb potential.

We did not extend our calculations for the values of κ smaller than 1. In fact, the PB potential was derived in the limit $\kappa \rightarrow \infty$.[6] Although in the CdS crystal this condition is not fulfilled, the potential had been found to be relatively successful also in this case and turned out to be one of the best potentials available. This has encouraged us to proceed with the study of the mass-ratio dependence for the corresponding value of κ, but would not justify the application of the potential for $\kappa < 1$.

The plot of Fig. 2, obtained for $K = 6.3725$ [$\epsilon_0 = 37.6$, $\epsilon_\infty = 5.1$ (Ref. 15)], $\kappa = 2.5672$, represents a typical situation for a TlCl-type crystal where the electron-phonon coupling is particularly strong. The σ dependence is in this case very unusual. The complex binding energy is an increasing, not a decreasing function of σ. Therefore, there is *no* critical value of the mass ratio for binding with respect to the neutral donor, which is the standard and most natural definition of the binding energy for the Coulomb potential. Since, however, the exciton energy is increasing more strongly with increasing σ, there is a point where the $E(\sigma)$ curve crosses the $E^{ex}(\sigma)$ curve. Consequently, there is some critical value above which the complex is no longer stable against decay into the free-exciton and ionized donor. Interestingly, this critical value ($\sigma_c = 0.07$) is much smaller than σ_c for the Coulomb potentials, corresponding to the decay into the neutral donor and free-hole.

We have investigated the dependence of the shape of the $E(\sigma)$ curve on polaron radius. For $\kappa < 2.5672$ the plot is essentially similar, but much steeper, and σ_c shifts to smaller values (for $\kappa = 1.75$, $\sigma_c < 0.05$). For $\kappa > 2.5672$, the slope of the curve is smaller, and σ_c is larger; for $\kappa = 3.5672$, $\sigma_c \approx 0.13$. The shape of the curve also changes.

For a still shorter range of the exponential correction in the potential ($\kappa = 4.5672$), the change of the shape is even more striking. The behavior for larger σ already resembles that for the Coulomb potential, i.e., the function decreases with increasing σ. Although the critical value of the mass ratio is large ($\sigma_c \approx 0.7$), the exciton binding energy in the critical region is smaller than the donor binding energy and the stability of the complex should again be referred to the neutral donor. However, the dependence for small σ is still erratic. It passes through a minimum and a maximum, i.e., it is not even monotonic. The Coulomb-like behavior is found for $\kappa = 5.5672$, although $\sigma_c \approx 0.5$ still slightly exceeds the Coulomb value.

We have performed a set of calculations for the AB potential. The results differed from those obtained for the PB potential in the actual values of the binding energies, and consequently in the values of σ_c which were generally smaller. The overall appearance of the curves was, however, very similar to that obtained for the PB potential.

5. *Discussion*

The results presented above indicate, for the first thing, that the conclusions drawn for the Coulomb potential are not directly transferable to more realistic potentials, i.e., to the potentials actually operative between charged particles in polar solids. Interestingly, not only the values of the binding energies and critical values of the mass ratio are changed, but also the most general features of the σ dependence of the binding energies are affected. In particular, the argument based on the Hellmann-Feynman theorem for the Coulomb potential and (presumably) small deviations from the Coulombic behavior turns out to be invalid, since the deviations may actually be considerable, and for some (rather realistic) parameter sets $E(\sigma)$ is not even a monotonic function. Qualitatively, this was to be expected, and a correct form of expression for $d\Delta(\sigma)/d\sigma$ for the PB and AB potentials might be derived via the Hellmann-Feynman theorem. The final expression being, however, no longer positive definite, its utility would be very limited, since its application would necessitate the knowledge of the actual ground-state wave function which is different for each value of σ.

For the Coulomb potential the $E(\sigma)$ dependence was universal in the sense that no parameters other than σ were necessary to determine the binding energy. Once the $E(\sigma)$ function was calculated, and granted the value of σ for a given crystal, the complex binding energy (for the Coulomb potential) was unambiguously determined from the plot. This was particularly useful in interpreting new experimental data, as no new computations were then necessary.

Unfortunately, this is no longer true for more realistic interaction potentials where at least two more (in the case of the PB potential) material constants are necessary. In order to provide a tool of comparable versatility, we would have to produce a set of $E(\sigma)$ plots for an enormous number of parameter sets to make the interpolation between different parameter sets meaningful. The results would be extremely voluminous and hardly accessible. Owing to the widespread accessibility of computers, the same objective can be achieved for much smaller effort (also computational) by calculating the complex binding energy just when the need arises for a given crystal (i.e., for one parameter set) instead of calculating it in advance for many (some useful, some unnecessary) parameter sets. This conclusion is valid for the PB as well as AB potentials, since both yield qualitatively similar erratic $E(\sigma)$ plots. This situation is currently rather typical; the tabulation of the functions of many variables becomes less popular, being replaced by routine computer programs.

The quantitative differences between the results obtained for the AB and PB potentials suggest that for each crystal of interest such calculations should be repeated for both forms of the potential which agrees with our previous conclusions.[3-5] We hope that the future development in the theory of electron-hole interaction potentials will produce some other, more generally successful, form of the potential.

As was already pointed out, the critical value σ_c is not universal but depends on the values of a few parameters, and also on the detailed form of the interaction potential. It is therefore rather pointless to spend too much effort on estimating the critical mass ratio for any set of parameters. This motivated the fact that we did not attempt to approach the accuracy of Refs. 2 and 14 in estimating σ_c, except for a sample case $K=0.6546$, $\kappa=1.08$.

The critical mass ratio is (for not too large κ) sensitive enough to the changes of parameters to differ for reasonable parameter sets at least by 0.01 from the Coulomb-like estimate. This should be reckoned the inherent error due to the limitations of the Coulomb model in a polar solid. The more elaborate attempts to surpass the accuracy of this order for the Coulomb interaction potential are therefore of rather academic interest and from the physical point of view seem futile.

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