

Exchange and polaron corrections for excitons in the degenerate-band case

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Corrections to the exciton energies due to exchange interaction and polar electron-phonon coupling are considered for the degenerate-band case. Mass renormalization and electron-hole interaction potentials induced by the Fröhlich coupling to longitudinal-optical phonons have been established in a previous paper by a tensor operator formalism. Here we present a formulation of the electron-hole exchange in the same theoretical concept. The screening of the exchange interaction is rediscussed. We conclude that the exchange term is screened by a background dielectric constant whose origin is the exchange coupling between all excited electronic states. On the basis of this theory exciton energies for cubic III-V, II-VI semiconductors and CuBr are computed and the influence of band degeneracy, polar electron-phonon coupling, and exchange interaction on the exciton states is discussed.

I. INTRODUCTION

Shallow excitons, whose binding energy is much smaller than the width of the valence or conduction band, can be treated in the frame of the effective-mass approximation. Since Wannier and Mott introduced the hydrogenic model, shallow excitons in semiconductors have been the subject of a large number of studies which either deal with the effective electron-hole interaction or consider the details of the energy bands. Among the first group of studies we mention the influence of electron-phonon interaction in polar semiconductors,¹⁻⁶ the many-particle aspects of the electron-hole interaction,^{7,8} and the effect of dynamical screening^{9,10} of local-field corrections⁹ and of the electron-hole exchange interaction.¹¹⁻¹⁵ Most of these studies were based on the assumption of simple isotropic energy bands. The second group of papers is concerned with band-structure effects, in particular with the degeneracy of the valence bands in cubic semiconductors. After previous attempts,¹⁶⁻¹⁸ essential progress was made only recently by use of tensor operator techniques.^{19,20} In this second group of papers, electron and hole were assumed to interact by a Coulomb potential screened by the static dielectric constant.

In a previous paper (Ref. 6) the exciton Hamiltonian was treated by one of us without electron-hole exchange interaction in two limiting cases: for weak electron-phonon interaction and weak binding the exciton was assumed to consist of an electron-polaron and a hole polaron. This model applies to excitons in III-V compounds and to excited states in II-VI compounds and copper halides. For stronger binding, when the exciton radius is smaller than the sum of the polaron radii, the exciton was coupled as a whole to the longitudinal-optical phonons. This model introduced by Haken¹ and refined by Pollmann and Büttner⁵ for the non-

degenerate-band case, is more realistic for the exciton ground state in II-VI compounds and copper halides. In the degenerate-band case the electron-phonon interaction is the origin of the well known phonon-induced scalar electron-hole interaction (Haken potential), as well as of a tensor force.⁶

The intention of the present paper is to consider the combined effect of electron-phonon interaction, band degeneracy, and exchange interaction on exciton states in polar cubic semiconductors with direct gap. For this purpose we discuss the screening of the electron-hole exchange interaction and reformulate it in terms of tensor operators (Sec. II). The essence of the treatment of electron-phonon interaction in the degenerate band case⁶ will be reported in Sec. III together with an interpretation of the resulting Hamiltonian. Some details of the numerical procedure and representative results for some III-V, II-VI compounds, and for CuBr are presented in Sec. IV. Finally we discuss the validity of the model for the interpretation of experiments, to obtain band parameters from exciton data.

II. EXCHANGE INTERACTION

If for the moment we disregard the electron-phonon interaction, the envelope function $B_{cv}(\vec{k}, \vec{Q})$ for an excitonic state of wave vector \vec{Q} is determined by the Schrödinger equation in \vec{k} space:

$$\sum_{c'v'\vec{k}'} [H_{cc'}(\vec{k})\delta_{vv'}\delta_{\vec{k}\vec{k}'} - H_{vv'}(\vec{k} - \vec{Q})\delta_{cc'}\delta_{\vec{k}\vec{k}'} + H_{cvc'v'}^c(\vec{k}, \vec{k}', \vec{Q}) + H_{cvc'v'}^{ex}(\vec{k}, \vec{k}', \vec{Q})] B_{c'v'}(\vec{k}', \vec{Q}) = E(\vec{Q})B_{cv}(\vec{k}, \vec{Q}) \quad (1)$$

[Ref. 12 and Ref. 13, Eq. (2.48)]. Here a direct gap at the center of the Brillouin zone is assumed.

Pseudo-Bloch functions are used for the one-particle states²¹ which, for the valence-band states, are time reversed. $H_{cc'}$ and $H_{vv'}$ are the Luttinger matrices for the electron and hole kinetic energies. The Coulomb interaction H^c is screened by the optic dielectric constant ϵ_{∞} .⁷ It should be noted that the leading term of $H_{cvcv'}$ is diagonal in the band indices, i.e., proportional to $\delta_{cc'} \delta_{vv'}$.

The exchange interaction can be separated into two parts, which in the limit of vanishing \vec{Q} are (a) the analytic exchange interaction:

$$H_{cvcv'}^{\text{exa}} = \frac{4\pi e^2}{V} \sum_{\vec{G} \neq 0} \frac{1}{\vec{G}^2} \langle c | e^{i\vec{G}\cdot\vec{r}} (T | v) \rangle \times \langle v' | T^\dagger e^{-i\vec{G}\cdot\vec{r}} | c' \rangle, \quad (2)$$

and (b) the nonanalytic exchange interaction:

$$H_{cvcv'}^{\text{exna}} = \lim_{Q \rightarrow 0} M_{cv}(\vec{Q}) M_{c'v'}(\vec{Q}), \quad (3)$$

where

$$M_{cv}(\vec{Q}) = \left(\frac{4\pi e^2}{VQ^2} \right)^{1/2} \frac{\hbar}{m} \frac{\langle c | \vec{Q} \cdot \vec{p} (T | v) \rangle}{E_c - E_v}. \quad (4)$$

$|c\rangle$ and $|v\rangle$ are the zone-center Bloch states for electrons of energies E_c and E_v , respectively, serving as the basis for the matrix representation of the effective mass Hamiltonians. The integration volume is the unit cell. \vec{G} denotes a reciprocal-lattice vector, T the time inversion operator, and V the crystal volume.

In the many-body treatment of the exciton problem,^{7,10} electron-hole exchange is part of the irreducible particle-hole interaction. In the diagrammatic formulation the exchange interaction enters with a bare Coulomb line, i.e., it is unscreened. However, in contrast to the Coulomb interaction even the leading terms of the exchange interaction are nondiagonal with respect to pairs of band indices (cv). Thus excitonic states associated with the lowest conduction and uppermost valence bands are coupled by H^{ex} to particle-hole states of all other pairs of conduction and valence bands, which constitute the dielectric background. This coupling leads to an effective screening of H^{exna} , as derived below.

If H^{ex} is formulated in a basis of Wannier functions, it also falls into two parts: a short- and a long-range part. There is a close correspondence but no identity between the short-range part and the analytic exchange on one side, and the long-range part and the nonanalytic exchange on the other side.^{22,23}

A. Screening of the exchange interaction

The Schrödinger equation (1), which due to the exchange interaction is of infinite rank with re-

spect to the band indices and does not divide into block-diagonal form, can be reduced to finite size by a renormalization of the nonanalytic exchange, as shown by Kiselev and Zhilich.¹² These authors transform Eq. (1) into an expression identical with the phenomenological equation for the energy of longitudinal excitons:

$$\epsilon_{\alpha\beta}(\vec{Q}, \omega) Q_\alpha Q_\beta / Q^2 = 0, \quad \omega = E/\hbar. \quad (5)$$

For this purpose they assume Eq. (1) to be solved without H^{exna} , the envelopes and energies of the solution being $C_{cv}^\mu(\vec{k}, \vec{Q})$ and $\tilde{E}^\mu(\vec{Q})$, respectively. The eigenfunctions of the complete Hamiltonian are then expanded as

$$B_{cv}(\vec{k}, \vec{Q}) = \sum_\mu \phi^\mu(\vec{Q}) C_{cv}^\mu(\vec{k}, \vec{Q}), \quad (6)$$

where $\phi^\mu(\vec{Q})$ is determined by the equation

$$[E - \tilde{E}^\mu(\vec{Q})] \phi^\mu(\vec{Q}) - M_\mu(\vec{Q}) \sum_{\mu'} M_{\mu'}^*(\vec{Q}) \phi^{\mu'}(\vec{Q}) = 0, \quad (7)$$

$$M_\mu(\vec{Q}) = \sum_{cv\vec{k}} C_{cv}^\mu(\vec{k}, \vec{Q})^* M_{cv}(\vec{Q}) = \sum_{cv} \varphi_{cv}^\mu(\vec{r}=0, \vec{Q})^* M_{cv}(\vec{Q}). \quad (8)$$

φ_{cv}^μ is the Fourier transform of $C_{cv}^\mu(\vec{k}, \vec{Q})$ for fixed c , v , and \vec{Q} . Since

$$\epsilon_{\alpha\beta}(\vec{Q}, \omega) = \delta_{\alpha\beta} - \sum_\mu \frac{P_\alpha^\mu(\vec{Q}) P_\beta^\mu(\vec{Q})^*}{E - \tilde{E}^\mu(\vec{Q})} \quad (9)$$

and

$$P_\alpha^\mu(\vec{Q}) = \sum_{cv} \varphi_{cv}^\mu(\vec{r}=0, \vec{Q})^* \frac{\hbar}{m} \left(\frac{4\pi e^2}{V} \right)^{1/2} \frac{\langle c | p_\alpha (T | v) \rangle}{E_c - E_v}, \quad (10)$$

Eq. (7) can be cast into the form of Eq. (5). This reformulation is obviously only possible because H^{exna} can be factorized. No similar treatment is possible for H^{exa} . Equation (5) and (9) are equivalent to the implicit equation

$$E^\mu(\vec{Q}) = \tilde{E}^\mu(\vec{Q}) + \frac{|M_\mu(\vec{Q})|^2}{\epsilon'_{\alpha\beta}(\vec{Q}, \omega^\mu(\vec{Q})) Q_\alpha Q_\beta / Q^2} \quad (11)$$

$$\hbar \omega^\mu(\vec{Q}) = E^\mu(\vec{Q})$$

for the exact exciton energy $E^\mu(\vec{Q})$.

Thus the correction of the unperturbed energies is equal to a first-order perturbation term of the screened nonanalytic exchange interaction. The screening is due to the electronic dielectric constant of Eq. (9), evaluated at the frequency of the excitonic state considered, but without its contribution and therefore denoted by a prime.

The preceding analysis opens a way for a practical solution of the exciton binding energies under the following additional approximations:

(a) We replace the "background" dielectric con-

stant in the denominator of Eq. (11) by the optic dielectric constant ϵ_∞ . This constant has been introduced phenomenologically already by Skettrup and Balslev.¹¹

(b) As experimental and numerical data indicate, H^{exa} does not have a profound influence on binding energies and can be treated as a first-order perturbation.

Under these assumptions, the solution of Eq. (11) is equivalent to the eigenvalue problem of Hamiltonian (1) projected onto the space of the band-edge states, with H^{exna} screened by ϵ_∞ . After a Fourier transformation the exchange interaction terms assume the following form:

$$H_{cvc',v'}^{\text{exa}} = \sum_{\vec{G} \neq 0} \frac{4\pi e^2}{G^2} \langle c | e^{i\vec{G} \cdot \vec{r}} (T | v) \rangle \langle v' | T^\dagger \rangle e^{-i\vec{G} \cdot \vec{r}} | c' \rangle \delta(\vec{r}), \quad (12)$$

$$H_{cvc',v'}^{\text{exna}} = \lim_{Q \rightarrow 0} \frac{4\pi e^2 \hbar^2}{Q^2 m^2 \epsilon_\infty} \times \frac{\langle c | \vec{Q} \cdot \vec{p} (T | v) \rangle \langle v' | T^\dagger \rangle \vec{p} \cdot \vec{Q} | c' \rangle}{E_g^2} \delta(\vec{r}), \quad (13)$$

where c, c' and v, v' refer to the Bloch states at the conduction-band minimum and valence-band maximum, respectively; thus $E_c - E_v = E_{c'} - E_{v'} = E_g$ is the gap energy.

B. Tensor formulation of the exchange terms

For cubic or tetrahedral semiconductors the exciton effective-mass Hamiltonian is usually expanded into products of angular momentum operators. In order to implement the exchange interaction terms into this formalism we specialize to the standard situation of cubic semiconductors with direct gap and restrict ourselves to a basis consisting of the two states of the conduction-band minimum and the six states of the uppermost valence band at the zone center.

We introduce the basis sets

$|v\rangle = |jS_h\rangle; j = -(X + iY)/\sqrt{2}, Z, (X - iY)/\sqrt{2}, S_h = \uparrow \downarrow$ for the valence band, and $|c\rangle = |RS_c\rangle, S_c = \uparrow, \downarrow$ for the conduction band, where X, Y, Z , and R denote the orbital parts of the zone-center Bloch functions. The analytic exchange term can immediately be factorized into an orbital and a spin part and, after minor regrouping of terms, be written as

$$H_{cvc',v'}^{\text{exa}} = \langle j | \left(\sum_{\vec{G} \neq 0} \frac{4\pi e^2}{G^2} e^{i\vec{G} \cdot \vec{r}} (T^\dagger | R) \right) \langle (R | T) e^{i\vec{G} \cdot \vec{r}} | j' \rangle \times \langle S_c | (T | S_h) \rangle \langle (S_h' | T^\dagger) | S_c' \rangle \delta(\vec{r}). \quad (14)$$

The orbital part is diagonal in j and j' , since the operator in the large parentheses is invariant under all operations of the crystal point group, which is O_h or T_d . The matrix for the spin part is $\frac{1}{2}(1 - \vec{\sigma}_e \cdot \vec{\sigma}_h)$, where $\vec{\sigma}_e$ and $\vec{\sigma}_h$ denote the vector operators whose components are the Pauli matrices for electron and hole, respectively. This operator contributes only to exciton states of zero total spin $\frac{1}{2}(\vec{\sigma}_e + \vec{\sigma}_h)$ (singlet states). Thus the analytic exchange terms can be formulated as matrix representation of the operator

$$H^{\text{exa}} = C \frac{1}{2} (1 - \vec{\sigma}_e \cdot \vec{\sigma}_h) \delta(\vec{r}), \quad (15)$$

where

$$C = \sum_{\vec{G} \neq 0} \frac{4\pi e^2}{G^2} |\langle R | e^{-i\vec{G} \cdot \vec{r}} | Z \rangle|^2. \quad (16)$$

If for the nonanalytic exchange term the spin-orbit splitting is neglected in the energy denominators, H^{exna} also can be factorized, the spin part being identical to that of H^{exa} . The orbital part equals

$$\frac{4\pi e^2}{Q^2 E_g \epsilon_\infty} \left(\frac{\hbar^2}{m^2 E_g} \langle j | \vec{Q} \cdot \vec{p} (T^\dagger | R) \rangle \langle (R | T) \vec{Q} \cdot \vec{p} | j' \rangle \right). \quad (17)$$

The expression in large parentheses is equal to the usual $\vec{k} \cdot \vec{p}$ perturbation matrix, where \vec{k} is replaced by \vec{Q} and only the interaction with the lowest conduction band is regarded. One obtains the expansion of this operator into $l=1$ angular momentum operators from the Luttinger matrix by retaining only the interaction matrix element

$$F = \frac{P^2}{E_g}, \quad P^2 = \frac{2}{m} |\langle R | p_x | Z \rangle|^2$$

and subtracting the free-particle kinetic energy $+\hbar^2 Q^2/2m$, where m is the free-electron mass. Upon introduction of the spherical tensor operators $\hat{Q}^{(2)}$ and $I^{(2)}$ (Refs. 19 and 24), H^{exna} assumes the following form:

$$H^{\text{exna}} = \frac{4\pi e^2}{E_g^2 \epsilon_\infty} \frac{\hbar^2 P^2}{2m} \frac{1}{2} (1 - \vec{\sigma}_e \cdot \vec{\sigma}_h) \left[\frac{1}{3} - (\hat{Q}^{(2)} \cdot \vec{I}^{(2)}) \right]$$

$$\hat{Q}^{(2)} = Q^{(2)}/Q^2. \quad (18)$$

Out of the manifold of exciton states upon which these operators act, we restrict ourselves to those formed by the Γ_6 conduction and Γ_8 valence band, neglecting the influence of the split-off band. This can be done by projecting the spin operators

\vec{I} , $\vec{\sigma}_h$, and products thereof to the space of $J = \frac{3}{2}$ eigenfunctions of the spin operator $\vec{J} = \vec{I} + \frac{1}{2}\vec{\sigma}_h$. Diagonalization of H^{exa} and H^{exna} in the basis consisting of the eigenfunctions of the total spin operator

$$\vec{F} = \vec{J} + \frac{1}{2}\vec{\sigma}_e$$

leads to the following results: the triplet states $F = 2$ are unaffected, since the projection of F into their eigenspace vanishes. For the singlet states $F = 1$ we obtain the following representations:

$$\begin{aligned} H^{\text{exa}} &= \frac{4}{3} C \delta(\vec{r}), \\ H^{\text{exna}} &= \frac{4}{3} \frac{4\pi e^2 \hbar^2 P^2}{E_g^2 \epsilon_\infty 2m} \left[\frac{1}{3} - (\hat{Q}^{(2)} \cdot \vec{F}^{(2)}) \right] \delta(\vec{r}), \end{aligned} \quad (19)$$

where $F^{(2)}$ is formed from $F = 1$ angular momentum matrices. For $\hat{Q} = (001)$, the term in square brackets becomes the matrix

$$\delta_{F_x 0} \delta_{0 F'_x}$$

in a standard basis. Thus only the $F = 1$ exciton of magnetic quantum number $F_x = 0$ with respect to the wave vector \vec{Q} as quantization axis, i.e., the longitudinal exciton, is affected by the nonanalytic exchange interaction. The splitting pattern for the eight exciton states is given schematically in Fig. 1. The $\Gamma_6 \times \Gamma_8$ manifold is decomposed into irreducible components $\Gamma_3 + \Gamma_4 + \Gamma_5$. No exchange corrections result for the $\Gamma_3 + \Gamma_4$ states ($F = 2$ triplet excitons), while the analytic exchange reduces the binding energy of Γ_5 excitons ($F = 1$ singlet excitons). The nonanalytic exchange splits the longitudinal exciton Γ_{5L} ($F = 1$, $F_x = 0$) from the transverse excitons Γ_{5T} ($F = 1$, $F_x = \pm 1$). Some remarks about the general background of the invariant expansion of the exchange interaction, together with hints for a generalization, are given in the Appendix.

III. EXCITON-PHONON INTERACTION

In the spherical model the effective-mass Hamiltonian for excitons interacting with longitudinal-optical phonons, but without the exchange interaction, has the following form:

$$\begin{aligned} H_x &= \frac{p_e^2}{2m_e} + T \left(\frac{\vec{p}_h}{\hbar} \right) - \frac{e^2}{\epsilon \mathcal{J}} + \sum_{\vec{q}} \hbar \omega_{\text{LO}} b_{\vec{q}}^\dagger b_{\vec{q}} \\ &+ \sum_{\vec{q}} [\Gamma_{\vec{q}} b_{\vec{q}} (e^{i\vec{q} \cdot \vec{r}_e} - e^{i\vec{q} \cdot \vec{r}_h}) + \text{h.c.}] \end{aligned} \quad (20)$$

Here the influence of the split-off band is neglected. The electron kinetic energy is described by a single parabolic band of bare mass m_e .

$$T \left(\frac{\vec{p}_h}{\hbar} \right) = \frac{\gamma_1}{2m} [P_h^2 - \mu_h (P_h^{(2)} \cdot g^{(2)})] \quad (21)$$

is the spherically averaged Luttinger Hamiltonian for the hole kinetic energy,²⁵ where γ_1/m is the mean inverse hole mass and $\mu_h = (6\gamma_3 + 4\gamma_2)/5\gamma_1$ is a band-splitting factor given in terms of the Luttinger parameters $\gamma_1, \gamma_2, \gamma_3$. The coupling to the phonons is expressed by the last term, where

$$\Gamma_{\vec{q}} = -i \left(\frac{2\pi e^2 \hbar \omega_{\text{LO}}}{V \epsilon^* q^2} \right)^{1/2}, \quad \frac{1}{\epsilon^*} = \frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \quad (22)$$

denotes the Fröhlich coupling factor. V is the crystal volume, ϵ_0 the static dielectric constant, ω_{LO} the longitudinal-optical frequency (assumed dispersionless), and $b_{\vec{q}}^\dagger, b_{\vec{q}}$ are the creation and annihilation operators, respectively, for an LO-phonon of wave vector \vec{q} . In Ref. 6 this Hamiltonian has been dealt with by two methods. In both, the phonon variables are eliminated by a variational procedure and effective Hamiltonians are established in configuration-spin space. In method I the polaron aspect of electron and hole is stressed. Accordingly the exciton wave function

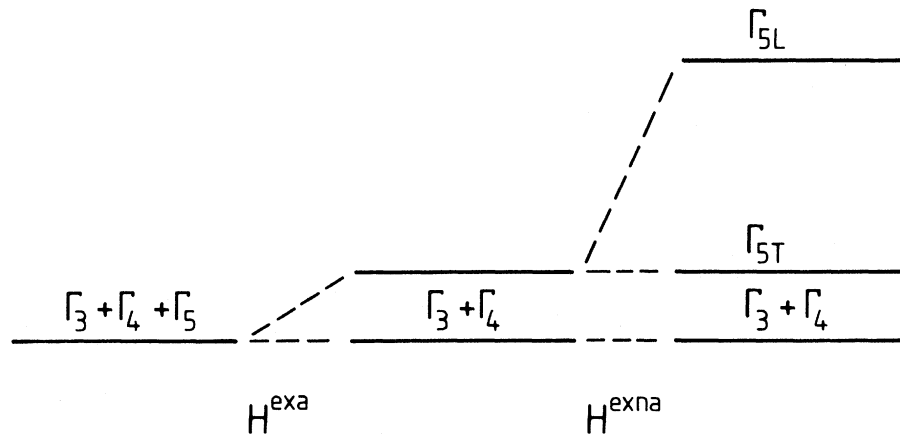


FIG. 1. Splitting of the eightfold exciton ground state due to analytic (H^{exa}) and nonanalytic exchange (H^{exna}).

is expanded into products of electron-polaron and hole-polaron wave functions. The resulting effective Hamiltonian contains a constant self-energy term and a phonon-induced electron-hole potential consisting of two parts: The first is equal to Haken's potential,¹ averaged over the light- and heavy-hole band. The second is a tensor force term proportional to $(\hat{r}^{(2)} \cdot \mathbf{J}^{(2)})$. Renormalized band parameters are inserted in the kinetic-energy terms. The eigenvalue problem of this Hamiltonian was solved by expanding the wave functions into eigenfunctions of total angular momentum $\vec{F} = \vec{J} + \vec{L}$, where \vec{L} denotes the orbital angular momentum. The radial parts were expanded into Gaussian functions, just as Baldereschi and Lipari did for determining the eigenstates of their spherical model Hamiltonian.²⁵

In method II, the trial wave function is

$$\psi_x = \exp\left(-i \sum_{\vec{q}} b_{\vec{q}}^\dagger b_{\vec{q}} \vec{q} \cdot \vec{R}\right) e^\alpha \phi_x |0\rangle, \quad (23)$$

where $|0\rangle$ is the phonon vacuum, $\vec{R} = S_2 \vec{r}_e + S_1 \vec{r}_h$ the center-of-mass coordinate of electron and hole,

$$\begin{aligned} \phi_x = f(r) |L=0, \mathcal{J}=\frac{3}{2}, F=\frac{3}{2}, F_z\rangle \\ + g(r) |L=2, \mathcal{J}=\frac{3}{2}, F=\frac{3}{2}, F_z\rangle, \end{aligned} \quad (24)$$

an ansatz for the ground-state wave function in configuration-spin space according to Baldereschi and Lipari,²⁵ with

$$\begin{aligned} f(r) = 2c_1 \alpha^{3/2} \exp(-\alpha r) \\ g(r) = \frac{2c_2}{\sqrt{3}} \beta^{5/2} r \exp(-\beta r). \end{aligned} \quad (25)$$

The operator

$$\alpha = \sum_{\vec{q}} \frac{\Gamma_{\vec{q}}^*}{\hbar \omega_{LO}} [f_1(\vec{q}) e^{iS_2 \vec{q} \cdot \vec{r}} - f_2(\vec{q}) e^{-iS_1 \vec{q} \cdot \vec{r}}] b_{\vec{q}}^\dagger + \text{h.c.}$$

$$S_1 = (m/\gamma_1)/M, \quad S_2 = m_e/M, \quad M = m_e + m/\gamma_1, \quad (26)$$

contains spin-dependent displacement amplitudes $f_l(\vec{q})$, $l=1,2$, which are expanded into projection operators:

$$\begin{aligned} f_l(\vec{q}) = f_l^+(q, \phi_x) P_+(\hat{q}) + f_l^-(q, \phi_x) P_-(\hat{q}) \\ P_\pm(\hat{q}) = \frac{1}{2} [1 \mp (\hat{q}^{(2)} \cdot \mathcal{J}^{(2)})], \end{aligned} \quad (27)$$

where the scalar functions $f_l^s(q, \phi_x)$, $s \in \{+, -\}$, $l=1,2$, depend on the parametrized function ϕ_x .

For the transformed Hamiltonian

$$\begin{aligned} H_x^{\text{eff}} = \langle 0 | U^\dagger H_x U | 0 \rangle \\ U = \exp\left(-i \sum_{\vec{q}} b_{\vec{q}}^\dagger b_{\vec{q}} \vec{q} \cdot \vec{R}\right) e^\alpha, \end{aligned} \quad (28)$$

we refer to Ref. 6. To the variational expression

$$E = \langle \phi_x | H_x^{\text{eff}} | \phi_x \rangle / \langle \phi_x | \phi_x \rangle, \quad (29)$$

three contributions

$$E = E_0 + E_s + E_{ph}$$

are obtained. E_0 is the energy of an exciton decoupled from phonons, as in Ref. 25, the static dielectric constant ϵ_0 being replaced by the optic dielectric constant ϵ_∞ . E_s is the polaron self-energy and E_{ph} is the mean value of the phonon-induced electron-hole potential. $E_s + E_{ph}$ vanishes when the exciton radius becomes much smaller than the polaron radii. E_{ph} is the mean value of the phonon-induced electron-hole potential. E_s and E_{ph} are lengthy rational functions of the polaron radii. In E the only parameters left are the mixing coefficients c_1, c_2 , and the exponents α and β . Minimization was performed by a standard variational program for four parameters. The exchange correction was performed perturbatively with ϕ_x and the operators H^{ex} and H^{exna} of Eq. (19). Caution must be exercised in the numerical variation for the following reason: a number of higher-order commutators of the form

$$[f_l(\vec{q}), [f_l(\vec{q}'), f_l(\vec{q}'')]] \quad (30)$$

had to be omitted in H_x^{eff} which are proportional to powers of $|f_l^+ - f_l^-|$, $l=1,2$. To keep the influence of the commutators small, the range of variation of c_1, c_2, α, β , should be restricted such that

$$\text{Max}_{q \geq 0^+} |f_l^+(q) - f_l^-(q)| \leq \frac{\sqrt{1+\mu_h} - \sqrt{1-\mu_h}}{\sqrt{1+\mu_h} + \sqrt{1-\mu_h}}, \quad l=1,2. \quad (31)$$

This value is the maximum value for the case of shallow excitons where the neglect of the commutators was found to be reasonable.

A critical remark is in place concerning the simultaneous treatment of electron-phonon and exchange interaction. The exciton wave vector \vec{Q} in Sec. II refers to the electronic part of the exciton wave function only and is, therefore, not a good quantum number of the eigenstates of H_x [Eq. (20)] since the total exciton momentum contains also the momenta of the virtually excited phonons. Hence \vec{Q} has to be interpreted as an operator mean value. In an exact treatment of both interactions one would expect a mutual influence of electron-phonon and exchange interaction in the exciton problem. We believe, however, that this effect does not become important in the relative motion of the electron-hole pair.

IV. RESULTS AND DISCUSSION

In this section we present the numerical results obtained for some representative III-V and II-VI

compounds and for CuBr.

A. Input parameter

Table I contains the input parameters for the calculation of the exciton binding energies of Table III. Since the accuracy of these parameters and the experiments from which they are obtained differ strongly for the different compounds, these input data require some comments. The most reliable band parameters are those for GaAs, for which we quote the parameter sets obtained from magneto-optic data of excitons²⁶ and from cyclotron resonance.²⁷ Both experiments yield polaron data. Moreover, from these parameters a polariton dispersion relation²⁸ has been deduced which is consistent with data from resonant Brillouin scattering. The data quoted for GaSb originate from interband magneto-optic experiments²⁹ and are interpreted as bare-mass parameters. For ZnSe the first set of parameters is obtained by using the model of method I and fitting the calculated $2P$ -exciton states to the two-photon absorption data of Ref. 30. In a spherical model, these correspond to the binding energies $E(P_{1/2}) = 4.18$ meV, $E(P_{3/2}) = 5.90$ meV, and $E(P_{5/2}) = 4.97$ meV. The second set of parameters for

ZnSe is taken from Ref. 31. In this reference, doubts are expressed concerning the effective rydberg derived in Ref. 30. For ZnTe we used cyclotron resonance data, and for CdTe, theoretical bare-mass parameters. The band parameters for CuBr were obtained from the two-photon-absorption data of excitonic P states³² in the same way as the corresponding parameter set for ZnSe. The binding energies in the spherical model are $E(P_{1/2}) = 14.74$ meV, $E(P_{3/2}) = 19.34$ meV, and $E(P_{5/2}) = 16.84$ meV. Since the two-photon experiments of Ref. 32 yielded only the reduced effective mass for method I (however, the masses of both electron and hole are required), we used in addition, the electron-to-hole mass ratio obtained from electron-exciton collision experiments. The conversion between bare and polaron mass parameters was performed according to Ref. 24. To determine the exchange splitting of the exciton ground state we calculated the constant C of Eq. (16) and the momentum matrix element P from band-edge wave functions obtained with the pseudopotential method. Alternatively P can be determined also from the electron effective mass values, which yield within 30% the same values as the pseudopotential calculation.

TABLE I. Parameters for calculating exciton binding energies. Experimental mass parameters are polaron or bare-mass parameters indicated by the references. The renormalization is considered according to Ref. 24.

	E_g (eV)	$\hbar\omega_{LO}$ (meV)	ϵ_0	ϵ_∞	m_e^*/m	γ_1^*	γ_2^*	γ_3^*	m_e/m	γ_1	γ_2	γ_3
GaAs	1.519 ^a	36.2 ^b	12.87 ^b	10.9 ^b	0.0665 ^b	6.85 ^a	2.10 ^a	2.90 ^a	0.0657	7.12	2.19	3.02
						6.84 ^c	2.11 ^c	2.74 ^c		7.11	2.19	2.84
GaSb	0.81 ^d	29.8 ^b	15.69 ^b	14.44 ^b	0.0405 ^e	13.12	4.34	5.62	0.0403	13.3 ^d	4.4 ^d	5.7 ^d
InP	1.42 ^f	43.3 ^b	12.30 ^b	9.56 ^b	0.0803 ^a	4.95 ^a	1.65 ^a	2.35 ^a	0.0788	5.40	1.80	2.56
ZnSe	2.82 ^g	30.5 ^b	8.66 ^g	5.90 ^b	0.16 ^g	3.00 ^h	0.53 ^h	0.92 ^h	0.149	3.45	0.64	1.09
						4.3 ^g	0.59 ^g	1.34 ^g		4.8	0.67	1.53
ZnTe	2.25 ⁱ	25.4 ^b	9.67 ^j	7.28 ^j	0.11 ^j	4.0 ^k	1.15 ^k	1.29 ^k	0.104	4.484	1.307	1.464
CdTe	1.49 ⁱ	20.83 ^b	10.23 ^b	7.21 ^b	0.101	4.23	1.52	1.98	0.096 ^l	5.29 ^l	1.89 ^l	2.46 ^l
CuBr	3.07 ^m	20.0	6.0 ^m	5.4	0.21	0.84	0.207 ^m	0.49 ^m	0.20 ^{m,n}	1.1	0.26	0.62

^aReference 26.

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^cReference 27.

^dReference 29.

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TABLE II. Exciton and polaron parameters derived from the input parameters of Table I.

	R_{eff} (meV)	ρ_e (Å)	ρ_{hh} (Å)	ρ_{lh} (Å)	a_{eff} (Å)
GaAs	3.75	40	13.5	36.2	149.1
	3.75	40	14.3	35.9	149.2
GaSb	1.46	56.3	19.4	55	314.2
InP	5.17	33.4	8.8	29.5	113.2
ZnSe	19.61	28.9	14.3	25.6	42.4
	17.19	28.9	17.5	30	48.4
ZnTe	11.11	37.6	15.9	33	67
CdTe	9.21	43.6	12.3	42.2	76.4
CuBr	66.6	30.8	5.2	19.8	18.0

For CuBr the value of P is reduced due to the fact that the uppermost valence band is derived mainly from Cu d states which do not contribute to the dipole matrix element. The p admixture to the topmost valence-band states is about 35% (Ref. 33). The pseudopotential values of the constant C [Eq. (16)] are so small that the calculated splitting between $\Gamma_3 + \Gamma_4$ and Γ_{5T} excitons is within the numerical errors. Obviously the pseudopotential wave functions do not contain the higher Fourier coefficients which are important for C .

B. Results

From the input parameters of Table I we first calculate the relevant parameters characterizing the system, such as the effective atomic units:

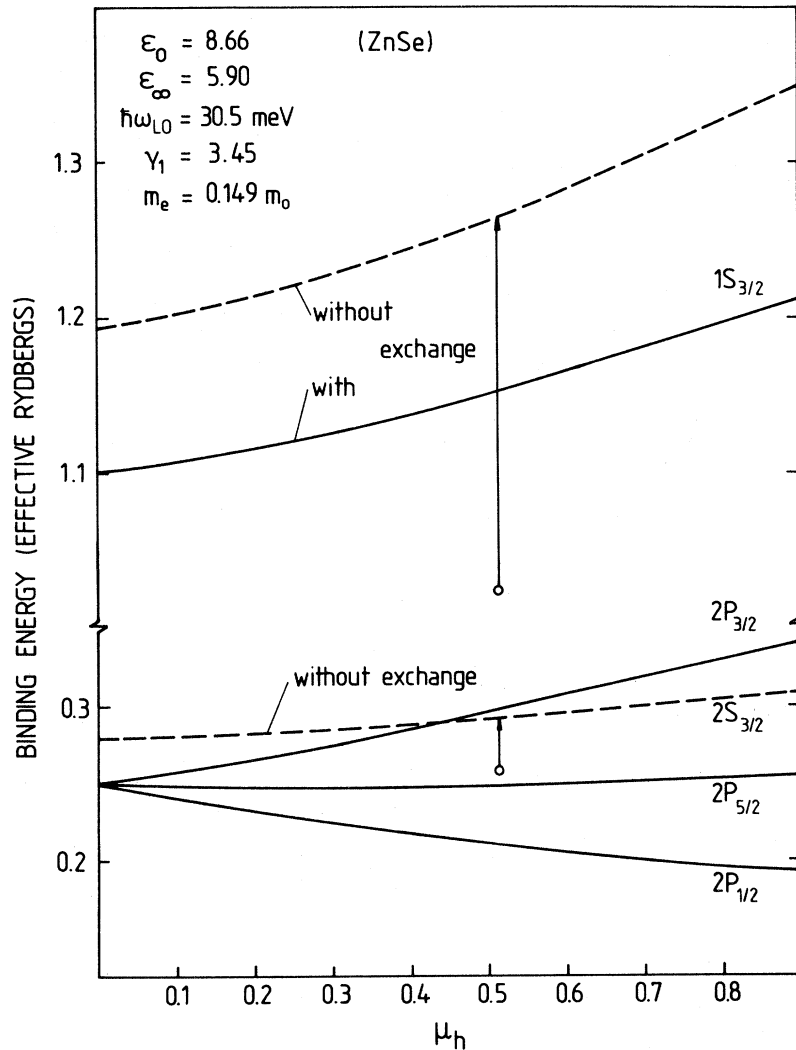


FIG. 2. Exciton binding energies as a function of the valence-band-splitting parameter μ_h . The fixed input parameters are those for ZnSe (Table I). For $\mu_h = 0.512$ the binding energies in the ϵ_0 approximation are indicated for $1S_{3/2}$ and $2S_{3/2}$ (circles).

TABLE III. Binding energies of excitons (in meV) calculated from the parameters of Table I. For method I and II see text. For $1S_{3/2}$ and $2S_{3/2}$ the energy refers to the transverse exciton. Δ_{LT} (in meV) is the correction due to the nonanalytic exchange interaction (longitudinal-transverse splitting).

	Method I		Method II		$2S_{3/2}$	$2P_{1/2}$	$2P_{5/2}$	$2P_{3/2}$
	$1S_{3/2}$	Δ_{LT}	$1S_{3/2}$	Δ_{LT}				
GaAs	4.09	0.09	3.94	0.08	1.02	0.75	0.95	1.18
	4.08	0.09	3.92	0.08	1.02	0.76	0.95	1.17
GaSb	1.58	0.02	1.56	0.02	0.40	0.29	0.38	0.48
InP	5.81	0.29	5.41	0.23	1.43	1.04	1.31	1.64
ZnSe	27.05	2.9	22.62	2.0	5.72	4.18	4.93	5.92
	23.74	2.0	20.12	1.4	5.08	3.56	4.35	5.36
ZnTe	13.54	0.75	12.01	0.5	3.12	2.32	2.79	3.38
CdTe	12.10	0.9	10.23	0.6	2.74	1.81	2.36	3.07
CuBr	74.71	10.5	69.1	9.3	19.89	14.78	16.79	19.33

$$R_{\text{eff}} = \frac{m_e^4}{2\hbar^2} \frac{1}{\gamma_1 \epsilon_0^2}, \quad \gamma_1' = \frac{m}{m_e^*} + \gamma_1^*$$

$$a_{\text{eff}} = \frac{\hbar^2}{m_e^2 \epsilon_0 \gamma_1'},$$

and the polaron radii

$$\rho_s = \left(\frac{\hbar^2}{2m_s \hbar \omega_{L0}} \right)^{1/2}, \quad S = e, lh, hh,$$

where the masses for light (lh) and heavy holes (hh) are

$$m_{lh} = \frac{m}{\gamma_1(1 + \mu_h)} \quad \text{and} \quad m_{hh} = \frac{m}{\gamma_1(1 - \mu_h)}.$$

The numerical values of Table II demonstrate that the sum of electron and hole polaron radii is definitely smaller than the Bohr radius a_{eff} for III-V compounds and for excited states of the II-VI compounds. This justifies the application of the polaron concept (method I). For the exciton ground states of II-VI compounds and of CuBr, the sum of the polaron radii is larger than the exciton radius which favors the application of method II.

TABLE IV. Exciton binding energies (in meV) for ϵ_0 approximation (using renormalized band parameters and a Coulomb potential screened with ϵ_0) and ϵ_∞ approximation (using bare-mass parameters and a Coulomb potential screened by ϵ_∞). The $1S_{3/2}$ energies correspond to the transverse exciton states. For GaAs and ZnSe the first set of parameters of Table I was used.

		$1S_{3/2}$	$2S_{3/2}$	$2P_{1/2}$	$2P_{5/2}$	$2P_{3/2}$
GaAs	ϵ_∞	5.41	1.38	1.03	1.30	1.62
	ϵ_0	3.95	1.01	0.76	0.95	1.18
ZnSe	ϵ_∞	39.6	9.97	8.1	9.6	11.3
	ϵ_0	20.1	5.05	4.19	4.88	5.70
CuBr	ϵ_∞	78.2	19.63	16.46	19.0	22.0
	ϵ_0	67.5	16.89	14.62	16.45	18.65

C. Discussion

The data of Tables III and IV and of Fig. 2 will be used to discuss the influence of the electron-phonon interaction on the exciton binding energies. A comparison with experimental results is made only for some of the compounds.

For GaAs the experimental value of $E(1S_{3/2}) - E(2S_{3/2}) = 3.15 \pm 0.15$ meV (Ref. 34) is reproduced most appropriately by the unperturbed polaron model (method I). The electron-phonon coupling, in general, increases the binding energy of the $1S$ excitons significantly compared to the ϵ_0 approximation (compare Tables III and IV). It causes a remarkable Lamb shift, lifting the degeneracy of the $2S$ and $2P$ states (see Fig. 2 for $\mu_h = 0$). Accurate experimental data for this shift are not available yet, and a simultaneous evaluation of the existing S and P exciton series data has not been performed. In Ref. 3 an experimental value of 13 ± 0.3 meV is reported for the $1S_{3/2} - 2S_{3/2}$ separation of excitons in ZnSe. This splitting cannot be reproduced with either of the parameter sets discussed so far. Even the parameters of Venghaus *et al.*³¹ yield too large a separation, since the model from which the parameters were extracted does not include a phonon-induced electron-hole potential. Thus a consistent evaluation of exciton data is still missing for ZnSe, which is mainly due to the uncertainty of the experimental value for the effective rydberg. For CuBr the parameter set producing the proper energies of the $2P$ states does not provide the correct binding energy of 110 meV (Ref. 35) for the $1S_{3/2}$ state. Since, however, the experimental binding energy of 20 meV (Ref. 35) is reproduced quite well for the $2S_{3/2}$ state, the most likely deficiency of our calculation is a breakdown of the continuum approximation. The $1S_{3/2}$ exciton radius of 5.86 Å becomes comparable to the lat-

tice constant for CuBr. In Refs. 30 and 32 the ϵ_0 approximation was applied to deduce the following parameters: for ZnSe (Ref. 30) $\gamma_1^* = 3.23$, $\gamma_2^* = 0.59$, and $\gamma_3^* = 1.01$, with $m_e^* = 0.17m_0$, and $\epsilon_0^* = 8.66$; for CuBr (Ref. 32): $\gamma_1^* = 5.84$, $\gamma_2^* = 0.2$, and $\gamma_3^* = 0.56$, with $m_e^* = 0.20$, and $\epsilon_0 = 6.0$. We included in the fit the electron-phonon interaction by method I and obtained parameters which are consistent with these (see Table I). It is evident, however, from Table III and IV and Fig. 2 that the influence of the electron-phonon interaction on the energies is not negligible. A more accurate fitting of the parameters is not reasonable since the k linear terms have been neglected. This only slightly influences S states, but for P states it may become more important with increasing ionicity of the compounds.

Finally, we want to emphasize the overall good agreement of the calculated longitudinal-transverse splitting Δ_{LT} (Table III) with more recent experimental data: GaAs, 0.08 meV (Refs. 36, 37), InP, 0.1 meV (Ref. 37) and 0.2 meV (Ref. 38), ZnSe, 1.5 meV (Ref. 39), ZnTe, 1.1 meV (Ref. 40), CdTe, 0.4 meV (Ref. 36), and CuBr, 12.2 meV (Ref. 41).

In conclusion, we have calculated excitonic binding energies for semiconductors including exchange, electron-phonon interaction, and valence-band degeneracy. All the terms modify significantly the hydrogenic exciton model and have to be considered if band parameters are determined from exciton data. Concerning the phonon Lamb shift, experiments determining both S and P states of the same crystal with comparable accuracy would be desirable. For deep exciton states, as the exciton ground state in CuBr, the continuum approximation is insufficient and central cell corrections must be considered.

APPENDIX

The basis sets $\{|c\rangle, |v\rangle\}$ which are used for the representation of the exchange Hamiltonian, can be chosen so as to transform according to irreducible representations $D^{(c)}$ and $D^{(v)}$:

$$g|v\rangle = \sum_{\tilde{v}} |\tilde{v}\rangle D_{\tilde{v}v}^{(v)}(g)$$

$$g|c\rangle = \sum_{\tilde{c}} |\tilde{c}\rangle D_{\tilde{c}c}^{(c)}(g), \quad g \in T_d.$$

A change to the basis $\{g^{-1}|c\rangle, g^{-1}|v\rangle\}$, $g \in T_d$ and simultaneous change of the wave vector from \vec{Q} to $g^{-1}\vec{Q}$ must leave the Hamiltonian invariant, which, accordingly, has to satisfy the invariance condition

$$D_{\tilde{c}c}^{(c)}(g)D_{\tilde{v}v}^{(v)}(g)H_{\tilde{c}\tilde{v}}^{\text{ex}}(g^{-1}\vec{Q})D_{\tilde{c}c}^{(c)}(g^{-1})D_{\tilde{v}v}^{(v)}(g^{-1}) = H_{\tilde{c}\tilde{v}}^{\text{ex}}(\vec{Q}).$$

For the zinc-blende-structure compounds we can choose the irreducible representation matrices of $O(3)$:

$$D^{(c)} = D_{1/2}^+,$$

$$D^{(v)} = D_1^- \otimes D_{1/2}^+, \quad (\text{A1})$$

which allows a change to a basis of total spin $F = \vec{l} + \frac{1}{2}\vec{\sigma}_e + \frac{1}{2}\vec{\sigma}_h$ by Clebsch-Gordon coupling. Note that for this, one has to choose hole states $\{T|v\rangle\}$ in the construction of H^{ex} ; otherwise $D^{(v)}$ has to be replaced by $D^{(v)*}$ and the angular-momentum calculus cannot be applied. Due to the choice (A1) of the representation matrices, the effective-mass Hamiltonian for the exchange operators can be expanded into polynomials in $Q_i, I_j, \sigma_k^e, \sigma_k^h$, $ijkl \in \{1, 2, 3\}$, which transform according to Γ_1 . In Eq. (18) the most important of these polynomials are retained.

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