

Unified theory of symmetry-breaking effects on excitons in cubic and wurtzite structures

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A general group-theoretical scheme is developed to discuss any symmetry-breaking effects on the 12-fold 1s-exciton states originating from an *s*-like and *p*-like electron-hole pair. All the possible effects on the conduction and valence bands are taken into account by an effective Hamiltonian formalism. For the electron-hole exchange interaction, the simplest term (including dipole-dipole interaction) is considered. The symmetry-breaking effects treated here can be anything; e.g., a magnetic field, an electric field, stress, the finiteness of exciton wave vector, etc., and even the products of them. As a group-theoretical treatment, this theory includes all the relevant previous theories as special cases.

I. INTRODUCTION

The simple model of excitons in solids has long been established as a composite particle of an electron and a hole which is specified by a wave vector for the translational motion, and a set of hydrogen-like quantum numbers for the relative motion. In a realistic system, however, one has very often to face an additional complexity, namely, the degeneracy or near degeneracy of the Bloch states which compose electron-hole pairs. Since this aspect leads to the existence of degenerate or nearly degenerate exciton states which respond sensitively to any perturbations, it has been studied rather extensively for various cases. A list of existing theories includes: (a) exchange mixing of spin-orbit partners¹; (b) finite wave vector of excitons (wurtzite^{2,3} and zinc-blende⁴ structures); (c) stress-induced exchange splitting⁵ (wurtzite structure); (d) stress-induced *k* linear term⁶ (zinc-blende structure); (e) stress effect⁷; (f) magnetic field mixing^{8,9}; (g) electric field mixing.^{10,11}

In each case the electron-hole exchange interaction and/or some of the symmetry-breaking effects were considered for a group of exciton states which are mixed by the perturbation. They lead to different energy-level schemes and corresponding optical selection rules. Studying various effects on a certain group of exciton states, we sometimes note the similarity or complementarity between two different effects. This must arise from the symmetry properties of the perturbation and the exciton states. Thus one may arrive at the idea that all the symmetry-breaking effects can be discussed in a single group-theoretical framework. It is the purpose of this paper to show it explicitly in the cases of direct allowed excitons at the Γ point of cubic and wurtzite structures.

The arrangement of the paper is the following: in Sec. II are the preliminaries, Sec. III discusses

the electron-hole exchange interaction, and Sec. VI gives concluding remarks which are common to both cubic and wurtzite structures. Sections IV and V are devoted to the detailed formulation and discussion of the cubic and wurtzite structures, respectively. Therefore, each set of Secs. I-IV and VI and Secs. I-III, V, VI provides a closed theoretical scheme.

II. PRELIMINARIES

Throughout the paper, we consider the 12-fold 1s exciton states arising from *s*-like conduction and *p*-like valence bands at the Γ point of the Brillouin zone. Although the energy of each state may change by symmetry operations, the whole energy scheme must be invariant for any symmetry operation of the system including time-reversal operation \hat{K} . Hereafter we use the following notation:

\hat{K}_+ : time-reversal symmetric;

\hat{K}_- : time-reversal antisymmetric.

There exists an effective Hamiltonian \mathcal{H} for the subspace of the 12-fold exciton states. By solving the eigenvalue problem for this Hamiltonian, one gets the energy levels and the optical selection rules.

In order to express the $12 \times 12 = 144$ matrix elements of \mathcal{H} , it is convenient to introduce an effective spin operator $\tilde{\sigma}_e$ ($\sigma_e = \frac{1}{2}$) for the conduction band, and effective spin and orbital angular momentum operators, $\tilde{\sigma}$ ($\sigma = \frac{1}{2}$) and \tilde{l} ($l = 1$), respectively, for the valence bands. The spin operator $\tilde{\sigma}_e$ ($\tilde{\sigma}$) operates only on the conduction- (valence-) band spin states, and \tilde{l} operates only on the orbital parts of the valence-band states. The products of all the independent components in each subspace

$$[(1, \sigma_{ex}, \sigma_{ey}, \sigma_{ez}) \otimes (1, \sigma_x, \sigma_y, \sigma_z) \\ \otimes (1, l_x, l_y, l_z, l_x l_x, l_x l_y, l_x^2 - l_y^2, l_z^2)]$$

exhaust all the independent forms of the 144 matrix elements.

If we have any symmetry breaking effects, the Hamiltonian \mathcal{H} depends on a set of physical quantities, Ξ , which can be, for example, a magnetic field, an electric field, a stress, the translational wave vector of the exciton, or their products. Since symmetry operations also affect Ξ , we must look for the invariant form of \mathcal{H} consisting of the quantities $\bar{\sigma}_e$, $\bar{\sigma}$, $\bar{\Gamma}$, and Ξ .

All the invariant terms can be classified into the following three categories: (i) $\text{inv.}(\bar{\sigma}_e, \Xi) = H^{(c)}$; (ii) $\text{inv.}(\bar{\sigma}, \bar{\Gamma}, \Xi) = H^{(v)}$; (iii) $\text{inv.}(\bar{\sigma}_e, \bar{\sigma}, \bar{\Gamma}, \Xi) = H_{ex}$. They correspond to the invariant form for the conduction band (i), valence bands (ii), and the electron-hole exchange interaction (iii). Since the third group depends on both $\bar{\sigma}_e$ and $\bar{\sigma}$ at the same time, we call it, in a generalized sense, the exchange interaction.

At this stage we introduce a simplifying assumption, namely, we neglect the $\bar{\Gamma}$ and Ξ dependence of the exchange-type invariant terms, H_{ex} . Since the normal exchange interaction, proportional to $(\bar{\sigma} \cdot \bar{\sigma}_e + \frac{1}{4})$,¹² is already a rather small effect, it will be very difficult to identify the higher-order effects without ambiguity except for the case where a higher-order effect produces some qualitatively new feature. Moreover, the inclusion of the Ξ dependence in $H^{(c)}$ and $H^{(v)}$ exhausts most of the presently interesting mixing schemes. Therefore, we leave the $\bar{\Gamma}$ and Ξ dependence of H_{ex} for future study when it becomes definitely necessary.¹³

The procedure to obtain the invariant expressions $H^{(c)}$ and $H^{(v)}$ is an extended version of Luttinger's effective Hamiltonian theory¹⁴ which treats the cyclotron motion of a valence electron in cubic semiconductors. But the meaning of the coefficient for each invariant term is not the same in the cases of an exciton and a Bloch electron. As shown explicitly in the case of magneto-optics of excitons in the zinc-blende structure,⁸ the coefficients for excitons are functions of those for Bloch electrons. Here is another point about the general nature of the formulation. One may regard $H^{(v)}$, for example, as the definition of valence-band parameters for a given Ξ . (If Ξ is a magnetic field, a part of $H^{(v)}$ gives Luttinger's Hamiltonian—see Sec. IV E 1.) Then, in the next step, we take it as a part of the exciton energy by adopting new coefficients which are functions of old ones. During this procedure, we must be careful about the following point: As shown in Appendix A of Ref. 8, if we use the missing electron picture, a matrix element with respect to valence-band states appears as (-1) times

its complex conjugate in the corresponding exciton problem.

III. ELECTRON-HOLE EXCHANGE INTERACTION

Here we give a general argument of the exchange interaction without depending on any crystal symmetry. We use a notation $|\phi(\chi)\rangle$ for the normalized Slater determinant where the valence state χ is missing and the conduction band state ϕ is occupied. The ordering of the orbitals is such that $|\chi(\chi)\rangle$ is the ground state without any permutation for all χ . The exchange part of the Coulomb matrix element between the two arbitrary exciton states

$$\sum_{\bar{q}} A(\bar{q}) |\phi_{\bar{q}+\bar{k}}^*(\chi_{\bar{q}})| \quad \text{and} \quad \sum_{\bar{q}'} \bar{A}(\bar{q}') |\bar{\phi}_{\bar{q}'+\bar{k}'}(\bar{\chi}_{\bar{q}'})|$$

can be written

$$J_{ex} = \sum_{\bar{q}} \sum_{\bar{q}'} A(\bar{q})^* \bar{A}(\bar{q}') \\ \times \int \int \phi_{\bar{q}+\bar{k}}^*(1) \chi_{\bar{q}}(1) \frac{e^2}{r_{12}} \\ \times \bar{\phi}_{\bar{q}'+\bar{k}'}(2) \bar{\chi}_{\bar{q}'}(2) d\tau_1 d\tau_2. \quad (3.1)$$

Introducing the Wannier functions a , \bar{a} , b , and \bar{b} for ϕ , $\bar{\phi}$, χ , and $\bar{\chi}$, respectively, we can rewrite Eq. (3.1)

$$J_{ex} = \delta_{\bar{k}, \bar{k}'} \sum_{\bar{R}} e^{i\bar{k} \cdot \bar{R}} \int \int \frac{d\bar{r}_1 d\bar{r}_2 \rho(\bar{r}_1)^* \bar{\rho}(\bar{r}_2)}{|\bar{r}_1 - \bar{r}_2 - \bar{R}|}, \quad (3.2)$$

where ρ ($\bar{\rho}$) is the spin singlet part of the localized charge density of the corresponding exciton state, and is defined in terms of the Fourier transform G (\bar{G}) of A (\bar{A}) as

$$\rho(\mathbf{r}) = e \sum_{\bar{R}} G(\bar{R}) \sum_{\sigma} a(\bar{r}) b(\bar{r} + \bar{R})^*, \quad \text{etc.} \quad (3.3)$$

Because of the localized character of Wannier functions, it is often approximated as

$$\rho(\bar{r}) = e G(0) \sum_{\sigma} a(\bar{r}) b(\bar{r})^*. \quad (3.4)$$

For spin-triplet excitons, the summation over spin states in Eq. (3.3) leads to the vanishing ρ (and J_{ex}). The contribution of the $R \neq 0$ terms in Eq. (3.2) can be calculated in terms of the dipole moments

$$\vec{\mu} = \int d\bar{r} \bar{r} \rho(\bar{r}), \quad \vec{\nu} = \int d\bar{r} \bar{r} \bar{\rho}(\bar{r}) \quad (3.5)$$

as¹⁵

$$J_D = \frac{4}{3} (\pi/\Omega) [3\vec{\mu}^* \nu \cos \theta \cos \bar{\theta} - (\vec{\mu}^* \cdot \vec{\nu})], \quad (3.6)$$

where Ω is the volume of the unit cell, and θ ($\bar{\theta}$) is

the angle between \vec{K} and $\vec{\mu}^*$ ($\vec{\nu}$). In Eq. (3.6) we have neglected a small contribution of the core part which should be excluded from the R summation (Ref. 15, Heller and Marcus), since K is small enough in most cases. J_D is called the long range or dipole-dipole contribution, and is not analytic at $K=0$. Thus, the total exchange energy is given by

$$J_{\text{ex}} = \delta_{\vec{k}, \vec{k}'} \left(J_D + \int \int \frac{d\vec{r}_1 d\vec{r}_2 \rho(r_1)^* \bar{\rho}(r_2)}{r_{12}} \right). \quad (3.7)$$

If one makes the approximation [Eq. (3.4)], J_{ex} is proportional to $G(0)^* \bar{G}(0)$.

In some of the recent literature,¹⁶ the nonanalytic part of J_{ex} is defined in a different way. Using the Fourier expansion

$$\frac{1}{r} = 4\pi \sum_n \int \frac{d\vec{k} \exp[i(\vec{k} + \vec{K}_n) \cdot \vec{r}]}{(\vec{k} + \vec{K}_n)^2}, \quad (3.8)$$

where \vec{K}_n is a reciprocal-lattice vector; one rewrites Eq. (3.2) as

$$J_{\text{ex}} = \delta_{\vec{k}, \vec{k}'} \frac{4\pi}{\Omega} \sum_n \frac{M_{\vec{k} + \vec{K}_n}^* \bar{M}_{\vec{k} + \vec{K}_n}}{(\vec{k} + \vec{K}_n)^2}, \quad (3.9)$$

where

$$M_{\vec{q}} = \int d\vec{r} \rho(\vec{r}) e^{-i\vec{q} \cdot \vec{r}}, \quad \text{etc.} \quad (3.10)$$

The nonanalytic part is defined as the term for $K_n=0$ of Eq. (3.9), namely

$$\begin{aligned} J_{\text{ex,NA}} &= \frac{\delta_{\vec{k}, \vec{k}'} 4\pi M_{\vec{k}}^* \bar{M}_{\vec{k}}}{\Omega K^2}, \\ &= \frac{\delta_{\vec{k}, \vec{k}'} 4\pi \mu^* \nu \cos\theta \cos\bar{\theta}}{\Omega}, \quad (Kr \ll 1) \\ &= \delta_{\vec{k}, \vec{k}'} \left(J_D + \frac{4\pi}{3\Omega} (\vec{\mu}^* \cdot \vec{\nu}) \right). \end{aligned} \quad (3.11)$$

The last line of the equation clarifies the relation between the two types of division of the exchange interaction, i.e., "short-range plus dipole-dipole" and "analytic plus nonanalytic."

IV. CUBIC STRUCTURE

In this section we give a detailed treatment of zinc-blende structure which has the crystal point group T_d . In Sec. IV D, it is shown that most of the results can be directly applied to the case of the O_h crystal point group.

Throughout this section, the Cartesian coordinates (x, y, z) are defined along the three cubic axes, which is different from the wurtzite case (Sec. V).

A. Bloch band contributions

We first define the components of the representative variable Ξ , which is introduced in Sec. II, as follows:

$$\begin{aligned} \Gamma_1: & S [1]; \\ \Gamma_2: & T [xl_x + yl_y + zl_z]; \\ \Gamma_3: & (U, V) [\sqrt{3}(x^2 - y^2), 2z^2 - x^2 - y^2]; \\ \Gamma_4: & (P, Q, R) [l_x, l_y, l_z]; \\ \Gamma_5: & (X, Y, Z) [x, y, z]. \end{aligned} \quad (4.1)$$

Their transformation properties are indicated on the right in the square brackets. It is very useful to classify the products of $\Xi = (S, T, U, V, P, Q, R, X, Y, Z)$ and $\Xi' = (S', T', U', V', P', Q', R', X', Y', Z')$ again into symmetry adapted components given in Eq. (4.1). The results are given in Table I. The repeated use of the table enables us to ascribe any products of given quantities to the components of

TABLE I. Multiplication table for the components of the irreducible representations of T_d group. The components are defined in Eq. (4.1). This table is equivalent to that of coupling coefficients in G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of Thirty-two Point Groups* (M.I.T., Cambridge, 1963).

S	SS'	TT'	UU' + VV'		PP' + QQ' + RR'		XX' + YY' + ZZ'
T	ST'		UV' - VU'			PX' + QY' + RZ'	
U	SU'	-TV'	UV' + VU'		$\sqrt{3}(PP' - QQ')$	$2RZ' - PX' - QY'$	$\sqrt{3}(XX' - YY')$
V	SV'	TU'	UU' - VV'		$2RR' - PP' - QQ'$	$\sqrt{3}(QY' - PX')$	$2ZZ' - XX' - YY'$
P	SP'	TX'	$(\sqrt{3}U - V)P'$	$-(\sqrt{3}V + U)X'$	$QR' - RQ'$	$QZ' + RY'$	$YZ' - ZY'$
Q	SQ'	TY'	$-(\sqrt{3}U + V)Q'$	$(\sqrt{3}V - U)Y'$	$RP' - PR'$	$RX' + PZ'$	$ZX' - XZ'$
R	SR'	TZ'	$2VR'$	$2UZ'$	$PQ' - QP'$	$PY' + QX'$	$XY' - YX'$
X	SX'	TP'	$-(\sqrt{3}V + U)P'$	$(\sqrt{3}U - V)X'$	$QR' + RQ'$	$QZ' - RY'$	$YZ' + ZY'$
Y	SY'	TQ'	$(\sqrt{3}V - U)Q'$	$-(\sqrt{3}U + V)Y'$	$RP' + PR'$	$RX' - PZ'$	$ZX' + XZ'$
Z	SZ'	TR'	$2UR'$	$2VZ'$	$PQ' + QP'$	$PY' - QX'$	$XY' + YX'$

irreducible representations. For example, starting from $(P, Q, R) = (P', Q', R') = (l_x, l_y, l_z)$, we get all the independent forms of the operators from the table as

$$S = l_x^2 + l_y^2 + l_z^2, \quad (U, V) = (\sqrt{3}(l_x^2 - l_y^2), 2l_z^2 - l_x^2 - l_y^2),$$

$$(X, Y, Z) = (\{l_y l_z\}, \{l_z l_x\}, \{l_x l_y\}),$$

where $\{AB\} = \frac{1}{2}(AB + BA)$. Their products with $(P'', Q'', R'') = (\sigma_x, \sigma_y, \sigma_z)$ give all the 36 independent products of operators acting on the sixfold valence bands. Their time-reversal properties are easily obtained. Since each angular momentum operator has \hat{K}_- character, the product consisting of an even (odd) number of them is of \hat{K}_+ (\hat{K}_-) type.

In Table II, simple examples of Ξ are given for certain cases of physical interest.

Although the Hamiltonian itself is time-reversal invariant, it is useful to separate it into two parts, H_s and H_{as} , which consist of the \hat{K}_+ and \hat{K}_- parts of Ξ , respectively.

The contribution from the conduction band is

$$H_s^{(c)} = \tau S, \quad (4.2)$$

$$H_{as}^{(c)} = 2\bar{\lambda}(P\sigma_{ex} + Q\sigma_{ey} + R\sigma_{ez}), \quad (4.3)$$

where τ and $\bar{\lambda}$ are effective constants. As the coefficients for the effective Hamiltonian, we use Greek (Roman) letters for the conduction (valence) bands, with and without bars for \hat{K}_- and \hat{K}_+ types of Ξ , respectively. Although we use the same

TABLE II. Examples of Ξ in T_d symmetry. \vec{E} : electric field, \vec{H} : magnetic field, ϵ : strain tensor, k : wave vector.

		\hat{K}_-	\hat{K}_+
Γ_1	S		E^2
Γ_2	T		$\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$
Γ_3	U		$\sqrt{3}(E_x^2 - E_y^2)$
	V		$3E_z^2 - E^2$
Γ_4	P	H_x	
	Q	H_y	
	R	H_z	
Γ_5	X	k_x	$E_x E_z$
	Y	k_y	$E_y E_x$
	Z	k_z	$E_z E_y$
			ϵ_{yz}
			ϵ_{zx}
			ϵ_{xy}

symbols irrespective of the physical content of Ξ , the meaning and the value of them should vary according to the choice of Ξ . For example, e_1 for $(X, Y, Z) = (E_x, E_y, E_z)$ and e_1 for $(X, Y, Z) = (\epsilon_{yz}, \epsilon_{zx}, \epsilon_{xy})$ have nothing to do with each other. They should be distinguished although we use a common notation for simplicity.

The contribution from the valence bands, which is much more complicated, is as follows:

$$H_s^{(v)} = (a_1 + 2a_2\vec{\sigma} \cdot \vec{1})S + c_1[\sqrt{3}U(l_x^2 - l_y^2) + V(3l_z^2 - 2)] + \sqrt{2}c_2[\sqrt{3}U(l_x\sigma_x - l_y\sigma_y) + V(3l_z\sigma_z - \vec{\sigma} \cdot \vec{1})]$$

$$+ \sqrt{8}d_1[P(l_y\sigma_z - l_z\sigma_y) + \text{c.p.}] + \sqrt{8}e_1[X\{l_y l_z\} + \text{c.p.}] + \sqrt{8}e_2[X(l_y\sigma_z + l_z\sigma_y) + \text{c.p.}], \quad (4.4)$$

where c.p. means the additional two terms obtained from the cyclic permutations of the first term.

$$H_{as}^{(v)} = 4\bar{b}_1(\sigma_x\{l_y l_z\} + \sigma_y\{l_z l_x\} + \sigma_z\{l_x l_y\})T + \sqrt{8}\bar{c}_1[U(2\{l_x l_y\}\sigma_z - \{l_y l_z\}\sigma_x - \{l_z l_x\}\sigma_y) + \sqrt{3}V(\{l_x l_x\}\sigma_y - \{l_y l_z\}\sigma_x)]$$

$$+ \sqrt{2}\bar{d}_1(P l_x + Q l_y + R l_z) + 2\bar{d}_2(P\sigma_x + Q\sigma_y + R\sigma_z) + 4\bar{d}_3[P(\{l_x l_z\}\sigma_z + \{l_y l_x\}\sigma_y) + \text{c.p.}]$$

$$+ 4\bar{d}_4(P\sigma_x l_x^2 + \text{c.p.}) + \sqrt{8}\bar{e}_1[X(\{l_z l_x\}\sigma_z - \{l_y l_x\}\sigma_y) + \text{c.p.}] + 4\bar{e}_2[X(l_y^2 - l_x^2)\sigma_x + \text{c.p.}]. \quad (4.5)$$

The numerical factor for each invariant is arbitrarily chosen to simplify some matrix representations.

B. Exciton basis functions

According to our basic assumption, the conduction band has atomic s character, and the valence bands p character. Thus, we denote the Bloch functions at the Γ point as

$$s\alpha(=\alpha_e), \quad s\beta(=\beta_e) \quad (4.6)$$

for the conduction bands which belong to Γ_6 , and

$$\alpha|m_j\rangle, \quad \beta|m_j\rangle \quad (4.7)$$

for the valence bands, where α and β are usual spin functions, and $|m_j\rangle$ is the eigenfunction of the

operator l_z , namely,

$$l_z|m_j\rangle = m_j|m_j\rangle, \quad (m_j = 1, 0, -1). \quad (4.8)$$

Sometimes it is more convenient to use x, y , and z character of the p functions explicitly. For that purpose we use the definition

$$|1\rangle = -(x + iy)/\sqrt{2},$$

$$|0\rangle = z,$$

$$|-1\rangle = (x - iy)/\sqrt{2}. \quad (4.9)$$

The spin-orbit interaction ($\sim\vec{\sigma} \cdot \vec{1}$) can be diagonalized by the following linear combinations:

$$\begin{aligned}
\phi_1 &= -(x + iy)\alpha/\sqrt{2}, \\
\phi_2 &= [2z\alpha - (x + iy)\beta]/\sqrt{6}, \\
\phi_3 &= [2z\beta + (x - iy)\alpha]/\sqrt{6}, \\
\phi_4 &= (x - iy)\beta/\sqrt{2}, \\
\phi_5 &= [z\alpha + (x + iy)\beta]/\sqrt{3}, \\
\phi_6 &= [-z\beta + (x - iy)\alpha]/\sqrt{3}.
\end{aligned} \tag{4.10}$$

They split into two irreducible representations, i.e., $\Gamma_8(\phi_1 \sim \phi_4)$ and $\Gamma_7(\phi_5, \phi_6)$. We now introduce the following 12 electron-hole pair states

$$\begin{aligned}
\Psi_1 &= |\alpha_e(\phi_1)|, & \Psi_5 &= |\beta_e(\phi_1)|, & \Phi_1 &= |\alpha_e(\phi_5)|, \\
\Psi_2 &= |\alpha_e(\phi_2)|, & \Psi_6 &= |\beta_e(\phi_2)|, & \Phi_2 &= |\alpha_e(\phi_6)|, \\
\Psi_3 &= |\alpha_e(\phi_3)|, & \Psi_7 &= |\beta_e(\phi_3)|, & \Phi_3 &= |\beta_e(\phi_5)|, \\
\Psi_4 &= |\alpha_e(\phi_4)|, & \Psi_8 &= |\beta_e(\phi_4)|, & \Phi_4 &= |\beta_e(\phi_6)|.
\end{aligned} \tag{4.11}$$

For simplicity, the k vector of each Bloch state is not explicitly written for the time being. These states can be classified according to the system's total angular momentum J and its z component M_J as in Table III.

The electric-dipole transition from the ground state $|0\rangle$ is nonvanishing only to the states with $J=1$. The dipole matrix elements are given in Table IV for the (ξ, η, ζ) polarized light [by taking all the Bloch states in Eq. (4.11) at $k=0$]. From this result it is easy to construct x -, y -, and z -polarized pair states as

$$\begin{aligned}
|x\rangle &= [|1, 1\rangle - |1, -1\rangle]/\sqrt{2}, & (2\xi) \\
|y\rangle &= [|1, 1\rangle + |1, -1\rangle]/i\sqrt{2}, & (2\eta) \\
|z\rangle &= -|1, 0\rangle, & (2\xi) \\
|x\rangle_C &= [|1, 1\rangle_C - |1, -1\rangle_C]/\sqrt{2}, & (\sqrt{2}\xi) \\
|y\rangle_C &= [|1, 1\rangle_C + |1, -1\rangle_C]/i\sqrt{2}, & (\sqrt{2}\eta) \\
|z\rangle_C &= -|1, 0\rangle_C, & (\sqrt{2}\xi).
\end{aligned} \tag{4.12}$$

The quantities on the right in parentheses are the dipole matrix elements in units of $M_0 = \langle s|ex|x\rangle/\sqrt{3}$.

TABLE III. $|J, M_J\rangle$ representation of the electron-hole pair states.

$ 2, 2\rangle$	Ψ_4	$ 1, 1\rangle$	$\frac{1}{2}(\Psi_3 + \sqrt{3}\Psi_8)$
$ 2, 1\rangle$	$\frac{1}{2}(\Psi_8 - \sqrt{3}\Psi_3)$	$ 1, 0\rangle^a$	$-(\Psi_2 + \Psi_7)/\sqrt{2}$
$ 2, 0\rangle$	$(\Psi_2 - \Psi_7)/\sqrt{2}$	$ 1, -1\rangle^a$	$\frac{1}{2}(\sqrt{3}\Psi_1 + \Psi_6)$
$ 2, -1\rangle$	$\frac{1}{2}(\sqrt{3}\Psi_6 - \Psi_1)$	$ 1, 1\rangle_C$	Φ_2
$ 2, -2\rangle$	$-\Psi_5$	$ 1, 0\rangle_C$	$(\Phi_4 - \Phi_1)/\sqrt{2}$
$ 0, 0\rangle$	$(\Phi_1 + \Phi_4)/\sqrt{2}$	$ 1, -1\rangle_C$	$-\Phi_3$

^aDefinition of $|1, 0\rangle$ and $|1, -1\rangle$ is different from that of Ref. 8 by the factor (-1) .

TABLE IV. Dipole matrix elements in unit of $M_0 = \langle s|ex|x\rangle/\sqrt{3}$.

$(1, 1 \hat{M} 0)$	$\sqrt{2}(\xi - i\eta)$	$c(1, 1 \hat{M} 0)$	$\xi - i\eta$
$(1, 0 \hat{M} 0)$	-2ξ	$c(1, 0 \hat{M} 0)$	$-\sqrt{2}\xi$
$(1, -1 \hat{M} 0)$	$-\sqrt{2}(\xi + i\eta)$	$c(1, -1 \hat{M} 0)$	$-(\xi + i\eta)$

An exciton state is a linear combination of the electron-hole pair states [Eq. (4.11)] for various possible \vec{k} values, for example,

$$\sum_{\vec{q}} A(\vec{q}) |\alpha_{e, \vec{q} + \vec{k}}(\phi_1, \vec{q})|, \tag{4.13}$$

where \vec{q} and \vec{k} are wave vectors, and $A(\vec{q})$ is the Fourier component of one of the hydrogen-like wave functions. Using such exciton basis functions, we can construct the whole interaction scheme for the 12 fold hydrogen-like series (12 times ∞ -dimensional states). Then, we extract the part for the 12 1s exciton states in such a way that all the effects from the rest are renormalized into the coefficients of their matrix elements and wave functions. This is the very scheme which we have in mind as the effective Hamiltonian formalism.

Since the dipole matrix elements for the exciton states are obtained from Table IV [or Eq. (4.12)] by multiplying by a factor $\sum_{\vec{q}} A(\vec{q})$, we can use the values in Table IV as the relative ones also for exciton states.

The linear combinations of the $J=2$ states give the basis for the Γ_3 and Γ_4 irreducible representations as

$$\begin{aligned}
\Gamma_3: |2+\rangle &= [|2, 2\rangle + |2, -2\rangle]/\sqrt{2}, \\
&|2, 0\rangle,
\end{aligned} \tag{4.14a}$$

$$\begin{aligned}
\Gamma_4: |1+\rangle &= -[|2, 1\rangle + |2, -1\rangle]/\sqrt{2}, \\
|1-\rangle &= i[|2, -1\rangle - |2, 1\rangle]/\sqrt{2}, \\
|2-\rangle &= [|2, 2\rangle - |2, -2\rangle]/\sqrt{2}.
\end{aligned} \tag{4.14b}$$

C. Matrix representation of the invariants

Using the basis functions in Sec. IV B, we express the invariants in matrix forms. We generally specify $\frac{1}{2}$ of the nondiagonal elements, since the other $\frac{1}{2}$ are easily obtained by hermiticity.

1. Bloch basis

As mentioned at the end of Sec. II, one may regard $H^{(c)}$ and $H^{(v)}$ as the definitions of the most general forms of the energies of the Bloch states in the presence of Ξ .

TABLE V. $H_s^{(v)}$ on the basis of valence electron functions (H.c.): Hermitian conjugate.

$ \frac{3}{2}, \frac{3}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{1}{2}, \frac{1}{2}\rangle$	$ \frac{1}{2}, -\frac{1}{2}\rangle$
$3a$	$\sqrt{6}d + \sqrt{3}h$	$\sqrt{3}f + \sqrt{6}k$	0	$\sqrt{3}d - \sqrt{6}h$	$\sqrt{6}f - \sqrt{3}k$
$2b + c + \sqrt{2}g_+$	0	$\sqrt{6}k + \sqrt{3}f$	$\sqrt{2}(b - c) + g^* - 2g$	$3e$	$\sqrt{2}(c - b) + 2g^* - g$
	$2b + c + \sqrt{2}g_+$	$-\sqrt{6}d - \sqrt{3}h$	$3a$	$\sqrt{3}k^* - \sqrt{6}f^*$	$-\sqrt{6}h^* + \sqrt{3}d^*$
(H.c.)				$b + 2c - \sqrt{2}g_+$	0
					$b + 2c - \sqrt{2}g_+$

$\frac{1}{3}$

$$a = (a_1 + a_2)S + (c_1 + \sqrt{2}c_2)V, \quad f = \sqrt{3}c_1U - i\sqrt{2}e_1Z$$

$$b = a_1S - 2c_1V, \quad g = \sqrt{2}a_2S - c_2V - 2id_1R$$

$$c = (a_1 - a_2)S + (c_1 - \sqrt{2}c_2)V, \quad h = \sqrt{2}d_1(Q + iP) + \sqrt{2}e_2(Y - iX)$$

$$d = -d_1(Q + iP) + (e_1 + e_2)(Y - iX), \quad k = \sqrt{3}c_2U - 2ie_2Z$$

$$e = -d_1(Q + iP) - (e_1 - e_2)(Y - iX), \quad g_+ = g + g^* = 2\sqrt{2}a_2S - 2c_2V$$

The matrix for $H_s^{(c)}$ and $H_{as}^{(c)}$ is obvious, i.e.,

$$\tau S + \bar{\lambda} \begin{pmatrix} R & P - iQ \\ P + iQ & -R \end{pmatrix} \quad (4.15)$$

on the basis (α_e, β_e) . In terms of the basis [Eq. (4.10)] we obtain Tables V and VI for $H_s^{(v)}$ and $H_{as}^{(v)}$, respectively.

2. Exciton basis

The matrix for the exchange interaction [Eq. (3.7)] is given in Table VII where we use the definition

$$j_0 = \frac{1}{3} \iint \frac{d\vec{r}_1 d\vec{r}_2 \rho_x(\vec{r}_1) \rho_x(\vec{r}_2)}{r_{12}},$$

$$j_1 = \frac{4\pi}{9\Omega} \left(\int d\vec{r} x \rho_x(r) \right)^2, \quad (4.16)$$

$$\rho_x(\vec{r}) = e \sum_{\vec{R}} G(\vec{R}) a_s(\vec{r}) b_x(\vec{r} + \vec{R}) \cong eG(0) a_s(\vec{r}) b_x(\vec{r}).$$

$a_s(\vec{r})$ and $b_x(\vec{r})$ are the s - and x -like orbitals of the Wannier functions, respectively.

In terms of the exciton basis functions [Eqs. (4.12) and (4.14)] and $|0, 0\rangle$ in Table III, $H_s^{(v)}$ and $H_{as}^{(v)}$ are given in Tables VIII and IX, respectively. The notations are defined as

TABLE VI. $H_{as}^{(v)}$ on the basis of valence electron functions (H.c.): Hermitian conjugate.

$ \frac{3}{2}, \frac{3}{2}\rangle$	$ \frac{3}{2}, \frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{1}{2}\rangle$	$ \frac{3}{2}, -\frac{3}{2}\rangle$	$ \frac{1}{2}, \frac{1}{2}\rangle$	$ \frac{1}{2}, -\frac{1}{2}\rangle$
$3\bar{a}$	$\sqrt{6}\bar{d} + \sqrt{3}\bar{h}$	$\sqrt{3}\bar{f} + \sqrt{6}\bar{r}$	$3\bar{s}$	$\sqrt{3}\bar{d} - \sqrt{6}\bar{h}$	$\sqrt{6}\bar{f} - \sqrt{3}\bar{r}$
$2\bar{b} - \bar{c} + \sqrt{2}\bar{g}_+$	$2\bar{t} + \bar{u} + \sqrt{8}\bar{e}$	$-\sqrt{6}\bar{r} - \sqrt{3}\bar{f}$	$\sqrt{2}(\bar{b} + \bar{c}) + \bar{g}^* - 2\bar{g}$	$\sqrt{2}(\bar{u} - \bar{t}) + \bar{e}$	
	$\bar{c} - 2\bar{b} - \sqrt{2}\bar{g}_+$	$\sqrt{3}\bar{h} + \sqrt{6}\bar{d}$	$\sqrt{2}(\bar{t} - \bar{u})^* - \bar{e}^*$	$\sqrt{2}(\bar{b} + \bar{c}) + \bar{g} - 2\bar{g}^*$	
		$-3\bar{a}$	$\sqrt{6}\bar{f}^* - \sqrt{3}\bar{r}^*$	$\sqrt{6}\bar{h}^* - \sqrt{3}\bar{d}^*$	
(H.c.)			$\bar{b} - 2\bar{c} - \sqrt{2}\bar{g}_+$	$\sqrt{8}\bar{e} - (2\bar{u} + \bar{t})$	
				$2\bar{c} - \bar{b} + \sqrt{2}\bar{g}_+$	

$\frac{1}{3}$

$$\bar{a} = (\sqrt{2}\bar{d}_1 + \bar{d}_2 + 2\bar{d}_4)R, \quad \bar{g} = -i\sqrt{3}\bar{c}_1V + 2\bar{d}_3R, \quad \bar{g}_+ = 4\bar{d}_3R$$

$$\bar{b} = \bar{d}_2R, \quad \bar{h} = (\bar{d}_2 + \bar{d}_4)(P - iQ) - \bar{e}_2(X + iY),$$

$$\bar{c} = (-\sqrt{2}\bar{d}_1 + \bar{d}_2 + 2\bar{d}_4)R, \quad \bar{r} = -i\sqrt{2}\bar{b}_1T + i\bar{c}_1U - 2\bar{e}_1Z,$$

$$\bar{d} = (\bar{d}_1 + \bar{d}_3)(P - iQ) + \bar{e}_1(X + iY), \quad \bar{s} = (\bar{d}_4 - \sqrt{2}\bar{d}_3)(P + iQ) + (\sqrt{2}\bar{e}_1 - \bar{e}_2)(X - iY),$$

$$\bar{e} = (\bar{d}_1 - \bar{d}_3)(P - iQ) - \bar{e}_1(X + iY), \quad \bar{t} = (\bar{d}_2 + 2\bar{d}_4)(P - iQ) + 2\bar{e}_2(X + iY),$$

$$\bar{f} = -i\bar{b}_1T - i\sqrt{2}\bar{c}_1U + 2\bar{e}_2Z, \quad \bar{u} = (\bar{d}_4 + \sqrt{2}\bar{d}_3)(P - iQ) - (\sqrt{2}\bar{e}_1 + \bar{e}_2)(X + iY),$$

(For Table VIII):

$$\begin{aligned}
 S_2 &= 3a_2S; (U_j, V_j) = (\gamma_j U, \gamma_j V), (j=1, 2); (P_1, Q_1, R_1) = (d_1 P, d_1 Q, d_1 R); \\
 (X_j, Y_j, Z_j) &= (\epsilon_j X, \epsilon_j Y, \epsilon_j Z), (j=1, 2); \gamma_1 = \frac{1}{2}(c_1 + \sqrt{2}c_2); \\
 \gamma_2 &= \frac{1}{2}(\sqrt{2}c_1 - c_2); \epsilon_1 = (e_1 + 2e_2)/\sqrt{6}; \epsilon_2 = (e_1 - e_2)/\sqrt{3}.
 \end{aligned}
 \tag{4.17}$$

(For Table IX):

$$\begin{aligned}
 T_1 &= (\sqrt{3}/2)\bar{d}_1 T; (U_1, V_1) = (\bar{\gamma}_1 U, \bar{\gamma}_1 V); (P_j, Q_j, R_j) = (\bar{d}_j P, \bar{d}_j Q, \bar{d}_j R), (j=3, 4); \\
 (X_j, Y_j, Z_j) &= (\bar{\epsilon}_j X, \bar{\epsilon}_j Y, \bar{\epsilon}_j Z), (j=1, 2); g_1 = \frac{1}{2}(12\bar{d}_1 + 27\bar{d}_2); g_2 = \frac{1}{2}(4\bar{d}_1 + \bar{d}_2); \\
 g_3 &= \frac{1}{2}(12\bar{d}_1 + 15\bar{d}_2), g_4 = \frac{1}{2}(4\bar{d}_1 + 13\bar{d}_2)\sqrt{3}; g_5 = \frac{1}{2}(20\bar{d}_1 + 41\bar{d}_2); \bar{\gamma}_1 = \frac{1}{2}\sqrt{3}\bar{c}_1; \\
 \bar{d}_1 &= \frac{1}{24}(2\sqrt{2}\bar{d}_1 + 2\bar{d}_2 + 9\sqrt{2}\bar{d}_3 - 5\bar{d}_4); \bar{d}_2 = \frac{1}{8}(\bar{d}_4 - \sqrt{2}\bar{d}_3); \bar{d}_3 = \frac{1}{3}(2\sqrt{2}\bar{d}_1 - \bar{d}_2 - 4\sqrt{2}\bar{d}_3 - 4\bar{d}_4); \\
 \bar{d}_4 &= \frac{1}{3}(\bar{d}_1 - \sqrt{2}\bar{d}_2 + \bar{d}_3 - \sqrt{2}\bar{d}_4); \bar{\epsilon}_1 = (\sqrt{2}\bar{e}_1 - \bar{e}_2)/\sqrt{3}; \bar{\epsilon}_2 = (\bar{e}_1 + \sqrt{2}\bar{e}_2)/\sqrt{3}.
 \end{aligned}
 \tag{4.18}$$

The matrix for $H_{ss}^{(c)}$ splits into two diagonal blocks, one for

$$\{|2+\rangle, |2, 0\rangle, |1+\rangle, |1-\rangle, |2-\rangle, |x\rangle, |y\rangle, |z\rangle\}$$

and the other for $\{|x\rangle_c, |y\rangle_c, |z\rangle_c, |0, 0\rangle\}$: The former can be obtained from Table IX by replacing $(g_1, g_2, g_3, g_4, g_5)$ with $(\frac{1}{2}\bar{\lambda}, -\frac{1}{2}\bar{\lambda}, \frac{1}{2}\bar{\lambda}, -\frac{1}{2}\sqrt{3}\bar{\lambda}, -\frac{1}{2}\bar{\lambda})$ and making all the other terms zero. The latter is given by

$$\bar{\lambda} \begin{pmatrix} 0 & -iR & iQ & P \\ & 0 & -iP & Q \\ \text{(H.c.)} & & 0 & R \\ & & & 0 \end{pmatrix}. \tag{4.19}$$

The sign of the fourth column is different from that of Table IX relative to the rest of the matrix.

D. Case of O_h symmetry

In order to treat the direct excitons in alkali halides, rare gas solids, etc., we have to consider the O_h crystal point group. The extension of the above theory to this case is very easy. The new

TABLE VII. Matrix for the exchange interaction. \hat{U} is a 2×2 matrix:

$$\hat{U} = \begin{pmatrix} 4 & 2\sqrt{2} \\ 2\sqrt{2} & 2 \end{pmatrix}, \quad j(u) = j_0 + j_1(3u^2 - 1).$$

$(\bar{\xi}, \bar{\eta}, \bar{\zeta})$ are the direction cosines of \vec{K} with respect to the (x, y, z) axes.

$ x\rangle$	$ x\rangle_c$	$ y\rangle$	$ y\rangle_c$	$ z\rangle$	$ z\rangle_c$
$j(\bar{\xi})\hat{U}$		$3j_1\bar{\xi}\bar{\eta}\hat{U}$		$3j_1\bar{\xi}\bar{\zeta}\hat{U}$	
		$j(\bar{\eta})\hat{U}$		$3j_1\bar{\eta}\bar{\zeta}\hat{U}$	
(H.c.)				$j(\bar{\zeta})\hat{U}$	

symmetry operations are those involving the space inversion. Since all the products of angular momentum operators $\bar{\sigma}_e, \bar{\sigma}$, and \bar{l} have even parity, one may take only even-parity Ξ 's. We define the components $S, T, U, V, P, Q, R, X, Y,$ and Z as before [Eq. (4.1)] for $\Gamma_1^+, \Gamma_2^+, \Gamma_3^+, \Gamma_4^+,$ and Γ_5^+ irreducible representations, but the transformation properties indicated in Eq. (4.1) are not all valid, since, in the O_h group (x, y, z) and (l_x, l_y, l_z) belong to Γ_4^- and Γ_4^+ , respectively. If one makes an extra consideration about parity, one can use Table I as it stands. The form of the effective Hamiltonian is the same as in Eqs. (4.2)–(4.5).

From the required restrictions on the choice of Ξ , we must drop out such effects as k -linear terms, linear electric field, stress induced k -linear terms, etc., although they can of course contribute as interactions with outer $(2p, 3p, \dots,$ excitons) subspace.

Thus all the results in the previous sections can be used with the proper choice of Ξ .

E. Comparison with existing theories

In order to demonstrate the general nature of the present theory, we derive various known examples as special cases of the above results.

As the basis of the following discussion, we describe the fundamental structure of the exciton level scheme in the absence of any symmetry breaking effects and the exchange interaction. For that purpose, we take that part of the effective Hamiltonian which does not depend on Ξ , in other words, we take only the terms including S (and put $S=1$) out of Eqs. (4.2) and (4.4). This gives the diagonal energies

$$\tau - a_1 - a_2$$

for

$$\{|2+\rangle, |2, 0\rangle, |1+\rangle, |1-\rangle, |2-\rangle, |x\rangle, |y\rangle, |z\rangle\},$$

and

TABLE VIII. $H_s^{(v)}$ on the exciton basis. Note: To avoid congestion of symbols, the (P, Q, R) matrix elements are written in the lower left corner, and the rest in the upper right corner. The complete matrix is Hermitian, i.e., one should add their complex conjugates in the opposite corners. For the notations, see the text. The diagonal element $-(a_1 + a_2)S$ is omitted.

$ 2+\rangle$	$ 2,0\rangle$	$ 1+\rangle$	$ 1-\rangle$	$ 2-\rangle$	$ x\rangle$	$ y\rangle$	$ z\rangle$	$ x\rangle_C$	$ y\rangle_C$	$ z\rangle_C$	$ 0,0\rangle$
$-2V_1$	$-2U_1$	$-i\sqrt{3}X_1$	$i\sqrt{3}Y_1$		$-iX_1$	$-iY_1$	$2iZ_1$	iX_2	iY_2	$-2iZ_2$	$-2iU_2$
	$2V_1$	iX_1	iY_1	$-2iZ_1$	$-i\sqrt{3}X_1$	$i\sqrt{3}Y_1$		$i\sqrt{3}X_2$	$-i\sqrt{3}Y_2$		$-2iV_2$
		$V_1 - \sqrt{3}U_1$	$\sqrt{3}Z_1$	$\sqrt{3}Y_1$	$\sqrt{3}V_1 - U_1$	Z_1	$-Y_1$	$-\sqrt{3}V_2 - U_2$	$-Z_2$	Y_2	$-2X_2$
			$V_1 + \sqrt{3}U_1$	$\sqrt{3}X_1$	$-Z_1$	$-\sqrt{3}V_1 - U_1$	X_1	Z_2	$\sqrt{3}V_2 - U_2$	$-X_2$	$-2Y_2$
				$-2V_1$	Y_1	$-X_1$	$2U_1$	$-Y_2$	X_2	$2U_2$	$-2Z_2$
					$-V_1 + \sqrt{3}U_1$	$\sqrt{3}Z_1$	$\sqrt{3}Y_1$	$-V_2 + \sqrt{3}U_2$	$\sqrt{3}Z_2$	$\sqrt{3}Y_2$	
						$-V_1 - \sqrt{3}U_1$	$\sqrt{3}X_1$	$\sqrt{3}Z_2$	$-V_2 - \sqrt{3}U_2$	$\sqrt{3}X_2$	
							$2V_1$	$\sqrt{3}Y_2$	$\sqrt{3}X_2$	$2V_2$	
$-i\sqrt{3}P_1$	iP_1		$\sqrt{3}R_1$	$\sqrt{3}Q_1$		$-R_1$	Q_1	S_2			
$i\sqrt{3}Q_1$	iQ_1	$\sqrt{3}R_1$		$\sqrt{3}P_1$	R_1		$-P_1$		S_2		
	$-2iR_1$	$\sqrt{3}Q_1$	$\sqrt{3}P_1$		$-Q_1$	P_1				S_2	
					$2P_1$	$2Q_1$	$2R_1$				S_2

$$\tau - a_1 + 2a_2$$

for $[|x\rangle_C, |y\rangle_C, |z\rangle_C, |0,0\rangle]$. Omitting the common part $(\tau - a_1)$, we hereafter use Δ_{so} instead of a_2 , where

$$\Delta_{so} = 3a_2. \quad (4.20)$$

It is obvious that Δ_{so} represents the spin-orbit

splitting of the valence bands.

These diagonal energies must always be superimposed on any effects discussed below, considering Δ_{so} as a given material constant.

1. Luttinger theory (Ref. 14)

If we take $H_s^{(v)}$ with $S = k_x^2 + k_y^2 + k_z^2$, $U = \sqrt{3}(k_x^2 - k_y^2)$, $V = 3k_z^2 - k^2$, $X = k_y k_z$, $Y = k_z k_x$, $Z = k_x k_y$ and $H_{as}^{(v)}$

TABLE IX. $H_{as}^{(v)}$ on the exciton basis. Note: To avoid the congestion of symbols, the (X, Y, Z) matrix elements are written in the lower left corner, and the rest in the upper right corner. The complete matrix is Hermitian, namely, one should add their complex conjugates in the opposite corners. For the notations, see the text.

$ 2+\rangle$	$ 2,0\rangle$	$ 1+\rangle$	$ 1-\rangle$	$ 2-\rangle$	$ x\rangle$	$ y\rangle$	$ z\rangle$	$ x\rangle_C$	$ y\rangle_C$	$ z\rangle_C$	$ 0,0\rangle$
0	$-iT_1$	$-g_1P$	$-g_1Q$	$2g_1R$	$-\sqrt{3}g_2P$	$\sqrt{3}g_2Q$		$\sqrt{3}P_4$	$-\sqrt{3}Q_4$		$2iU_1$
	0	$-\sqrt{3}g_1P$	$\sqrt{3}g_1Q$		g_2P	g_2Q	$-2g_2R$	$-P_4$	$-Q_4$	$2R_4$	$-2iV_1$
$-\sqrt{3}X_1$	X_1	0	ig_3R	$-ig_3Q$	$-iT_1$	ig_4R	ig_4Q	$i\sqrt{3}V_1 - iU_1$	$-i\sqrt{3}R_4$	$-i\sqrt{3}Q_4$	
$\sqrt{3}Y_1$	Y_1		0	ig_3P	ig_4R	$-iT_1$	ig_4P	$-i\sqrt{3}R_4$	$-i\sqrt{3}V_1 - iU_1$	$-i\sqrt{3}P_4$	
	$-2Z_1$			0	ig_4Q	ig_4P	$-iT_1$	$-i\sqrt{3}Q_4$	$-i\sqrt{3}P_4$	$2iU_1$	
X_1	$\sqrt{3}X_1$		$-2iZ_1$	$2iY_1$	0	$-ig_5R$	ig_5Q	$iV_1 + i\sqrt{3}U_1$	$-iR_4$	iQ_4	$2P_4$
Y_1	$-\sqrt{3}Y_1$	$2iZ_1$		$-2iX_1$		0	$-ig_5P$	iR_4	$iV_1 - i\sqrt{3}U_1$	$-iP_4$	$2Q_4$
$-2Z_1$		$-2iY_1$	$2iX_1$				0	$-iQ_4$	iP_4	$-2iV_1$	$2R_4$
X_2	$\sqrt{3}X_2$		iZ_2	$-iY_2$		$i\sqrt{3}Z_2$	$i\sqrt{3}Y_2$	0	$-iR_3$	iQ_3	$-P_3$
Y_2	$-\sqrt{3}Y_2$	$-iZ_2$		iX_2	$i\sqrt{3}Z_2$		$i\sqrt{3}X_2$		0	$-iP_3$	$-Q_3$
$-2Z_2$		iY_2	$-iX_2$		$i\sqrt{3}Y_2$	$i\sqrt{3}X_2$				0	$-R_3$
		$-2X_2$	$-2Y_2$	$-2Z_2$							0

parameters \bar{k} , \bar{q} , \bar{g}_c , \bar{c} , \bar{c}_2 , \bar{c}_3 in Ref. 8 are given by

$$\begin{aligned}\bar{k}\mu_B &= -4\bar{\delta}_1, & \bar{q}\mu_B &= -4\bar{\delta}_2, \\ \bar{g}_c\mu_B &= 2\bar{\lambda}, & \bar{c} &= (\tau - a_1 - a_2)H^2, \\ \bar{c}_2 &= -4\gamma_1 H^2, & \bar{c}_3 + 2\bar{c}_2 &= -4\epsilon_1 H^2/\sqrt{3}.\end{aligned}\quad (4.25)$$

5. Stress-induced \vec{k} -linear term (Ref. 6)

In order to explain the unusual aspects of the exciton spectra in uniaxially stressed CuCl,¹⁷ a mechanism involving the strain tensor ϵ_{ij} and the exciton wave vector \vec{K} was proposed by Sakoda and Onodera.⁶ Among various possibilities, they took two terms proportional to

$$(\epsilon_{xy}K_y - \epsilon_{zx}K_z)l_x + c.p., \quad (4.26)$$

and

$$(\epsilon_{yy} - \epsilon_{zz})K_x l_x + c.p. \quad (4.27)$$

Both of them correspond to the fourth term of Eq. (4.5) which has the coefficient \bar{d}_1 . This means that the effect is equivalent to a certain magnetic field. It is generally true that a longitudinal exciton state becomes allowed in the σ spectrum of the Voigt configuration ($\vec{K} \perp \vec{H} \perp \vec{E}_{\text{photon}}$). Actually the most unusual feature of the experiment was the growth of the longitudinal Z_3 exciton state in certain geometries. Thus it would be interesting to reinterpret the results from the standpoint of equivalent magnetic fields. Let us denote the effective fields

$$H'_x = (\epsilon_{yy} - \epsilon_{zz})K_x, \quad \text{etc.} \quad (4.28)$$

$$H''_x = \epsilon_{xy}K_y - \epsilon_{zx}K_z, \quad \text{etc.} \quad (4.29)$$

Since $\vec{K} \cdot \vec{H}'' = 0$, the field \vec{H}'' always gives the Voigt configuration. In Table XI, the directions of \vec{H}' and \vec{H}'' are given for a given uniaxial stress and \vec{K} direction in the cases of the configurations actually measured. The observation of the longitudinal exciton state does correspond to the cases of "Voigt" configuration in the Table with the sign σ in the

TABLE XI. Orientation of the effective magnetic field \vec{H}' and \vec{H}'' . The signs F and V indicate the Faraday and Voigt configurations. E_{\parallel} and E_{\perp} are the components of the electric-field vector of the incident light with respect to the direction of the uniaxial stress, and σ and π are the corresponding notations in the analogy of a magnetic field. $\Delta' = -2\epsilon_{xz}/\epsilon_{xy}$.

Stress	\vec{K}	\vec{H}'	\vec{H}''	E_{\parallel}	E_{\perp}
[001]	[100]	[100] (F)	0	σ	σ
[001]	[110]	[110] (V)	0	σ	π
[111]	arbitrary	0	$\vec{K} \times [111]$ (V)	σ	π
[110]	[112]	[110] (V)	[110] (V)	π	σ
[112]	[110]	[110] (V)	[11 Δ'] (V)	π, σ	π, σ

last two columns. Based on this simpler picture, one may call the effect "stress Zeeman effect" in analogy with the magneto-Stark effect.¹⁸

6. Electric field effects (Refs. 10 and 11)

A linear splitting of the $Z_3(\Gamma_8 \times \Gamma_7)$ excitons in CuCl was observed in a electric field by Mohler.¹⁰ It is interpreted as the combined effect of an electric field and the exchange interaction: As seen in Table VIII, the states $\{|x\rangle, |y\rangle, |z\rangle\}$ show a linear splitting through $(X, Y, Z) = (E_x, E_y, E_z)$. It is obvious that the exchange mixing (Table V) between $\{|x\rangle, |y\rangle, |z\rangle\}$ and $\{|x\rangle_c, |y\rangle_c, |z\rangle_c\}$ transfers some of the linear splitting effect in the former subset into the latter.

Since (E_x, E_y, E_z) , $(E_y E_z, E_z E_x, E_x E_y)$, and $(\epsilon_{yz}, \epsilon_{zx}, \epsilon_{xy})$ have the same transformation properties as (X, Y, Z) , we can expect similar effects for the Z_3 excitons under a uniaxial stress or a (quadratic) electric field.

A combined effect of \vec{E} and \vec{K} was theoretically studied in the case of the Z_3 excitons in CuCl.¹¹ Since the only products appearing in the $\Gamma_8 \times \Gamma_7$ subspace are the three components of

$$\vec{K} \times \vec{E},$$

as seen in Table IX, this is again equivalent to a certain magnetic field like the one discussed in Sec. IV E 5. Since the vector $\vec{K} \times \vec{E}$ is perpendicular to \vec{K} , the effective field is in the Voigt configuration. The prediction in Ref. 11 about the appearance of the longitudinal and triplet (*para*) excitons just corresponds to the situations of the σ and π magneto-optical spectra, respectively.

F. Discussion

Simple examples of Ξ are given in Table II, but there are still empty columns in it. If we consider the higher-order effects of the quantities already included there, we can fill the empty part, and also find similar effects to the lower-order ones. By this procedure one may lead to new mixing schemes, or to simpler interpretations of complicated effects as mentioned in Sec. IV E ("magnetic-field"-like effect caused by stress or electric field in combination with the finite wave vector of the exciton). Therefore it is interesting to list the transformation properties of the products of simpler quantities. This can be easily done by the use of Tables I and II. Here we show an example of how to classify the products in the case of stress-induced k -linear effects. All the other cases can be treated similarly. We start with

$$\begin{aligned}
S &= \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} (= \epsilon_{00}), \\
(U, V) &= (\sqrt{3}(\epsilon_{xx} - \epsilon_{yy}), 2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}), \\
(X, Y, Z) &= (\epsilon_{yz}, \epsilon_{zx}, \epsilon_{xy}), \\
(X', Y', Z') &= (K_x, K_y, K_z).
\end{aligned} \tag{4.30}$$

Since a strain tensor and a wave vector have \hat{K}_+ and \hat{K}_- properties, respectively, all the products are of \hat{K}_- type. Then, we simply look for the expressions of symmetry-adapted products of primed and unprimed quantities in Table I, and we get the following 18 linear combinations of the products:

$$\begin{aligned}
\tilde{S} &= K_x \epsilon_{yz} + K_y \epsilon_{zx} + K_z \epsilon_{xy}; \\
\tilde{U} &= \sqrt{3}(K_x \epsilon_{yz} - K_y \epsilon_{zx}); \\
\tilde{V} &= 2K_z \epsilon_{xy} - K_x \epsilon_{yz} - K_y \epsilon_{zx}; \\
(\tilde{P}_1, \tilde{Q}_1, \tilde{R}_1) &= \sqrt{3}((\epsilon_{yy} - \epsilon_{zz})K_x, (\epsilon_{zz} - \epsilon_{xx})K_y, (\epsilon_{xx} - \epsilon_{yy})K_z); \\
(\tilde{P}_2, \tilde{Q}_2, \tilde{R}_2) &= (K_y \epsilon_{xy} - K_z \epsilon_{zx}, K_z \epsilon_{yz} - K_x \epsilon_{xy}, K_x \epsilon_{zx} - K_y \epsilon_{yz}); \\
(\tilde{X}_1, \tilde{Y}_1, \tilde{Z}_1) &= \epsilon_{00}(K_x, K_y, K_z); \\
(\tilde{X}_2, \tilde{Y}_2, \tilde{Z}_2) &= ((3\epsilon_{xx} - \epsilon_{00})K_x, (3\epsilon_{yy} - \epsilon_{00})K_y, (3\epsilon_{zz} - \epsilon_{00})K_z); \\
(\tilde{X}_3, \tilde{Y}_3, \tilde{Z}_3) &= (K_y \epsilon_{xy} + K_z \epsilon_{zx}, K_z \epsilon_{yz} + K_x \epsilon_{xy}, K_x \epsilon_{zx} + K_y \epsilon_{yz}).
\end{aligned} \tag{4.31}$$

In this way we can at once obtain correct forms of the products which fit to our theory as they stand.

Instead of repeating the same procedure for all the combinations of \tilde{H} , \tilde{E} , ϵ , and \tilde{K} , we simply mention some examples of product quantities which fill the empty columns of Table II: for \hat{K}_+ ,

$$\begin{aligned}
T &= K_x H_x + K_y H_y + K_z H_z; \\
(P, Q, R) &= (E_y \epsilon_{xy} - E_z \epsilon_{zx}, E_z \epsilon_{yz} - E_x \epsilon_{xy}, E_x \epsilon_{zx} - E_y \epsilon_{yz}).
\end{aligned} \tag{4.32}$$

$$H_s^{(c)} = \tau S, \tag{5.2}$$

$$H_{as}^{(c)} = 2\bar{\lambda} T \sigma_{ez} + 2\bar{\mu} (Y \sigma_{ex} - X \sigma_{ey}), \tag{5.3}$$

$$\begin{aligned}
H_s^{(v)} &= [a_1 + a_2 l_x^2 + 2a_3 l_x l_y + 2a_4 (l_x \sigma_x + l_y \sigma_y)] S + \sqrt{2} b_1 (l_x \sigma_y - l_y \sigma_x) T + 2\sqrt{2} e_1 (X l_x + Y l_y) \sigma_z + 2e_2 (X \sigma_x + Y \sigma_y) l_z \\
&\quad + 2\sqrt{2} e_3 (X \{l_x l_z\} + Y \{l_y l_z\}) + f_1 [W (l_x^2 - l_y^2) + 2Z \{l_x l_y\}] + \sqrt{2} f_2 [(l_x \sigma_x - l_y \sigma_y) W + (l_x \sigma_y + l_y \sigma_x) Z],
\end{aligned} \tag{5.4}$$

$$\begin{aligned}
H_{as}^{(v)} &= 2\sqrt{2} \bar{a}_1 (\{l_x l_z\} \sigma_y - \{l_y l_z\} \sigma_x) S + [\bar{b}_1 l_z + 2\bar{b}_2 \sigma_z + 2\bar{b}_3 l_x^2 \sigma_x + 2\sqrt{2} \bar{b}_4 (\{l_x l_z\} \sigma_x + \{l_y l_z\} \sigma_y)] T \\
&\quad + \bar{c}_1 [(l_x^2 - l_y^2) \sigma_x - 2 \{l_x l_y\} \sigma_y] U + \bar{d}_1 [(l_x^2 - l_y^2) \sigma_y + 2 \{l_x l_y\} \sigma_x] V + \sqrt{2} \bar{e}_1 (l_x Y - l_y X) + 2(\bar{e}_2 + \bar{e}_4 l_x^2) (\sigma_x Y - \sigma_y X) \\
&\quad + 4\sqrt{2} \bar{e}_3 (\{l_x l_z\} Y - \{l_y l_z\} X) \sigma_z + \bar{e}_5 [(l_x^2 - l_y^2) \sigma_x + 2 \{l_x l_y\} \sigma_y] Y + [(l_x^2 - l_y^2) \sigma_y - 2 \{l_x l_y\} \sigma_x] X \\
&\quad + 2\bar{f}_1 [(l_x^2 - l_y^2) \sigma_z Z - 2 \{l_x l_y\} \sigma_z W] + 2\sqrt{2} \bar{f}_2 [\{l_x l_z\} \sigma_y + \{l_y l_z\} \sigma_x] W - (\{l_x l_z\} \sigma_x - \{l_y l_z\} \sigma_y) Z.
\end{aligned} \tag{5.5}$$

For \hat{K}_- ,

$$\begin{aligned}
T &= E_x H_x + E_y H_y + E_z H_z, \\
S, U, V, \dots,
\end{aligned} \tag{4.33}$$

see Eq. (4.31).

The \tilde{I} and $\tilde{\Xi}$ dependence of H_{ex} , which is neglected in this paper, can be similarly constructed with the aid of Table I.

V. WURTZITE STRUCTURE

The Cartesian coordinates (x, y, z) for wurtzite structure are chosen in such a way that z is parallel to the c axis.

A. Bloch band contributions

Corresponding to the six irreducible representations of the C_{6v} single group which is the crystal point group of wurtzite, we introduce a set of representative variables for a physical quantity

$$\begin{aligned}
\Gamma_1: & S [z]; \\
\Gamma_2: & T [l_z]; \\
\Gamma_3: & U [(3x^2 - y^2)y]; \\
\Gamma_4: & V [(3y^2 - x^2)x]; \\
\Gamma_5: & (X, Y) [x, y]; \\
\Gamma_6: & (W, Z) [x^2 - y^2, 2xy].
\end{aligned} \tag{5.1}$$

The transformation properties of each variable are indicated on the right in the square brackets. Simple examples of Ξ are given in Table XII. The product of two Ξ 's are reduced into symmetry adapted components in Table XIII. The repeated use of Table XIII gives us all the independent forms of the products of the operators $\tilde{\sigma}_e$, $\tilde{\sigma}$, and \tilde{I} .

The invariant forms for the \hat{K}_+ and \hat{K}_- parts of the contributions from the conduction and valence bands are

TABLE XII. Simple examples of Ξ in C_{6v} symmetry. \vec{E} : electric field; \vec{H} : magnetic field; ϵ : strain tensor; \vec{K} : wave vector.

		\hat{K}_-			\hat{K}_+			
Γ_1	S	K_z		$K_x^2 + K_y^2$	$H_x^2 + H_y^2$	E_z	$E_x^2 + E_y^2$	$\epsilon_{zz} \epsilon_{xx} + \epsilon_{yy}$
Γ_2	T		H_z					
Γ_3	U							
Γ_4	V							
Γ_5	X	K_x	H_y	$K_x K_z$	$H_x H_z$	E_x	$E_x E_z$	ϵ_{xz}
	Y	K_y	$-H_x$	$K_y K_z$	$H_y H_z$	E_y	$E_y E_z$	ϵ_{yz}
Γ_6	W			$K_x^2 - K_y^2$	$H_x^2 - H_y^2$		$E_x^2 - E_y^2$	$\epsilon_{xx} - \epsilon_{yy}$
	Z			$2K_x K_y$	$2H_x H_y$		$2E_x E_y$	$2\epsilon_{xy}$

The small Greek and Roman letters are arbitrarily defined (real) coefficients with and without bars on them corresponding to the \hat{K}_- and \hat{K}_+ characters of Ξ , respectively.

B. Basis functions

The conduction-band functions transform as the Γ_7 irreducible representation. We denote them as before by

$$s\alpha(\alpha_e), \quad s\beta(\beta_e). \quad (5.6)$$

In this case, however, the orbital part s may contain some z character, since both of them belong to Γ_1 . The valence-band functions consisting of the products of (x, y, z) and (α, β) can be reduced into $\Gamma_9 + \Gamma_7 + \Gamma_7$. The most general forms of the symmetry-adapted linear combinations of the spin-orbitals can be obtained by noting the Kramers degeneracy and the conservation of the z component of the total angular momentum ($l_z + \sigma_z$). The

more intuitive method is to diagonalize the spin-orbit interaction ($-\vec{l} \cdot \vec{\sigma}$) and an effective stress energy along the z axis (quasicubic model¹⁹). The eigenfunctions are given by²⁰

$$\begin{aligned} \Gamma_7(B): \quad & \phi_1 = \delta|0\rangle\alpha - \gamma|1\rangle\beta, \\ & \phi_2 = \gamma|-1\rangle\alpha - \delta|0\rangle\beta; \\ \Gamma_7(C): \quad & \phi_3 = -\gamma|0\rangle\alpha - \delta|1\rangle\beta, \\ & \phi_4 = \delta|-1\rangle\alpha + \gamma|0\rangle\beta; \\ \Gamma_9(A): \quad & \phi_5 = -|1\rangle\alpha, \\ & \phi_6 = |-1\rangle\beta, \end{aligned} \quad (5.7)$$

where $\{|1\rangle, |0\rangle, |-1\rangle\}$ are the eigenfunctions of l_z and defined in the same way as in Eq. (4.9). The parameters γ and δ are defined as

$$\begin{aligned} \gamma &= [2/(2 + B_0^2)]^{1/2}, \\ \delta &= B_0/(2 + B_0^2)^{1/2}, \\ B_0 &= -2 + 3\Delta E/\Delta_{so}, \end{aligned} \quad (5.8)$$

TABLE XIII. Multiplication table for the components of irreducible representations. This table is equivalent to that of coupling coefficients in G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of Thirty-Two Point Groups* (M.I.T., Cambridge, 1963).

Γ_1	S	SS'	TT'	UU'	VV'	$XX' + YY'$	$WW' + ZZ'$
Γ_2	T	ST'		UV'		$XY' - YX'$	$WZ' - ZW'$
Γ_3	U	SU'	TV'			$XZ' + YW'$	
Γ_4	V	SV'	TU'			$YZ' - XW'$	
Γ_5	X	SX'	TY'	UZ'	$-VW'$	$XZ' - YW'$	
	Y	SY'	$-TX'$	UW'	VZ'	$YZ' + XW'$	
Γ_6	W	SW'	TZ'	$-UX'$	$-VX'$	$XX' - YY'$	$ZZ' - WW'$
	Z	SZ'	$-TW'$	UY'	VY'	$XY' + YX'$	$WZ' + ZW'$

where ΔE is the energy of the $\Gamma_7(B)$ state measured from that of $\Gamma_9(A)$, and Δ_{so} is the spin-orbit splitting of the valence bands in the virtual cubic limit. Note that γ and δ are normalized, i.e., $\gamma^2 + \delta^2 = 1$. In the limit of strong crystal field as in ZnO, $\gamma = 0$ and $\delta = 1$, and for the weak crystal field limit, $\gamma = 1/\sqrt{3}$ and $\delta = -\sqrt{2/3}$, which correspond to the case of cubic structure.

In terms of the wave functions [Eqs. (5.6) and (5.7)] we form electron-hole pair states just in the same way as in Eq. (4.11).

Then, the wave functions with appropriate polarization character are given for the A , B , and C excitons as follows:

$$\begin{aligned}
\Gamma_5(A): |x\rangle_A &= (\Phi_1 + \Phi_4)/\sqrt{2}, \quad (\sqrt{3}\xi), \\
|y\rangle_A &= i(\Phi_1 - \Phi_4)/\sqrt{2}, \quad (\sqrt{3}\eta); \\
\Gamma_8(A): |t\rangle_A &= -i(\Phi_3 + \Phi_2)/\sqrt{2}, \quad (0), \\
|t'\rangle_A &= (\Phi_3 - \Phi_2)/\sqrt{2}, \quad (0); \\
\Gamma_5(B): |x\rangle_B &= (\Psi_5 + \Psi_2)/\sqrt{2}, \quad (\sqrt{3}\gamma\xi), \\
|y\rangle_B &= i(\Psi_5 - \Psi_2)/\sqrt{2}, \quad (\sqrt{3}\gamma\eta); \\
\Gamma_1(B): |z\rangle_B &= (\Psi_1 - \Psi_6)/\sqrt{2}, \quad (\sqrt{6}\delta\xi); \\
\Gamma_2(B): |t\rangle_B &= -i(\Psi_1 + \Psi_6)/\sqrt{2}, \quad (0); \\
\Gamma_5(C): |x\rangle_C &= (\Psi_7 + \Psi_4)/\sqrt{2}, \quad (\sqrt{3}\delta\xi), \\
|y\rangle_C &= i(\Psi_7 - \Psi_4)/\sqrt{2}, \quad (\sqrt{3}\delta\eta); \\
\Gamma_1(C): |z\rangle_C &= (\Psi_8 - \Psi_3)/\sqrt{2}, \quad (\sqrt{6}\gamma\xi), \\
\Gamma_2(C): |t\rangle_C &= i(\Psi_8 + \Psi_3)/\sqrt{2}, \quad (0),
\end{aligned} \tag{5.9}$$

where the quantities on the right in parentheses are the dipole moment of each state for the light polarized along (ξ, η, ζ) in units of M_0 ($=\langle s|ex|x\rangle/\sqrt{3}$).

C. Matrix representations

Corresponding to the dual character of the invariants, the one as the definition of Bloch band parameters and the other as the partial contributions to the exciton energies, we give matrices on both Bloch and exciton bases.

1. Bloch basis

Using the basis (α_e, β_e) , we get the matrix for the conduction-band contributions, $H_s^{(c)} + H_{as}^{(c)}$, as

$$\tau S + \begin{pmatrix} \bar{\lambda}T & \bar{\mu}(Y + iX) \\ \bar{\mu}(Y - iX) & -\bar{\lambda}T \end{pmatrix}. \tag{5.10}$$

For the valence-band contribution, we define the following combinations of parameters: for the \hat{K}_+ quantities,

$$\begin{aligned}
\alpha'_1 &= a_1 + \gamma^2(a_2 - a_3) - 2\gamma\delta a_4, \quad \alpha'_2 = a_1 + a_2 + a_3, \\
\alpha'_3 &= a_1 + \delta^2(a_2 - a_3) + 2\gamma\delta a_4, \\
\alpha_4 &= (\gamma^2 - \delta^2)a_4 + \gamma\delta(a_2 - a_3), \\
\epsilon_1 &= \gamma e_2 - \delta(e_1 + e_3), \quad \epsilon_2 = \delta e_2 + \gamma(e_1 + e_3), \quad \epsilon_3 = e_1 - e_3, \\
\eta_1 &= \delta f_2 - \gamma f_1, \quad \eta_2 = -\gamma f_2 - \delta f_1,
\end{aligned} \tag{5.11}$$

and for the \hat{K}_- quantities,

$$\begin{aligned}
\bar{\beta}_1 &= \bar{b}_1 + \bar{b}_2 + \bar{b}_3, \quad \bar{\beta}_2 = \delta^2\bar{b}_2 + \gamma^2(\bar{b}_1 - \bar{b}_2 - \bar{b}_3) - 2\gamma\delta\bar{b}_4, \\
\bar{\beta}_3 &= \gamma^2\bar{b}_2 + \delta^2(\bar{b}_1 - \bar{b}_2 - \bar{b}_3) + 2\gamma\delta\bar{b}_4, \\
\bar{\beta}_4 &= (\gamma^2 - \delta^2)\bar{b}_4 - \gamma\delta(2\bar{b}_2 + \bar{b}_3 - \bar{b}_1), \\
\bar{\epsilon}_1 &= \gamma(\bar{e}_2 + \bar{e}_4) - \delta(\bar{e}_1 + \bar{e}_3), \quad \bar{\epsilon}_2 = \delta(\bar{e}_2 + \bar{e}_4) + \gamma(\bar{e}_1 + \bar{e}_3), \\
\bar{\epsilon}_3 &= 2\gamma\delta(\bar{e}_1 - \bar{e}_3) - \gamma^2\bar{e}_3 - \delta^2\bar{e}_2, \\
\bar{\epsilon}_4 &= 2\gamma\delta(\bar{e}_3 - \bar{e}_1) - \delta^2\bar{e}_3 - \gamma^2\bar{e}_2, \\
\bar{\epsilon}_5 &= (\delta^2 - \gamma^2)(\bar{e}_1 - \bar{e}_3) + \gamma\delta(\bar{e}_2 - \bar{e}_5), \\
\bar{\eta}_1 &= -\gamma\bar{f}_1 - \delta\bar{f}_2, \quad \bar{\eta}_2 = \gamma\bar{f}_2 - \delta\bar{f}_1.
\end{aligned} \tag{5.12}$$

In terms of these newly defined constants, $H_s^{(v)}$ and $H_{as}^{(v)}$ are given in Tables XIV and XV, respectively.

2. Exciton basis

Using the basis [Eq. (5.9)] we obtain the Tables XVI and XVII for $H_s^{(c)} + H_s^{(v)}$ and $H_{as}^{(c)} + H_{as}^{(v)}$, respectively. In Table XVI we used the notations:

$$\alpha_j = \tau - \alpha'_j \quad (j = 1, 2, 3). \tag{5.13}$$

TABLE XIV. Matrix representation of $H_s^{(v)}$.

	ϕ_5	ϕ_6	ϕ_1	ϕ_2	ϕ_3	ϕ_4
$\alpha'_2 S$	0	$\epsilon_1(X - iY)$	$\eta_1(W - iZ)$	$\epsilon_2(X - iY)$	$\eta_2(W - iZ)$	
$\alpha'_3 S$		$\eta_1(W + iZ)$	$-\epsilon_1(X + iY)$	$\eta_2(W + iZ)$	$-\epsilon_2(X + iY)$	
$\alpha'_1 S$			0	$\alpha_4 S + i\beta_1 T$	$\epsilon_3(X - iY)$	
			$\alpha'_1 S$	$-\epsilon_3(X + iY)$	$\alpha_4 S - i\beta_1 T$	
(H.c.)				$\alpha'_3 S$	0	
					$\alpha'_2 S$	

D. Comparison with existing theories

The energy-level scheme without any symmetry breaking effect is obtained from $H_s^{(c)} + H_s^{(v)}$ with $S=1$ and H_{ex} . Table XVI apparently suggests the existence of a nondiagonal element with the coefficient α_4 . Actually the parameters γ and δ are so chosen that this nondiagonal term becomes zero. Thus we ascribe the diagonal energies

$$\begin{aligned} 0 & \text{ to the } A\text{-excitons,} \\ \Delta_{AB} & \text{ to the } B\text{-excitons,} \\ \Delta_{AC} & \text{ to the } C\text{-excitons,} \end{aligned} \quad (5.16)$$

by arbitrarily choosing the zero of energy.

The fundamental framework of the problem is, therefore, the exchange matrix, (5.14), plus the diagonal energies, (5.16). This part corresponds to Sec. IVE 2 (exchange mixing of spin-orbit partners). In the wurtzite structure also, the exchange interaction mixes the different exciton series A , B , and C . One of the direct consequences of this mixing effect is the stress splitting of these exciton states (see Sec. VD 1).

1. Stress-exchange splitting (Ref. 5)

No stress can lift the degeneracy of the Γ_7 or Γ_9 band edges each of which forms a Kramers doublet, while a linear splitting of Γ_5 exciton states (x and y polarized) can be expected from group theory for a uniaxial stress perpendicular to the c axis ($\Gamma_5 \times \Gamma_5$ contains Γ_8). This apparent paradox was solved by introducing an interplay between stress and exchange interaction.⁵

If we take $\vec{K} \parallel \vec{c}$ ($\xi = \bar{\eta} = 0$, $\bar{\zeta} = 1$) and the uniaxial stress perpendicular to c ($W \neq 0$, $S \neq 0$, $T = U = V = X = Y = Z = 0$) corresponding to the experimental situation,²¹ the relevant matrix is given by

$$\begin{pmatrix} J_L & 0 & i\bar{\mu}K & 0 & \gamma J_L & 0 & i\bar{\epsilon}_1 K & 0 \\ & J & 0 & -i\bar{\mu}K & 0 & \gamma J & 0 & -i\bar{\epsilon}_1 K \\ & & 0 & 0 & i\bar{\epsilon}_1 K & 0 & 0 & 0 \\ & & & 0 & 0 & -i\bar{\epsilon}_1 K & 0 & 0 \\ & & & & \gamma^2 J_L + \Delta_{AB} & 0 & -i\bar{\epsilon}_3 K & 0 \\ & & & & & \gamma^2 J + \Delta_{AB} & 0 & -i\bar{\epsilon}_3 K \\ & & & & & & 2\delta^2 J + \Delta_{AB} & 0 \\ \text{(H.c.)} & & & & & & & \Delta_{AB} \end{pmatrix}, \quad (5.21)$$

$$\begin{pmatrix} J & \gamma J \pm \eta_1 W & \delta J \pm \eta_2 W \\ & \gamma^2 J + \Delta_{AB} & \gamma \delta J - \alpha S \\ \text{(H.c.)} & & \delta^2 J + \Delta_{AC} \end{pmatrix}, \quad (5.17)$$

where the “+” and “-” signs are for $\{|x\rangle_A, |x\rangle_B, |x\rangle_C\}$ and $\{|y\rangle_A, |y\rangle_B, |y\rangle_C\}$, respectively, and

$$J = 3(j_0 - j_1), \quad (5.18)$$

$$\alpha S = \alpha_4 \epsilon_{zz} + \alpha'_4 (\epsilon_{xx} + \epsilon_{yy}), \quad (5.19)$$

$$W = \epsilon_{xx} - \epsilon_{yy}. \quad (5.20)$$

Without strain, Eq. (5.17) leads to three doubly degenerate energies. Each pair includes an x - and a y -polarized state. For finite value of W , they all split linearly, since the sign of the W terms is different for the x - and y -polarized states.

Thus the observation of the stress splitting of the exciton states clearly indicates the importance of the electron-hole exchange interaction in semiconductors.

2. Wave-vector-dependent selection rules (Refs. 2 and 3)

The basis functions (5.9) have vanishing wave vector. Optically excited states, however, have finite values of the translational wave vector \vec{K} . This small but finite \vec{K} can act as a perturbation which mixes the basis states defined for $\vec{K}=0$, and consequently gives rise to additional selection rules. Some mechanisms of such mixings were discussed in earlier works.^{2,3} Here we derive a generalized version of such interaction schemes among the A and B exciton states.

(a) K -linear contribution. Since K_z belongs to Γ_1 , interesting effects occur only in the case $\vec{K} \perp \vec{c}$. Thus we here choose $(K_x, K_y, K_z) = (K, 0, 0)$ in Table XVII. The mixing matrix for

$$\{|x\rangle_A, |y\rangle_A, |t'\rangle_A, |t\rangle_A, |x\rangle_B, |y\rangle_B, |z\rangle_B, |t\rangle_B\}$$

is given by

TABLE XVII. Matrix representation of $H_{as}^{(c)} + H_{as}^{(v)}$ on the exciton basis. The contribution of $H_{as}^{(c)}$ is written in the lower left corner to avoid the congestion of symbols. The complete matrix is obtained by adding the complex conjugates of all the elements to their opposite corners.

$ x\rangle_A$	$ y\rangle_A$	$ t'\rangle_A$	$ t\rangle_A$	$ x\rangle_B$	$ y\rangle_B$	$ z\rangle_B$	$ t\rangle_B$	$ x\rangle_C$	$ y\rangle_C$	$ z\rangle_C$	$ t\rangle_C$
$\left[\begin{array}{cccccccccccc} 0 & -i\bar{\beta}_1 T & -i\bar{d}_1 V & i\bar{c}_1 U & i\eta_1 \begin{pmatrix} W & Z \\ Z & -W \end{pmatrix} & i\bar{\epsilon}_1 \begin{pmatrix} X & Y \\ Y & -X \end{pmatrix} & i\bar{\eta}_2 \begin{pmatrix} W & Z \\ Z & -W \end{pmatrix} & i\epsilon_2 \begin{pmatrix} -X & -Y \\ -Y & X \end{pmatrix} \\ -i\bar{\lambda} T & 0 & i\bar{c}_1 U & -i\bar{d}_1 V & & & & & & & & \\ i\bar{\mu} \begin{pmatrix} -X & Y \\ Y & X \end{pmatrix} & & 0 & i\bar{\beta}_1 T & i\bar{\epsilon}_1 \begin{pmatrix} X & -Y \\ -Y & -X \end{pmatrix} & i\bar{\eta}_1 \begin{pmatrix} -W & Z \\ Z & W \end{pmatrix} & i\bar{\epsilon}_2 \begin{pmatrix} X & -Y \\ -Y & -X \end{pmatrix} & i\bar{\eta}_2 \begin{pmatrix} W & -Z \\ -Z & -W \end{pmatrix} \\ & & & & 0 & -i\bar{\beta}_2 T & i\bar{\epsilon}_3 \begin{pmatrix} -X & Y \\ -Y & -X \end{pmatrix} & i\bar{a}_1 S & -i\bar{\beta}_4 T & i\bar{\epsilon}_5 \begin{pmatrix} X & -Y \\ Y & X \end{pmatrix} \\ & & & & i\bar{\lambda} T & 0 & & i\bar{\beta}_4 T & i\bar{a}_1 S & & & \\ & & & & i\bar{\mu} \begin{pmatrix} X & Y \\ Y & -X \end{pmatrix} & & 0 & i\bar{\beta}_2 T & i\bar{\epsilon}_5 \begin{pmatrix} X & Y \\ -Y & X \end{pmatrix} & -i\bar{a}_1 S & -i\bar{\beta}_4 T \\ & & & & & & & & & & & \\ & & & & & & & & 0 & -i\bar{\beta}_3 T & i\bar{\epsilon}_4 \begin{pmatrix} X & -Y \\ Y & X \end{pmatrix} \\ & & & & & & & & i\bar{\lambda} T & 0 & & \\ & & & & & & & & & & & \\ & & & & & & & & & & i\bar{\mu} \begin{pmatrix} -X & -Y \\ -Y & X \end{pmatrix} & i\bar{\beta}_3 T \\ & & & & & & & & & & i\bar{\lambda} T & 0 \end{array} \right]$											

where

$$J_L = 3(j_0 + 2j_1). \quad (5.22)$$

From this scheme we can easily see the possibility of the following mixings: (i) $\Gamma_{5L}(A)$ and $\Gamma_1(B)$, (L : longitudinal); (ii) $\Gamma_6(A)$ and $\Gamma_5(B)$; (iii) $\Gamma_6(A)$ and $\Gamma_5(A)$; (iv) $\Gamma_{5T}(B)$ and $\Gamma_2(B)$, $\Gamma_{5L}(B)$ and $\Gamma_1(B)$, (T : transverse).

Case (i) was suggested by Hopfield and Thomas,² and case (iv) was treated by Mahan and Hopfield.³ Cases (ii) and (iii) may be relevant to the newly found $\Gamma_6(A)$ magnetoluminescence line in the configuration $\vec{E} \perp \vec{c}$ and $\vec{H} \parallel \vec{c}$.²² It should be noted that the mixings (i) and (ii) occur with the same magnitude. The exchange mixing also can help the appearance of $\Gamma_6(A)$ in the $\vec{E} \perp \vec{c}$ configuration.

The A - C mixing has just the same form as (5.21) except for the different numerical coefficients.

(b) K^2 -contribution. We omit here the terms proportional to K_z^2 and $K_x^2 + K_y^2$, because they simply shift the energies of the whole A (B) states by an equal amount. Then, the only nonvanishing part of the matrix is the nondiagonal block between the A and B states. In terms of the basis functions ordered in the same way as in Eq. (5.21) this nondiagonal block matrix (in the upper right corner) is given by

$$\begin{pmatrix} -\eta_1 \begin{pmatrix} K_x^2 - K_y^2 & 2K_x K_y \\ 2K_x K_y & K_y^2 - K_x^2 \end{pmatrix} & \epsilon_1 \begin{pmatrix} -K_x K_z & -K_y K_z \\ -K_y K_z & K_x K_z \end{pmatrix} \\ \epsilon_1 \begin{pmatrix} -K_x K_z & K_y K_z \\ K_y K_z & K_x K_z \end{pmatrix} & \eta_1 \begin{pmatrix} K_x^2 - K_y^2 & -2K_x K_y \\ -2K_x K_y & K_y^2 - K_x^2 \end{pmatrix} \end{pmatrix}. \quad (5.23)$$

For $\vec{K} \perp \vec{c}$, mixing between $\Gamma_6(A)$ and $\Gamma_1(B)$ can be expected. This leads to the appearance of $\Gamma_6(A)$ in the $\vec{E} \parallel \vec{c}$ configuration.²

Since the transformation properties of the strain tensor ϵ_{ij} are the same as those of $K_i K_j$, one can use Eq. (5.23) as the general mixing scheme due to strain by replacing $K_i K_j$ with ϵ_{ij} .

Finally we summarize the selection rules for the $\Gamma_6(A)$ exciton.

(i) $\vec{E} \parallel \vec{c}$. In this case, $\Gamma_6(A)$ must be mixed with some Γ_1 states in order to be observable. Since $\Gamma_6 \times \Gamma_1 = \Gamma_6$, the perturbation must have Γ_6 symmetry, which is the case for $(K_x^2 - K_y^2, 2K_x K_y)$ and $(\epsilon_{xx} - \epsilon_{yy}, 2\epsilon_{xy})$.

(ii) $\vec{E} \perp \vec{c}$. Here we need the mixing of the $\Gamma_6(A)$ with some Γ_5 states. The relation $\Gamma_6 \times \Gamma_5 = \Gamma_3 + \Gamma_4 + \Gamma_5$ requires mechanisms which have the symmetry Γ_3 , Γ_4 , or Γ_5 . Examples of such perturbations are (K_x, K_y) , $(K_x K_z, K_y K_z)$, and $(\epsilon_{xz}, \epsilon_{yz})$ for Γ_5 , stress-induced K -linear terms

$$[2K_x \epsilon_{xy} + K_y (\epsilon_{xx} - \epsilon_{yy}), 2K_y \epsilon_{xy} - K_x (\epsilon_{xx} - \epsilon_{yy})] \quad (5.24)$$

for Γ_3 and Γ_4 .

E. Discussion

1. Comparison between wurtzite and $\langle 111 \rangle$ -stressed zinc-blende structures

According to the well-known quasicubic model,¹⁹ it might seem that a wurtzite structure could be approximated by a $\langle 111 \rangle$ -stressed zinc-blende structure with respect to not only the valence-band energies at $k=0$ but also other quantities such as mass parameters, k -linear terms, the effects of external perturbations, etc. Since the symmetries of these two systems are different from each other, this kind of generalization is not always allowed group theoretically. Therefore it would be interesting to give a criterion about what is allowed and what is forbidden. Of course, there still remains a problem of quantitative accuracy even in the allowed case of such generalization just as in the original model. This is related to the size of the subspace of wave functions, but we do not discuss it any further. Instead, we concentrate on the above-mentioned criterion.

When a zinc-blende structure is uniaxially distorted along a $\langle 111 \rangle$ axis, the crystal point group at $k=0$ is C_{3v} which is a subgroup of C_{6v} (wurtzite). The compatibility relation between $C_{6v} - C_{3v} - T_d$ is given in Table XVIII. Because of the lower symmetry, the effective Hamiltonian in the case of C_{3v} symmetry for a given Ξ can contain more invariant terms than that of C_{6v} case. This will be explicitly shown in the following example.

The original quasicubic Hamiltonian¹⁹ which leads to the valence-band energies at $k=0$ can be written

$$H_{qc} = \lambda_{so} \vec{1} \cdot \vec{\sigma} + P_o (\{l_{\bar{y}} l_{\bar{z}}\} + \{l_{\bar{z}} l_{\bar{x}}\} + \{l_{\bar{x}} l_{\bar{y}}\}), \quad (5.25)$$

where λ_{so} and P_o are the parameters representing spin-orbit and noncubic crystal-field effects, respectively, and the coordinates $(\bar{x}, \bar{y}, \bar{z})$ are defined along the three principal axes of cubic structure and related with (x, y, z) as

$$\begin{aligned} x &= (\bar{x} - \bar{y})/\sqrt{2}, \\ y &= (\bar{x} + \bar{y} - 2\bar{z})/\sqrt{6}, \\ z &= (\bar{x} + \bar{y} + \bar{z})/\sqrt{3}. \end{aligned} \quad (5.26)$$

TABLE XVIII. Compatibility relation.

C_{6v}	C_{3v}	T_d
Γ_1, Γ_3	Γ_1	Γ_1, Γ_5
Γ_2, Γ_4	Γ_2	Γ_2, Γ_4
Γ_5, Γ_6	Γ_3	$\Gamma_3, \Gamma_4, \Gamma_5$

In terms of (x, y, z) , Eq. (5.25) can be rewritten

$$H_{qc} = \lambda_{so} \vec{1} \cdot \vec{\sigma} + \frac{1}{2} P_o (2l_z^2 - l_x^2 - l_y^2). \quad (5.27)$$

Both terms are clearly invariant not only in C_{3v} but also in C_{6v} . Now we try to extend the above procedure to the k dependence of the valence-band energies. Let us consider the kinetic energy

$$\begin{aligned} H_{kin c} &= Lk^2 + (M - L)(k_x^2 l_x^2 + k_y^2 l_y^2 + k_z^2 l_z^2) \\ &\quad - 2N(k_x k_z \{l_{\bar{y}} l_{\bar{z}}\} + \text{c.p.}) \end{aligned} \quad (5.28)$$

in the cubic structure, where L , M , and N are well-known inverse mass parameters.²³ Here we neglect the spin-dependent kinetic-energy terms which can in principle be expected from the general expression (4.4). On the other hand, the corresponding energy in C_{6v} is given by

$$\begin{aligned} H_{kin w} &= A_1 k_x^2 + A_2 (k_x^2 + k_y^2) + B_1 k_x^2 l_x^2 + B_2 (k_x^2 + k_y^2) l_x^2 \\ &\quad + C_1 [(k_x^2 - k_y^2)(l_x^2 - l_y^2) + 4k_x k_y \{l_x l_y\}] \\ &\quad + D_1 (k_x k_z \{l_x l_z\} + k_y k_z \{l_y l_z\}). \end{aligned} \quad (5.29)$$

Using the transformation (5.26) we can put most of Eq. (5.28) into the form of Eq. (5.29) where

$$\begin{aligned} A_1 &= \frac{1}{3}(4L - M + 2N), \quad A_2 = \frac{1}{3}(4L - M - N), \\ B_1 &= -N, \quad B_2 = \frac{1}{2}N, \\ C_1 &= \frac{1}{6}(M - L - 2N), \quad D_1 = \frac{2}{3}(2M - 2L - N), \end{aligned} \quad (5.30)$$

but there remain the following terms which are invariant in C_{3v} but *not* in C_{6v} :

$$\begin{aligned} &(\frac{1}{3}\sqrt{2}N)[2k_x k_y \{l_x l_z\} + (k_x^2 - k_y^2)\{l_y l_z\}] \\ &\quad + 2k_x k_z \{l_x l_y\} + k_y k_z (l_x^2 - l_y^2). \end{aligned} \quad (5.31)$$

Although the above procedure leads to partially erroneous results, the relation (5.30) may be used to guess the approximate values of the valence-band parameters in C_{6v} from those in T_d .

There are, however, examples which do not lead to noninvariant terms. The Zeeman energy of the form

$$g\mu_B \vec{H} \cdot \vec{1} + g'\mu_B \vec{H} \cdot \vec{\sigma}$$

and the Stark energy

$$q(E_x \{l_y l_z\} + E_y \{l_z l_x\} + E_z \{l_x l_y\})$$

are such examples. If we take the uniaxial stress along $\langle 111 \rangle$, one of the stress-induced \vec{k} -linear terms [Eq. (4.29)] also belongs to this category.

Thus we are led to the following conclusion: The generalization of the quasicubic model produces both invariant and noninvariant terms in wurtzite structure. The noninvariant terms can be checked by comparing them with the general expression of invariants in C_{6v} , i.e., Eqs. (5.2)–(5.5). The merit of this generalization is that it

provides the relationships between some of the (independent) parameters in Eqs. (5.2)–(5.5).

2. Composite effects

Higher-order effects of the symmetry-breaking entities listed in Table XII can be easily discussed in terms of Tables XII and XIII. Here we take two examples: (i) \vec{H} -induced \vec{k} -linear term and (ii) stress-induced \vec{k} -linear term.

According to Table XIII, the products of \vec{K} and \vec{H} can be decomposed as

$$\begin{aligned} S &= K_x H_y - K_y H_x, & T_1 &= K_x H_x + K_y H_y, \\ T_2 &= K_z H_z, & (X_1, Y_1) &= (K_z H_y, -K_x H_x), \\ (X_2, Y_2) &= (K_y H_z, -K_x H_z), \\ (W, Z) &= (K_x H_y + K_y H_x, K_y H_y - K_x H_x). \end{aligned} \quad (5.32)$$

The above S component was used as an effective electric field along the c axis by Thomas and Hopfield¹⁸ in the consideration of the magneto-Stark effect of excitons with finite \vec{K} . The (X, Y) components can be also regarded as such type of “Stark” field.

Among the 18 stress-induced \vec{k} -linear terms, we list here only the products which fill the empty columns in Table XII:

$$\begin{aligned} U &= 2K_x \epsilon_{xy} + K_y (\epsilon_{xx} - \epsilon_{yy}), \\ V &= 2K_y \epsilon_{xy} - K_x (\epsilon_{xx} - \epsilon_{yy}), \\ (W, Z) &= (K_x \epsilon_{xz} - K_y \epsilon_{yz}, K_x \epsilon_{yz} + K_y \epsilon_{xz}). \end{aligned} \quad (5.33)$$

In a similar way, we can construct the correct forms of the higher-order products which can be used directly in Tables XVI and XVII.

VI. CONCLUDING REMARKS

A. Validity of the theory

Although we have assumed the pure atomic p character of the orbital parts of the valence electron states at the beginning of the formulation, it is possible to have orbital admixture of d -character such as

$$|p_x\rangle + \nu |d_{yz}\rangle, \text{ etc.},$$

since it only changes the values of matrix elements without any alteration of the symmetry properties. Therefore the theory can also be applied to the cases where one should expect a considerable amount of p - d mixing.

As long as we treat the coefficients of the effective Hamiltonian as renormalized constants, the matrix itself is always correct. One should, however, expect the limit of the applicability of this formalism, when some of the other exciton states,

e.g., $2s, 2p, \dots$, happen to couple very strongly to the 12-fold $1s$ exciton states considered here.

B. Line-shape analysis

An important development to be expected in the future is to establish a practical way of line-shape analysis of reflectance spectra. (Except for special cases as in Ref. 2, absorption spectroscopy is not possible with high accuracy.) Since we have to deal with many oscillators lying very closely to each other and interacting through various mechanisms, we cannot easily estimate the resonance energies and oscillator strengths of the oscillators simply from the appearance of reflectance spectra. Thus we cannot avoid line-shape analysis in order to obtain correct informations from experiments. This is a very important step in carrying out the analysis of measurements in terms of the general theory developed here.

C. Meaning of the parameters

When we analyze measurements in terms of this theory, we obtain the values of the effective parameters (as defined as the coefficients of invariants in the effective Hamiltonian) of a given exciton problem, for example, exciton masses, g -values, deformation potential constants, and so on. These parameters are related with more fundamental material constants which are defined with respect to Bloch bands. As mentioned in Sec. IV E 4, this relation was calculated in the case of the magneto-optical problem of the $\Gamma_8 \times \Gamma_6$ excitons by means of second-order perturbation theory.⁸ Since the contribution of the exciton excited states proved to be important in this case,²⁴ it is expected to be appreciable also in some of the other cases. But there is no other example of such a detailed calculation in wurtzite structure and for other symmetry-breaking effects. It is desirable to have such relationships in various cases. It is one of the most important future problems of this theory.

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APPENDIX: MIXING SCHEME DUE TO K -LINEAR TERM

In Ref. 4 this effect is considered in connection with magneto-optical studies. Therefore the representation of the mixing scheme for various quantization axes is desirable. Here we reproduce the cases of the other two principal crystal axes.

TABLE XIX. The k -linear matrix for the [111] quantization axis.

	$ 2,2\rangle$	$ 2,1\rangle$	$ 2,0\rangle$	$ 2,-1\rangle$	$ 2,-2\rangle$	$ 1,1\rangle$	$ 1,0\rangle$	$ 1,-1\rangle$
$\frac{4}{\sqrt{3}}\bar{\epsilon}_1 K$	0	$-i\sqrt{3}\bar{\xi}$	$-\bar{\xi}$	$-\sqrt{6}\bar{\xi}$	0	$i\bar{\xi}$	$\bar{\xi}$	$3\sqrt{2}\bar{\xi}$
		0	$i\sqrt{2}\bar{\xi}$	0	$-\sqrt{6}\bar{\xi}$	0	$-i\sqrt{8}\bar{\xi}$	$-\sqrt{2}\bar{\xi}$
			0	$i\sqrt{2}\bar{\xi}$	$\bar{\xi}$	$i\sqrt{6}\bar{\xi}$	0	$i\sqrt{6}\bar{\xi}$
(H.c.)				0	$-i\sqrt{3}\bar{\xi}$	$-\sqrt{2}\bar{\xi}$	$-i\sqrt{8}\bar{\xi}$	0
					0	$-3\sqrt{2}\bar{\xi}$	$\bar{\xi}$	$i\bar{\xi}$

TABLE XX. The k -linear matrix for the [110] quantization axis.

	$ 2,2\rangle$	$ 2,1\rangle$	$ 2,0\rangle$	$ 2,-1\rangle$	$ 2,-2\rangle$	$ 1,1\rangle$	$ 1,0\rangle$	$ 1,-1\rangle$
$-\bar{\epsilon}_1 K$	$-2\sqrt{3}\bar{\xi}$	$-i\sqrt{3}\bar{\xi}$	$\sqrt{2}\bar{\xi}$	$-i\sqrt{27}\bar{\xi}$	0	$i\bar{\xi}$	$-\sqrt{2}\bar{\xi}$	$9i\bar{\xi}$
		$4\sqrt{3}\bar{\xi}$	$i\sqrt{2}\bar{\xi}$	0	$-i\sqrt{27}\bar{\xi}$	$-6\bar{\xi}$	$-i\sqrt{8}\bar{\xi}$	$2\bar{\xi}$
			0	$i\sqrt{2}\bar{\xi}$	$-\sqrt{2}\bar{\xi}$	$i\sqrt{6}\bar{\xi}$	$6\sqrt{3}\bar{\xi}$	$i\sqrt{6}\bar{\xi}$
(H.c.)				$-4\sqrt{3}\bar{\xi}$	$-i\sqrt{3}\bar{\xi}$	$2\bar{\xi}$	$-i\sqrt{8}\bar{\xi}$	$-6\bar{\xi}$
					$2\sqrt{3}\bar{\xi}$	$9i\bar{\xi}$	$-\sqrt{2}\bar{\xi}$	$i\bar{\xi}$

[111] and [110]. We omit the diagonal block for $\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}$, since it is always zero.

For the [111] axis, Eq. (4.24) leads to the matrix in Table XIX, where $K\bar{\xi}$ and $K\bar{\xi}$ are the [111] and $[1\bar{1}0]$ components of \bar{K} , respectively, and the third component is assumed to be zero.

For the [110] axis, H_K can be expressed as in Table XX, where $K\bar{\xi}$ and $K\bar{\xi}$ are defined as the [110] and $[1\bar{1}0]$ components of \bar{K} , respectively, and the third component is assumed to be zero.

From these matrices, we see the following

peculiar aspects: (i) There is a mixing between the $J=1$ and 2 states. (ii) This mixing is very selective between the components of the $|J, M_J\rangle$ states, depending on the quantization axis and the direction of \bar{K} . (iii) There is a further splitting of the exciton states.²⁵

Consequently, (a) there occurs a relaxation of the optical selection rules, namely, the $J=2$ states become allowed without any external perturbation, and (b) the allowed components can be selectively observed by splitting the states in a magnetic field.

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¹³The $\vec{\Gamma}$ dependence of the H_{ex} leads to the nonspherical exchange interaction of the form $(j_x^2 \sigma_x + j_y^2 \sigma_y + j_z^2 \sigma_z)$ in a zinc-blende structure, where $\vec{j} = \vec{\Gamma} + \vec{\sigma}$, ($j = \frac{3}{2}$). This term is not of interest to us, because the assumption of s - and p -like Bloch states as the basis automatically gives a vanishing coefficient for this term. This is still true, even if one considers the orbital mixing of d -like states into p -like ones (e.g., $d_{yz} - p_x$ mixing). One gets a finite contribution only when one uses such wave functions that the Bloch states with $j_x = \pm \frac{3}{2}$ are spin mixed, which is a rather higher-order effect.

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