

Theory of degenerate 1s excitons in zinc-blende-type crystals in a magnetic field: Exchange interaction and cubic anisotropy

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The magneto-optical behavior of the eightfold 1s-exciton states arising from the Γ_6 conduction and Γ_8 valence-band pair is studied. The effective Hamiltonian for these states is obtained by symmetry considerations as the sum of invariant terms with appropriate coefficients. The explicit forms of the coefficients are described in terms of the band parameters by using the perturbational scheme proposed by Altarelli and Lipari. The most general forms for the Γ_6 and Γ_8 band edges are considered as well as the electron-hole exchange interaction. By separating the problem into a spherical part and an anisotropic part of cubic symmetry, a clear-cut view is obtained with respect to the dependence of the optical spectrum on the direction of the magnetic field. The result is expressed in matrix forms for the magnetic field along the $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ crystal axes.

I. INTRODUCTION

Although there have been many studies on various aspects of excitons in solids, the nature of the highly degenerate exciton states resulting from the degeneracy of the bands is still one of the main points of interest to be clarified. For the study of these kinds of systems, magneto-optical measurements are very powerful, because in a magnetic field all the degenerate levels split into sublevels, each of which has its own characteristic oscillator strength and polarization. The theory applicable to such measurements has not yet been fully developed. Recently Altarelli and Lipari¹ (hereafter referred to as AL) proposed a perturbational approach to the 1s excitons in zinc-blende-type semiconductors by extending the method of Baldereschi and Lipari² (BL, hereafter) in the presence of a magnetic field. In this approach, one treats the effect of the magnetic field and the nonspherical part of the valence bands as perturbations. Thus one can write down all the matrix elements in terms of the hydrogenlike wave functions, which provides a good view through this complicated problem. What AL have actually calculated, however, is not satisfactory for experimental analysis for the following reasons: (a) The calculation was done only for $\vec{H} \parallel \langle 001 \rangle$, where one has no essential contribution from the anisotropic terms (in contrast to the other configurations). (b) The electron-hole exchange interaction which was neglected by them turns out to be very important for the low-field splitting patterns in many substances. (c) Some important correction terms are missing in their results within the second-order perturbation.

In this paper, we study the problem from a more general point of view with respect to the above-mentioned drawbacks and the perturbational approach. We first derive the general form of the effective Hamiltonian for the eightfold states of the

1s exciton from symmetry considerations. In this paper we restrict the treatment to excitons with vanishing translational wave vector $\vec{k}$. (The effect of the finiteness of $\vec{k}$ is discussed separately.³) Then the effective Hamiltonian is a sum of invariant terms composed of the magnetic field $\vec{H}$ and the effective spin operators $\vec{\sigma}$ ($\sigma = \frac{1}{2}$) and $\vec{J}$ ($J = \frac{3}{2}$) for the electron and hole, respectively. This Hamiltonian contains all the information about the energies of the exciton states and their optical selection rules including their dependences on the direction of the magnetic field. As the next stage, we calculate the explicit forms of the coefficients of the invariant terms by means of AL's perturbational scheme and see the contribution of the first- and second-order perturbations. Finally we reduce the general expression for the exciton energies to a matrix form with the basis quantized along the magnetic field. This representation makes it easier to compare the result with experiments.

II. EFFECTIVE HAMILTONIAN

The exciton states under consideration consist of eight pair states arising from the Γ_6 and Γ_8 bands. The degeneracy of each band can be described in terms of the effective spin operators $\vec{\sigma}$ or $\vec{J}$ according to the method of Luttinger.⁴ The effective Hamiltonian should be expressed as the sum of invariant terms which can be formed by the various combination of $\vec{\sigma}$, $\vec{J}$, and $\vec{H}$. Since we are interested in the low field case in this paper, we drop the terms of order higher than H^2 . In Table I, we list the transformation properties of the independent components of these three quantities. From this table together with their time-reversal properties, one can easily form various invariant expressions. Since the coefficients of the invariant terms obtainable from the products given in Table II turn out to be zero within the following perturba-

TABLE I. Transformation properties of $\vec{\sigma}$, $\vec{J}$, and $\vec{H}$.

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
$\vec{\sigma}$	1			$(\sigma_x, \sigma_y, \sigma_z)$	
$\vec{J}$	1	$J_x J_y, J_z$ $+ J_z J_y J_x$	(J_x^2, J_y^2)	(J_x, J_y, J_z)	$(V_x, V_y, V_z)^a$ $(U_x, U_y, U_z)^a$
$\vec{H}$	H^2		(H_x^2, H_y^2)	(H_x, H_y, H_z)	$(H_y H_z, H_z H_x, H_x H_y)$

$$^a V_x = \{(J_y^2 - J_z^2)J_x\}, U_x = \{J_y J_z\}, \{AB\} = (AB + BA)/2.$$

$$V_y = \{(J_z^2 - J_x^2)J_y\}, U_y = \{J_z J_x\},$$

$$V_z = \{(J_x^2 - J_y^2)J_z\}, U_z = \{J_x J_y\}.$$

The axes x , y , and z are parallel to the three $\langle 001 \rangle$ crystal axes.

tional calculation of Sec. III, we omit these terms from the following equation. With this condition, the general form of the effective Hamiltonian is given by

$$E = E_B + \tilde{\Delta}_1 \vec{J} \cdot \vec{\sigma} + \tilde{\Delta}_2 (\sigma_x J_x^3 + \sigma_y J_y^3 + \sigma_z J_z^3) + \tilde{g}_C \mu_B \vec{\sigma} \cdot \vec{H} - 2\mu_B [\tilde{\kappa} \vec{J} \cdot \vec{H} + \tilde{q} (H_x J_x^3 + H_y J_y^3 + H_z J_z^3)] + (ea_0^*/2c)^2 \frac{1}{\mu_0} [c_1 H^2 + c_2 (\vec{J} \cdot \vec{H})^2 + c_3 (H_x H_y \{J_x J_y\} + H_y H_z \{J_y J_z\} + H_z H_x \{J_z J_x\})], \quad (2.1)$$

where $\{J_x J_y\} = (J_x J_y + J_y J_x)/2$ etc., and μ_0 and a_0^* are the mass and the Bohr radius of the exciton defined later in terms of the spherical parts of the band masses [see Eqs. (3.12) and (3.18)]. The axes x , y , and z refer to the three $\langle 001 \rangle$ crystal axes, μ_B is the Bohr magneton, $-e$ is the electron charge, and c is the light velocity. The nine parameters (E_B , $\tilde{\Delta}_1$, $\tilde{\Delta}_2$, $\tilde{g}_C$, $\tilde{\kappa}$, $\tilde{q}$, c_1 , c_2 , c_3) describe the exciton energies in low magnetic fields completely. The splitting pattern and the optical selection rules will be discussed in later sections.

III. EFFECTIVE-MASS EQUATIONS AND A PERTURBATIONAL TREATMENT

A.

For the excitons arising from the Γ_6 and Γ_8 band pair, the effective-mass equations without exchange interaction are given by

$$EB_{ij}(\vec{r}_e, \vec{r}_h) = \sum_{i'} \sum_{j'} \{ \delta_{ij}, H_{ii'}^{(e)} [\vec{p}_e + (e/c)\vec{A}_e] - \delta_{ii'}, H_{jj'}^{(v)} [\vec{p}_h - (e/c)\vec{A}_h] - \delta_{ii'}, \delta_{jj'}, e^2/\epsilon |\vec{r}_e - \vec{r}_h| \} B_{i',j'}(\vec{r}_e, \vec{r}_h). \quad (3.1)$$

The indexes $i(i')$ and $j(j')$ refer to the conduction and valence bands, respectively; $\vec{r}$, $\vec{p}$, and $\vec{A}$ are the coordinate, its conjugate momentum, and the vector potential, respectively, with suffixes e for the electron and h for the hole; and ϵ is the static

dielectric constant. It should be emphasized that the function B_{ij} is the amplitude of the exciton state on the i th conduction band and on the j th hole states (not the j th missing electron state). The effective Hamiltonian formalism by Luttinger⁴ provides the most general forms of $H^{(e)}$ and $H^{(v)}$. But $H^{(v)}$ in Eq. (3.1) is not the so-called Luttinger Hamiltonian itself. As seen in Appendix A, all the signs of the effective angular momentum operators in Luttinger's formalism, J_x , J_y , and J_z , should be reversed, which changes the signs of the terms in the original Luttinger Hamiltonian with odd powers of $\vec{J}$, that is, $H^{(v)}$ in Eq. (3.1) is the Luttinger Hamiltonian with reversed signs for the κ , q , and $\vec{k}$ linear terms. Thus,

$$H^{(e)}(\vec{k}) = k^2/2m_e^* + g_c \mu_B \vec{\sigma} \cdot \vec{H}, \quad (3.2)$$

$$-H^{(v)}(\vec{k}) = (1/m_0) [(\gamma_1 + \frac{5}{2}\gamma_2)k^2/2 - \gamma_2(k_x^2 J_x^2 + k_y^2 J_y^2 + k_z^2 J_z^2) - 2\gamma_3(\{k_x k_y\}\{J_x J_y\} + \text{cycl. perm.})] - 2\mu_B \kappa \vec{J} \cdot \vec{H} - 2\mu_B q (H_x J_x^3 + H_y J_y^3 + H_z J_z^3) + K_l (k_x \{J_y^2 - J_z^2\} J_x + \text{cycl. perm.}), \quad (3.3)$$

where m_e^* and g_c are the mass and the g factor of the conduction electron, m_0 is the free-electron mass, $(\gamma_1, \gamma_2, \gamma_3, \kappa, q)$ are the Luttinger parameters,⁴ K_l is the coefficient of the $\vec{k}$ linear term, and cycl. perm. means the cyclic permutation of the preceding term. As for the electron-hole exchange interaction, we add to the effective-mass Hamiltonian in (3.1) the following terms,⁵

$$H_{\text{exch}} = \Delta_0 + \Delta_1 \vec{J} \cdot \vec{\sigma} + \Delta_2 (\sigma_x J_x^3 + \sigma_y J_y^3 + \sigma_z J_z^3). \quad (3.4)$$

Concerning the approximation used in (3.4) see the last paragraph of Appendix A.

B.

For the further calculation, we rewrite Eq. (3.1) in terms of the coordinates for the relative and the

TABLE II. Omitted invariant terms.^a

$\Gamma_1(H^2) \times \Gamma_1(\Gamma_4(\vec{\sigma}) \times \Gamma_4(\vec{J}))$
$\Gamma_1(H^2) \times \Gamma_1(\Gamma_4(\vec{\sigma}) \times \Gamma_4(J^3))$
$\Gamma_4(\Gamma_2(J^3) \times \Gamma_5(H^2)) \times \Gamma_4(\vec{\sigma})$
$\Gamma_4(\Gamma_3(J^2) \times \Gamma_4(\vec{H})) \times \Gamma_4(\vec{\sigma})$
$\Gamma_4(\Gamma_5(\vec{V}) \times \Gamma_3(H^2)) \times \Gamma_4(\vec{\sigma})$
$\Gamma_4(\Gamma_5(\vec{V}) \times \Gamma_5(H^2)) \times \Gamma_4(\vec{\sigma})$
$\Gamma_4(\Gamma_5(\vec{U}) \times \Gamma_4(\vec{H})) \times \Gamma_4(\vec{\sigma})$

^a $\Gamma_i(X)$ means the Γ_i component of the quantity X tabulated in Table I. The first invariant term of this table, for example, is therefore $H^2 \vec{\sigma} \cdot \vec{J}$.

translational motions,

$$\vec{r} = \vec{r}_e - \vec{r}_h, \quad (3.5)$$

$$\vec{R} = (m_e^* \vec{r}_e + m_h^* \vec{r}_h) / (m_e^* + m_h^*). \quad (3.6)$$

Although $m_e^* = m_h^*$ was chosen in the former treatments,^{6,7} we choose here as the hole mass

$$m_h^* = m_0 / \gamma_1. \quad (3.7)$$

The final form of the effective-mass Hamiltonian is given by

$$H = H^{(0)} [\vec{p} + (e/c) \vec{A} + m_e^* \hbar \vec{K} / (m_e^* + m_h^*)] \\ - H^{(v)} [-\vec{p} + (e/c) \vec{A} + m_h^* \hbar \vec{K} / (m_e^* + m_h^*)]$$

$$- e^2 / \epsilon r + H_{\text{exch}}, \quad (3.8)$$

where $\vec{K}$ is the wave vector corresponding to the coordinate $\vec{R}$, and $\vec{p}$ and $\vec{A}$ refer to the relative motion. Since the magnitude of $\vec{K}$ is very small in the case of our interest, we neglect the terms containing $\vec{K}$ in (3.8). Then we divide H into two parts

$$H = H_s + H', \quad (3.9)$$

where

$$H_s = (p^2 / 2\mu_0 - e^2 / \epsilon r) \delta_{ii} \delta_{jj'}, \quad (3.10)$$

$$H' = H_d + H_l + H_q + H_{k1} + H_{k2} + H_{\text{exch}}, \quad (3.11)$$

$$1/\mu_0 = 1/m_e^* + \gamma_1/m_0, \quad (3.12)$$

$$H_d = (\gamma_2/m_0) [\frac{5}{4} p^2 - (p_x^2 J_x^2 + p_y^2 J_y^2 + p_z^2 J_z^2)] - (2\gamma_3/m_0) (p_x p_y \{J_x J_y\} + \text{cycl. perm.}), \quad (3.13)$$

$$H_l = \frac{eH}{2c} \left(\frac{1}{m_e^*} - \frac{\gamma_1 + \frac{5}{2} \gamma_2}{m_0} \right) [\bar{\xi} (y p_z - z p_y) + \text{cycl. perm.}] + \frac{eH}{m_0 c} \gamma_2 [(\bar{\eta} z - \bar{\xi} y) p_x J_x^2 + \text{cycl. perm.}] \\ + \frac{eH}{m_0 c} \gamma_3 [\bar{\xi} (x p_z - y p_y) - \bar{\xi} z p_x + \bar{\eta} z p_y] \{J_x J_y\} + \text{cycl. perm.} + \mu_B [-2\kappa \vec{J} \cdot \vec{H} - 2qH(\bar{\xi} J_x^2 + \bar{\eta} J_y^2 + \bar{\xi} J_z^2) + g_c \vec{\sigma} \cdot \vec{H}], \quad (3.14)$$

$$H_q = \left(\frac{eH}{2c} \right)^2 \left\{ \left(\frac{1}{2\mu_0} + \frac{5}{4} \frac{\gamma_2}{m_0} \right) [(\bar{\eta} z - \bar{\xi} y)^2 + \text{cycl. perm.}] - \frac{\gamma_2}{m_0} [(\bar{\eta} z - \bar{\xi} y)^2 J_x^2 + \text{cycl. perm.}] \right. \\ \left. - 2 \frac{\gamma_3}{m_0} [(\bar{\eta} z - \bar{\xi} y)(\bar{\xi} x - \bar{\xi} z) \{J_x J_y\} + \text{cycl. perm.}] \right\}, \quad (3.15)$$

$$H_{k1} = -K_l [p_x \{J_y^2 - J_z^2\} J_x + \text{cycl. perm.}], \quad (3.16)$$

$$H_{k2} = \frac{eH}{2c} K_l [(\bar{\eta} z - \bar{\xi} y) \{J_y^2 - J_z^2\} J_x + \text{cycl. perm.}], \quad (3.17)$$

where $(\bar{\xi}, \bar{\eta}, \bar{\xi})$ are direction cosines of the magnetic field $\vec{H}$. Following the method of BL and AL, we take H_s as the unperturbed Hamiltonian. Then the Rydberg energy $\mathcal{R}^*$ and the Bohr radius a_0^* of the exciton and the γ factor are given by

$$\mathcal{R}^* = \mu_0 e^4 / 2 \hbar^2 \epsilon^2, \quad a_0^* = \epsilon \hbar^2 / \mu_0 e^2, \quad \gamma = e \hbar H / 2 \mu_0 c \mathcal{R}^*. \quad (3.18)$$

Before going into the details of the perturbational calculation, it is useful to note the character of each term in H' : In the first order, only parts of H_d , H_l , and H_{exch} give nonvanishing contributions. In the second order, the nd states of the hydrogen-like series contribute through H_d , H_l , and H_q , the np states through H_{k1} and H_{k2} , and the ns states through H_q . After lengthy calculations we are able to express the coefficients of the invariant terms in (2.1) in terms of the more fundamental material parameters in (3.2)–(3.4):

$$E_B = -\mathcal{R}^* + \Delta_0 - b_1 - b_2, \quad (3.19a)$$

$$\tilde{\Delta}_1 = \Delta_1, \quad (3.19b)$$

$$\tilde{\Delta}_2 = \Delta_2, \quad (3.19c)$$

$$\tilde{g}_c = g_c, \quad (3.19d)$$

$$\tilde{\kappa} = \kappa - d - \frac{13}{6} d(\tau - 1) + \frac{1}{6} f, \quad (3.19e)$$

$$\tilde{q} = q + \frac{2}{3} d(\tau - 1) - \frac{2}{3} f, \quad (3.19f)$$

$$c_1 = 1 - \nu - \frac{5}{4} \delta', \quad (3.19g)$$

$$c_2 = \delta', \quad (3.19h)$$

$$c_3 = 2\delta' \left(\frac{1}{\tau} - 1 \right) + 2\sigma', \quad (3.19i)$$

where b_1 and b_2 are the corrections for the binding energy due to the H_d^2 and H_{k1}^2 terms, respectively, which were calculated by BL [see their Eqs. (13a) and (22)]. Their H_p and μ_3 correspond to our H_{k1} and $2m_0\mu_0/K_l$, respectively], and

$$d = \frac{32}{5} (\mu_0/m_0) \gamma_3^2 M, \quad (3.20a)$$

$$\tau = \gamma_2/\gamma_3, \quad (3.20b)$$

$$f = 4(m_0/\mu_0) G(\mu_0 a_0^* K_l / \hbar)^2, \quad (3.20c)$$

$$\nu = \frac{16}{15} (\mu_0 \gamma_2 / m_0)^2 (2 + 3/\tau^2) (3N + W), \quad (3.20d)$$

$$\delta' = (1 + 16W/15) \mu_0 \gamma_2 / m_0, \quad (3.20e)$$

$$\sigma' = 2F(\mu_0 a_0^* K_l / \hbar)^2. \quad (3.20f)$$

The definition of the constants M , G , N , W , and F is given in Appendix B, and their numerical values are given by

$$M = 0.281, \quad (3.21a)$$

$$G = 0.375, \quad (3.21b)$$

$$N = 0.469, \quad (3.21c)$$

$$W = 0.719, \quad (3.21d)$$

$$F = 0.844. \quad (3.21e)$$

In the above expressions (3.19a-i), the terms d and $d(\tau-1)$ are due to $H_d H_l$. This contribution was calculated by AL, but a part of the term, i. e., τd , is missing in their result. The terms f and σ' are due to $H_{k1} H_{k2}$ and H_{k2}^2 , respectively, δ' comes from H_q and $H_d H_q$, and ν is due to H_l^2 and $H_d H_q$. AL neglected the contribution from $H_d H_q$, but it turns out to be important because the terms containing W make considerable contributions.

IV. SPLITTING PATTERNS AND SELECTION RULES

Since we are now able to estimate the values of the coefficients of the invariant terms in (2.1) from a given set of material constants, we discuss the splitting patterns and the optical selection rules of the 1s-exciton states in a magnetic field by using the effective Hamiltonian (2.1). We use a matrix representation of (2.1) which is convenient for the analysis of experiments. For the quantization axis of the basis functions, *we always take the axis along the magnetic field H (ξ axis)*. We denote the eigenfunctions of σ_z and J_z as $\{\alpha, \beta\}$ and $\{|\frac{3}{2}, \pm\frac{3}{2}\rangle, |\frac{3}{2}, \pm\frac{1}{2}\rangle\}$, respectively. In the present treatment of the excitons, we are emphasizing the importance of the exchange interaction. Therefore we use the $|J^{(t)}, J_z^{(t)}\rangle$ basis, where

$$\vec{J}^{(t)} = \vec{J} + \vec{\sigma} \quad (J^{(t)} = 2 \text{ or } 1). \quad (4.1)$$

This basis diagonalizes the Δ_1 -exchange interaction. The relation between $|J^{(t)}, J_z^{(t)}\rangle$ and $\{\alpha, \beta\} \times |J, J_z\rangle$ is given by

$$|2, 2\rangle = \left| \frac{3}{2}, \frac{3}{2} \right\rangle \alpha, \quad (4.2a)$$

$$|2, 1\rangle = \frac{\sqrt{3}}{2} \left| \frac{3}{2}, \frac{1}{2} \right\rangle \alpha + \frac{1}{2} \left| \frac{3}{2}, \frac{3}{2} \right\rangle \beta, \quad (4.2b)$$

$$|2, 0\rangle = \frac{1}{\sqrt{2}} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle \alpha + \frac{1}{\sqrt{2}} \left| \frac{3}{2}, \frac{1}{2} \right\rangle \beta, \quad (4.2c)$$

$$|2, -1\rangle = \frac{1}{2} \left| \frac{3}{2}, -\frac{3}{2} \right\rangle \alpha + \frac{\sqrt{3}}{2} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle \beta, \quad (4.2d)$$

$$|2, -2\rangle = \left| \frac{3}{2}, -\frac{3}{2} \right\rangle \beta, \quad (4.2e)$$

$$|1, 1\rangle = -\frac{1}{2} \left| \frac{3}{2}, \frac{1}{2} \right\rangle \alpha + \frac{\sqrt{3}}{2} \left| \frac{3}{2}, \frac{3}{2} \right\rangle \beta, \quad (4.2f)$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle \alpha - \frac{1}{\sqrt{2}} \left| \frac{3}{2}, \frac{1}{2} \right\rangle \beta, \quad (4.2g)$$

$$|1, -1\rangle = \frac{\sqrt{3}}{2} \left| \frac{3}{2}, -\frac{3}{2} \right\rangle \alpha - \frac{1}{2} \left| \frac{3}{2}, -\frac{1}{2} \right\rangle \beta. \quad (4.2h)$$

Among these states $|1, 1\rangle$, $|1, 0\rangle$, and $|1, -1\rangle$ are electric dipole active for the σ_+ , π , and σ_- polarizations, respectively, and other states are dipole inactive in the absence of the external perturbations.

The expression (2.1) can be divided into two parts: The one is spherical and the other is anisotropic with respect to the dependence of the optical spectrum on the direction of the applied magnetic field.

A. Spherical case

This case is defined by the relations

$$\tilde{\Delta}_2 = 0, \quad \tilde{q} = 0, \quad c_3 = 0. \quad (4.3)$$

Then the 8×8 matrix (2.1) can be reduced into three 2×2 and two 1×1 matrices by choosing the quantization axis along the magnetic field. They are given by the sum of the common diagonal term

$$(E_B + \bar{c}) \underline{1} \quad (4.4)$$

and the following submatrices; for the states $|2, 2\rangle$ and $|2, -2\rangle$ (the order along the rows and columns)

$$\left(\frac{3}{4} \tilde{\Delta}_1 + \bar{c}_2 \right) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \left(\frac{1}{2} \bar{g}_c - 3\bar{\kappa} \right) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad (4.5a)$$

for the states $|2, 1\rangle$ and $|1, 1\rangle$,

$$-2\bar{\kappa} \underline{1} + \frac{1}{4} \tilde{\Delta}_1 \begin{pmatrix} 3 & 0 \\ 0 & -5 \end{pmatrix} + \frac{1}{4} (\bar{g}_c + 2\bar{\kappa} - 2\bar{c}_2) \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}; \quad (4.5b)$$

for the states $|2, -1\rangle$ and $|1, -1\rangle$,

$$+2\bar{\kappa} \underline{1} + \frac{1}{4} \tilde{\Delta}_1 \begin{pmatrix} 3 & 0 \\ 0 & -5 \end{pmatrix} - \frac{1}{4} (\bar{g}_c + 2\bar{\kappa} + 2\bar{c}_2) \begin{pmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{pmatrix}; \quad (4.5c)$$

and for the states $|2, 0\rangle$ and $|1, 0\rangle$,

$$\begin{pmatrix} \frac{3}{4} \tilde{\Delta}_1 - \bar{c}_2 & \bar{\kappa} + \frac{1}{2} \bar{g}_c \\ \bar{\kappa} + \frac{1}{2} \bar{g}_c & -\frac{5}{4} \tilde{\Delta}_1 - \bar{c}_2 \end{pmatrix}; \quad (4.5d)$$

where

$$\bar{g}_c = \tilde{g}_c \mu_B H, \quad (4.6a)$$

$$\bar{\kappa} = \tilde{\kappa} \mu_B H, \quad (4.6b)$$

$$\bar{c} = \frac{1}{2} \gamma^2 \mathcal{R}^*(c_1 + \frac{5}{4} c_2), \quad (4.6c)$$

$$\bar{c}_2 = \frac{1}{2} \gamma^2 \mathcal{R}^* c_2. \quad (4.6d)$$

Since the system is axially symmetric along the ξ axis, only the states with the same J_z values mix

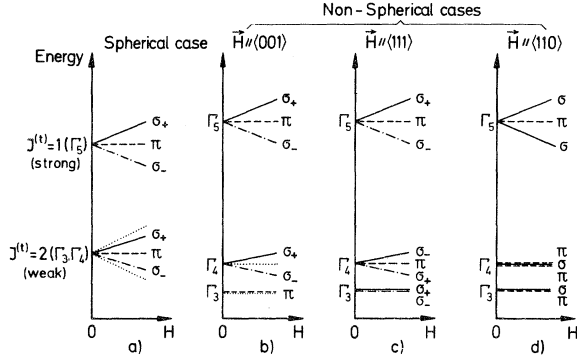


FIG. 1. Examples of the initial splitting. The ordering and the separation of the σ spectrum is arbitrarily taken. Negative values of $\tilde{\Delta}_1$ and $\tilde{\Delta}_2$ are used. Dotted lines are not observable. The energies at zero field are $E(\Gamma_5) = -\frac{5}{4}\tilde{\Delta}_1 - \frac{41}{16}\tilde{\Delta}_2$, $E(\Gamma_3) = \frac{3}{4}\tilde{\Delta}_1 + \frac{39}{16}\tilde{\Delta}_2$, $E(\Gamma_4) = \frac{3}{4}\tilde{\Delta}_1 + \frac{15}{16}\tilde{\Delta}_2$.

with each other. We can observe the $|2, 1\rangle$, $|2, 0\rangle$, and $|2, -1\rangle$ states as weak lines in the σ_+ , π , and σ_- spectra, respectively. The states $|2, \pm 2\rangle$ are not observable in this case. An example of the linear splitting pattern is given in Fig. 1(a).

One may regard the spherical case as the main framework of the magneto-optical spectrum of the $1s$ -exciton states. While the splitting pattern is independent of the direction of the magnetic field in this case, the remaining terms ($\tilde{\Delta}_2$, $\tilde{q}$, c_3) do give the directional dependence which leads to some extra complications in the splitting pattern as described in the next subsection.

B. Nonspherical cases

Here we consider the effects of the $\tilde{\Delta}_2$, $\tilde{q}$, and c_3 terms which depend on the choice of the ξ axis. We now need the explicit forms of J_ξ (σ_ξ) and J_η (σ_η) which together with J_z (σ_z) compose the three perpendicular components of the angular momentum vector $\vec{J}$ ($\vec{\sigma}$). We choose the following representation:

$$J_\xi + iJ_\eta = \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad J_\xi = \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}, \quad (4.7)$$

$$J_\xi - iJ_\eta = \begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix},$$

$$\sigma_\xi + i\sigma_\eta = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \sigma_\xi = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (4.8)$$

$$\sigma_\xi - i\sigma_\eta = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

For a given direction of the magnetic field, we first rewrite the anisotropic terms in (2.1) in terms of the (ξ, η, ζ) components of $\vec{J}$ and $\vec{\sigma}$, and then, with the aid of (4.7) and (4.8), we get the matrix representation of the anisotropic terms for the basis functions (4.2).

1. $\vec{H} \parallel \langle 001 \rangle$

The additional terms to the spherical part, (4.4) and (4.5), are reduced to the following four 2×2 submatrices: for the states $|2, 2\rangle$ and $|2, -2\rangle$ (the order along the rows and columns)

$$\frac{1}{16} \begin{pmatrix} 27(\tilde{\Delta}_2 - 4\tilde{q}) & 12\tilde{\Delta}_2 \\ 12\tilde{\Delta}_2 & 27(\tilde{\Delta}_2 + 4\tilde{q}) \end{pmatrix}; \quad (4.9a)$$

for the states $|2, 1\rangle$ and $|1, 1\rangle$,

$$\frac{1}{16} \begin{pmatrix} 15(\tilde{\Delta}_2 - 2\tilde{q}) & -26\sqrt{3}\tilde{q} \\ -26\sqrt{3}\tilde{q} & -41(\tilde{\Delta}_2 + 2\tilde{q}) \end{pmatrix}; \quad (4.9b)$$

for the states $|2, -1\rangle$ and $|1, -1\rangle$,

$$\frac{1}{16} \begin{pmatrix} 15(\tilde{\Delta}_2 + 2\tilde{q}) & 26\sqrt{3}\tilde{q} \\ 26\sqrt{3}\tilde{q} & -41(\tilde{\Delta}_2 - 2\tilde{q}) \end{pmatrix}; \quad (4.9c)$$

and for the states $|2, 0\rangle$ and $|1, 0\rangle$,

$$\frac{1}{16} \begin{pmatrix} 39\tilde{\Delta}_2 & 4\tilde{q} \\ 4\tilde{q} & -41\tilde{\Delta}_2 \end{pmatrix}; \quad (4.9d)$$

where

$$\tilde{q} = \tilde{q} \mu_B H. \quad (4.10)$$

The matrices (4.9) have essentially the same structure as those of (4.5): The states $|2, 1\rangle$, $|2, 0\rangle$, and $|2, -1\rangle$ can be seen as weak lines in the σ_+ , π , and σ_- spectra, respectively. Although the states $|2, \pm 2\rangle$ mix with each other, they still remain dipole inactive. An example of the initial splitting is shown in Fig. 1(b). The only qualitative difference between this and the spherical cases is the existence of the Γ_3 - Γ_4 splitting, that is, the weak lines in σ and π spectra converge to different energies at zero field. The effect of the $\tilde{q}$ term appears as a correction to the effective g values. The c_3 term makes no contribution in this case.

2. $\vec{H} \parallel \langle 111 \rangle$

The additional matrix is reduced to the following two 3×3 and one 2×2 matrices: for the states $|2, 2\rangle$, $|2, -1\rangle$, and $|1, -1\rangle$ (the order along the rows and columns),

$$\frac{1}{16} \begin{pmatrix} 23(\tilde{\Delta}_2 - 4\bar{q}) + 4\bar{c}_3 & -i8\sqrt{2}(\tilde{\Delta}_2 - \bar{q}) & -i8\sqrt{6}\bar{q} \\ i8\sqrt{2}(\tilde{\Delta}_2 - \bar{q}) & 31(\tilde{\Delta}_2 + 2\bar{q}) - 2\bar{c}_3 & 2\sqrt{3}(5\bar{q} + \bar{c}_3) \\ i8\sqrt{6}\bar{q} & 2\sqrt{3}(5\bar{q} + \bar{c}_3) & -41(\tilde{\Delta}_2 - 2\bar{q}) + 2\bar{c}_3 \end{pmatrix}; \quad (4.11a)$$

for the states $|2, -2\rangle$, $|2, 1\rangle$, and $|1, 1\rangle$,

$$\frac{1}{16} \begin{pmatrix} 23(\tilde{\Delta}_2 + 4\bar{q}) + 4\bar{c}_3 & -i8\sqrt{2}(\tilde{\Delta}_2 + \bar{q}) & i8\sqrt{6}\bar{q} \\ i8\sqrt{2}(\tilde{\Delta}_2 + \bar{q}) & 31(\tilde{\Delta}_2 - 2\bar{q}) - 2\bar{c}_3 & 2\sqrt{3}(-5\bar{q} + \bar{c}_3) \\ -i8\sqrt{6}\bar{q} & 2\sqrt{3}(-5\bar{q} + \bar{c}_3) & -41(\tilde{\Delta}_2 + 2\bar{q}) + 2\bar{c}_3 \end{pmatrix}; \quad (4.11b)$$

and for the states $|2, 0\rangle$ and $|1, 0\rangle$,

$$\frac{1}{16} \begin{pmatrix} 15\tilde{\Delta}_2 - 4\bar{c}_3 & 52\bar{q} \\ 52\bar{q} & -41\tilde{\Delta}_2 - 4\bar{c}_3 \end{pmatrix}; \quad (4.11c)$$

where

$$\bar{c}_3 = \frac{1}{2} \gamma^2 \mathcal{R}^* c_3. \quad (4.12)$$

In this case the states $|2, \pm 2\rangle$ become observable in the σ_- and σ_+ spectra, respectively. Since they are allowed only through the cubic anisotropy, their observation will give a good estimate of the $\tilde{\Delta}_2$, $\bar{q}$, and $\bar{c}_3$ coefficients. An example of the initial splitting is given in Fig. 1(c).

3. $\vec{H} \parallel \langle 110 \rangle$

In this case the additional matrix is reduced to two 4×4 submatrices; for the states $|2, 2\rangle$, $|2, 0\rangle$, $|2, -2\rangle$, and $|1, 0\rangle$ (the order along the rows and columns)

$$\frac{1}{16} \begin{pmatrix} 24(\tilde{\Delta}_2 - 4\bar{q}) + 6\bar{c}_3 & \sqrt{6}(3\tilde{\Delta}_2 - 6\bar{q} - \bar{c}_3) & 9\tilde{\Delta}_2 & -\sqrt{6}(6\bar{q} + \bar{c}_3) \\ \sqrt{6}(3\tilde{\Delta}_2 - 6\bar{q} - \bar{c}_3) & 21\tilde{\Delta}_2 - 6\bar{c}_3 & \sqrt{6}(3\tilde{\Delta}_2 + 6\bar{q} - \bar{c}_3) & 40\bar{q} \\ 9\tilde{\Delta}_2 & \sqrt{6}(3\tilde{\Delta}_2 + 6\bar{q} - \bar{c}_3) & 24(\tilde{\Delta}_2 + 4\bar{q}) + 6\bar{c}_3 & -\sqrt{6}(6\bar{q} - \bar{c}_3) \\ -\sqrt{6}(6\bar{q} + \bar{c}_3) & 40\bar{q} & -\sqrt{6}(6\bar{q} - \bar{c}_3) & -41\tilde{\Delta}_2 - 6\bar{c}_3 \end{pmatrix}; \quad (4.13a)$$

and for the states $|2, 1\rangle$, $|2, -1\rangle$, $|1, 1\rangle$, and $|1, -1\rangle$,

$$\frac{1}{16} \begin{pmatrix} 27(\tilde{\Delta}_2 - 2\bar{q}) - 3\bar{c}_3 & -3(4\tilde{\Delta}_2 + \bar{c}_3) & \sqrt{3}(3\bar{c}_3 - 14\bar{q}) & \sqrt{3}(12\bar{q} - \bar{c}_3) \\ -3(4\tilde{\Delta}_2 + \bar{c}_3) & 27(\tilde{\Delta}_2 + 2\bar{q}) - 3\bar{c}_3 & -\sqrt{3}(12\bar{q} + \bar{c}_3) & \sqrt{3}(3\bar{c}_3 + 14\bar{q}) \\ \sqrt{3}(3\bar{c}_3 - 14\bar{q}) & -\sqrt{3}(12\bar{q} + \bar{c}_3) & -41(\tilde{\Delta}_2 + 2\bar{q}) + 3\bar{c}_3 & 3\bar{c}_3 \\ \sqrt{3}(12\bar{q} - \bar{c}_3) & \sqrt{3}(3\bar{c}_3 + 14\bar{q}) & 3\bar{c}_3 & -41(\tilde{\Delta}_2 - 2\bar{q}) + 3\bar{c}_3 \end{pmatrix}. \quad (4.13b)$$

In this case, four lines are, in principle, observable in each of the σ and π spectra. The mixing of the σ_+ and σ_- spectra is possible through the cubic anisotropy. The states $|2, \pm 2\rangle$ are observable in the π spectrum in contrast to the previous case, $\vec{H} \parallel \langle 111 \rangle$, where they appear in the σ spectrum. An example of the initial splitting is shown in Fig. 1(d).

V. DISCUSSION

In this section we discuss the results of the pre-

vious sections from a physical point of view, which clarifies the role of each parameter.

A. Effect of the exchange interaction

The eightfold degeneracy of the 1s-exciton states is lifted by the $\tilde{\Delta}_1$ exchange interaction into threefold ($J^{(t)} = 1$, Γ_3) and fivefold ($J^{(t)} = 2$, $\Gamma_3 + \Gamma_4$) degenerate sets. The latter splits further due to the $\tilde{\Delta}_2$ -exchange interaction. The explicit forms of the wave functions belonging to each irreducible representation depend on the choice of the quantiza-

tion axis:

for a $\langle 001 \rangle$ axis

$$\Gamma_3: |2, 0\rangle, [|2, 2\rangle + |2, -2\rangle]/\sqrt{2}, \quad (5.1)$$

$$\Gamma_4: |2, \pm 1\rangle, [|2, 2\rangle - |2, -2\rangle]/\sqrt{2}; \quad (5.2)$$

for a $\langle 111 \rangle$ axis

$$\Gamma_3: [|2, 2\rangle + i\sqrt{2}|2, -1\rangle]/\sqrt{3}, \\ [|2, -2\rangle + i\sqrt{2}|2, 1\rangle]/\sqrt{3}, \quad (5.3)$$

$$\Gamma_4: [\sqrt{2}|2, 2\rangle - i|2, -1\rangle]/\sqrt{3}, \\ [\sqrt{2}|2, -2\rangle - i|2, 1\rangle]/\sqrt{3}, |2, 0\rangle; \quad (5.4)$$

for a $\langle 110 \rangle$ axis

$$\Gamma_3: [|2, 1\rangle - |2, -1\rangle]/\sqrt{2}, \\ [\sqrt{3}|2, 2\rangle + \sqrt{2}|2, 0\rangle + \sqrt{3}|2, -2\rangle]/\sqrt{8}, \quad (5.5)$$

$$\Gamma_4: [|2, 1\rangle + |2, -1\rangle]/\sqrt{2}, [|2, 2\rangle - |2, -2\rangle]/\sqrt{2}, \\ [|2, 2\rangle - \sqrt{6}|2, 0\rangle + |2, -2\rangle]/\sqrt{8}; \quad (5.6)$$

for any axis

$$\Gamma_5: |1, \pm 1\rangle, |1, 0\rangle. \quad (5.7)$$

Thus we get various splitting patterns depending on the direction of the magnetic field, as shown in Fig. 1.

The existence of the exchange splitting gives rise to the magnetic field dependence of the oscillator strength ratio between the strong and weak components of the spectrum. The oscillator strength of the Γ_3 and Γ_4 components starts from zero at $H=0$ and increases quadratically with H and then saturates. If we neglect the exchange splitting, however, the ratio of the oscillator strengths is quite different from the above case: In the non-spherical case, with $\vec{H} \parallel \langle 001 \rangle$ and $\tilde{A}_1 = \tilde{A}_2 = 0$, for example, the ratio of the two lines in each of the σ_+ , σ_- , and π spectra is (3:1), (3:1), and (1:1), respectively, independent of the magnitude of the magnetic field. This of course applies also to the spherical case. These values are the saturation values at high field in the case of the finite exchange splitting.

In both cases of GaAs and InP,⁸ one sees only strong components at low fields, and the weaker components begin to appear only at finite magnetic fields with much lower intensity ratio than the $\frac{1}{3}$ (σ) or 1 (π) expected in the absence of the exchange interaction. Therefore, it is clear that the exchange splitting exists at zero field in these materials, although we do not see it clearly when we extrapolate the high-field pattern to zero field. In the cases of CdTe,⁹ and CuBr,¹⁰ we can see the exchange splitting of ~ 0.6 meV and ~ 4 meV, respectively, by direct extrapolation of the high-field pattern. In both of them one sees a small structure in the reflectance spectrum at zero field at the energy position

of the $J^{(t)} = 2$ exciton states. It is interpreted as due to the effect of the finite translational wave vector of the exciton connected with the $\vec{k}$ -linear term of the valence band.³

In contrast to the $\tilde{A}_1$ -exchange splitting, the existence of the $\tilde{A}_2$ -exchange splitting is not definitely established. Although there is one report on CuBr,¹⁰ the assignment is not unique, and furthermore our recent measurement on the single crystal of CuBr disproves the existence of $\tilde{A}_2$ exchange splitting.¹¹

B. g factors

In the presence of the exchange splitting, the initial splitting of the $|1, \pm 1\rangle$ states in magnetic fields is given by $g_w \mu_B H$, where

$$g_w = -5\tilde{\kappa} - \tilde{g}_c/2 - 41\tilde{q}/4. \quad (5.8)$$

This value does not depend on the direction of the magnetic field, as we see from (4.9)–(4.13).

The weak-field g values of the $J^{(t)} = 2$ components show a peculiar behavior in the presence of the $\tilde{A}_2$ -exchange splitting: The Γ_3 states do not split linearly for any direction of the magnetic field. If we denote the splitting of the Γ_4 states as $f_t \mu_B H$, then we get the relations

$$f_{\langle 001 \rangle} = -3\tilde{\kappa} + \tilde{g}_c/2 - 15\tilde{q}/4, \quad (5.9a)$$

$$f_{\langle 111 \rangle} = -f_{\langle 001 \rangle}, \quad (5.9b)$$

$$f_{\langle 110 \rangle} = 0. \quad (5.9c)$$

The second equation means that the order of the σ_+ and σ_- lines of the Γ_4 states is reversed between the cases $\vec{H} \parallel \langle 001 \rangle$ and $\langle 111 \rangle$. For $\vec{H} \parallel \langle 111 \rangle$, the Γ_3 states are active for the $\sigma_{\pm}$ polarizations, but they have no linear splitting. If $\tilde{A}_2 = 0$, the splitting pattern looks more or less like that of Fig. 1(a) (with somewhat different selection rules). Therefore, we can use the above result to check the existence of an appreciable $\tilde{A}_2$ splitting.

Besides the above-mentioned g factors, we can define various effective g values; for example, the g factors for the case of $\tilde{A}_2 = 0$, or the coefficient of the nondiagonal element between $|2, 0\rangle$ and $|1, 0\rangle$ which determines the oscillator strength of the weak π line originating from $|2, 0\rangle$. All of them can be easily calculated from the matrices in Sec. 4 and the eigenstates (5.1)–(5.7). Since the effective g values are linear combinations of $\tilde{\kappa}$, $\tilde{g}_c$, and $\tilde{q}$, the measurement of several different g values is useful to determine the values of these parameters.

C. Clamping effect between the sublevels

As we see in the previous sections, the diamagnetic energies are different from sublevel to sublevel. Since c_2 (γ_2) is positive and $c_2 \gg |c_3|$ in most cases,¹² the diamagnetic shift is biggest for the

$|2, \pm 2\rangle$ states. Combining this with the fact that the $J^{(t)} = 1$ states have higher energy than the $J^{(t)} = 2$ states at zero field, we can expect a level crossing between the $|2, \pm 2\rangle$ and $J^{(t)} = 1$ states at certain finite fields. As long as the spherical assumptions (4.3) are valid, nothing happens at this crossing point in the optical spectrum. When we switch on the nonspherical interactions, however, the crossing levels interact with each other, giving rise to a clamping (anticrossing) effect. This effect depends strongly on the direction of the magnetic field.

1. $\vec{H} \parallel \langle 001 \rangle$

No clamping occurs, because the $|2, \pm 2\rangle$ states do not interact with the other states [cf. Eq. (4.9)].

2. $\vec{H} \parallel \langle 111 \rangle$

In this case the states $|2, \pm 2\rangle$ appear in the $\sigma_{\pm}$ spectra, respectively, as seen from (4.11). Therefore there occurs one clamping in each of the $\sigma_{\pm}$ spectra. This clamping will occur at higher magnetic fields than in the case of $\vec{H} \parallel \langle 110 \rangle$, because the difference in the diamagnetic energies between the clamping states is smaller for $\vec{H} \parallel \langle 111 \rangle$ than for $\vec{H} \parallel \langle 110 \rangle$.

3. $\vec{H} \parallel \langle 110 \rangle$

The clamping occurs in the π spectrum between $|1, 0\rangle$ and $|2, \pm 2\rangle$ states, as seen from (4.13a). An example is shown in Fig. 2. The corresponding σ spectrum shows nothing peculiar in this case.

The importance of the clamping effect is that it provides a peculiar way to observe the strongly forbidden states $|2, \pm 2\rangle$. Outside the clamping re-

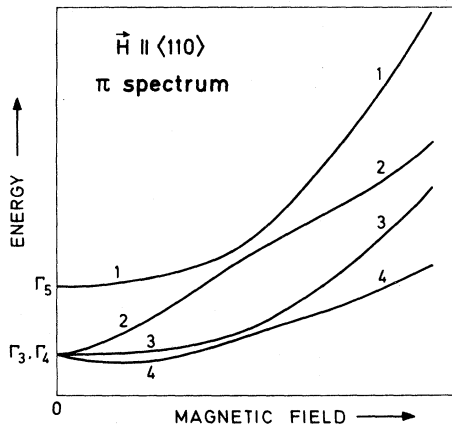


FIG. 2. An example of clamping in the π spectrum for $\vec{H} \parallel \langle 110 \rangle$. The lines 2 and 4 at lower fields and 1 and 3 at higher fields correspond to the states $|2, \pm 2\rangle$. Δ_2 is taken to be zero in this case.

gion they normally have very small oscillator strengths. As we approach the crossing point, their oscillator strengths increase very rapidly, which makes the observation easier. Although the clamping effect may not always be observed because of the linewidth, the effect will provide a peculiar spectrum in favorable cases. One can use this effect as a measure of the degree of cubic anisotropy.

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APPENDIX A

Here we discuss the proper way to connect the Luttinger Hamiltonian with the effective-mass equations of the exciton. We start from a many-electron formalism and finally give the correct description of the electron-hole two-particle picture.

We denote the one-electron band functions with the wave vector $\vec{k}$ by $\chi_{j\vec{k}}(\vec{r})$ for the j th valence band and by $\phi_{i\vec{k}}(\vec{r})$ for the i th conduction band. They form an orthonormal set (together with the higher and lower band states, whose contribution to the formation of the excitons can be neglected). Now, an electron-hole pair state can be expressed by a Slater determinant

$$\Phi_{ij}(\vec{k}, \vec{q}) = |\phi_{i\vec{k}}, \chi_{j\vec{q}}|, \quad (\text{A1})$$

which represents a state where the valence-band state $\chi_{j\vec{q}}$ is missing and the conduction-band state $\phi_{i\vec{k}}$ is occupied. All the other valence-band states are occupied. An exciton state is a linear combination of such electron-hole pair states

$$\Psi = \sum_i \sum_j \sum_k \sum_q A_{ij}(\vec{k}, \vec{q}) \Phi_{ij}(\vec{k}, \vec{q}), \quad (\text{A2})$$

which diagonalizes the many-electron Hamiltonian

$$\hat{H}_t = \sum_{l=1}^N \hat{h}(\vec{r}_l, \vec{p}_l) + \frac{1}{2} \sum_l \sum_{m (l \neq m)}^N \hat{g}(\vec{r}_l, \vec{r}_m), \quad (\text{A3})$$

where $\hat{h}$ and $\hat{g}$ are the one- and two-electron operators, respectively, of the many-electron system, namely, $\hat{h}$ is the sum of the kinetic and effective one-electron potential energies and $\hat{g}$ is the Coulomb repulsive energy between each pair of electrons. The one-electron wave functions χ 's and ϕ 's are related to the eigenfunctions of $\hat{h}$. From

$$\hat{H}_t \Psi = E \Psi \quad (\text{A4})$$

we get the secular equation for $A_{ij}(\vec{k}, \vec{q})$:

$$\begin{aligned}
& \sum_{i'} \sum_{j'} \sum_{\vec{k}'} \sum_{\vec{q}'} [\delta_{ij'} \delta_{\vec{q}\vec{q}'} \langle \phi_{i\vec{k}} | \hat{h} | \phi_{i'\vec{k}'} \rangle \\
& - \delta_{ii'} \delta_{\vec{k}\vec{k}'} \langle \chi_{j'\vec{q}'} | \hat{h} | \chi_{j\vec{q}} \rangle \\
& + \langle \phi_{i\vec{k}}(1) \chi_{j'\vec{q}'}(2) | \hat{g} | \chi_{j\vec{q}}(1) \phi_{i'\vec{k}'}(2) \rangle \\
& - \langle \phi_{i\vec{k}}(1) \chi_{j\vec{q}}(2) | \hat{g} | \chi_{j'\vec{q}'}(2) \phi_{i'\vec{k}'}(1) \rangle] \\
& \times A_{i'j'}(\vec{k}', \vec{q}') = EA_{ij}(\vec{k}, \vec{q}) . \quad (A5)
\end{aligned}$$

Note that the order of the wave function is reversed in the second term on the left-hand side. This is because it comes from the missing orbital in (A1). The third and fourth terms in the left-hand side are the exchange and Coulomb interaction between electron and hole, respectively. Although the reversal of the order of χ 's also occurs in the Coulomb and exchange terms, it is not important within the approximation of this paper. By using this equation we can precisely follow the argument of Luttinger and Kohn.¹³ Therefore, we do not give the details in the intermediate stages. We first make a canonical transformation $A_{ij} \rightarrow \bar{A}_{ij}$ which eliminates the first-order interband matrix elements of the momentum operator, and we rewrite the resulting secular equations for $\bar{A}_{ij}$ in terms of the Fourier transform

$$\bar{B}_{ij}(\vec{r}_e, \vec{r}_h) = \sum_{\vec{k}} \sum_{\vec{q}} \exp(i\vec{k} \cdot \vec{r}_e - i\vec{q} \cdot \vec{r}_h) \bar{A}_{ij}(\vec{k}, \vec{q}) , \quad (A6)$$

which results in

$$\begin{aligned}
& \sum_{i'} \sum_{j'} \left[\delta_{ij'} H_{ii'}^{(c)} \left(\vec{p}_e + \frac{e}{c} \vec{A}_e \right) - \delta_{ii'} H_{jj'}^{(L)} \left(-\vec{p}_h + \frac{e}{c} \vec{A}_h \right) \right. \\
& \left. - \delta_{ii'} \delta_{jj'} e^2 / \epsilon |\vec{r}_e - \vec{r}_h| \right] \bar{B}_{i'j'}(\vec{r}_e, \vec{r}_h) = E \bar{B}_{ij}(\vec{r}_e, \vec{r}_h) . \quad (A7)
\end{aligned}$$

In this equation the exchange term is neglected for the time being, and the usual form of the Coulomb term¹⁴ is used. The exchange term is discussed at the end of this appendix. The matrix $H^{(L)}$ is the transposed form of the Luttinger Hamiltonian: The reversed order of the indexes j and j' is still kept in (A7).

The transformation property of the function (A.1) under all the possible symmetry operations is the same as that of the product

$$\phi_{ik} \chi_{j\vec{q}_k} , \quad (A8)$$

where $\chi_{j\vec{q}_k}$ is the time-reversed state of $\chi_{j\vec{q}}$ [$q_t = -q$; for j see (A11)]. Therefore we may work with the more convenient function

$$\alpha_{ij}(\vec{k}, \vec{q}_t) = A_{ij}(\vec{k}, \vec{q}) \quad (A9)$$

and its canonical transform $\bar{\alpha}_{ij}$ and the Fourier transform $B_{ij}(\vec{r}_e, \vec{r}_h)$ of $\bar{\alpha}_{ij}(\vec{k}, \vec{q}_t)$ instead of $A_{ij}(\vec{k}, \vec{q})$, $\bar{A}_{ij}(\vec{k}, \vec{q})$, and $\bar{B}_{ij}(\vec{r}_e, \vec{r}_h)$. In this picture, one must change the signs of certain matrix elements of

$$\langle \chi_{j'\vec{q}'} | \hat{h} | \chi_{j\vec{q}} \rangle \quad (A10)$$

because of the transformation properties of the χ 's under the time-reversal operation $\hat{K}$. If we choose the phases of χ 's as

$$\hat{K} | \frac{3}{2}, \pm \frac{3}{2} \rangle = \pm | \frac{3}{2}, \mp \frac{3}{2} \rangle, \quad \hat{K} | \frac{3}{2}, \pm \frac{1}{2} \rangle = \mp | \frac{3}{2}, \mp \frac{1}{2} \rangle, \quad (A11)$$

the matrix element (A10) should be multiplied by the factor $(-1)^{j+j'}$ in this new picture. Here j and j' take the values 1, 2, 3, and 4 corresponding to the band indices $|\frac{3}{2}, \frac{3}{2}\rangle$, $|\frac{3}{2}, \frac{1}{2}\rangle$, $|\frac{3}{2}, -\frac{1}{2}\rangle$, and $|\frac{3}{2}, -\frac{3}{2}\rangle$, respectively. Thus, in order to obtain the secular equations for B_{ij} , we must use the Luttinger Hamiltonian with the following modifications:

$$(I) \quad \text{transposition}, \quad (A12)$$

$$(II) \quad \text{reindexing } j \rightarrow \bar{j}, \quad (A13)$$

$$(III) \quad \text{sign changes as in (A11)}. \quad (A14)$$

The processes (A12)–(A14) applied to the $\vec{J}$ operator simply change its sign. Since the Luttinger Hamiltonian is expressed in terms of the linear, quadratic, and cubic forms of the components of the $\vec{J}$ operator, we finally get the Luttinger Hamiltonian with reversed sign of $\vec{J}$ in the secular equations for B_{ij} . Since κ -, q -, and $\vec{k}$ -linear terms are odd in the $\vec{J}$ operator, these three terms appear with reversed signs in the equations for B_{ij} , i.e., (3.3). AL recently corrected the wrong signs of κ and q in Ref. 1. As we have just seen, the $\vec{k}$ -linear term also suffers from the sign change.

One can summarize the result as follows: We can choose one of the two representations, the missing electron picture with transposed Luttinger Hamiltonian or the hole picture with negative signs for κ , q , and K_L .

Finally we give a short comment on the exchange interaction which is neglected in (A7). From the symmetry argument the exchange term should have the form

$$\hat{f}_0 + \hat{f}_1 \vec{\sigma} \cdot \vec{J} + \hat{f}_2 (\sigma_x J_x^3 + \sigma_y J_y^3 + \sigma_z J_z^3), \quad (A15)$$

where $\hat{f}$'s are the operators acting on the functions of $\vec{r}_e$ and $\vec{r}_h$. From the localized nature of the Wannier functions it is reasonable to assume¹⁴

$$\hat{f}_1 \propto \delta(\vec{r}_e - \vec{r}_h). \quad (A16)$$

The third term in (A15) originates from the fact that none of the valence band functions are simple products of the orbital and spin functions because of the cubic symmetry. Although there is a contribution to the $\hat{f}_2$ term from the (A16) type of operator, it is not yet clear if it is the main contribution to that term. Therefore we take the simplest assumption in this paper, i.e., we use constants Δ_0 , Δ_1 , and Δ_2 for the 1s states of the exciton, instead of the operators $\hat{f}_0$, $\hat{f}_1$, and $\hat{f}_2$ which

connect different hydrogenlike states [see (3.4)]. This assumption reduces the number of nonvanishing coefficients of the invariant terms discussed in Sec. II. If one uses a more elaborate operator form for the exchange term, most of the invariants in Table II have nonzero coefficients in the second-order perturbation.

APPENDIX B

Here we give the definition of the constants W , F , and G which appear in the text. The constants M and N arise from the second-order perturbation due to $H_d H_l$ and H_l^2 , respectively, and their expressions are already given by AL.

The constant W comes from the term $H_d H_q$ and is given by

$$W = \frac{1}{4} \sum_{n=2}^{\infty} \frac{\langle 1s | (r/a_0^*)^2 | nd \rangle \langle nd | (1 + a_0^*/r) | 1s \rangle}{1 - 1/n^2}, \quad (\text{B1})$$

where bra and ket are the normalized radial eigenfunctions of the hydrogenlike solutions of H_s (with principal quantum number n), (3.10), and the integration is carried out only over the radial variable r . The symbol $\mathbf{S}$ denotes a sum over discrete (n) and an integral over continuous (k) states (see BL and AL). Only the d -like states contribute to the constant W . The constants F and G arise from the terms $H_{k2} H_{k2}$ and $H_{k1} H_{k2}$, respectively, and are defined by

$$F = \frac{1}{4} \sum_{n=2}^{\infty} \frac{\langle np | r/a_0^* | 1s \rangle^2}{1 - 1/n^2}, \quad (\text{B2})$$

$$G = \frac{1}{4} \sum_{n=2}^{\infty} \frac{\langle 1s | r/a_0^* | np \rangle \langle np | 1s \rangle}{1 - 1/n^2}. \quad (\text{B3})$$

In these cases, only the p -like states contribute to the sums.

The values of the constants W , F , and G can be calculated by the aid of the expressions

$$\langle nd | (r/a_0^*)^2 | 1s \rangle = \frac{64n^4 [n(n^2 - 1)(n^2 - 4)]^{1/2} \left(\frac{n-1}{n+1}\right)^n}{(n^2 - 1)^4}, \quad (\text{B4})$$

$$\langle np | 1s \rangle = 8 \frac{n^{3/2}}{(n^2 - 1)^{3/2}} \left(\frac{n-1}{n+1}\right)^n, \quad (\text{B5})$$

$$\langle np | r/a_0^* | 1s \rangle = 16 \frac{n^{7/2}}{(n^2 - 1)^{5/2}} \left(\frac{n-1}{n+1}\right)^n, \quad (\text{B6})$$

$$\begin{aligned} \langle kd | (r/a_0^*)^2 | 1s \rangle \\ = 64 \left(\frac{K(1 + 4K^2)}{(1 - e^{-2/K})(1 + K^2)^7} \right)^{1/2} e^{-2 \tan^{-1} K/K}, \end{aligned} \quad (\text{B7})$$

$$\langle kp | 1s \rangle = 8 \left(\frac{K}{(1 - e^{-2/K})(1 + K^2)^3} \right)^{1/2} e^{-2 \tan^{-1} K/K}, \quad (\text{B8})$$

$$\langle kp | r/a_0^* | 1s \rangle = 16 \left(\frac{K}{(1 - e^{-2/K})(1 + K^2)^5} \right)^{1/2} e^{-2 \tan^{-1} K/K}, \quad (\text{B9})$$

where

$$K = ka_0^*. \quad (\text{B10})$$

The matrix element $\langle np | 1s \rangle$ corresponds to K_n of BL except for the factor 2 coming from the definition of $|1s\rangle$. Numerical calculation leads to the values given in Eq. (3.21).

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