

## Direct excitons in cubic semiconductors in a magnetic field

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The influence of the degeneracy and anisotropy of the valence band of a cubic semiconductor on the exciton 1s and 2s states in a weak magnetic field is investigated. Using the reduced Coulomb Green's function, purely analytical expressions for the wave functions in the first order and energies up to second order of the perturbation theory are obtained.

### I. INTRODUCTION

A description of shallow exciton states in semiconductors with degenerate bands requires an investigation of a system of differential equations. An exact solution is not known for this system. McLean and Loudon,<sup>1</sup> using a variational technique, computed an approximate wave function for the ground state of the direct and indirect excitons in Ge and Si. Abe,<sup>2</sup> by a variational method, computed the wave function of the direct excitons in Ge and GaAs.

Baldereschi and Lipari<sup>3,4</sup> and Czaja<sup>5</sup> proposed a new method to investigate shallow excitons in semiconductors with degenerate bands. This method is based on the remark that the warping of the valence band in most semiconductors is relatively small. Thus the perturbation theory can give a general and accurate description of the lowest discrete exciton states in semiconductors. Altarelli and Lipari<sup>6</sup> used this method to compute the splitting of the exciton levels in a weak magnetic field.

The purpose of the present paper is to give a general investigation of the direct exciton states 1s

and 2s of diamond and zinc-blende-type semiconductors at low magnetic field, taking into account both the Coulomb interaction and the actual degeneracy and warping of the two upper valence subbands. Using the reduced Coulomb Green's function given by Hostler<sup>7</sup> and by Świerkowski and Suffczyński,<sup>8</sup> purely analytical expressions are obtained for the wave functions in the first order and for energies up to second order of the perturbation theory.

### II. PERTURBATION THEORY

The Hamiltonian for the relative electron-hole motion in a magnetic field is

$$H = H_e(\vec{p} + (e/c)\vec{A}) - H_h(-\vec{p} + (e/c)\vec{A}) - \frac{e^2}{\epsilon r}, \quad (1)$$

where  $\vec{p}$  is the relative electron-hole momentum,  $\epsilon$  is the static dielectric constant,  $\vec{r}$  is the electron-hole radius vector, and

$$H_e(\vec{k}) = \frac{1}{2m_e^*} k^2 + \mu^* \vec{\sigma} \cdot \vec{B}, \quad (2)$$

$$\begin{aligned} -H_h(\vec{k}) = & \frac{1}{m_0} [(\gamma_1 + \frac{5}{2}\gamma_2)\frac{1}{2}k^2 - \gamma_2(k_x^2J_x^2 + k_y^2J_y^2 + k_z^2J_z^2) \\ & - 2\gamma_3(\{k_xk_y\}\{J_xJ_y\} + \{k_yk_z\}\{J_yJ_z\} + \{k_zk_x\}\{J_zJ_x\}) \\ & - (e\hbar/c)\kappa\vec{J} \cdot \vec{B} - (e\hbar/c)q(J_x^3B_x + J_y^3B_y + J_z^3B_z)]. \end{aligned} \quad (3)$$

Here the constants  $\gamma_1, \gamma_2, \gamma_3, \kappa, q$ , and the spin- $\frac{3}{2}$  matrices  $J_x, J_y, J_z$  have been defined by Luttinger<sup>9</sup>;  $m_e^*$  is the electron effective mass,  $\mu^*$  is the effective magnetic moment of the conduction electron,  $\{ab\} \equiv \frac{1}{2}(ab + ba)$ . In Eqs. (1)–(3) we have neglected the effects of the splitoff valence band,<sup>4</sup> of the electron-hole exchange interaction,<sup>10–13</sup> and of the terms linear in  $\vec{p}$  which arise from the lack of inversion symmetry in zinc-blende semiconductors.<sup>4</sup> We now assume that the constant magnetic field  $\vec{B}$  is along the [001] direction of the crystal and we

choose the gauge  $\vec{A}$  in the form

$$\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r}) = \frac{1}{2}B(-y, x, 0).$$

Altarelli and Lipari<sup>6</sup> write Eq. (1) as

$$H = H_s + H_d + H_l + H_q, \quad (4)$$

where  $H_s$  represents the Coulomb interaction between the electron and the isotropic part of the hole,  $H_d$  represents the anisotropic hole contribution<sup>3,4</sup>:

$$H_s = p^2/2\mu_0 - e^2/\epsilon r, \quad (5)$$

$$H_d = \frac{5}{4\mu_1} p^2 - \frac{1}{\mu_1} (p_x^2 J_x^2 + p_y^2 J_y^2 + p_z^2 J_z^2) - \frac{1}{\sqrt{3}\mu_2} (p_x p_y \{J_x J_y\} + p_y p_z \{J_y J_z\} + p_x p_z \{J_x J_z\}). \quad (6)$$

$H_l$  and  $H_q$  are, respectively, the linear and quadratic terms in  $B$ :

$$H_l = \frac{eB}{c} \left[ \left( \frac{1}{2m_e^*} - \frac{\gamma_1}{2m_0} - \frac{5}{4\mu_1} \right) (xp_y - yp_x) + \frac{1}{\mu_1} (xp_y J_y^2 - yp_x J_x^2) + \frac{1}{2\sqrt{3}\mu_2} [(xp_x - yp_y) \{J_x J_y\} + xp_z \{J_y J_z\} - yp_z \{J_x J_z\}] - \frac{\hbar}{m_0} (\kappa J_x + q J_z^3) \right] + \mu^* \sigma_z B, \quad (7)$$

$$H_q = \frac{e^2 B^2}{4c^2} \left[ \left( \frac{1}{2\mu_0} + \frac{5}{4\mu_1} \right) (x^2 + y^2) - \frac{1}{\mu_1} (y^2 J_x^2 + x^2 J_y^2) + \frac{1}{\sqrt{3}\mu_2} xy \{J_x J_y\} \right]. \quad (8)$$

The masses  $\mu_0$ ,  $\mu_1$ ,  $\mu_2$  are related to the Luttinger<sup>9</sup> parameters  $\gamma_1$ ,  $\gamma_2$ ,  $\gamma_3$  by

$$\frac{1}{\mu_0} = \frac{1}{m_e^*} + \frac{\gamma_1}{m_0}, \quad \frac{1}{\mu_1} = \frac{\gamma_2}{m_0}, \quad \frac{1}{\mu_2} = 2\sqrt{3} \frac{\gamma_3}{m_0}.$$

$H_s$  is the Hamiltonian of a hydrogen atom with reduced mass  $\mu_0$  and dielectric constant  $\epsilon$ . The eigenfunctions of  $H_s$  can be classified with the quantum numbers  $n$ ,  $l$ ,  $m$ ,  $\mu$  and  $\sigma$ , where the first three are the usual hydrogen-atom quantum numbers, and where  $\mu$  and  $\sigma$  are, respectively, hole and electron spin projections on the  $z$  direction. The wave functions, i. e., exciton envelopes, can be written

$$|nlm\mu\sigma\rangle = |nlm\rangle |\mu\rangle |\sigma\rangle, \quad (9a)$$

where  $|nlm\rangle$  are the usual hydrogen-atom wave functions and

$$J_z |\mu\rangle = \mu |\mu\rangle, \quad \mu \equiv \pm \frac{3}{2}, \pm \frac{1}{2} \quad (9b)$$

$$\frac{1}{2} \sigma_z |\sigma\rangle = \sigma |\sigma\rangle, \quad \sigma = \pm \frac{1}{2}. \quad (9c)$$

The corresponding eigenvalues are

$$E_n = -\frac{\mu_0 e^4}{2\hbar^2 \epsilon^2} \frac{1}{n^2}, \quad (10)$$

for the continuum, the energies are still given by (10) with the replacement  $n = -i/k$ .

It was previously shown<sup>3-5</sup> that  $H_d$  can be treated as a small perturbation with respect to  $H_s$ . Therefore, at low magnetic fields, the states of the Hamiltonian (4) can be investigated by using perturbation theory with the perturbation  $V = H_d + H_l + H_q$ . Perturbed discrete exciton levels and exciton wave functions can be computed using the reduced Coulomb Green's function.<sup>7</sup>

The Green's-function operator  $G^n$  is defined by expression

$$G^n = \frac{\hbar^2}{2\mu_0} \mathbf{S} \sum_{l, m} \frac{|klm\rangle \langle klm|}{E_n - E_k}. \quad (11)$$

The symbol  $\mathbf{S}$  means summation over discrete states and integration over continuum states. The reduced Coulomb Green's function was given by Hostler<sup>7</sup> and by Świerkowski and Suffczyński.<sup>8</sup> Operating with  $G^n$  on the wave function  $\psi$  can be expressed by

$$(G^n \psi)(\vec{r}_2) = \int d^3 r_1 G^n(\vec{r}_2, \vec{r}_1) \psi(\vec{r}_1). \quad (12)$$

Now, for any  $n$

$$\langle n00\mu\sigma | H_d | n00\mu'\sigma' \rangle = 0. \quad (13)$$

In the Coulomb potential the states  $2s$  have the states  $2p$  degenerate with it. Valence-band warping removes this degeneracy. In the semiconductors of diamond-type symmetry the perturbation by the magnetic field  $\vec{B} = (0, 0, B)$  has vanishing matrix elements between the  $2s$  and  $2p$  states and the resulting secular determinant for  $2s$  states is diagonal. Thus the nondegenerate perturbation theory for energies is still valid. Moreover, from Wigner-Eckart theorem one can see that

$$\langle 21m\mu\sigma | V G^n V | 200\mu'\sigma' \rangle = 0, \quad m = 0, \pm 1. \quad (14)$$

Further considerations will relate to  $1s$  and  $2s$  states only. The round bracket  $| \ )$  will be adopted for the perturbed wave function. The wave functions in the first-order perturbation theory up to terms linear in  $B$  can be written, using (14), in the form

$$|n00\mu\sigma\rangle = |n00\mu\sigma\rangle + \frac{2\mu_0}{\hbar^2} G^n (H_d + H_l) |n00\mu\sigma\rangle, \quad n = 1, 2. \quad (15)$$

The corresponding energies in first- and second-order perturbation theory are

$$E_{\mu\sigma}(ns) = E_n + \langle n00\mu\sigma | V | n00\mu\sigma \rangle + \frac{2\mu_0}{\hbar^2} \langle n00\mu\sigma | VG^nV | n00\mu\sigma \rangle, \quad n=1, 2. \quad (16)$$

Retaining only linear and quadratic terms in  $B$  we have, using (13):

$$E_{\mu\sigma}(ns) = E_n + \langle n00\mu\sigma | \frac{2\mu_0}{\hbar^2} H_d G^n H_d | n00\mu\sigma \rangle + \langle n00\mu\sigma | H_i + \frac{2\mu_0}{\hbar^2} (H_d G^n H_i + H_i G^n H_d) | n00\mu\sigma \rangle + \langle n00\mu\sigma | H_q + \frac{2\mu_0}{\hbar^2} (H_d G^n H_q + H_q G^n H_d) | n00\mu\sigma \rangle + \langle n00\mu\sigma | \frac{2\mu_0}{\hbar^2} H_i G^n H_i | n00\mu\sigma \rangle, \quad n=1, 2. \quad (17)$$

The term in Eq. (17) containing  $H_d G^n H_q + H_q G^n H_d$  was not considered in Ref. 6.

### III. EXCITON $1s$ AND $2s$ STATES

From now on, we will use effective Rydberg and effective Bohr radius as units of energy and length, respectively:

$$R_0 = \mu_0 e^4 / 2\hbar^2 \epsilon^2, \quad a_0 = \epsilon \hbar^2 / \mu_0 e^2. \quad (18a)$$

The ratio of half cyclotron to Rydberg energy is

$$\gamma = e\hbar B / 2c\mu_0 R_0. \quad (18b)$$

Equation (15), after integration prescribed by (12), yields

$$|n00\mu\sigma\rangle = |n00\mu\rangle |\sigma\rangle, \quad n=1, 2 \quad (19a)$$

$$|100\mu\rangle = \frac{1}{\sqrt{\pi}} e^{-r} |\mu\rangle + \left( \sqrt{\frac{2}{5}} \frac{\mu_0}{\mu_1} v_1^a(\mu) + \frac{1}{2\sqrt{5}} \frac{\mu_0}{\mu_2} v_2^a(\mu) \right) f_{1a}(r) + \gamma \left( -\frac{1}{\sqrt{5}} \frac{\mu_0}{\mu_1} v_1^i(\mu) - \frac{1}{2\sqrt{30}} \frac{\mu_0}{\mu_2} v_2^i(\mu) \right) r^2 e^{-r}, \quad (19b)$$

$$|200\mu\rangle = \frac{1}{4\sqrt{2\pi}} (2-r)e^{-r/2} |\mu\rangle + \left( \frac{1}{2\sqrt{5}} \frac{\mu_0}{\mu_1} v_1^a(\mu) + \frac{1}{4\sqrt{10}} \frac{\mu_0}{\mu_2} v_2^a(\mu) \right) f_{2a}(r) + \gamma \left( -\frac{1}{4\sqrt{10}} \frac{\mu_0}{\mu_1} v_1^i(\mu) - \frac{1}{16\sqrt{15}} \frac{\mu_0}{\mu_2} v_2^i(\mu) \right) (2-r)r^2 e^{-r/2}. \quad (19c)$$

Here

$$v_1^a(\frac{3}{2}) = \begin{bmatrix} -(1/\sqrt{2})Y_0^2 \\ 0 \\ \frac{1}{2}(Y_2^2 + Y_{-2}^2) \\ 0 \end{bmatrix}, \quad v_2^a(\frac{3}{2}) = \begin{bmatrix} 0 \\ \sqrt{\frac{2}{3}}iY_1^2 \\ (1/\sqrt{6})(Y_2^2 - Y_{-2}^2) \\ 0 \end{bmatrix}, \quad v_1^i(\frac{3}{2}) = \begin{bmatrix} 0 \\ 0 \\ 1/\sqrt{2}(Y_2^2 - Y_{-2}^2) \\ 0 \end{bmatrix}, \quad v_2^i(\frac{3}{2}) = \begin{bmatrix} 0 \\ iY_1^2 \\ (Y_2^2 + Y_{-2}^2) \\ 0 \end{bmatrix}$$

$$v_1^a(\frac{1}{2}) = \begin{bmatrix} 0 \\ (1/\sqrt{2})Y_0^2 \\ 0 \\ \frac{1}{2}(Y_2^2 + Y_{-2}^2) \end{bmatrix}, \quad v_2^a(\frac{1}{2}) = \begin{bmatrix} -\sqrt{\frac{2}{3}}iY_{-1}^2 \\ 0 \\ 0 \\ (1/\sqrt{6})(Y_2^2 - Y_{-2}^2) \end{bmatrix}, \quad v_1^i(\frac{1}{2}) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ (1/\sqrt{2})(Y_2^2 - Y_{-2}^2) \end{bmatrix}, \quad v_2^i(\frac{1}{2}) = \begin{bmatrix} iY_{-1}^2 \\ 0 \\ 0 \\ (Y_2^2 + Y_{-2}^2) \end{bmatrix} \quad (20)$$

$$v_1^a(-\frac{1}{2}) = \begin{bmatrix} \frac{1}{2}(Y_2^2 + Y_{-2}^2) \\ 0 \\ (1/\sqrt{2})Y_0^2 \\ 0 \end{bmatrix}, \quad v_2^a(-\frac{1}{2}) = \begin{bmatrix} -(1/\sqrt{6})(Y_2^2 - Y_{-2}^2) \\ 0 \\ 0 \\ -\sqrt{\frac{2}{3}}iY_1^2 \end{bmatrix}, \quad v_1^i(-\frac{1}{2}) = \begin{bmatrix} (1/\sqrt{2})(Y_2^2 - Y_{-2}^2) \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad v_2^i(-\frac{1}{2}) = \begin{bmatrix} -(Y_2^2 + Y_{-2}^2) \\ 0 \\ 0 \\ -iY_1^2 \end{bmatrix}$$

$$v_1^i(-\frac{3}{2}) = \begin{bmatrix} 0 \\ \frac{1}{2}(Y_2^2 + Y_{-2}^2) \\ 0 \\ -(1/\sqrt{2})Y_0^2 \end{bmatrix}, \quad v_2^i(-\frac{3}{2}) = \begin{bmatrix} 0 \\ -(1/\sqrt{6})(Y_2^2 - Y_{-2}^2) \\ \sqrt{\frac{2}{3}}iY_{-1}^2 \\ 0 \end{bmatrix}, \quad v_1^i(-\frac{3}{2}) = \begin{bmatrix} 0 \\ (1/\sqrt{2})(Y_2^2 - Y_{-2}^2) \\ 0 \\ 0 \end{bmatrix}, \quad v_2^i(-\frac{3}{2}) = \begin{bmatrix} 0 \\ -(Y_2^2 + Y_{-2}^2) \\ -iY_{-1}^2 \\ 0 \end{bmatrix},$$

where

$$Y_m^l(\theta, \varphi) = \left( \frac{(l-|m|)!}{(l+|m|)!} \frac{2l+1}{4\pi} \right)^{1/2} \frac{(-1)^l e^{im\varphi}}{2^l l!} \sin^{|m|} \theta \frac{d^{l+|m|} \sin^{2l} \theta}{d(\cos \theta)^{l+|m|}},$$

$$f_{1s}(r) = \frac{2}{r} e^{-r} \left\{ \frac{6}{r} + 6 + \frac{17}{6} r + r^2 + \left( \frac{3}{r^2} - \frac{3}{2r} \right) e^{2r} g(-2r) \right. \\ \left. + \left[ \left( \frac{3}{r^2} - \frac{3}{2r} \right) e^{2r} - \left( \frac{3}{r^2} + \frac{9}{2r} + 3 + r \right) \right] (\ln 2r + \gamma_E) \right\}, \quad (21a)$$

$$f_{2s}(r) = \frac{2}{r} e^{-r/2} \left\{ - \left( \frac{24}{r} + 18 + \frac{22}{3} r + \frac{19}{12} r^2 + \frac{1}{4} r^3 \right) - \frac{24}{r^2} e^r g(-r) \right. \\ \left. + \left( -\frac{24}{r^2} e^r + \frac{24}{r^2} + \frac{24}{r} + 12 + 4r + r^2 \right) (\ln r + \gamma_E) \right\}, \quad (21b)$$

$$g(x) = \int_0^x \frac{e^t - 1}{t} dt, \quad \gamma_E = 0.577215\dots$$

is the Euler-Mascheroni constant.

In Eqs. (19b) and (19c) the first terms are the hydrogen-atom wave functions. The second terms represent the effect of the valence-band structure in the absence of magnetic field. The form of these terms is similar to Schechter's<sup>14,15</sup> or McLean and Loudon's<sup>1</sup> trial functions, but it is important to point out that for  $n=1, 2$  the radial function  $f_{ns}(r)$  for  $r \rightarrow 0$  behave as  $r$ , not as  $r^2$ . The last terms in (19b) and (19c), proportional to  $\gamma$ , describe the effect of the magnetic field.

From (11)–(13), we get after analytical integrations with the reduced Coulomb Green's function, the energies

$$E_{\mu\sigma}(1s) = -1 - \frac{4}{5} \phi S_1 + (g_1 \mu + g_2 \mu^3 + g_e \sigma) \gamma \\ + (q_1 + q_2' \mu^2) \gamma^2, \quad (22a)$$

where, from Refs. 4, 16, and 17,

$$S_1 = 1 + \frac{1}{4} + \frac{1}{8} + \frac{1}{12} - \frac{1}{8} \pi^2 = 0.22463278\dots, \quad (22b)$$

and the constants  $g_1, g_2, q_1, q_2'$  for 1s states are

$$g_1 = -2\kappa \frac{\mu_0}{m_0} + \frac{13\sqrt{3}}{10} \frac{\mu_0}{\mu_2} \frac{\mu_0}{\mu_1} - \frac{7}{20} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ g_2 = -2q \frac{\mu_0}{m_0} - \frac{2\sqrt{3}}{5} \frac{\mu_0}{\mu_2} \frac{\mu_0}{\mu_1} + \frac{1}{5} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ q_1 = \frac{1}{2} - \frac{53}{48} \frac{\mu_0}{\mu_1} - \frac{34}{15} \left( \frac{\mu_0}{\mu_1} \right)^2 - \frac{17}{60} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ q_2' = \frac{53}{60} \frac{\mu_0}{\mu_1}; \quad (22c)$$

$$E_{\mu\sigma}(2s) = -\frac{1}{4} - \frac{1}{16} \phi S_2 + (g_1 \mu + g_2 \mu^3 + g_e \sigma) \gamma \\ + (q_1 + q_2' \mu^2) \gamma^2, \quad (23a)$$

where, from Refs. 4 and 17,

$$S_2 = \pi^2 - \frac{1}{6} - 9 = 0.70293769\dots, \quad (23b)$$

and the constants  $g_1, g_2, q_1, q_2'$  for 2s states are

$$g_1 = -2\kappa \frac{\mu_0}{m_0} + \frac{13\sqrt{3}}{15} \frac{\mu_0}{\mu_2} \frac{\mu_0}{\mu_1} - \frac{7}{30} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ g_2 = -2q \frac{\mu_0}{m_0} - \frac{4\sqrt{3}}{15} \frac{\mu_0}{\mu_2} \frac{\mu_0}{\mu_1} + \frac{2}{15} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ q_1 = 7 - \frac{61}{6} \frac{\mu_0}{\mu_1} - \frac{349}{15} \left( \frac{\mu_0}{\mu_1} \right)^2 - \frac{349}{120} \left( \frac{\mu_0}{\mu_2} \right)^2, \\ q_2' = \frac{122}{15} \frac{\mu_0}{\mu_1}. \quad (23c)$$

Here  $\phi = 8(\mu_0/\mu_1)^2 + (\mu_0/\mu_2)^2$ ,  $\bar{\mu}^* = \mu^*/\mu_B$  is the effective magnetic moment expressed in Bohr magnetic moments  $\mu_B = e\hbar/2m_0c$ , and  $g_e = 2\bar{\mu}^* \mu_0/m_0$ . In Eqs. (22a) and (23a) the second term, with  $\phi$ , represents the contributions from  $H_d$ . The third term, linear in  $B$ , gives the Zeeman splitting of the octuplet of exciton states, symmetric with respect to the zero-field level. The term  $(\mu_0/\mu_1)(\mu_0/\mu_2)$ , stemming from  $H_d G^n H_i + H_i G^n H_d$  term of Eq. (17), is absent in Eq. (8) of Ref. 6. The last term in Eqs. (22a) and (23a) gives the diamagnetic shift. The last two terms were written in the form corresponding to that which Bhattacharjee and Rodriguez<sup>18</sup> obtained in their group-theoretical analysis of the Zeeman effect of acceptors.

## IV. CONCLUSIONS

It is worth to recall that the perturbative treatment is valid only for values of the energy shifts

$$\Delta E_{\mu\sigma}(1s) < \frac{3}{4}R_0 \quad \text{and} \quad \Delta E_{\mu\sigma}(2s) < \left(\frac{1}{4} - \frac{1}{9}\right)R_0.$$

In the present paper the errors detected in Eq. (8) of Ref. 6 are corrected. It is important to stress that in the present paper and in the paper of Altarelli and Lipari<sup>6</sup> the energy corrections were calculated to second order of the perturbation theory while the terms of the same order of magnitude, i. e., proportional to  $\gamma_2\gamma_3\gamma$  and to  $\gamma_2\gamma_3\gamma^2$ , appear

also in the third-order perturbation theory.

The wave functions presented here can be used, *inter alia*, to compute effects of stress on the exciton levels. Further, they may be used to compute the absolute intensities of the magnetically split components of the exciton lines, which could be observed with good spectral resolution.<sup>19,20</sup>

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