EXCITONS BOUND TO IONIZED DONOR

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The exciton bound to an ionized donor by Coulomb forces is investigated in the effective mass approximation. The case of anisotropic effective masses of electron and hole, and anisotropic dielectric constant, is considered. A variational method for computing the ground state energy of the complex is described. Expectation values of the interparticle distances are computed. Numerical results for CdS and CdSe are given.

Introduction

Excitons bound to imperfections in solids form complexes which give rise to observable line spectra [1–4]. The simplest of such complexes is an exciton bound to an ionized donor. This is a three-particle complex consisting of the fixed donor center plus one electron and one hole. Within the framework of the effective-mass approximation the mass of the conduction band minimum is ascribed to the electron, the mass of the valence band maximum to the hole. Assuming the coulombic interaction between all three particles, and neglecting any other interactions like the short range interactions which give rise to the central cell corrections, we will look for the ground state of the complex.

The hamiltonian

Since exciton complexes are observed in several compounds with wurtzite structure [3–5], the description appropriate for anisotropic, axially symmetric, effective masses and dielectric constant is relevant.

We consider a crystal with one preferred axis, the c axis, along which we take the z direction. With the origin taken at the donor center, the electron and hole coordinates are x_e, y_e, z_e and x_h, y_h, z_h, respectively. The electron and hole effective masses are $m_{e\perp}(m_{e||})$ and $m_{h\perp}(m_{h||})$ perpendicular (parallel) to the c axis. The low frequency dielectric constant perpendicular (parallel) to the c axis is $\varepsilon_\perp(\varepsilon_{||})$. Furthermore $\varepsilon_0 = (\varepsilon_\perp \varepsilon_{||})^{1/2}$ and $\eta = \varepsilon_{||}/\varepsilon_\perp$.

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The hamiltonian of the complex is

$$H = T + V \tag{1}$$

where the kinetic energy is

$$T = -\frac{\hbar^2}{2}\left[\frac{1}{m_{e\perp}}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2}\right) + \frac{1}{m_{e\parallel}}\frac{\partial^2}{\partial z_e^2} + \frac{1}{m_{h\perp}}\left(\frac{\partial^2}{\partial x_h^2} + \frac{\partial^2}{\partial y_h^2}\right) + \frac{1}{m_{h\parallel}}\frac{\partial^2}{\partial z_h^2}\right] \tag{2}$$

and the potential energy, with a singly ionized donor, is

$$V = \frac{e^2}{\varepsilon_0}[(x_h^2 + y_h^2 + \eta^{-1}z_h^2)^{-\frac{1}{2}} - (x_e^2 + y_e^2 + \eta^{-1}z_e^2)^{-\frac{1}{2}} - ((x_e - x_h)^2 + (y_e - y_h)^2 + \eta^{-1}(z_e - z_h)^2)^{-\frac{1}{2}}]. \tag{3}$$

The coordinates modified by the anisotropic dielectric constant are

$$\boldsymbol{r}'_e = (x'_e, y'_e, z'_e) = (x_e, y_e, \eta^{-\frac{1}{2}}z_e),$$
$$\boldsymbol{r}'_h = (x'_h, y'_h, z'_h) = (x_h, y_h, \eta^{-\frac{1}{2}}z_h). \tag{4}$$

The kinetic energy (2) is

$$T = -\frac{\hbar^2}{2}\left[\frac{1}{m_{e\perp}}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2}\right) + \frac{1}{\eta m_{e\parallel}}\frac{\partial^2}{\partial z_e'^2} + \frac{1}{m_{h\perp}}\left(\frac{\partial^2}{\partial x_h^2} + \frac{\partial^2}{\partial y_h^2}\right) + \frac{1}{\eta m_{h\parallel}}\frac{\partial^2}{\partial z_h'^2}\right]. \tag{5}$$

In terms of modified distances, $r'_e = |\boldsymbol{r}'_e|$, $r'_h = |\boldsymbol{r}'_h|$ and $r'_{eh} = |\boldsymbol{r}'_e - \boldsymbol{r}'_h|$, the potential energy (3) is simply

$$V = \frac{e^2}{\varepsilon_0}\left(\frac{1}{r'_h} - \frac{1}{r'_e} - \frac{1}{r'_{eh}}\right). \tag{6}$$

It is appropriate now to introduce the harmonic mean of the effective masses, modified by the anisotropic dielectric constant,

$$m_e = 3\left/\left(\frac{2}{m_{e\perp}} + \frac{1}{\eta m_{e\parallel}}\right)\right., \qquad m_h = 3\left/\left(\frac{2}{m_{h\perp}} + \frac{1}{\eta m_{h\parallel}}\right)\right.. \tag{7}$$

With the anisotropy parameters for the electron and the hole

$$\gamma_e = m_e\left(\frac{1}{m_{e\perp}} - \frac{1}{\eta m_{e\parallel}}\right), \qquad \gamma_h = m_h\left(\frac{1}{m_{h\perp}} - \frac{1}{\eta m_{h\parallel}}\right) \tag{8}$$

the kinetic energy can be rewritten as [5]

$$T = -\frac{\hbar^2}{2}\left[\frac{1}{m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e'^2}\right) + \frac{\gamma e}{3m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} - 2\frac{\partial^2}{\partial z_e'^2}\right) + \right.$$
$$\left. + \frac{1}{m_h}\left(\frac{\partial^2}{\partial x_h^2} + \frac{\partial^2}{\partial y_h^2} + \frac{\partial^2}{\partial z_h'^2}\right) + \frac{\gamma_h}{3m_h}\left(\frac{\partial^2}{\partial x_h^2} + \frac{\partial^2}{\partial y_h^2} - 2\frac{\partial^2}{\partial z_h'^2}\right)\right]. \tag{9}$$

The variational method

To find the ground state energy of the complex we use a variational method. It is well known that in the case of an isotropic hamiltonian, the total angular momentum of the system commutes with the hamiltonian [6–8]. The ground state energy of such hamiltonian has a wave function which depends only on the interparticle distances.

In the case of an anisotropic hamiltonian, with either $\gamma_e \neq 0$, or $\gamma_h \neq 0$, or both, the form of the ground state wave function is unknown. We approximate the ground state wave function by a variational function which depends only on the distances r'_e, r'_h and r'_{eh}. These are precisely the distances which determine the coulombic potential energy (6). For such wave function, $\psi = \psi\,(r'_e, r'_h, r'_{eh})$, we have

$$\left\langle \psi, \frac{\partial^2}{\partial x_e^2}\,\psi \right\rangle = \left\langle \psi, \frac{\partial^2}{\partial y_e^2}\,\psi \right\rangle = \left\langle \psi, \frac{\partial^2}{\partial z_e'^2}\,\psi \right\rangle,$$

and

$$\left\langle \psi, \frac{\partial^2}{\partial x_h^2}\,\psi \right\rangle = \left\langle \psi, \frac{\partial^2}{\partial y_h^2}\,\psi \right\rangle = \left\langle \psi, \frac{\partial^2}{\partial z_h'^2}\,\psi \right\rangle \tag{10}$$

since for any function of the distances only, $f = f(r_e, r_h, r_{eh})$, integrals over all space of $dv = d^3r_e d^3r_h$ satisfy

$$\int x_e^2 f dv = \int y_e^2 f dv = \int z_e^2 f dv,$$
$$\int x_h^2 f dv = \int y_h^2 f dv = \int z_h^2 f dv, \tag{11}$$
$$\int (x_e - x_h)^2 f dv = \int (y_e - y_h)^2 f dv = \int (z_e - z_h)^2 f dv.$$

Thus the wave function $\psi(r'_e, r'_h, r'_{eh})$ depending only on the distances gives vanishing expectation value of the anisotropic terms, *i. e.* proportional to γ_e and γ_h, in the kinetic energy (9). We stress, however, the following fact. The assumption that the ground state wave function depends only on the distances r'_e, r'_h, r'_{eh} is not well motivated in the anisotropic case.

The energy expectation value

To compute the expectation value of the hamiltonian H with the wave function $\psi = \psi(r'_e, r'_h, r'_{eh})$ we introduce dimensionless distances by a scale transformation

$$R_n = r'_n/a_h, \qquad n = e, h, eh, \tag{12}$$

with $a_h = \hbar^2\varepsilon_0/e^2 m_h =$ the Bohr radius corresponding to the mass of the hole. The rydberg corresponding to the mass of the hole is $E_h = e^2/2\varepsilon_0 a_h = e^4 m_h/2\hbar^2\varepsilon_0^2$. The expectation value of the hamiltonian $E' = \langle \psi, H\psi \rangle/\langle \psi, \psi \rangle$ can be expressed in terms of twice the rydberg of the hole, $E = E'/2E_h$.

The coulombic potential energy (6) is a homogeneous function of the distances r'_e, r'_h, r'_{eh}. Hence, the isotropic part of the hamiltonian H can be written

$$H = 2E_h H_0 = 2E_h(T_0 + V_0) \tag{13}$$

with

$$T_0 = -\frac{1}{2\sigma}\Delta_e - \frac{1}{2}\Delta_h,$$

$$\Delta_e = \frac{\partial^2}{\partial X_e^2} + \frac{\partial^2}{\partial Y_e^2} + \frac{\partial^2}{\partial Z_e^2}, \quad (X_e, Y_e, Z_e) = (x_e', y_e', z_e')/a_h, \tag{14}$$

$$\Delta_h = \frac{\partial^2}{\partial X_h^2} + \frac{\partial^2}{\partial Y_h^2} + \frac{\partial^2}{\partial Z_h^2}, \quad (X_h, Y_h, Z_h) = (x_h', y_h', z_h')/a_h, \tag{15}$$

$$V_0 = \frac{1}{R_h} - \frac{1}{R_e} - \frac{1}{R_{eh}}. \tag{16}$$

Since we shall only be using a wave function depending on the distances R_n, we neglect the anisotropic part of the kinetic energy. Thus the hamiltonian $T_0 + V_0$ depends only on the ratio $\sigma = m_e/m_h$ of the effective masses of electron and hole. Moreover its ground state energy E_0 depends on this ratio monotonically [9–10]. This is seen by considering the derivative of the expectation value with respect to σ. For normalized eigenfunction ψ, $\langle \psi, \psi \rangle = 1$, $\partial\langle \psi, \psi \rangle/\partial\sigma = 0$,

$$\frac{\partial E_0}{\partial\sigma} = \frac{\partial}{\partial\sigma}\langle \psi, H_0\psi \rangle = E_0\frac{\partial}{\partial\sigma}\langle \psi, \psi \rangle + \left\langle \psi, \frac{\partial H_0}{\partial\sigma}\psi \right\rangle$$

$$= \left\langle \psi, \frac{\partial H_0}{\partial\sigma}\psi \right\rangle = \left\langle \psi, \frac{\partial}{\partial\sigma}\left(-\frac{1}{2\sigma}\Delta_e\right)\psi \right\rangle = -\frac{1}{\sigma}\left\langle \psi, -\frac{1}{2\sigma}\Delta_e\psi \right\rangle \leqslant 0. \tag{17}$$

The complex remains bound if its energy is more negative than the ground state energy of the neutral donor $E_D = -\sigma E_h$ [11]. Since

$$\frac{E' - E_D}{E_D} = \frac{-E - \sigma/2}{\sigma/2}, \tag{18}$$

the criterion for binding the exciton to an ionized donor is $E < -\sigma/2$.

The matrix elements

We take now the wave function in the form [12–13]

$$\psi = \sum_{i=1}^{N} X_i\psi_i,$$

$$\psi_i = S^3(SR_h)p_i \exp\left[-S(A_iR_e + B_iR_{eh} + C_iR_h)\right]. \tag{19}$$

The exponents p_i have to be positive integers, or, if all p_i are equal, they can be also half integral. S is a scale parameter.

The matrix elements of an operator o between the wave functions ψ_i and ψ_j will be

written $\langle o \rangle_{ij}$. The relevant matrix elements are expressible in terms of the integrals [13–14]

$$I_{k,l,m}(a, b, c) = 8\pi^2 \int\limits_0^\infty dr_e \int\limits_0^\infty dr_h \int\limits_{|r_e - r_h|}^{r_e + r_h} dr_{eh} r_e^k r_{eh}^l r_h^m \exp\left[-(ar_e + br_{eh} + cr_h)\right]$$

$$= 8\pi^2 \cdot 2 \cdot k!l!m! \sum_{p=0}^k \sum_{q=0}^l \sum_{r=0}^m \frac{\binom{p+q}{q}}{(a+b)^{p+q+1}} \frac{\binom{k-p+r}{r}}{(a+c)^{k-p+r+1}} \frac{\binom{l-q+m-r}{m-r}}{(b+c)^{l-q+m-r+1}}. \tag{20}$$

We write for brevity

$$I_{klm} = I_{k,l,m+p_i+p_j-1}(A_i + A_j, B_i + B_j, C_i + C_j). \tag{21}$$

The overlap integrals are

$$\langle \psi_i, \psi_j \rangle = \langle 1 \rangle_{ij} = I_{112}. \tag{22}$$

The terms in the potential energy V_0 are

$$\langle R_e^{-1} \rangle_{ij} = SI_{012}, \quad \langle R_{eh}^{-1} \rangle = SI_{102}, \quad \langle R_h^{-1} \rangle = SI_{111}. \tag{23}$$

The kinetic energy matrix element is

$$\langle T_0 \rangle_{ij} = \frac{1}{2} S^2 \left[\left(\frac{1}{\sigma} A_i A_j + \left(\frac{1}{\sigma} + 1 \right) B_i B_j + C_i C_j \right) I_{112} + \right.$$

$$+ \frac{1}{2\sigma} (A_i B_j + A_j B_i)(I_{202} + I_{022} - I_{004}) + \frac{1}{2}(B_i C_j + B_j C_i)(I_{121} + I_{103} - I_{301}) -$$

$$\left. - \frac{1}{2}(B_i p_j + B_j p_i)(I_{120} + I_{102} - I_{300}) - (C_i p_j + C_j p_i)I_{111} + p_i p_j I_{110} \right]. \tag{24}$$

The energy expectation value of the ground state is obtained as the lowest root of the characteristic equation

$$\det\left(\langle H_0 \rangle_{ij} - \langle 1 \rangle_{ij} E\right) = 0. \tag{25}$$

The corresponding linear coefficients X_j satisfy

$$\sum_{j=1}^N \left(\langle H_0 \rangle_{ij} - \langle 1 \rangle_{ij} E\right) X_j = 0. \tag{26}$$

The exponents p_i and the parameters A_i, B_i, C_i have to be chosen so as to make the energy a minimum.

To get an idea about the distribution of charge in the complex one can compute the expectation value of the three distances R_e, R_h and R_{eh} with the wave function obtained from minimalization of energy [15]. The necessary matrix elements are

$$\langle R_e \rangle_{ij} = S^{-1} I_{212}, \quad \langle R_{eh} \rangle_{ij} = S^{-1} I_{122}, \quad \langle R_h \rangle_{ij} = S^{-1} I_{113}, \tag{27}$$

and

$$\langle R_n \rangle = \sum_{i,j=1}^N \langle R_n \rangle_{ij} X_i X_j \bigg/ \sum_{i,j=1}^N \langle 1 \rangle_{ij} X_i X_j, \quad n = e, h, eh. \tag{28}$$

Numerical results

The numerical results of the described computation scheme have been partly published [16–18]. We give here as an example the ground state of the exciton bound to an ionized donor in CdS and CdSe. The hole from the highest, Γ_9, valence subbands is considered.

For CdS

the effective masses in units of the free electron mass are [5]

$$m_{e\perp} = 0.171, \quad m_{e\parallel} = 0.153, \quad m_{h\perp} = 0.7, \quad m_{h\parallel} = 5.0.$$

The dielectric constant is [19]

$$\varepsilon_\perp = 9.35, \quad \varepsilon_\parallel = 10.33.$$

Hence, $m_e = 0.17034$, $m_h = 0.9874$. The effective mass ratio is $\sigma = 0.1725$, $\gamma_e = -0.0115$, $\gamma_h = 1.23$.

The donor ground state energy is $E_D = -e^4 m_e / 2\hbar\varepsilon_0^2 = -23.994$ meV. The donor radius is $a_D = \hbar^2\varepsilon_0 / e^2 m_e = 30.5$ Å.

The reduced mass of the electron and hole is $\mu = (m_e^{-1} + m_h^{-1})^{-1}$, $\mu = 0.145$. The radius of the free exciton is $a_{Ex} = \hbar^2\varepsilon_0 / e^2\mu$, $a_{Ex} = 35.8$ Å.

We used wave function (19) with $N = 4$ and $p_i = p = 3$. The best wave function was found when the parameters had the values:

A_i 0.1881693,	0.1585773,	0.05079477,	0.2515395,
B_i 0.02864492,	-1.015322×10^{-4}	0.1619302,	0.1428984,
C_i 0.2070215,	0.1393884,	0.2241851,	0.5784894,
X_i 1.2124386×10^{-6}	3.9410149×10^{-8}	1.5087599×10^{-6}	1.3214599×10^{-5}

The linear parameters X_i yield $\psi(R_e, R_h, R_{eh})$ normalized to unity. The ground state energy has been found $(E' - E_D)/E_D = 4.04 \times 10^{-2}$. Thus $E' - E_D = -0.97$ meV.

The mean distances between the particles are, in Ångstrom units,

$$\langle R_e \rangle = 55 \text{ Å}, \quad \langle R_h \rangle = 104 \text{ Å}, \quad \langle R_{eh} \rangle = 93 \text{ Å}.$$

The ratios of the distances are

$$\langle R_e \rangle / \langle R_h \rangle = 0.527, \langle R_{eh} \rangle / \langle R_h \rangle = 0.898,$$

$$\langle R_e \rangle / a_D = 1.79, \quad \langle R_{eh} \rangle / a_{Ex} = 2.6$$

The distances with these ratios are shown in Fig. 1.

For CdSe

the effective masses have been assumed [20–21]

$$m_{e\perp} = m_{e\parallel} = 0.13, \quad m_{h\perp} = 0.45, \quad m_{h\parallel} = 1.0,$$

and the dielectric constant [19] $\varepsilon_\perp = 9.7$, $\varepsilon_\parallel = 10.65$. Hence, $m_e = 0.134$, $m_h = 0.5602$, $\gamma_e = 0.0919$, $\gamma_h = 0.735$, $\sigma = 0.2392$.

$$E_D = -17.645 \text{ meV}, \quad a_D = 40.1 \text{ Å}$$

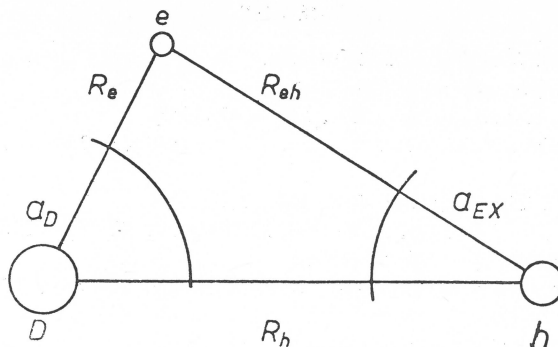$$\mu = 0.108, \quad a_{Ex} = 49.7 \text{ Å}.$$

Fig. 1. The interparticle distances in the exciton-ionized donor complex in CdS, *i.e.* at the electron-to-hole effective-mass ratio $\sigma = 0.1725$. The neutral donor orbit, centered at the donor center, and the free-exciton orbit, centered at the hole, are indicated

The wave function (19) with $N = 4$ and $p_i = p = 2.5$ was found best when the parameters had the values:

A_i 0.2525879,	0.2277946,	0.07251129,	0.2880866,
B_i 0.0351769,	-4.50194×10^{-3},	0.2146009,	0.1779778,
C_i 0.2140925,	0.1379945,	0.245199,	0.6087717,
X_i 1.0184183 $\times 10^{-5}$,	3.8346148 $\times 10^{-7}$,	1.2378762 $\times 10^{-5}$,	1.1101309 $\times 10^{-4}$.

The ground state energy has been found $(E' - E_D)/E_D = 1.98 \times 10^{-2}$, $E' - E_D = 0.35$ meV, and the distances

$$\langle R_e \rangle = 69 \text{ Å}, \quad \langle R_h \rangle = 167 \text{ Å}, \quad \langle R_{eh} \rangle = 157 \text{ Å}.$$

The ratios of the distances are

$$\langle R_e \rangle / \langle R_h \rangle = 0.414, \quad \langle R_{eh} \rangle / \langle R_h \rangle = 0.94$$
$$\langle R_e \rangle / a_D = 1.72, \quad \langle R_{eh} \rangle / a_{Ex} = 3.16.$$

Thus, with increasing σ the hole gets further away from the donor, the electron gets nearer to the donor, while the electron-hole distance increases.

With the wave function (19) with $N = 4$ and $p_i = p = 2.5$ the largest ratio σ for which binding still exists [22–24] has been found at $\sigma = 0.3902$. For this ratio of the effective masses we found $(E' - E_D)/E_D = 1.43 \times 10^{-6}$, and the mean distances, in units of the Bohr radius corresponding to the mass of the hole,

$$\langle R_e \rangle = 3.99, \quad \langle R_h \rangle = 23.74, \quad \langle R_{eh} \rangle = 23.72,$$

with the ratios

$$\langle R_e \rangle / \langle R_h \rangle = 0.168, \quad \langle R_{eh} \rangle / \langle R_h \rangle = 0.999.$$

It is to be noted that for $E' \cong E_D$, that is for vanishing binding, our variational function (19) does not give infinite $\langle R_h \rangle$. It only yields $\langle R_{eh} \rangle \cong \langle R_h \rangle$, *i. e.* equal distance of the hole from the electron and from the donor center.

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