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Exciton Energy Levels in Wurtzite-Type Crystals[*]

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The exciton problem in wurtzite-type crystals is investigated taking into full account the structure of the valence bands. Using perturbation theory, after a proper rotation of the exciton Hamiltonian, we obtain analytical expressions for the exciton ground states originating from the Γ_9, Γ_7, and Γ_7 valence subbands. These expressions are valid for any value of the crystal field splitting. Results are given for CdSe and CdS and the agreement with experiment is good.

Structure due to excitons was first observed in II-VI wurtzite compounds by Gross and co-workers[1] and by Thomas and Hopfield.[2] Since then, many authors[3] have investigated direct excitons in these materials. From the theoretical point of view, however, little work has been done.

It is well known that crystals with diamond and zinc-blende lattices have valence-band states originating from atomic *p* states and that the maximum of the valence band is at $\vec{k}=0$.[4] The valence bands of wurtzite-type materials also originate from atomic *p* states[5] but, because the symmetry is lower than that of the diamond and zinc-blende cases, the situation is more complicated. It is known, however, that the maximum is still exactly (or very nearly) at $\vec{k}=0$. The minimum of the conduction band is also at $\vec{k}=0$ (Γ_7 symmetry). In conjunction with the conduction band, each of the three valence bands gives rise to a series of exciton states which are called $A(\Gamma_9)$, $B(\Gamma_7)$, and $C(\Gamma_7)$.

The exciton Hamiltonian in the case of degenerate bands has been derived by Dresselhaus[6] and has been solved quite accurately for the case of direct[7] and indirect[8] excitons in diamond and zinc-blende semiconductors. For the case of wurtzite materials no exact solutions are known and only rough estimates of the binding energies have been obtained using a simple model in which the complicated valence bands are replaced by "average" simple bands. The valence-band structure of wurtzite-type materials has been studied by several investigators.[9] Most of these investigations, however, have restricted themselves to the limiting cases in which the crystal field splitting is small or large compared to the spin-orbit splitting. Such approximations, however, are hardly justified for most wurtzite-type crystals. Recently a more general treatment of these bands has been done by Jahne and Gutsche[10] using the $\vec{k}\cdot\vec{p}$ method. It would, therefore, be desirable to obtain values of the exciton binding energies taking into account the structure of the valence bands. In this paper, we give simple analytical expressions for the binding energy of the three exciton series which take into full account the details of the valence bands.

In the case of wurtzite-type compounds, the Hamiltonian for the relative electron-hole motion is

$$H_{ex}(\vec{p})=H_{el}(\vec{p})-H_h(\vec{p})+H_{int}(\vec{r})\ , \tag{1}$$

where $\vec{p}$ is the relative electron-hole momentum, $\vec{r}$ is the electron-hole distance, $H_{el}(\vec{p})$ is the electron Hamiltonian,

$$H_{el}(\vec{p})=\frac{p_x^2+p_y^2}{2m_{e\perp}}+\frac{p_z^2}{2m_{e\parallel}}\ , \tag{2}$$

where $m_{e\perp}$ and $m_{e\parallel}$ are the perpendicular and parallel electron masses, respectively, and

$$H_{int}(\vec{r})=-\frac{e^2}{[\epsilon_\parallel\epsilon_\perp(x^2+y^2)+\epsilon_\perp^2 z^2]^{1/2}} \tag{3a}$$

$$=-\frac{e^2}{\bar{\epsilon}_s[x^2+y^2+(\epsilon_\perp/\epsilon_\parallel)z^2]^{1/2}}\ , \tag{3b}$$

where $\bar{\epsilon}_s=(\epsilon_\parallel\epsilon_\perp)^{1/2}$, $\epsilon_\perp$ and $\epsilon_\parallel$ being the transverse and longitudinal dielectric constants. H_h is the 6×6 matrix which describes the hole kinetic energy near $\vec{k}=0$ as given by Jahne and Gutsche.[10] It is useful to change variables as follows:

$$x'=x\ ,\quad y'=y\ ,\quad z'=(\epsilon_\perp/\epsilon_\parallel)^{1/2}z\ . \tag{4}$$

Hamiltonian (1) can therefore be written as follows:

$$H_{ex}=\begin{vmatrix} P_0-Gp^2+BP_{20}-E_5^- & -\Delta_1^* & 0 & W'P_{21} & -2UP_{22} & 0 \\ -\Delta_1 & P_0+Gp^2+DP_{20}-E_1 & -W'P_{21} & 0 & 0 & -W'P_{2-1} \\ 0 & -W'P_{2-1} & P_0-Gp^2+BP_{20}-E_5^- & -\Delta_1 & 0 & -2UP_{2-2} \\ W'P_{2-1} & 0 & -\Delta_1^* & P_0+Gp^2+BP_{20}-E_1 & W'P_{21} & 0 \\ -2UP_{2-2} & 0 & 0 & W'P_{2-1} & P_0-Gp^2+BP_{20}-E_5^+ & 0 \\ 0 & -W'P_{21} & -2UP_{22} & 0 & 0 & P_0-Gp^2+BP_{20}-E_5^+ \end{vmatrix} \tag{5}$$

where

$$P_0 = F p^2 - \frac{e^2}{\bar{\epsilon}_s r} ,$$

$$\Delta_1 = \tfrac{1}{3}\sqrt{2}\,\Delta_7 , \quad E_5^- = E_5 - \tfrac{1}{3}\Delta_5 , \qquad E_5^+ = E_5 + \tfrac{1}{3}\Delta_5 , \tag{6a}$$

$$P_{20} = p_x{}^2 + p_y{}^2 - 2p_z{}^2 , \tag{6b}$$

$$P_{21} = (1/\sqrt{2})(p_x + ip_y)\,p_z , \qquad P_{2-1} = (1/\sqrt{2})(p_x - ip_y)p_z , \tag{6c}$$

$$P_{22} = \tfrac{1}{2}(p_x + ip_y)^2 , \quad P_{2-2} = \tfrac{1}{2}(p_x - ip_y)^2 , \tag{6d}$$

$$F = -\frac{1}{6}\left(\frac{\epsilon_\perp}{\epsilon_\parallel}\,(R+T) + 2(Q+S)\right) + \frac{1}{3}\left(\frac{2}{2m_{e\perp}} + \frac{1}{2m_{e\parallel}}\,\frac{\epsilon_\perp}{\epsilon_\parallel}\right) = \frac{1}{2\mu} , \tag{6e}$$

$$G = \frac{1}{6}\left(\frac{\epsilon_\perp}{\epsilon_\parallel}\,(R-T) + 2(Q-S)\right) , \tag{6f}$$

$$B = -\frac{1}{3}\left(Q - \frac{\epsilon_\perp}{\epsilon_\parallel}\,R\right) + \frac{1}{3}\left(\frac{1}{2m_{e\perp}} - \frac{1}{2m_{e\parallel}}\,\frac{\epsilon_\perp}{\epsilon_\parallel}\right) , \tag{6g}$$

$$D = -\frac{1}{3}\left(S - \frac{\epsilon_\perp}{\epsilon_\parallel}\,T\right) + \frac{1}{3}\left(\frac{1}{2m_{e\perp}} - \frac{1}{2m_{e\parallel}}\,\frac{\epsilon_\perp}{\epsilon_\parallel}\right) , \tag{6h}$$

$$W' = (\epsilon_\perp/\epsilon_\parallel)^{1/2}\,W . \tag{6i}$$

The parameters Q, R, S, T, U, and W are those used by Jahne and Gutsche[10] to describe the hole Hamiltonian. Since F is in general much greater than G, B, D, U, and W', we divide the exciton Hamiltonian into two parts. The first part—the main part—is given by

$$H_0 = \left|\begin{array}{cccccc} P_0 - E_5^- & -\Delta_1^* & 0 & 0 & 0 & 0 \\ -\Delta_1 & P_0 - E_1 & 0 & 0 & 0 & 0 \\ 0 & 0 & P_0 - E_5^- & -\Delta_1 & 0 & 0 \\ 0 & 0 & -\Delta_1^* & P_0 - E_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & P_0 - E_5^+ & 0 \\ 0 & 0 & 0 & 0 & 0 & P_0 - E_5^+ \end{array}\right| , \tag{7}$$

and a perturbation part is given by

$$H_{\text{pert}} = H_{\text{ex}} - H_0 . \tag{8}$$

Hamiltonian (7) can be exactly diagonalized if one applies a similarity transformation. The results of such diagonalization[11] are the three following hydrogenic series:

$$E_A^0(1s) = -R_0(1 + \bar{E}_5^+) , \tag{9a}$$

$$E_B^0(1s) = -R_0(1 - \bar{a}_0) , \tag{9b}$$

$$E_C^0(1s) = -R_0(1 - \bar{b}_0) , \tag{9c}$$

where

$$a_0 = -\left(\frac{E_5^- + E_1}{2}\right) - \left[\left(\frac{E_5^- - E_1}{2}\right)^2 + \Delta_1^2\right]^{1/2} , \tag{10a}$$

$$b_0 = -\frac{E_5^- + E_1}{2} + \left[\left(\frac{E_5^- - E_1}{2}\right)^2 + \Delta_1^2\right]^{1/2} , \tag{10b}$$

$$\bar{a}_0 = a_0/R_0 , \quad \bar{b}_0 = b_0/R_0 , \quad R_0 = \mu e^4/2\hbar^2\bar{\epsilon}_s^2 . \tag{10c}$$

After applying the same similarity transformation to H_{pert} and following straightforward but lengthy calculations,[11] we get the following corrections (up to second-order perturbation theory):

$$\Delta E_A(1s) = R_0\{B_1 - A_0[A_1 S_1(0) + A_2 S_1(\bar{a}_0 + E_5^-) + A_3 S_1(\bar{b}_0 + \bar{E}_5^+)]\} , \tag{11a}$$

$$\Delta E_B(1s) = R_0\{B_2 - A_0[A_4 S_1(0) + A_5 S_1(\bar{b}_0 - \bar{a}_0) + A_2 S_1(-\bar{a}_0 - \bar{E}_5^+)]\} , \tag{11b}$$

$$\Delta E_C(1s) = R_0\{-B_2 - A_0[A_6 S_1(0) + A_5 S_1(\bar{a}_0 - \bar{b}_0) + A_3 S_1(-\bar{b}_0 - \bar{E}_5^+)]\} , \tag{11c}$$

TABLE I. Parameters used for the calculations. All quantities are defined in the text. The units are meV for the energies, m_0 (free-electron mass) for the conduction-band masses, and $h^2/2m_0$ for the valence-band parameters.

Crystal	$m_{e\perp}$	$m_{e\parallel}$	$\epsilon_\perp$	$\epsilon_\parallel$	$E_5 - E_1$	Δ_5	Q	R	S	T	U	W
CdS	0.205[a]	0.205[a]	8.28[a]	8.64[a]	29.4[b]	59.6[b]	−2.38[b]	−0.33[b]	−0.33[b]	−4.15[b]	−2.00[b]	−1.18[b]
CdSe	0.130[a]	0.130[a]	8.75[a]	9.25[a]	39.0[b]	418[b]	−3.57[b]	−0.44[b]	−0.44[b]	−4.08[b]	−2.00[b]	−1.18[b]

[a] From Ref. 3.

[b] From Ref. 10.

TABLE II. Exciton energy levels for wurtzite-type compounds. All quantities are defined in the text. The energy unit is meV. In parentheses are the experimental values, taken from Ref. 3.

Crystal	Series	R_0	a_0	b_0	ΔE	$E_b = R_0 + \Delta E$
	A	29.5			0.9	30.4 (29.4)
Cds	B	29.5	16 (15)		1.4	30.9 (29.5)
	C	29.5		74 (78)	0.4	29.9 (• • •)
	A	17.5			−0.6	16.9 (15.7)
CdSe	B	17.5	25 (25)		0.4	17.9 (16.7)
	C	17.5		432 (433)	−0.3	17.2 (• • •)

where

$$A_0 = \tfrac{16}{15}\mu^2, \quad A_1 = 12B^2, \quad A_2 = 8a^2U^2 + b^2W'^2,$$

$$A_3 = 8b^2U^2 + a^2W'^2, \quad A_4 = 12(a^2B + b^2D)^2,$$

$$A_5 = 12[ab(B-D)]^2 + W'^2, \quad A_6 = 12(b^2B + a^2D)^2,$$

$$a = c/(c^2+1)^{1/2}, \quad b = 1/(c^2+1)^{1/2},$$

$$B_1 = -2\mu G, \quad B_2 = 2\mu(b^2 - a^2)G,$$

$$c = -\frac{E_5^- - E_1}{2\Delta_1} - \left[\left(\frac{E_5^- - E_1}{2\Delta_1}\right)^2 + 1\right]^{1/2},$$

and $S_1(x)$ is the same dimensionless series as in the diamond and zinc-blende cases.[7,8] Expressions (9a)–(9c) together with (11a)–(11c) completely describe the ground-state exciton binding energies. We have applied such expressions to CdS and CdSe for which almost all parameters necessary for the calculations are known, shown in Table I. The parameters U and W are not known and have been estimated.[10] However, these contributions are small and an uncertainty in their values should not appreciably affect the final results, which are shown in Table II. We see that the perturbative contributions are small so that the perturbation treatment is certainly valid. The agreement with the experimental results is good; in particular, we predict, for band B, a binding energy larger than that of band A, in agreement with experiment. Such agreement could be improved if one had more accurate valence-band parameters. It would be highly desirable, therefore, to have a good determination of such parameters, especially for ZnS and ZnO, where such parameters are not known, and where, therefore, we cannot carry out the calculation. In the cases in which some of the parameters are accurately known, one could use our expressions in conjunction with some experimental information to determine those parameters which are not known. Such analysis could prove to be very useful especially if one wants to use the valence-band parameters to describe other properties of these solids such as acceptor levels, density of states, etc. It is finally clear that the present method can also be applied to the excited states, such as the 2s states, and to the determination of the lifetime of the C-series exciton states which are frequently experimentally unobservable.[3]

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