move to a deeper position, i.e., from near the conduction band toward the valence band.

[19]All of the proposed mechanisms, should, generally, lead to first-order kinetics.

[20]C. P. Carnes, P. J. Drevinsky, and H. M. DeAngelis, AFCRL Technical Report No. 70-0423, 1970 (unpublished).

Calculation of the Exchange Energy for Excitons in the Two-Body Model*

Peter G. Rohnert†

*II. Institut für Theoretische Physik, Technische Universität Berlin, 1 Berlin 12, Germany
and Department of Physics, University of Dayton, Dayton, Ohio 45409*
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The exchange energy for the Wannier exciton is calculated by solving a previously derived two-body Hamiltonian $H^{(2)}$. The solution of the eigenvalue problem of $H^{(2)}$ in the effective-mass approximation is performed with a numerical diagonalization method. The values obtained for the exchange energy in several II-VI compounds are between 10 and 20% of the binding energy of the pure hydrogenlike exciton. The comparison with experimental results shows a satisfactory agreement.

I. INTRODUCTION

The influence of the electron-hole exchange interaction on the energy spectrum of the Wannier exciton is generally said to be small for large exciton radii.[1] Therefore, this exchange interaction is normally neglected in deriving a two-particle equation for the exciton from the N-electron Hamiltonian.[2-4] In a previous paper,[5] we presented a two-body operator for the exciton which was also derived from the N-electron Hamiltonian, but which included an exchange term in the two-body picture. With this term it became possible to handle the exchange energy of the exciton in the two-particle formalism. We did this in the above-mentioned paper with a perturbation calculation and our results were comparable to those of Makarov.[6]

It is, however, not necessary to use a perturbation method to compute the exchange energy of the exciton. We will show that the calculation of the exchange interaction can be performed on the same footing as the calculation of the Coulomb interaction. We obtain the exchange energy for the Wannier exciton in the effective-mass approximation (EMA) without fitting parameters. The physical restrictions to the validity of the calculated values are caused by the approximations used in deriving the exciton Hamiltonian. The derivation of a two-body Hamiltonian is only possible with the assumption of one-particle excitations in the N-electron picture. This assumption and the EMA have to be discussed in order to decide to which crystals the obtained results may be applicable.

In Sec. II, we shall first consider the main points in formulating the eigenvalue problem for $H^{(2)}$. We shall see that there are two possible methods for obtaining the eigenvalue spectrum of $H^{(2)}$ in the EMA. Only the diagonalization method will be described in detail. Then, in Sec. III, we shall solve the eigenvalue problem of $H^{(2)}$ and, in Sec. IV, the results will be discussed. In Sec. V, finally, we shall compare the calculated energy spectra for several substances with experiment.

II. EIGENVALUE PROBLEM FOR EXCITON HAMILTONIAN

In order to calculate the exchange energy of the exciton, we solve the eigenvalue problem of the exciton Hamiltonian $H^{(2)}$ which includes an exchange term. This Hamiltonian has the form[5]

$$H^{(2)} = E_0 + h(\vec{r}_1) - h^*(\vec{r}_2) - \frac{e^2}{\epsilon|\vec{r}_1 - \vec{r}_2|} + \delta(\vec{r}_1 - \vec{r}_2)\delta_{\sigma_1\sigma_2} \sum_{\sigma_1'\sigma_2'} \delta_{\sigma_1'\sigma_2'} \int_\Omega \frac{e^2}{\epsilon|\vec{r}_1 - \vec{r}_1'|} \delta(\vec{r}_1' - \vec{r}_2') \cdots d\tau_1' d\tau_2' , \quad (1)$$

where E_0 is the ground-state energy of the whole crystal in the Hartree-Fock method[7] and is here a constant, and $h(\vec{r}_1)$ and $-h(\vec{r}_2)$ are the self-consistent one-particle Fock operators,[7]

$$h(\vec{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + V(\vec{r}_i) + \sum_v \sum_\sigma \int_\Omega \frac{e^2}{\epsilon|\vec{r} - \vec{r}_i|} |\varphi_v(\vec{r}, \sigma)|^2 d\tau - \sum_v \delta_{s_i s_v} \varphi_v(\vec{r}_i, \sigma_i) \sum_\sigma \int_\Omega \frac{e^2}{\epsilon|\vec{r} - \vec{r}_i|} \varphi_v^*(\vec{r}, \sigma) \cdots d\tau_1 , \quad (2)$$

with $\varphi_v(\vec{r}_i, \vec{\sigma}_i)$ the eigenfunctions of $h(\vec{r}_i)$ in the valence band. $\sum_v$ means the summation over all valence-band states, while $\sum_\sigma$ is the sum over the spin variable σ. The integral is to be taken over the crystal volume Ω. The fourth term in Eq. (1) is the Coulomb term and the last one is the exchange term; ϵ is the dielectric constant.

The operator $H^{(2)}$ was derived from the N-electron Hamiltonian $H^{(N)}$ by an equivalence principle. The equivalence of the two operators $H^{(N)}$ and $H^{(2)}$ was shown for the subspaces $\tau^{(N)}$ and $\tau^{(2)}$ of the whole N-particle and two-particle Hilbert spaces, respectively. Thereby, the basis of $\tau^{(N)}$ consisted of all determinants with one conduction-band function and $N-1$ valence-band functions, the so-called one-particle excitations. The basis of $\tau^{(2)}$ was given by the two-particle products $\varphi_c(\vec{r}_1, \sigma_1)$ $\times \varphi_v^*(\vec{r}_2, \sigma_2)$, with φ_c a conduction-band function and φ_v a valence-band function. The restriction of $H^{(N)}$ to the subspace $\tau^{(N)}$ is a common approximation in treating the exciton. One can say it defines the exciton. Only in this approximation does there exist an equivalent two-particle operator $H^{(2)}$. This one is also restricted to a subspace, namely, $\tau^{(2)}$. We can signify this fact by introducing the projection operator

$$P = P_c(1) P_v^*(2) , \qquad (3)$$

with

$$P_\alpha(i) = \sum_j \varphi_{\alpha j}(\vec{r}_i, \sigma_i) \sum_{\sigma_i'} \int_\Omega \varphi_{\alpha j}^*(\vec{r}_i', \sigma_i') \cdots d\tau_i'$$

$$(i = 1, 2; \alpha = c, v) . \qquad (4)$$

(The sum runs over all states j of the band α.) This operator projects on $\tau^{(2)}$ and makes certain that the "first" particle (electron, $\vec{r}_1$) is in the conduction band (c), while the "second" particle (hole, $\vec{r}_2$) is in the valence band (v). So P suppresses states which have, e.g., two electrons in the conduction band and which are not exciton states. With this operator, we obtain the correct two-particle operator

$$\overline{H}^{(2)} = P H^{(2)} P , \qquad (5)$$

which is defined in the whole two-particle Hilbert space and is called the exciton Hamiltonian. In constrast to otherwise derived exciton Hamiltonians, it includes an exchange term. This exchange term is considered fully in the following solution of the eigenvalue problem of $\overline{H}^{(2)}$.

Before diagonalizing $\overline{H}^{(2)}$ we perform the EMA. First we consider the Fock operators $h(\vec{r}_1)$ and $h(\vec{r}_2)$, which describe the electron in the conduction band and the hole in the valence band, respectively. Assuming isotropic band extrema (for anisotropic effects see, e.g., Dresselhaus[8]), we have approximately, for the Fock operators

$$h(\vec{r}_1) \to E_1 - (\hbar^2/2m_e) \nabla_1^2 ,$$
$$\qquad (6)$$
$$-h^*(\vec{r}_2) \to -E_2 - (\hbar^2/2m_h) \nabla_2^2 .$$

E_1 and E_2 are the energies of the band edges, and m_e and m_h are the effective masses of the electron and the hole, respectively. In addition to the two Fock operators the EMA also concerns the functions

$$\varphi_{\alpha j}(\vec{r}_i, \sigma_i) = \varphi_{\alpha \vec{k}}(\vec{r}_i) \zeta_{\alpha s}(\sigma_i) \quad (i = 1, 2; \alpha = c, v) \qquad (7)$$

in the projection operator (4). Corresponding to Eq. (6), we have to approximate the Bloch functions by plane waves and get the resulting projection operator[9]

$$P = P(\vec{r}_1, \vec{r}_2) = \frac{1}{\Omega^2} \sum_{\langle \vec{k}, \vec{k}' \rangle} e^{i(\vec{k}\vec{r}_1 - \vec{k}'\vec{r}_2)} \int_\Omega e^{-i(\vec{k}\vec{r}_1' - \vec{k}'\vec{r}_2')} \cdots d\tau_1' d\tau_2' \qquad (8)$$

With these approximations, and after diagonalization in spin space, the operator $\overline{H}^{(2)}$ has the form

$$\overline{H}^{(2)} = \overline{H}_c + A_c , \qquad (9)$$

with

$$\overline{H}_c = P H_c P , \qquad (10)$$

$$H_c = E_0 + E_f - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_h} \nabla_2^2 - \frac{e^2}{\epsilon |\vec{r}_1 - \vec{r}_2|} , \qquad (11)$$

$$A_c = P A_0 P$$
$$= \frac{\delta_t}{\Omega^2} \sum_{\langle \vec{k}, \vec{k}' \rangle} e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} \int_\Omega \frac{2e^2}{\epsilon \vec{r}_{11'}} e^{-i\vec{k}'(\vec{r}_1' - \vec{r}_2')} \cdots d\tau_1' d\tau_2' . \qquad (12)$$

$E_f = E_1 - E_2$ is the band gap; A_0 is the exchange term of Eq. (1); δ_t proceeds from the spin, and is 1 for that triplet state which has no projection in the z direction, and zero otherwise[10]; $1/\vec{r}_{11'}$ is a modified Coulomb potential caused by P.

After this preparation we are ready to solve the eigenvalue problem

$$\overline{H}^{(2)} \Phi^{(2)}(\vec{r}_1, \vec{r}_2) = E_{exc} \Phi^{(2)}(\vec{r}_1, \vec{r}_2) \qquad (13)$$

of the exciton Hamiltonian $\overline{H}^{(2)}$ given by Eqs. (8)–(12). We solve this by calculating the matrix elements of $\overline{H}^{(2)}$ in a known basis and then diagonalizing that matrix numerically.

It should be mentioned that there is another possible way to solve the eigenvalue equation (13). It is suggested by the special form of the exchange term A_0 in Eq. (1). The δ character of A_0 enables us to reduce the eigenvalue equation (13) to the definition equation of the Green's function of eigenvalue problems. By means of the Green's function of the hydrogen problem, one can obtain the solution of the eigenvalue problem of $\overline{H}^{(2)}$. The results are identi-

cal with those obtained by the diagonalization meth-
od.

III. SOLUTION OF EIGENVALUE PROBLEM

As mentioned in Sec. II, we solve the eigenvalue
problem of $\bar{H}^{(2)}$ by diagonalization of a matrix rep-
resentation of $\bar{H}^{(2)}$. First of all, we introduce, as
usual,[4] the average electron-hole coordinate $\vec{R}$ and
the electron-hole separation $\vec{r}$ with

$$\vec{R} = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2) , \tag{14a}$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2 , \tag{14b}$$

and call the new wave function Ψ,

$$\Psi(\vec{R}, \vec{r}) = \Phi^{(2)}(\vec{r}_1, \vec{r}_2) . \tag{15}$$

Further, we assume that Ψ is of the form

$$\Psi(\vec{R}, \vec{r}) = (1/\sqrt{\Omega}) e^{i\vec{K}\cdot\vec{R}} f(\vec{r}) . \tag{16}$$

Then the eigenvalue equation (13) is transformed
into an equation involving only the coordinate $\vec{r}$.
This is known for the part H_c of $\bar{H}^{(2)}$; see, e.g.,
Knox.[4] But the same is true if the projection opera-
tor P and the exchange operator A_c are included.
For that purpose we first calculate the expression

$$P(\vec{r}_1, \vec{r}_2)\Psi(\vec{R}, \vec{r}) = P(\vec{r}_1, \vec{r}_2)(1/\sqrt{\Omega}) e^{i\vec{K}\cdot\vec{R}} f(\vec{r})$$

$$= (1/\sqrt{\Omega}) e^{i\vec{K}\cdot\vec{R}} e^{i(\vec{K}/2)\cdot\vec{r}} P(\vec{r}) e^{-i(\vec{K}/2)\cdot\vec{r}} f(\vec{r}) , \tag{17}$$

with

$$P(\vec{r}) = \frac{1}{\Omega}\sum_{\langle\vec{k}\rangle} e^{i\vec{k}\cdot\vec{r}} \int e^{-i\vec{k}\cdot\vec{r}'} \cdots d\tau' . \tag{18}$$

We introduce now the new function

$$v(\vec{r}) = e^{-i(\vec{K}/2)\cdot\vec{r}} f(\vec{r}) , \tag{19}$$

and the abbreviations

$$\bar{v}(\vec{r}) = P(\vec{r}) v(\vec{r}) \tag{20}$$

and

$$\hat{P}(\vec{r}) = e^{i(\vec{K}/2)\cdot\vec{r}} P(\vec{r}) e^{-i(\vec{K}/2)\cdot\vec{r}} . \tag{21}$$

Then we obtain the following alternatively used ex-
pressions:

$$P(\vec{r}_1, \vec{r}_2)\Psi(\vec{R}, \vec{r}) = \hat{P}(\vec{r})\Psi(\vec{R}, \vec{r}) \tag{22}$$

$$= (1/\sqrt{\Omega}) e^{i\vec{K}\cdot\vec{R}} \hat{P}(\vec{r}) f(\vec{r}) \tag{23}$$

$$= (1/\sqrt{\Omega}) e^{i\vec{K}\cdot\vec{R}} e^{i(\vec{K}/2)\cdot\vec{r}} \bar{v}(\vec{r}) , \tag{24}$$

so the projection operator P influences only the
separation coordinate $\vec{r}$ and reproduces the function
$e^{i\vec{K}\cdot\vec{R}}$.

Next we consider the exchange term. With Eqs.
(12), (16), and (19) we obtain

$$A_c\Psi = \frac{8\pi^2 e^2 \delta_t \bar{v}(0)}{\epsilon K^2} \frac{1}{\sqrt{\Omega}} e^{i\vec{K}\cdot\vec{R}} e^{i(\vec{K}/2)\cdot\vec{r}} \bar{\delta}(\vec{r}) , \tag{25}$$

wherein $\bar{\delta}(\vec{r})$ is the partial δ function

$$\bar{\delta}(\vec{r}) = P^*(\vec{r})\delta(\vec{r}) = \frac{1}{\Omega}\sum_{\langle\vec{k}\rangle} e^{i\vec{k}\cdot\vec{r}} . \tag{26}$$

We see in (25) that A_c also reproduces $e^{i\vec{K}\cdot\vec{R}}$ and
changes only the $\vec{r}$-dependent part. Thus Eq. (13)
is reduced to the only $\vec{r}$-dependent equation

$$\hat{P}(\vec{r})\left(E_0 + E_\ell + \frac{\hbar^2 K^2}{8\mu} - \frac{\hbar^2}{2\mu}\nabla^2 - i\frac{\hbar^2\vec{K}}{2\nu}\cdot\vec{\nabla} - \frac{e^2}{\epsilon r}\right)\hat{P}(\vec{r})f(\vec{r}) + \frac{8\pi e^2 \delta_t \bar{v}(0)}{\epsilon K^2} e^{i(\vec{K}/2)\cdot\vec{r}} \bar{\delta}(\vec{r}) = E_{exc}\hat{P}(\vec{r})f(\vec{r}) , \tag{27}$$

with

$$1/\mu = 1/m_e + 1/m_h \tag{28}$$

and

$$1/\nu = 1/m_e - 1/m_h . \tag{29}$$

This reduction of the eigenvalue equation was the
reason for introducing the new coordinates $\vec{R}$ and $\vec{r}$.

The next step is the selection of a complete basis.
The choice of a basis to calculate the matrix ele-
ments is arbitrary, and therefore our selection
might be determined only by convenience. It is
evident that we choose the complete set of plane
waves $e^{i\vec{K}\cdot\vec{R}}/\sqrt{\Omega}$ related to the coordinate $\vec{R}$. Con-
cerning the coordinate $\vec{r}$, we construct a special
basis. It consists partially of hydrogen functions
and partially of Slater functions. The hydrogen

functions are chosen for $l \neq 0$:

$$U_\lambda(\vec{r}) = U_{nlm}(r, \vartheta, \varphi) = R_{nl}(r) Y_{lm}(\vartheta, \varphi) . \tag{30}$$

(For the explicit form, see, e.g., Bethe and Sal-
peter.[11]) The Slater functions, which were sug-
gested by Hylleraas and discussed by Shull and
Löwdin[12] and also by Slater,[13] are chosen for $l = 0$:

$$S_{n00}(r, \vartheta, \varphi) = R'_{n0}(r) Y_{00}(\vartheta, \varphi)$$

$$= \left(\frac{8}{a^3}\right)^{1/2} \frac{1}{(n+1)!} \frac{1}{[(n+1)n]^{1/2}}$$

$$\times e^{-r/a} L^2_{n+1}\left(\frac{2r}{a}\right) \frac{1}{(4\pi)^{1/2}} , \tag{31}$$

where L are the Laguerre polynomials

$$L_{n+1}^{2}(x) = \frac{d^2}{dx^2}\left[e^x \frac{d^{n+1}}{dx^{n+1}}(x^{n+1}e^{-x})\right]. \qquad (32)$$

The functions S_{n00} and U_{n00} differ mainly in the exponential function which is always the same in S_{n00} while n dependent in U_{n00}. For $n=1$, both functions are equal:

$$S_{100}(r,\,\vartheta,\,\varphi) = U_{100}(r,\,\vartheta,\,\varphi)\,. \qquad (33)$$

Since we are mainly interested in the $n=1$ exciton state, this equality (33) is a reason for choosing the above Slater functions.

The $R_{nl}(r)$ of Eq. (30) form a complete set of functions for each fixed l and current n. The same is true for the R'_{n0} of Eq. (31), which are orthonormal with respect to n. Further, the S_{n00} are orthogonal to the hydrogen functions U_{nlm} with $l \neq 0$, because the spherical harmonic

$$Y_{00}(\varphi,\,\varphi) = 1/(4\pi)^{1/2} \qquad (34)$$

of S_{n00} is orthogonal to the spherical harmonics $Y_{lm}(\vartheta,\,\varphi)$, $l \neq 0$, of the hydrogen functions. So the hydrogen functions (30) for $l \neq 0$ and the Slater functions (31) for $l = 0$ form a complete basis in the $\vec{r}$ space. This basis supplies, together with the plane waves $e^{i\vec{K}\cdot\vec{R}}/\sqrt{\Omega}$, a complete orthonormal set in the two-particle space.

The reason for constructing the mixed basis, consisting of U and S, is the form of Eq. (27). Neglecting the exchange term and the projection operator, it is a hydrogenlike equation and the solution is given by

$$f_q(\vec{r}) \equiv f_{\vec{K}\lambda}(\vec{r}) = e^{-i(\mu/2\nu)\vec{K}\cdot\vec{r}}U_\lambda(\vec{r})\,. \qquad (35)$$

We denote the state with the number q which involves the six quantum numbers $\vec{K}$ and $\lambda \equiv nlm$. $f_q(0)$ vanishes for $l \neq 0$, and with Eq. (19), so does $v_q(0)$. For the value of $\tilde{v}_q(0)$ in expression (25), one calculates slightly different amounts, but for $l \neq 0$, $\tilde{v}_q(0)$ practically vanishes too. So, in this case, the exchange term disappears in Eq. (27) and, aside from the projection operator, this is a hydrogenlike equation. Therefore, we use the hydrogen functions in the case of $l \neq 0$, for which the matrix of $\bar{H}^{(2)}$ is almost diagonal. For $l = 0$, the exchange term does not vanish, and the matrix is not diagonal, either for hydrogen or for Slater functions. We prefer the Slater functions for the necessary numerical calculation because they do not contain a continuum as the hydrogen functions do and, therefore, they are a proper basis for a matrix diagonalization method.

We calculate the matrix elements

$$\bar{H}_{q',q}^{(2)} = (\Psi_{q'},\,\bar{H}^{(2)}\Psi_q) \qquad (36)$$

separately for $\bar{H}_c$ and A_C. Using (9) and (24), we have for $\bar{H}_c$

$$(\Psi_{q'},\,\bar{H}_c\Psi_q) = \delta_{\vec{K}',\vec{K}}\,(v_{q'}(\vec{r}),\,\tilde{H}'_c v_q(\vec{r}))$$

$$\approx \delta_{\vec{K}',\vec{K}}\,(v_{q'}(\vec{r}),\,H'_c v_q(\vec{r}))\,, \qquad (37)$$

with

$$\tilde{H}'_c = P(\vec{r})\,H'_c\,P(\vec{r})$$

and

$$H'_c = E_0 + E_\ell - \frac{\hbar^2 K^2}{2m_e} - \frac{\hbar^2}{2\mu}\nabla^2 - i\frac{\hbar^2\vec{K}}{m_e}\vec{\nabla} - \frac{e^2}{\epsilon r}\,. \qquad (38)$$

$\delta_{\vec{K}',\vec{K}}$ means the Kronecker symbol. The approximation in Eq. (37) is not very serious. For example, the expectation values of the operators $\tilde{H}'_c$ and H'_c for the exciton $1s$ state differ by a factor of less than $1-10^{-4}$, which is irrelevant considering the other approximations made. In the case of the exchange term we calculate the matrix elements correctly and obtain, with (25),

$$(\Psi_{q'},\,A_C\Psi_q) = \frac{8\pi e^2 \delta_l \delta_{\vec{K}',\vec{K}}}{\epsilon K^2}\,\tilde{v}_{q'}^*(0)\,\tilde{v}_q(0)\,. \qquad (39)$$

The resulting matrix element is now

$$\bar{H}_{q'q}^{(2)} = \delta_{\vec{K}',\vec{K}}\left[(v_{q'}(\vec{r}),\,H'_c v_q(\vec{r})) + \frac{8\pi e^2 \delta_l}{\epsilon K^2}\,\tilde{v}_{q'}^*(0)\,\tilde{v}_q(0)\right]. \qquad (40)$$

With (19) and (35) we can deduce the $v_q(\vec{r})$ to our basis functions and then calculate the matrix elements (40) explicitly. The only approximation we make is the substitution of the sum over the first Brillouin zone (BZ) by an integral in the $\vec{k}$ space over a sphere, which has the same volume as the first BZ. The radius k_m of the sphere is given by

$$k_m = \gamma\pi/a_l\,, \qquad (41)$$

where a_l is the lattice constant and γ is a number which depends on the geometry of the BZ and has a value of about 1. The resulting expressions are very extensive; we do not present them here. We have diagonalized the matrix numerically on a computer. The results given in Sec. IV are obtained from matrices of order $d = 100$. The change in the values for the $1s$ exciton state resulting from diagonalizing a matrix of $d = 90$ and a matrix of $d = 120$ was smaller than 0.01%. Therefore, using a matrix of order $d = 100$ should be adequate to get correct values.

IV. RESULTS

First, we see from Eq. (40) that all matrix elements between states with a different total $\vec{K}$ vector vanish. This is obvious for the Coulomb term. But also the exchange interaction does not couple states with different $\vec{K}$ vectors in our approximation. Further, we see that only exciton s states

with $\delta_t = 1$ have a considerable amount of exchange energy. The exchange energies of the other states are negligible. This is in agreement with our previous results[5] and with Makarov.[6] The s states are shifted by the exchange interaction from the other states which remain hydrogenlike. The final result for the exciton energy, that is, the eigenvalue spectrum of the exciton Hamiltonian $H^{(2)}$, is given by the formula

$$E_{\text{exc}} \equiv E_{\bar{K}nlm} = E_0 + E_g + \frac{\hbar^2 K^2}{2(m_e + m_h)}$$

$$- \frac{\mu e^4}{2\epsilon^2 \hbar^2} \left(\frac{1 - \delta_t \delta_{l0}}{n^2} + \frac{\delta_t \delta_{l0}}{\rho_n^2} \right) . \quad (42)$$

Again δ_{l0} means the Kronecker symbol. The quantity

$$G = \mu e^4 / 2\epsilon^2 \hbar^2 = (\mu / m\epsilon^2) \times 13.6 \text{ eV} \quad (43)$$

is sometimes called one exciton Rydberg and differs from the Rydberg energy of the hydrogen atom by a factor of $\mu / m\epsilon^2$. ρ_n is a number which corresponds to the principal quantum number n but is slightly different from integers. It is discussed in detail below. For $l \neq 0$, the term with ρ_n^2 disappears and the remaining expression for the exciton energy is just the normally used formula for the Wannier exciton.[4] But for $l = 0$, we now have a changed value for the binding energy which is given by the last term in Eq. (42). Therein the ρ_n is not an integer but is somewhat larger than the corresponding n. Aside from the main quantum number n, ρ_n depends on the three parameters p, b, and c. Here, p is the product of the exciton radius

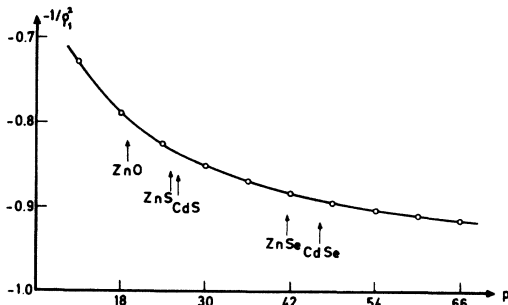$$a = (\epsilon m / \mu) a_B = (\epsilon m / \mu) \times 0.529 \text{ Å} \quad (44)$$

FIG. 1. Exciton binding energy for the exchange-influenced 1s state as a function of the parameter p for fixed values $b = 0.5$ and $c = 0.45$. The units are exciton Rydbergs [cf. Eq. (43)]. In the pure hydrogenlike case the binding energy is -1. The difference between $-1/\rho_1^2$ for a particular p and -1 is the exchange energy of the exciton. For some II-VI compounds the p values of Table III are entered.

TABLE I. Binding energies of the exchange-influenced exciton states. The values for $1/\rho_n^2$ are calculated for variable p and fixed $b = 0.5$ and $c = 0.45$. By multiplying the given values for $1/\rho_n^2$ with G [cf. Eq. (43)], one gets the binding energies of the exchange-influenced states.

P	$-1/\rho_1^2$	$-1/\rho_2^2$	$-1/\rho_3^2$	$-1/\rho_4^2$
12	-0.7284	-0.2117	-0.0993	-0.0574
18	-0.7890	-0.2211	-0.1023	-0.0587
24	-0.8257	-0.2265	-0.1040	-0.0595
30	-0.8510	-0.2302	-0.1051	-0.0599
36	-0.8686	-0.2327	-0.1059	-0.0603
42	-0.8832	-0.2346	-0.1066	-0.0606
48	-0.8946	-0.2362	-0.1069	-0.0608
54	-0.9032	-0.2374	-0.1074	-0.0610
60	-0.9099	-0.2383	-0.1077	-0.0612
66	-0.9156	-0.2391	-0.1079	-0.0613
72	-0.9026	-0.2397	-0.1080	-0.0614
$\cdot$				
$\cdot$				
$\cdot$				
$p \to \infty$	-1.0000	-0.2500	-0.1111	-0.0625

with the "radius" k_m of the first BZ [cf. Eq. (41)]:

$$p = a k_m . \quad (45)$$

It is a fixed value for each substance and varies for some typical II-VI semiconductors from 20 to 50. The parameter

$$b = a K \quad (46)$$

is the product of the exciton radius a and the absolute value of the total wave number $\vec{K}$ of the exciton;

$$c = (\mu / m_e) b = [m_h / (m_e + m_h)] a K \quad (47)$$

is b multiplied by a fraction of effective masses. For an optically excited exciton, the K value is very small and the calculated values for the parameters b and c are about 1. They have almost no influence on ρ_n. So only the parameter p is important here.

The dependence of the binding energy on the parameter p is given in Table I and in Fig. 1 for fixed values b and c. In Fig. 1, we see that for large p the value $-1/\rho_1^2$ approaches -1. The difference between the value on the curve and -1 is a measure of the exchange energy, which thus becomes smaller for large p. On the other hand, p is large in substances with large exciton radii [cf. Eq. (45)]. So it is verified that the exchange interaction becomes small for large exciton radii.

For small exciton radii, i.e., small p values, the exchange energy increases and reaches considerable amounts. But there we come to the limit of the described model. The size of the exciton in the 1s state should involve at least three lattice sites. With Eqs. (41) and (45) we have

$$p = \gamma \pi a / a_e , \quad (48)$$

TABLE II. Parameters used to calculate the exchange energy.

Sub-stance	Struc-ture[a]	ϵ[b]	μ/m[c]	a (Å)[d]	G_{calc}[e] (meV)
CdS	h	8.2	0.14	31	28
CdSe	h	9	0.09	53	15
ZnO	h	7	0.21	18	58
ZnSe	c	8.6	0.12	38	22
ZnS	c	7	0.17	22	47

[a]h means hexagonal (wurtzite) structure and c means cubic (zinc blende) structure.

[b]We used an averaged dielectric constant ϵ obtained from ϵ_0 and ϵ_∞ (Ref. 14) by Haken's formula (Ref. 2).

[c]Reference 14.

[d]Cf. Eq. (44).

[e]Cf. Eq. (43).

and for $a/a_e \approx 3$ we find a p of about 10, which is the lower limit for application of the above energy formula (42). But in practically all semiconductors, the p value is much larger, as seen in Table II. Therefore, if the parameters m_e, m_h, ϵ, and k_m are known, we can state the value of p and then obtain the exchange energy of the exciton from Table I. Unfortunately, the parameters m_e, m_h, and ϵ are not well known. So the determination of the exchange energy contains some uncertainty. On the other hand, if the exchange energy is known by experiments on excitons, one can obtain the values for the reduced effective mass and for ϵ.

V. COMPARISON WITH EXPERIMENT

In order to determine the exchange energy

$$A = \frac{\mu e^4}{2\epsilon^2 \hbar^2} \frac{1}{\rho_n^2} = G \frac{1}{\rho_n^2} \tag{49}$$

for some II-VI compounds, we need the parameters ϵ and μ. Since these are not precisely known, we give for control, in Table II, the values used. With these values we determined p and got from Table I the amounts of the exchange energy. In Table III

TABLE III. Calculated and measured values for the exciton exchange energy in some II-VI compounds.

Sub-stance	Struc-ture[a]	p[b]	A (%)	A[c] (meV)	$j = \frac{1}{2}A$	j_{expt}[d]
CdS	h	26.2	16.4	4.6	2.3	2.5
CdSe	h	46.3	10.8	1.6	0.8	0.4
ZnO	h	19.0	20.4	11.8	5.9	5.6
ZnSe	c	41.5	11.6	2.5	1.25	1.0
ZnS	c	25.0	17.0	8.0	4.0	4.0

[a]See Ref. a of Table II.   [c]Cf. Eq. (49).
[b]Cf. Eq. (45).   [d]Reference 15.

we list the calculated values for A – in column 4 in percentage of the binding energy and in column 5 in meV. One-half of this value, j, corresponds to the measured j_{expt}. These values originate from pressure measurements by Langer et al.[15] The agreement between the calculated values j and the measured values j_{expt}, is fairly good considering the approximations made and the uncertainty in the experimental parameters. The equality of the measured and calculated values for ZnS must be considered accidental.

The main result of these calculations is the fact that the exchange energy for Wannier excitons reaches values of 10 to 20% of the binding energy. Even for excitons with very large radii (cf. CdSe in Table II) the exchange energy has a reasonable value of about 10% of the binding energy. Thus the influence of the exchange interaction on the energy spectrum of the Wannier exciton is larger than estimated before and should not be neglected.

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Energy Levels of Direct Excitons in Semiconductors with Degenerate Bands*

A. Baldereschi and Nunzio O. Lipari
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 62802
(Received 2 September 1970)

A new method to investigate the direct-exciton spectrum in semiconductors with degenerate bands is described. This method, which solves the effective-mass Hamiltonian using symmetry arguments and second-order perturbation theory, gives a general and accurate description of exciton states in semiconductors. Direct excitons in group-IV elements, III-V compounds, and II-VI compounds are investigated. For Ge and GaAs, the binding energy is in excellent agreement with previous calculations. For all other substances, our treatment represents the first theoretical investigation. The results are in satisfactory agreement with available experimental data.

I. INTRODUCTION

Diamond and zinc-blende semiconductors have been studied extensively in recent years and a large amount of information is now available both experimentally and theoretically. Special attention has been given to the optical properties because they are one of the best tools for investigating band structures and electron states. Near the fundamental edge, the optical spectra of these semiconductors exhibit structure which is interpreted as due to direct-exciton formation. In large-gap semiconductors, additional structure due to indirect excitations is observed at lower energies.

The first observation of direct and indirect excitons was made in Si and Ge.[1] Since then, structure due to exciton formation has been observed in many zinc-blende III-V[2] and II-VI[3] compounds. These effects are generally small, owing to the large dielectric constants and small effective masses of these materials. For InSb, these effects are so small that they have not yet been observed in optical spectra. In this case, however, exciton effects have been observed in magneto-optical experiments[4] and the exciton binding energy can be estimated.

In contrast to such abundance of experimental data, little theoretical work has been done up to date. Most of these theoretical investigations have been concerned with the exciton energy spectrum and the optical absorption in a model semiconductor with simple valence and conduction bands. In this case, the Wannier exciton Hamiltonian[5] can be reduced to that of the hydrogen atom and exact solutions are easily obtained. Optical selection rules

and the absorption coefficient have been investigated[6] in detail too. Even though these investigations are useful from the theoretical point of view, they cannot be applied directly to the interpretation of most of the experimental data because degeneracies often occur in the energy bands. All crystals with the diamond and zinc-blende structure have a degenerate valence band at $\vec{k} = 0$, where the exciton is formed, and therefore the theory for simple bands cannot be applied.

A formal theoretical treatment of excitons in the case of degenerate bands has been done by Dresselhaus.[7] The resulting Hamiltonian is formally similar to that describing impurity states for degenerate bands[8] and, owing to its complexity, no exact solutions have been obtained. McLean and Loudon[9] have obtained an approximate solution for the ground state of the direct and the indirect excitons in Ge and Si using the variational technique previously introduced by Kohn and Schechter[10] in their treatment of shallow acceptor states. The same method was also used by Abe,[11] who considered the direct exciton in Ge and GaAs. So far, no one has considered the exciton series originating from the split-off valence band whose effects in optical spectra have been experimentally observed.[12-14] Furthermore, no calculations have been done to compute the energy of excited states which have been experimentally observed in some of the III-V compounds[15] and II-VI compounds.[16] The reason for these facts is that the variational technique, which involves elaborate computations for the ground state, becomes practically impossible when applied to excited states or to the split-off exciton series.