QUANTUM SIZE EFFECTS IN SEMICONDUCTOR CRYSTALLITES: CALCULATION OF THE ENERGY SPECTRUM FOR THE CONFINED EXCITON *

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For the exciton (e⁻, h⁺) confined to a sphere (a simple model for the light absorption of a small semiconductor particle) we calculate some of the electronic states. We use procedures similar to those for the two-electron atom. For radii R smaller than the "exciton radius" simple one-configuration wavefunctions suffice. For larger R a more accurate description involving Hylleraas functions is required.

1. Introduction

This Letter reports on the calculation of energy levels for the two-body system of the "confined exciton". The exciton model is able to describe the optical absorption of very small crystallites consisting of semiconducting material, e.g. cadmium sulfide, CdS [1–12]. CdS crystallites, which are approximately spherical, can be generated and stabilized with radii, R, reaching below the "exciton radius" $R_{exc} = \hbar^2 \epsilon / \mu e^2$ of the material (cf. eq. (2b) below); for CdS $R_{exc} \approx 20$ Å. As R decreases a blue-shift of the threshold of optical absorption is observed together with a growing "prominence" of the exciton peak in the spectrum.

In its simplest form the model of the confined exciton assumes infinitely high potential walls at the crystallite surface. Improved models [10,11] take into account penetration of the charge carriers into the outside space. Until a satisfactory theory (in the framework of the exciton model) is available, there appear to be two problems: The choice of a physically realistic model and the reliability of the calculations. This article considers the latter problem. Even the simple model (two Coulomb-interacting particles confined to a sphere) has only been approximately calculated [11]. Efros and Efros [13] have treated this model for the limiting cases of $R \ll R_{exc}$ and $R \gg R_{exc}$ and

have suggested a Born–Oppenheimer-like approximation for other values of R. Our point of departure is the close relationship of the problem to that of the two-electron atom. We discuss (see section 2) the use of configuration interaction and Hylleraas functions, as well as a perturbation expansion in R. Section 3 presents the results of our calculations and discusses briefly improvements to the simple model and comparison with the existing measurements.

2. Exciton energy levels for the hard sphere

The exciton consists of a conduction-band electron, e⁻, and a valence-band positive hole, h⁺. Let m_1 and m_2 be the effective masses (assumed to be isotropic) for the two particles. The Coulomb attraction between e⁻ and h⁺ is screened by the factor $1/\epsilon$ where ϵ is the high-frequency dielectric constant of the material

$$H = -(\hbar^2/2m_1) \nabla_1^2 - (\hbar^2/2m_2) \nabla_2^2 - e^2/\epsilon|r_1 - r_2| \quad (1)$$

is the Hamiltonian of the system [14]. The eigenvalues of (1) represent the excited energy levels of the crystal, counted from the lower edge of the conduction band. (Transition energies from the crystal ground state can be obtained by adding the gap energy E_g.)

We use the following units for mass, length and energy:

$$\mu = (1/m_1 + 1/m_2)^{-1} = 0.154 m_0, \quad (2a)$$

$$\text{bohr(exc)} = \hbar^2\epsilon/\mu e^2 = 19.3 \text{ Å}, \tag{2b}$$

$$\text{hartree(exc)} = \mu e^4/\hbar^2\epsilon^2 = 0.133 \text{ eV}. \tag{2c}$$

The numerical values in (2a)–(2c) refer to bulk CdS for which we take [15]: $m_1 = 0.19\,m_0$, $m_2 = 0.8\,m_0$ (m_0 denotes the free electron mass), $\epsilon = 5.6$ and $E_g = 2.5$ eV. In the infinitely extended crystal the exciton exhibits hydrogenic energy levels $-(1/2n^2)$ hartr(exc) with $n = 1, 2, 3...$. If the movement of e^- and h^+ is confined to a sphere of radius R, eq. (1) becomes a helium-like two-particle problem since the center-of-mass movement is no longer separable. In comparison with the $R = \infty$ hydrogenic case, the energy spectrum must become richer through the various combinations of two single-particle levels. The rough one-body model [8,10] (one electron of mass μ moves in the field of the walls and an h^+ fixed at the sphere centre) is in this respect inadequate.

Problem (1) can be treated by the same methods which are used for the two-electron atom [16–19]. The sphere radius R corresponds largely to the inverse nuclear charge $1/Z$. After the scale transformation $r \to r/R$ [16,17] the Hamiltonian (1) takes the form $H^0 + R(-1/r_{12})$ where H^0 is the sum of the kinetic energies from (1) and R appears as a perturbation parameter. Any eigenvalue can therefore be written as a power series in R (times a prefactor $1/R^2$); if R is small enough the series can be truncated at first order:

$$E(R) = (1/R^2)\,[E^{(0)} + R\,E^{(1)} + ...]. \tag{3}$$

In this approximation the eigenfunctions are products of two particle-in-a-box orbitals [20]. We denote these orbitals by 1s, 2s,... (for the angular momentum $l = 0$), by 2p, 3p,... (for $l = 1$), etc. The $E^{(0)}$ in (3) is the sum of two orbital energies (belonging to the masses m_1 and m_2), $E^{(1)}$ is the respective expectation value of $-1/r_{12}$. The *lowest state* of the exciton has the "configuration" $(1s)^2$. The corresponding product eigenfunction is:

$$\psi_A = \phi_{1s}(r_1)\,\phi_{1s}(r_s) \tag{4}$$

and $E^{(0)} = \frac{1}{2}\pi^2$, $E^{(1)} = -1.786$. Column A of table 1 gives the $(1s)^2$ energy in this approximation [11].

As R increases, (4) will no longer be sufficient. The set of all particle-in-a-box orbitals [20] forms a complete set and the exact $(1s)^2$ state of the exciton can be expanded (in the sense of configuration interaction [18,19]):

Table 1
Exciton "ground state" energy in different approximations. (A) Single configuration, eq. (4); (B) 25 s-orbital configurations, eq. (5); (C) Hylleraas-type function, eq. (6). Energies in hartr(exc), radii R in bohr(exc), see eqs. (2b) and (2c)

Radius R	A	B	C
0.5	16.167	16.112	16.039
1	3.149	3.091	3.017
1.5	1.003	0.942	0.869
2	0.341	0.277	0.207
3	−0.047	−0.117	−0.177
5	−0.160	−0.243	−0.276

$$\psi_B = \sum_{\alpha,\beta} c_{\alpha\beta}\phi_\alpha(r_1)\,\phi_\beta(r_2). \tag{5}$$

We have carried out an expansion, restricted to ss' configurations. The matrix elements of $1/r_{12}$ are sums of sine integrals Si($n\pi$) [21]. Using 25 configurations (those with the 25 lowest kinetic energies, E^0) column B of table 1 is obtained. Very accurate and compact wavefunctions for two-electron systems are provided by the Hylleraas method [16,17,22], which introduces the coordinate r_{12} explicitly. The simplest ansatz is:

$$\psi_C = (c + c'\,r_{12})\,\psi_A. \tag{6}$$

Evaluation of the matrix elements for (6), whilst more complicated than for the CI case (5), still leads exclusively to elementary integrals and Si($n\pi$). The resulting $(1s)^2$ energy is given in column C of table 1.

The Hylleraas-type function C, which automatically comprises contributions from pp', dd', etc. configurations, is seen to do better than B for all radii $R \lesssim 5$ bohr(exc). In comparison with A, C is lower by about 0.13 hartr(exc) = 17 meV, almost independent of R. For small radii, $R \lesssim 1$ bohr(exc) ≈ 20 Å, this correction is insignificant. The R independence of the difference (C−A) suggests that quite a large range of radii R ($R \lesssim 2$ bohr(exc)) is well described by the *second-order* perturbation expansion, i.e. the extension of (3) by the next term where $E^{(2)} \approx -0.13$. The improvement of C over A becomes important for $R \gtrsim 2.5$ bohr(exc) where $E < 0$, so that the exciton exists in a bound state without strong perturbation by the walls. For $R \to \infty$ $E(R)$ must tend to the free-exciton binding-energy -0.5 hartr(exc) and the wavefunction essential-

Table 2
Coefficients $E^{(0)}$ and $E^{(1)}$ (see eq. (3)) for the lowest energy levels (angular momenta $L = 0$ and $L = 1$) of the CdS exciton. In the given configurations the first label refers to the e^- (mass 0.19), the second to h^+ (mass 0.80)

L	Configuration	$E^{(0)}$	$-E^{(1)}$
0	$(1s)^2$	4.935	1.786
	1s2s	7.776	1.780
	$(2p)^2$	10.093	1.889
	1s3s	12.511	1.777
	2p3p	13.883	1.851
1	1s2p	5.926	1.620
	2p1s	9.104	1.620
	1s3p	9.715	1.724

ly to $\exp(-r_{12})$. Therefore, for radii in the range of several bohr(exc), (6) would have to be extended by terms in $(r_{12})^2$, $(r_{12})^3$, etc.

For the *higher energy levels* of the exciton, eq. (3)

with the appropriate coefficients $E^{(0)}$ and $E^{(1)}$ again holds as long as R is sufficiently small. Apart from $L = 0$ other angular momenta L can be of interest, since the crystallites of the experiment are never strictly spherical. Table 2 gives $E^{(0)}$ and $E^{(1)}$ for the five lowest ($L = 0$) and for the three lowest ($L = 1$) levels. (The evaluation of $E^{(1)}$ in terms of Si integrals becomes cumbersome for configurations containing p-orbitals; it is more convenient to replace the Bessel function j_1 by its series expansion [21].) For $L = 0$, the $E^{(1)}$ values are seen to be close together, while the $E^{(0)}$ are much wider separated. The energy curves (3) therefore do not cross in a large range of R suggesting that strong interaction between neighbouring configurations does not occur. Thus (3) appears to be a useful approximation, at least for the ($L = 0$) states. Fig. 1 displays the position of the levels for a few radii R.

In order to obtain an accurate level scheme *for large R*, one would do a Hylleraas-type calculation similar to (6) with several configurations included.
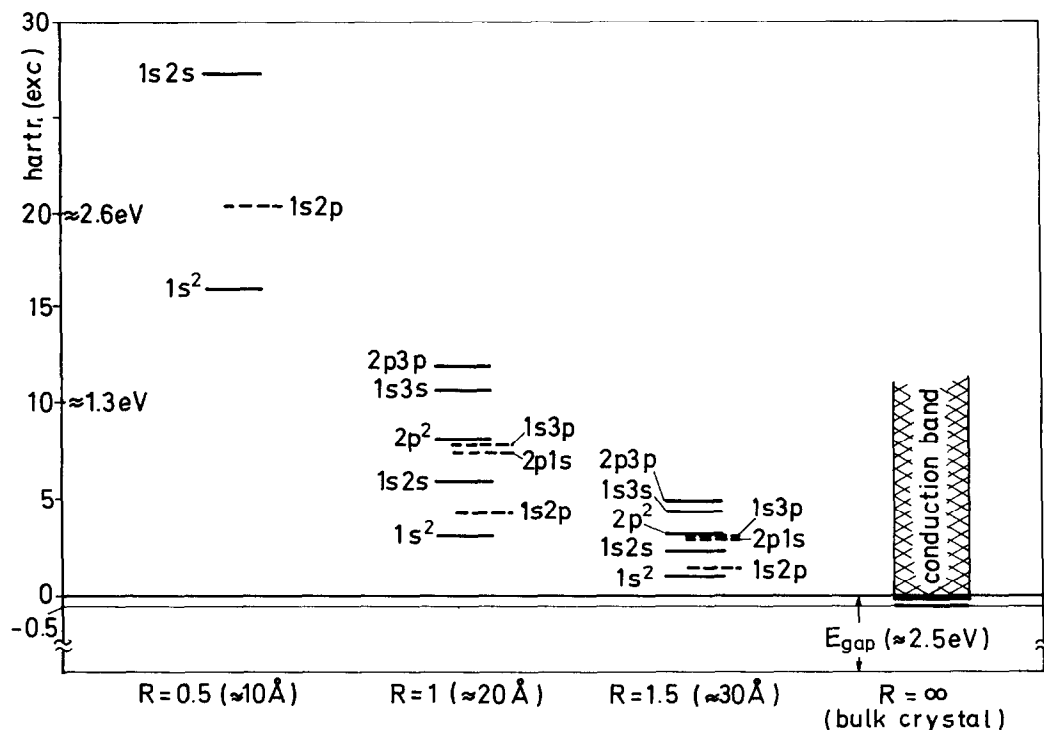

Fig. 1. CdS exciton confined to a sphere of radius R. The lowest energy levels (of angular momenta $L = 0$ and $L = 1$) are in the approximation of eq. (3). (Dotted levels refer to $L = 1$). Radii R are given in units of bohr(exc); cf. eq. (2b).

3. Discussion

In this article we have tested methods for calculating the energy levels for the spherically confined exciton. The results are: (i) For radii $R \lesssim 1$ bohr(exc) ≈ 20 Å (for CdS) the low-lying states of angular momentum $L = 0$ are well described by a simple one-configuration wavefunction. These levels, which at $R = \infty$ are hydrogen-like and energetically close (between -0.5 hartr(exc) and 0), become widely separated with roughly equal mutual energy gaps (see fig. 1). (ii) In order to obtain the smaller energy shifts occurring at larger R, Hylleraas-type wavefunctions are appropriate. For example at $R = 2$ bohr(exc) ≈ 40 Å the model gives a shift (compared with $R = \infty$) of 0.71 hartr(exc) $= 94$ meV for the lowest level.

Clearly, the hard-wall model cannot yield quantitative agreement with experimental results because it exaggerates the kinetic energy contribution to all levels. The qualitative changes in the energy spectrum with decreasing R should be given correctly. It would be interesting if the well-separated higher levels, which the model predicts, could be confirmed by experiment.

An improvement of the model, which at the same time does not unduly complicate the calculations, is the introduction [10] of a finite depth, V_0, for the potential box representing the crystallite. We have shown recently in the framework of the one-body model (see fig. 1 of ref. [8]) that, by assuming a value of $V_0 \approx 4$ eV, the predicted absorption threshold for CdS can be brought considerably closer to the values measured in the range $6 \lesssim R \lesssim 20$ Å. The two-body approach described above is directly transferable to the finite-V_0 case. One would replace the orbitals in eqs. (4) and (6) by the finite-V_0 ones [20].

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