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Calculation of exchange energy in quantum dots: application to porous silicon

G. FISHMAN, R. ROMESTAIN and J.C. VIAL

Laboratoire de Spectrométrie Physique, Université J. Fourier, Grenoble I, BP 87, 38402 St Martin d'Hères cedex, France

ABSTRACT: We present a variational calculation of the envelope wave function of an exciton inside a cube, in the effective mass approximation, with one parameter which plays the part of a Bohr radius. This geometry allows one to reduce the sixfold integrals to threefold integrals which shortens tremendously computer calculations. This wave function is used to obtain the exchange energy and the oscillator strength. The limiting cases (large or small cubes) are recovered. We show that recent experimental results in porous silicon can be explained without further hypothesis.

1. INTRODUCTION

In a quantum dot it is well known that the hamiltonian describing an exciton, i.e. an electron-hole pair correlated by the Coulomb interaction, has no analytical solution[1]. As a consequence it is necessary to look for approximate solutions. Inside the effective mass approximation framework, which we use in the present paper, it is possible either to develop the (envelope) wave function on an appropriate basis[2] or to use a trial function[3]. Here we shall adopt this last approach. To simplify the calculation as much as possible we describe the electron of the conduction band and the hole of the valence band by a average mass \( m_e \) and an average mass \( m_h \) respectively. Furthermore we assume infinite potential barriers, which is not a bad approximation for the case of porous silicon which will be considered more specifically later.

II. WAVE FUNCTION

In the quantum dot the hamiltonian is (with standard notations):

\[
H = \frac{p_e^2}{2m_e} + \frac{p_h^2}{2m_h} - \frac{e^2}{\epsilon r_{eh}}
\]  

We are looking for the ground state of this hamiltonian and we will consider the case of a cubic quantum dot as this is easier to solve for than a sphere. Inside a cube of side \( 2Q \) we will use the function \( \mathbf{r} = \pi / 2Q \):

\[
\psi_c(\mathbf{r}) = \cos qx \cos qy \cos qz
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and the normalized wave function

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\( \varphi_c(r) = Q^{-3/2} \phi_c(r) \)

The trial wave function for the exciton in the cube is then:

\[
\phi_{x,c}(\mathbf{r}_e, \mathbf{r}_h) = \phi_c(\mathbf{r}_e) \phi_c(\mathbf{r}_h) \exp(-\mathbf{r}_{eh}/a)
\]

where \( a \) plays the part of an effective Bohr radius. We have to minimize:

\[
\langle \phi_{x,c} | H | \phi_{x,c} \rangle / \langle \phi_{x,c} | \phi_{x,c} \rangle
\]

The results are given Fig. 1. If \( Q/a \) is very large, \( a/a \) tends to one as expected (\( a \) is the Bohr radius of the 1s bulk exciton). The limit is less obvious when \( Q/a \) is very small: in this case the limit of \( a/a \) is equal to 1.97 while in a sphere \([4]\) the limit is equal to 2.01. This indicates the small importance of the shape of the quantum dot.

The difference between the description by an exciton \( \psi_{x,c}(\mathbf{r}_e, \mathbf{r}_h) \) and by an uncorrelated electron-hole pair \( \psi_{eh,c}(\mathbf{r}_e, \mathbf{r}_h) \) where

is usefully described by the correlation energy

\[
E_{\text{cor}} = \langle \phi_{x,c} | H | \phi_{x,c} \rangle - \langle \phi_{eh,c} | H | \phi_{eh,c} \rangle
\]
E_{cor}/E_{x,1s} is given in Fig.2; 
E_{x,1s} is the binding energy of the 
1s bulk exciton. Although, in the 
limit Q/ax = 0, \Psi_{x,c} tends to 
\Psi_{eh,c}, E_{cor} does not tend to zero 
but to 0.251 E_{x,1s}. Again this 
points out the slight difference 
between the cube and the sphere 
where this limit is equal to 0.248 
E_{x,1s}[4].

Fig.2 Correlation energy versus the 
half-side of the cube. The energy 
unit is the binding energy of the 
1s bulk exciton. a_{x} is the same as 
in Fig.1.

3. EXCHANGE ENERGY AND OSCILLATOR STRENGTH

We are now in position to calculate the exchange energy[5]. For 
an uncorrelated electron hole pair the exchange energy is:

\[ E_{eh,c} = \pi a_{x}^{3} E_{x} \int d^{3}r \, |\Psi_{eh,c}(r,r)|^{2} \]  \hspace{1cm} (12)

where \( E_{x} \) is the exchange energy of the 1s bulk exciton. Now

\[ \int d^{3}r \, |\Psi_{eh,c}(r,r)|^{2} = \int d^{3}r \, |\Psi_{c}(r)|^{2} = \frac{27}{64} \frac{1}{Q^{3}} \]  \hspace{1cm} (13)

In a cube the exchange energy of an exciton is:

\[ E = \int d^{3}r \, |\Psi_{x,c}(r,r)|^{2} \pi a_{x}^{3} E_{x} \]  \hspace{1cm} (14)

Finally we obtain:

\[ \frac{E}{E_{eh,c}} = \frac{64}{27 \pi} \left( \frac{Q}{a_{x}} \right)^{3} \frac{E}{E_{x}} \]  \hspace{1cm} (15)

The ratio \( E/E_{eh,c} \) is plotted in Fig.3 and allows one to know the 
exchange energy \( E \) for an exciton for any value of \( Q/a_{x} \). This ratio can 
be also be written as:

\[ \frac{E}{E_{eh}} = \frac{Q^{6}}{N} \]  \hspace{1cm} (16)

It is straightforward to 
verify that i) if \( Q/a_{x} \) tends to 
zero, \( E \) tends to \( E_{eh} \) and ii) if 
\( Q/a_{x} \) tends to infinite, \( E \) tends to 
\( E_{x} \). This is what we expect.

Fig.3 Vertical axis: ratio of the 
exchange energy \( E \) of an exciton to 
the exchange energy \( E_{eh,c} \) of an 
uncorrelated electron-hole pair in 
a cube of half-side \( Q \). Horizontal 
axis: ratio of half-side \( Q \) to \( a_{x} \), 
the Bohr radius of the 1s bulk 
exciton. The vertical axis gives 
also the envelop function dependent 
part of the oscillator strength 
(see text).
Incidently we can note that the envelope function dependent part $F_0$ of the oscillator strength\[6\], i.e.:

$$F_0 = \left| \int d^3r \psi_{\epsilon,c}(r,r) \right|^2$$  \hspace{1cm} (17)

is equal to $Q^6/N$ so that the Fig.3 gives also $F_0$.

4. POROUS SILICON

We can now use the above results to explain recent experimental results in porous silicon\[7,8\]. For a luminescence energy equal to 1.77 eV, which corresponds roughly to a crystallite of 25 Å\[9\], the exchange energy is equal to 10 meV. In Ref.7 this result was interpreted as being the exchange energy of uncorrelated electron-hole pair, which leads to $2Q = 24$ Å (see Eq.12 and 13), using known values $a_x = 43$ Å\[10\] and $E_x = 0.15$ meV\[11\]. Now we can comment on whether this approximation is justified or not. Using the results given in Fig.3, we obtain $2Q = 26$ Å. (A discussion on the validity of all the values given here is postponed in a further publication). This shows that, in this particular case, a description of the exciton as an uncorrelated electron-hole pair is well justified.

5. CONCLUSION

We have shown that it is more simple to study the exciton inside a cube than inside a sphere, at least from the viewpoint of the unavoidable numerical calculation. We have pointed out the similarities (exchange energy, oscillator strength) and the differences (correlation energy) between an exciton and an uncorrelated electron hole-pair in very small crystallites. Finally we have applied our calculation to porous silicon and confirmed that the measured splittings can be due to exchange energy.

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