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CONFINEMENT ENERGY OF QUANTUM DOTS AND THE BRUS EQUATION

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ABSTRACT

A review of the ground state confinement energy term in the Brus equation for the bandgap energy of a spherically shaped semiconductor quantum dot was made within the framework of effective mass approximation. The Schrodinger wave equation for a spherical nanoparticle in an infinite spherical potential well was solved in spherical polar coordinate system. Physical reasons in contrast to mathematical expediency were considered and solution obtained. The result reveals that the shift in the confinement energy is less than that predicted by the Brus equation as was adopted in most literatures.

1. INTRODUCTION

Solid state materials, in general are classified either as metals, semiconductors or insulators. As the name implies, semiconductors are materials whose electrical/electronic properties are intermediate between those of metals and insulators. These intermediate properties are determined by their crystal structures, bonding characteristics, electronic energy level, just to mention but a few (Pillai, 2010). The energy band model or structure of materials dictates that unlike metals, gap, often referred to as forbidden energy gap exist between the valence band and the conduction band of semiconductors and insulators at room temperature. Thus, in loose terms, materials with zero energy gap are metals while those with energy gap greater than 3 eV are commonly referred to as insulators (Yu & Cardona, 2005). Semiconductors are one of the most useful class of materials ever known to man. Despite that they occupy mainly the groups III and IV in the periodic classification of elements, semiconductors also exist in many different chemical compositions with a large variety of crystal structures. Examples include silicon, germanium, gallium arsenide, cadmium selenide, cadmium sulphide, etc (Yu & Cardona, 2005).

The versatility and usefulness of a semiconductor lies in its band gap energy which in turn govern its optoelectronic properties. Band gap engineering refers to the process of altering the band gap energy of a semiconductor to meet specific requirement and application. It is distinct from doping which only shifts the femi level (or energy) within the bandgap of a given semiconductor, thereby creating band tail states either close to the valence band (acceptor state) or conduction band (donor state), leading to the formation of either P-type or N-type semiconductor respectively. Common bandgap engineering techniques include the use of heterostructures (Esaki & Tsu, 1970) and by alloying composition (Fox & Ispasoiu, 2017). Decreasing the physical size of a semiconductor into the nanometric region can also be regarded as a bandgap engineering technique as it alters the bandgap due to quantum confinement effects. Semiconductors have made in road into our lives as they are the workhorse of modern electronics. They form the foundation of both industrial and consumer electronics. Improvement in theoretical understanding of the physics of semiconductors coupled with advances in crystal growth and circuit fabrication techniques has led to the development of integrated circuits which come in sizes ranging from small scale integration (SSI) to ultra large scale integration (ULSI) depending on the number of components per chip (Gupta, 2014). This process, often referred to as miniaturization is not without an end. When the material or circuit dimension scales down into the nanometric region, quantum effects become prominent leading to confinement of carriers (electrons and holes). Carriers can be confined in one, two, or three dimensions leading to a quantum well, quantum wire or quantum dot respectively (Davies, 2005). Thus, quantum dots are semiconductor nanostructures (nanoparticles) in which carriers are confined in all three dimensions (Brus, 1984). They are formed predominantly by Stranski-Krastanow growth mode, a molecular beam epitaxy technique (Pohl, 2013) and by solution or wet chemistry (Brus, 1983), used to realize colloidal or stand alone quantum dots. Quantum dots exist in different shapes depending on the growth and material conditions. These include spherical, lens, pyramidal, cylindrical shapes, etc. (Pohl, 2013).

Carrier confinement increases the band gap energy of a semiconductor and alters the density of state of the bulk semiconductor material (Pohl, 2013). It therefore extends the frontiers of application of the semiconductor. The energy increase in the band gap is referred to as the confinement energy of the quantum dot.

Brus (1984) gave the first theoretical calculation for a spherical semiconductor colloidal (or stand alone) nanocrystal with CdS and CdSe as examples, based on effective mass approximation. The band gap energy according to Brus is

$$E_{g(qd)} = E_{bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r R^2} \quad (1)$$

Where,

$E_{g(qd)}$ = band gap energy of quantum dot

E_{bulk} = band gap energy of bulk semiconductor

R = radius of quantum dot

m_e^* = effective mass of excited electron

m_h^* = effective mass of excited hole

h = planck's constant

ε_0 = permittivity of vacuum

ε_r = relative permittivity

The first term in the right hand side of equation (1) denotes the band gap energy of the bulk semiconductor. The second additive term in the right hand side of equation (1) represents the additional energy due to quantum confinement. It can be thought of as the infinite square-well contribution to the band gap energy. The third subtractive term stands for the exciton's columbic interaction energy. The numerical factor in this term originates

from calculations of wave function overlap integrals. Thus, according to the brus equation, the confinement energy E_c is explicitly stated as (Brus, 1984):

$$E_c = \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \quad (2)$$

One of the short comings of the Brus equation is its failure to account for the electron-hole spatial correlation effect (Kayanuma, 1988). However, our focus in this paper is on the confinement energy term. Quantitatively, the effect of quantum confinement on the band gap energy of a semiconductor is chiefly determined by this term. The Brus equation shows that for a spherical shaped semiconductor nanocrystal, the confinement energy is inversely proportional to the square of the radius of the nanocrystal. The goal of this paper is to investigate this relationship and also ascertain the veracity or otherwise of the confinement energy term. The vast applications of quantum dots in technology is emission based. The confinement energy is important because it determines the emission energy as well as the wavelength of the quantum dot.

2. FORMALISM

An ideal spherical quantum dot is a spherical shaped semiconductor nano crystal in which excitons are confined in an infinite spherical well (Delerue & Lannoo, 2004). This corresponds to an impenetrable hard spherical wall. The confining potential is given by

$$V_{conf.}(r) = \begin{cases} 0, & r \leq a \\ \infty, & otherwise \end{cases} \quad (2)$$

Where,

R = radius of the confining potential

a = radius of the nanocrystal

Following Schrodinger's time-independent wave equation (Davies, 2005):

$$\frac{-h^2}{2\mu}\nabla^2\,\Psi(x,y,z) + V(x,y,z) = E\,\Psi(x,y,z) \quad (3)$$

Where,

μ = mass of particle

E = energy of particle

Ψ = wave function associated with particle

Since the potential depends on the radius from a fixed point of a spherical quantum dot, the Laplacian ∇^2 of the spherical polar coordinate is independent of the angular part and is given as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \quad (4)$$

Putting equation (4) into equation (3) for V = 0:

$$\frac{-h^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = E\,\Psi(x,y,z) \quad (5)$$

The confinement energy depends only on r.

Assume $\Psi(x, y, z)$ = R(r)G(θ)Q(∅) ; The radial part of equation (5) by the method of separation of variables yields:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu E r^2}{h^2} = l(l+1) \quad (6)$$

Where l = orbital angular momentum

Equation (6) is simplified and the result is stated as :

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[k^2 - \frac{l(l+1)}{r^2}\right] R(r) = 0 \quad (7)$$

Where k = $\frac{\sqrt{2\mu E}}{h}$

Equation (7) is reminiscent of spherical Bessel differential equation. The solutions are the spherical Bessel function of order l, $j_l(kr)$ and the spherical Neumann function of order l, $n_l(kr)$.

The general solution is :

$$R_{n,l}(r) = C_l\, j_l(kr) + D_l\, n(kr) \quad (8)$$

Where C_l and D_l are constants.

Unlike the spherical Neumann function, the behavior of the Bessel function is such that it is finite at the origin (Weber and Arfken, 2003). The finite requirement of the wave function suggest that D must be equal to zero. This reduces equation (9) to:

$$R_{n,l}(r) = C_l\, j_l(kr) \quad (9)$$

Where,

C_l = normalization constant

$R_{n,l}(r)$ = eigen function

The wave function must varnish at the boundary. However, in the formulation, due to mathematical expediency, one had used a confining potential that is central, which implies that there exist an explicit hard core potential at the centre. But, according to the physical description of the system, no boundary exist at r = 0, which would introduce a node in the wave function at that point. Rewriting equation (11) in consonance with Dey et al (2012) yields:

$$R_{n,l}(d) = C_l\, j_l(kd) \quad (10)$$

Where,

d = diameter of the sphere (distance between two directly opposite points on the sphere).

Also, the infinite potential barrier requires that R(d) = 0. This translates into

$$j_l(kd) = 0 \quad (11)$$

Where kd is a zero of the lth-order spherical Bessel function.

Unfortunately, the zeros are not located at good (sensible) points (like n or nπ).

The boundary condition requires that:

$$K = \frac{1}{d} X_{n,l} \quad (12)$$

Where $X_{n,l}$ is the nth zero of the lth-order spherical Bessel function.

Putting equation (12) into equation (7) yields:

$$\frac{1}{d^2} X_{n,l}^2 = \frac{2\mu E}{h^2} \quad (13)$$

Following equation (13), the allowed energies E_n become

$$E_n = \frac{h^2}{2\mu d^2} X_{n,l}^2 \quad (14)$$

Putting $\mu = m_e^*$ into equation (14) yields the electron confinement energy E_{en} as :

$$E_{en} = \frac{h^2}{2m_e^* d^2} X_{n,l}^2 \quad (15)$$

Where m_e^* is the effective mass of electron

Similarly, the hole confinement energy E_{hn} is obtained as:

$$E_{hn} = \frac{h^2}{2m_h^* d^2} X_{n,l}^2 \quad (16)$$

Where m_h^* is the effective mass of hole.

Adding equations (15) and (16) gives the total confinement energy (simply confinement energy), E_c as:

$$E_c = \frac{h^2}{2d^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) X_{n,l}^2 \quad (17)$$

Where,

n = radial quantum number

The ground state corresponds to n = 1 and $l = 0$. $X_{1,0}$ = 3.142 (Abramowitz and Stegun, 1970) which coincides with the well-known constant π. Therefore equation (19) becomes:

$$E_c = \frac{\pi^2 h^2}{2d^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \quad (18)$$

3. CONCLUSION

The confinement energy is inversely proportional to the square of the diameter of the quantum dot, in contrast to the Brus equation which predicts an inverse square relationship in the radius. The confinement energy based on the brus equation is not entirely new. Very few researches are ground breaking and entirely new. A good number of researches today are innovative and the brus equation is no exception. A “bird eye" view of the brus equation reveals that it is nothing but a Schrodinger equation modified to account for the effect of an electron-hole pair (exciton)

confined to a nanometric spherical shaped semiconductor referred to as quantum dot. It is blind to the varied crystal structures that exist for semiconductors.

The confinement energy obtained in equation (18) is less (about a quarter) than that predicted by the brus equation adopted in some articles and literatures (Chukwuocha & Onyeaju, 2012; Ikeri, Onyia, & Vwavware, 2019) . Unlike the brus equation, equation (19) gives values of the confinement energy for all excited states possible.

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CONFLICT OF INTEREST

The author have declared that no competing interests exist.

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