

CALCULATION OF BAND PROPERTIES OF QUANTUM DOT INTERMEDIATE BAND SOLAR CELLS WITH HYDROGENIC IMPURITIES

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ABSTRACT: The intermediate band solar cell (IBSC) has the potential of achieving 63.2 % efficiency under maximum concentrated sunlight. This efficiency relies on a material with three bands: a valence band, an intermediate metallic band and a conduction band. In order to achieve high efficiencies the Fermi level of the intermediate band (IB) must be well within the intermediate band. This ensures both a supply of electrons capable of photon induced transition to the conduction band as well as a large population of holes that allow electrons to transition from the valence band to the intermediate band. The use of quantum dot technology may be used to implement an IBSC by positioning the quantum dots close enough and periodically enough so that their wave functions couple to create an intermediate band. The effective half-filling of the IB could then be achieved by introducing some doping. However, the introduction of dopants, modifies the former energy spectra with respect to an undoped quantum dot. This paper explores the energy spectrum of the quantum dot system when an impurity is introduced in the center of a quantum dot. Results show that the inclusion of this impurity allows both a proper IBSC band structure and a Fermi level positioning.

Keywords: Fundamentals, Modeling, PV materials.

1 INTRODUCTION

The high efficiency of an IBSC hinges upon the existence of an intermediate band and an intermediate band whose quasi-Fermi energy is inside its band. This placement of the Fermi level is crucial as it optimizes the probabilities that empty states will exist in the IB to host electrons that are promoted from the valence band and that occupied states will exist in the IB in order to supply electrons to the conduction band when the corresponding photon absorption processes take place [1]. Quantum dots have been proposed as a means to implement the IBSC [1].

Although quantum dots can in principle provide the necessary energy configuration, the introduction of some doping is necessary in order to supply the electrons required to half-fill the IB. In the past, it was suggested to introduce this doping in the barrier region [2]. With barrier doping, the half-filling of the IB comes from the electron transfer from the impurity to the dot.

In the quantum dot implementation of an IBSC formulated in this paper, the intermediate band is also created by an array of quantum dots, but, the impurity, of a hydrogenic nature, is located within the center of the quantum dot.

2 QUANTUM DOT INTERMEDIATE BAND SOLAR CELLS

Previous work [3,4] indicates that the optimum gap from the lower edge of the conduction band to the upper edge of the valence band is 1.95 eV while the intermediate band should be centered either 0.71 eV or 1.24 eV below the lower edge of the conduction band.

When the IBSC is implemented with quantum dots,

the largest of these band gaps, assuming the valence-band offset of the heterojunction is zero, is equal to the band gap of the barrier material. It is hypothesized that the location of the intermediate band may be approximated as the ground state energy of an electron within the confining potential introduced by the conduction band offset of the heterojunction and the electrostatic potential or the hydrogenic impurity. Electrons are Fermions with 1/2 spin, therefore the ground state energy is double degenerate. Since there is one impurity per quantum dot, this ground state will be *de facto* half-filled with electrons. In the next section of this paper we calculate the spectrum of the stationary states of the electron bound within the quantum dot. The results of these calculations address whether the addition of the hydrogenic impurity within the dot provides a spectrum suitable for engineering an IBSC.

3 CALCULATING THE GROUND STATE ENERGY

In order to calculate the energy levels in a quantum dot with an impurity we are forced to return to the Schrödinger equation because the potential energy varies appreciably over distances shorter than the wavelength of the electrons [5]. In order to calculate the effect of the impurity on the ground state energy, we include an electrostatic potential in the Hamiltonian that is caused by the ionized donor impurity. We then calculate the expected value of the Hamiltonian using an approximation to the ground state eigenfunction. This approximation is a linear combination or orthonormal Laguerre-based wave functions. The contributions of the orthogonal wavefunctions are adjusted so that the expected value of the approximation is minimized.

Since the confining potential due to the conduction band offset of the heterojunction and the donor impurity is radially symmetric, we begin our work with the radial form of the Schrödinger equation for stationary states, which is given as:

$$\left[-\frac{\hbar^2}{2m_{\text{eff}}} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m_{\text{eff}}} \frac{1}{r} \frac{\partial}{\partial r} + \frac{\hbar^2}{2m_{\text{eff}}} \frac{l(l+1)}{r^2} + V(r) \right] R_{k,l}(r) = E_{k,l} \cdot R_{k,l}(r) \quad (1)$$

where r is the radial distance relative to the center of the QD, \hbar is Planck's constant, m_{eff} is the average of the electron effective masses in the dot and the barrier¹, l is the angular quantum number, $R_{k,l}$ is the radial wave function of an electron whose quantum numbers are k and l , $E_{k,l}$ is the energy eigenvalue corresponding to the radial wave function $R_{k,l}$ and, $V(r)$ is the potential energy of the confining potential which is described in equation (2). The bracketed term is called the Hamiltonian. The explicit form of the confining potential is given as:

$$V(r) = \begin{cases} -\frac{q^2}{4\pi\kappa\epsilon_0 r} - V_o & \text{for } r \leq r_{QD}, \\ -\frac{q^2}{4\pi\kappa\epsilon_0 r} & \text{for } r > r_{QD}, \end{cases} \quad (2)$$

where q is the magnitude of both the electron charge and the ionized impurity, κ is the average dielectric constant, ϵ_0 is the permittivity of free space, and V_o is the heterojunction's conduction band offset. The heterojunction interface occurs at radius r_{QD} .

In this paper we will only be concerned with wavefunctions whose angular quantum number, l , is equal to zero. When calculating the ground state energy, the quantum number k is set to unity. The ground state radial wavefunction, $R_{1,0}(r)$, will be approximated by a linear combination of Laguerre-based radial wavefunctions. The reason for this choice is as follows. The eigenfunctions of the Hamiltonian created by setting in equation (1) $l=0$, $k=n$ and $V_o=0$ are, in fact, wave function based upon Laguerre polynomials as follows:

$$R_{n,l}^L(r) = 2a^{-3/2} n^{-5/2} \exp\left(-\frac{r}{na}\right) L_{n-1}^1\left(\frac{2r}{na}\right). \quad (3)$$

In the hydrogenic model the quantum number n has a physical significance, here n is an index. a is the effective Bohr radius given as

$$a = \frac{4\pi\kappa\epsilon_0 \hbar^2}{m_{\text{eff}} q^2}. \quad (4)$$

The superscript L in equation (3) is used to distinguish

¹ In this paper both the dielectric constant and the electron effective mass are assumed to be constant throughout the entire intermediate band material.

between the approximate ground state wavefunction of the complete Hamiltonian given in equation (1), namely $R_{1,0}(r)$. L_{n-1}^1 is an associated Laguerre functions, which are defined as follows:

$$L_{v-1}^u\left(\frac{2r}{na}\right) = \sum_{k=0}^{v-1} \frac{(-1)^k (u+v-1)!}{(v-1-k)! (u+k)! k!} \left(\frac{2r}{na}\right)^k, \quad (5)$$

The set of wave functions defined in equation (3) define an orthonormal basis with respect to the dot product given by

$$\langle f | g \rangle = \int_0^\infty r^2 f^*(r) g(r) dr, \quad (6)$$

Thus using Laguerre-based radial wavefunctions in conjunction with the variation method, an upper bound for the expected value of the ground state energy, $\langle E_{1,0} \rangle$, may be obtained by minimizing, with respect to coefficients $\alpha_1, \alpha_2, \dots, \alpha_J$, the following quadratic form [6]:

$$\langle E_{1,0} \rangle \leq -V_o + \sum_{j=1}^J \sum_{k=1}^J \alpha_j \alpha_k (A_{j,k} + B_{j,k} + C_{j,k}), \quad (7)$$

Where J is an integer. For the results obtained in this paper, J is set to 14 because this value is found to offer a good compromise between computational accuracy and computational processing time. The other variables in equation (7) are defined as follows:

$$A_{j,k} = -\frac{\hbar^2}{2m_{\text{eff}} \cdot a^2} \frac{1}{j^2} \delta_{j,k}, \quad (8)$$

$$B_{j,k} = V_o \exp\left(\frac{-2r_{QD}}{j \cdot a}\right) \times \sum_{z=0}^2 \frac{1}{z!} \left(\frac{2r_{QD}}{j \cdot a}\right)^z \delta_{j,k}, \quad (9)$$

$$C_{j,k} = V_o \exp\left(\frac{r_{QD}(j+k)}{a \cdot j \cdot k}\right) \times \sum_{p=0}^j \sum_{q=0}^k \sum_{z=3}^{2+p+q} \frac{1}{z!} \left(\frac{r_{QD}(j+k)}{a \cdot j \cdot k}\right)^z w_{p,q}^{(j,k)}, \quad (10)$$

$$w_{p,q}^{(j,k)} = \frac{j!k!(2+p+q)!}{p!q!(1+p)!(j-1-p)!(1+q)!(k-1-q)!} \times \sqrt{j \cdot k} j^q k^p \frac{(-2)^{2+p+q}}{(j+k)^{3+p+q}} \quad (11)$$

$\delta_{j,k}$ is the delta function. The minimization of the ground state energy, with respect to coefficients $\alpha_1, \alpha_2, \dots, \alpha_J$, is constrained by the physical necessity that the norm of the wavefunction be equal to unity:

$$\sum_{j=1}^J \alpha_j^2 = 1. \quad (12)$$

Equation (7) may be simplified for two special cases: when $r_{QD} = 0$, and in the limit as $r_{QD} \rightarrow \infty$ [6]. With respect to the former special case,

$$\langle E_{1,0} \rangle \Big|_{r_{QD}=0} = -\frac{\hbar^2}{2m_{eff} \cdot a^2}. \quad (13)$$

With respect to the latter special case,

$$\langle E_{1,0} \rangle \Big|_{r_{QD} \rightarrow \infty} = -V_o - \frac{\hbar^2}{2m_{eff} \cdot a^2}. \quad (14)$$

Due to the fact that equation (7), which expresses the upper bound of the ground state energy, is given as a quadratic form, we recommend minimizing this expression with the gradient descent method [7].

4 RESULTS FOR TWO HYPOTHETICAL HETEROJUNCTIONS

The goal of this paper is to determine whether a quantum dot heterojunction with a centrally located hydrogenic impurity may be used to create an IBSC. In order to achieve the first goal it is necessary that the ground state energy is well separated from the first excited state (> 500 meV).

Using the results in section three, we have calculated the approximate energy level for two hypothetical heterojunctions. In both examples the effective mass is given as $0.098 \cdot 9.11 \cdot 10^{-31}$ kg and the dielectric constant is given as 11.7. In the first example the conduction band offset is given as 750 meV and in the second example the conduction band offset is given as 1250 meV. These values are reasonable with respect to an IBSC whose barrier material is AlGaAs [8]. The energy levels of the first ten bound states are shown below.

Figures one and two illustrate that the energies of the first four bound electron eigenstates decrease monotonically with an increase in the radius of the quantum dot. Beginning with the six eigenstate, there is a range of quantum dot radii for which the eigenstate is no longer bound. However, as theorized above, all the eigenstates will return to a predictable value at a suitable large QD radius.

The radius at which the ground state energy is equal to -710 meV is 17 nm and 8.8 nm when V_o is 750 meV and 1250 meV respectively. At this radius, in both figures one and two, the energies of the remaining bound states are grouped with 280 meV and 120 meV of each other nm when V_o is 750 meV and 1250 meV

respectively. The radius at which the ground state energy is equal to -1240 meV is 23 nm when V_o is 750 meV. At this same radius the energy of the first excited state is -700 meV and the remaining bound states are grouped within 200 meV of each other. For the case when V_o is 1250 meV, at a radius of 11 nm the energy difference between the first and second eigenstates is 710 meV. At this same radius the remaining bound states are within 200 meV of each other.

$\kappa = 11.7; m_{eff} = 0.098 \cdot 9.11 \cdot 10^{-31}$ kg; $V_o = 750$ meV; $l = 0$

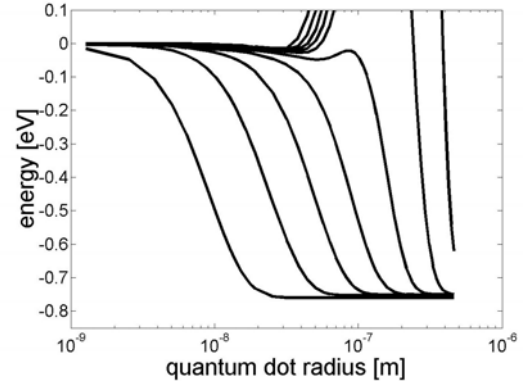


Figure 1: Energies of the first ten radially symmetric electron states in a quantum dot with a centrally located hydrogenic impurity. V_o is 750 meV.

$\kappa = 11.7; m_{eff} = 0.098 \cdot 9.1 \cdot 10^{-31}$ kg; $V_o = 1250$ meV; $l = 0$

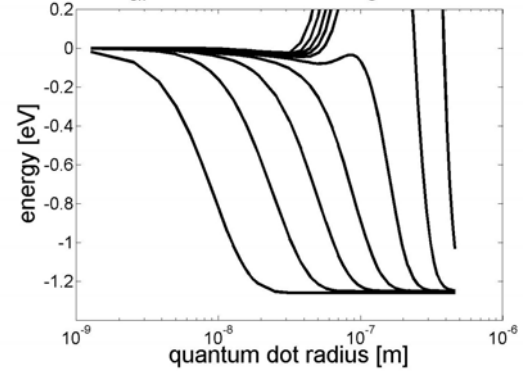


Figure 2: Energies of the first ten radially symmetric electron states in a quantum dot with a centrally located hydrogenic impurity. V_o is 1250 meV.

The significance of these results is as follows. The primary goal of the paper, to determine whether a quantum dot heterojunction with a centrally located hydrogenic impurity may be used to create an IBSC, is achieved for the conduction band offset of 1250 meV. This is because there exists a quantum dot radius at which the difference between the ground state energy and the first excited state energy is greater than 500 meV.

We assume that a periodic array of quantum dots with centrally located impurities will cause bands to appear around the energy levels shown in figures one and two. We further assume that any energy levels within $4kT$ (~ 100 meV) of each other will merge into a single band. We advise that the quantum dot radius be set to a value at which the ground state energy is greater than 500 meV below the energy of the first excited state. We further advise that the quantum dot radius be set to a value at which the energy of each bound excited state is within 100 meV of the energy of its nearest neighbor.

Having the energies of the remaining bound states closely grouped prevents the formation of a second intermediate band.

It is undesirable for more than one band to appear between the valence band and conduction band. This is because there is then the risk that these new bands will not provide significant photon absorption while they open new paths for non-radiative recombination. Finally, we assume that the bound states grouped closely near 0 eV will cause the band gap between the valence band and conduction to shrink as compared to a heterojunction without impurities.

5 CONCLUSIONS

We have calculated the first 10 energy levels of electrons in a quantum dot with a centrally located impurity whose stationary states have their angular quantum numbers set to zero. We have found that it is possible to obtain a ground state energy well separated from the energies of the excited states. This holds true for a wide range of quantum dot radii and over a wide range of possible ground state energies. In particular, within the bounds of currently fabricated quantum dot radii, it is possible to obtain an energy spectrum such that the ground state energy is 710 meV below the first excited state. This is important because it will lead to an intermediate band whose location meets the requirement for optimum conversion efficiency of the IBSC [3]. We conclude that an intermediate band solar cell may be implemented with ideal quantum dots with centrally located hydrogenic impurities.

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