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QUANTUM CONFINEMENT IN CORE-SHELL STRUCTURES

D. POKHREL[1], A. NDUWIMANA[2], AND X. Q. WANG[1]

[1]Department of Physics and Center for Theoretical Studies of Physical Systems,
Clark Atlanta University, Atlanta, Georgia 30314, USA
[2]Department of Science, Georgia Perimeter College, Decatur, Georgia 30034, USA

ABSTRACT. We have derived a secular equation approach to solve for a two-dimensional particle in a box model. The particle in a box model is relevant to the quantum confinement in nanowire structured nanomaterials. Numerical solutions of secular relations allow us to extract the energy and charge density for potential barrier and well cases, respectively. In the case of potential barrier, charge density is confined to the shell region, while in the case of potential well, charge density is confined to the core region. Our results provide useful insight to the quantum confinement effect in nanostructured materials.

AMS (MOS) Subject Classification. 82D77, 82D80

1. INTRODUCTION

The recent technological approach is based on two dimensional (2D) quantum wells, one dimensional (1D) quantum wires and zero dimensional (0D) quantum dots where carrier transport is entirely controlled by quantum effects [1, 2, 3]. The quantum confinement is observed when the size of the particle is too small as compared to the wavelength of the electron. Since the band gap and wavelength are inversely related to each other , the wavelength decreases with decrease in size. Qualitatively this effect is analogous to the problem of a particle in a box, and efforts to quantify confinement effects. Nonmaterial exhibit unique optical and electrical properties in connection with the quantum confinement effect and are increasingly used in electronic and optoelectronic devices including sensors, detectors, field effect transistors, solar cells, light-emitting diodes [4]. The size and shape of the materials affects the electronic and optical properties of materials. Nanomaterials have unexpected visual properties because they are small enough to confine their electrons and produce quantum effects. Core shell semiconductor nanocrystal properties are based on the relative conduction and valence band edge alignment of the core and the shell.

The semiconductor nanowires (NWs) structure is a favorable environment to achieve 1D system. The ability to control the physical and chemical properties of low

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dimensional nanomaterials by variation of their size is of crucial importance for nanotechnological applications. It is now well recognized that nanometer-scale silicon and germanium wires have immense potential for the fabrication of a new generation of optoelectronics devices within well-established silicon based microelectronic technology. More recently, due to the technological importance much effort has been focused on the core-shell structured semiconductor quantum wires. One of the distinctive features of the core-shell structured nanomaterials is the composition dependence of their electronic, structural and optical properties. One of the most important reason that nanoscale systems can show new properties is the size of nanomaterials. As a result, fundamental building blocks of matter such as an electrons experience "confinement" effects. This type of non-classical behavior can be explained by the "particle in a box" model, which is a result of the Schrodinger equation. The particle-in-a-box model is relevant to the quantum confinement in core-shell structured nanomaterials, which provides an insight into the behavior of the electrons and quantum mechanical description.

2. THEORETICAL MODEL

2.1. **One dimensional Secular equation.** A particle in one dimensional box is a fundamental quantum mechanical model describing the translational motion of a single particle confined inside an infinitely deep well from which it can't escape. The Schrodinger equation in one dimension is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi(x) = E\psi(x). \tag{1}$$

For a free particle with effective mass m confined by impenetrable barriers (i.e. infinite potential energy), the energy levels are given by $\frac{\hbar^2 k^2}{2m}$ where the wave vector, $k = n\pi/L$, $n = 1, 2, 3\ldots$ and L is the size of the box. Though this model is a good approximation for one-dimensional system such as nanowires, it is not adequate for core-shell nanowire or doped nanowires. For this reason, we study the confinement in a heterostructure by considering a particle in a potential central barrier and central well of height Δ (i.e. walls of infinite potential energy) with boundaries $x = 0$ and $x = a$ as shown in Figure1. For both cases, the regions $x < 0$ and $x > a$ are forbidden and the wavefunction is zero at these boundaries. In the case of a potential barrier, the potential is set to zero outside the barrier and to Δ in the barrier region.

Eq. (1) is solved by applying boundary conditions such that the wave function as well as it first derivative are continuous at the interface (b and a-b). The wave function vanishes at the edge ($x = 0$ and $x = a$) because the potential outside the well is infinity. The resulting secular equation for solving E for the central barrier

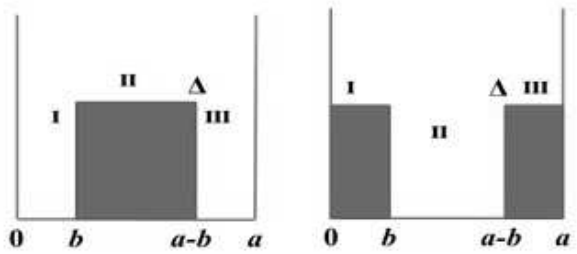

FIGURE 1. One dimensional central potential barrier (left panel) and well (right panel). The barrier has potential Δ and a width equal to $a - 2b$ centered at the middle of the box of width a.

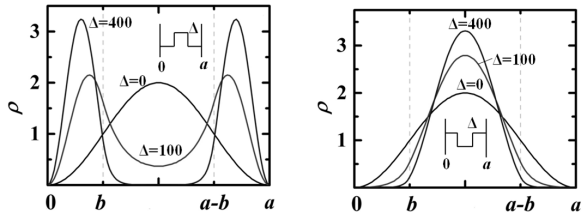

FIGURE 2. charge distribution for central barrier (left panel) and central well (right panel). The graphs represent the charge density for different values of barrier Δ.

case is given by

$$\begin{aligned}
&[\kappa\cos(\kappa b)\cosh(\lambda b) - \lambda\sinh(\lambda b)\sin(\kappa b)] \\
&\quad\times[\lambda\cosh(\lambda a - \lambda b)\sin(\kappa b) + \kappa\cos(\kappa b)\sinh(\lambda a - \lambda b)] \\
&= [\kappa\cos(\kappa b)\sinh(\lambda b) - \lambda\cosh(\lambda b)\sin(\kappa b)] \\
&\quad\times[\lambda\sinh(\lambda a - \lambda b)\sin(\kappa b) + \kappa\cos(\kappa b)\cosh(\lambda a - \lambda b)] \qquad (2)
\end{aligned}$$

where $\kappa = \sqrt{E}$ and $\lambda = \sqrt{\Delta - E}$.

Similarly, in the case of central well, the resulting secular equation is of the form

$$\begin{aligned}
&[\kappa\sin(\kappa b)\sinh(\lambda b) + \lambda\cosh(\lambda b)\cos(\kappa b)] \\
&\quad\times[\kappa\cos(\kappa a - \kappa b)\sinh(\lambda b) + \lambda\cosh(\lambda b)\sin(\kappa a - \kappa b)] \\
&= [\kappa\cos(\kappa b)\sinh(\lambda b) - \lambda\cosh(\lambda b)\sin(\kappa b)] \\
&\quad\times[\kappa\sin(\kappa a - \kappa b)\sinh(\lambda b) - \lambda\cosh(\lambda b)\cos(\kappa a - \kappa b)]. \qquad (3)
\end{aligned}$$

For general values of Δ, the classification of confined ($\Delta > E$) states for barrier and well can be obtained through numerical solutions of Eqs. 2 and 3, respectively. The calculated charge densities for the ground state of a central barrier and central well are shown in Figure 2. As expected, as Δ is set to zero, the charge density is a given by the square of a sine function, having its maximum at the center of the well. As the value of barrier is increased, the ground state moves from a core state

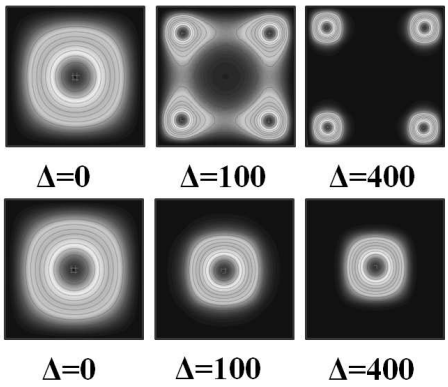

FIGURE 3. Charge distribution of central barrier (left panel) and well (right panel) in two dimensions. Δ is the height of the potential barrier.

to a shell state. As the barrier potential is increased, the density of a particle at the center decreases significantly. On the other side. For the central well case, the charge density gets more confined in the core as Δ increases.

The one-dimensional solution can be easily generalized for a two dimensional system. This is due to the fact Equation 1 becomes separable in x and y. Figure 3 depicts the wavefunction for a particle in a square box as the value of Δ is changed. For the case of a central barrier, the charges get more confined to the box corners as the potential barrier is increased. The case of a central well is very similar to the one dimensional case since charges get more confined to the core as Δ get higher.

2.2. **Cylindrical two dimensional Secular equation.** The secular equation for a cylindrical heterostructure has been derived previously [7]. The spatial separation of electron and holes are important for the practical application of solar cells [5], which is implied in coaxial silicon nanowires. While the spatial confinement in heterostructured nanowires is known to be attributed to a type-II (electrons and holes are confined in different materials) band offset [6], the nature of confinement in complementary doped coaxial silicon nanowires remains not fully understood. It have been shown that the dipoles of complementary doping generate confinement potentials for carriers across a p-type/intrinsic/n-type coaxial nanowire [8]. The effective type-II confinement potential for such as system is depicted in Figure 4. We derive the secular equation for such heterostructure.

The effect of this cascade shaped confinement potential on the band structure of a coaxial nanowire structure can be studied by a two-dimensional (2D) "particle-in-a-box" model [4]. Along the nanowire axis one has a continuous spectrum of plane waves, and the quantization arises from the radial confinement. The model is characterized by four parameters, the height of the dipole potential barrier, Δ; the core radius R_c; the inner shell radius R_s, and the radius of the nanowire R. The central barrier model corresponds to electrons (holes) in a p-i-n (n-i-p) coaxial

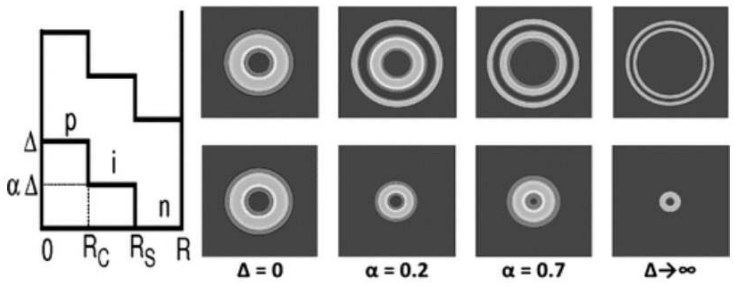

FIGURE 4. Model for a p-i-n doped coaxial nanowire. The core is p-doped while the shell is n doped. R_c is the potential barrier at the core while R_s is the beginning of the n-doped shell.

nanowire, while the central well model corresponds to holes (electrons) in a p-i-n (n-i-p) nanowire.

Considering a cylindrical multishell structured nanowire, the radial distribution functions can be obtained through a secular equation of the form

(4)
$$\begin{aligned}
&\kappa[J_l(\lambda R)Y_l(\lambda R_s) - J_l(\lambda R_s)Y_l(\lambda R)]\{I_l^{'}(\kappa R_s)[\kappa I_l(\eta R_c)K_l^{'}(\kappa R_c) - \eta I_l^{'}(\eta R_c)K_l(\kappa R_c)] \\
&\quad + K_l^{'}(\kappa R_s)[\eta I_l(\kappa R_c)K_l^{'}(\eta R_c) - \kappa I_l^{'}(\kappa R_c)I_l(\eta R_c]\} \\
&= \lambda[Y_l^{'}(\lambda R_s)J_l(\lambda R) - J_l^{'}(\lambda R_s)Y_l(\lambda R)]\{I_l(\kappa R_s)[\kappa I_l(\eta R_c)K_l^{'}(\kappa R_c) - \eta I_l^{'}(\eta R_c)K_l(\kappa R_c)] \\
&\quad + K_l(\kappa R_s)[\eta I_l(\kappa R_c)K_l^{'}(\eta R_c) - \kappa I_l^{'}(\kappa R_c)I_l(\eta R_c]\}
\end{aligned}$$

where ℓ is the angular momentum that labels the subband, J_ℓ and Y_ℓ are the Bessel functions of the first and second kinds, respectively. The three inverse length scales, $\eta = \sqrt{2m^*(E-\Delta)}/\hbar$, $\kappa = \sqrt{2m^*(E-\Delta/2)}/\hbar$, and $\lambda = \sqrt{2m^*E}/\hbar$, correspond to electrons (holes) in p-i-n (n-i-p) regions of coaxial nanowires, respectively. For holes (electrons) in p-i-n (n-i-p) regions, $\eta \leftrightarrow \lambda$. The energy and length units are $\hbar^2/2m^*R^2$ and R, respectively.

It is straightforward to study the limiting cases of Eq. (4), namely, $\Delta = 0$ and $\Delta \to \infty$. $\Delta = 0$ refers to an undoped nanowire. The energy spectrum is of the form $E_{n\ell} = \hbar^2\gamma_{n\ell}^2/2m^*R^2$, where $\gamma_{n\ell}$ is the n^{th} zero of ℓ^{th} Bessel function J_ℓ. For our purpose, we are interested in the charge distribution of $\ell = 0$ for conduction band minimum (CBM) and valence band maximum (VBM). The solution assumes the same charge density distribution centered at the core region for CBM and VBM, indicating no spatial charge separation. In contrast, for $\Delta \to \infty$, electrons (holes) in p-i-n (n-i-p) case are confined in the core with the spectrum $E_{n\ell} = \hbar^2\gamma_{n\ell}^2/2m^*R_c^2$, while holes (electrons) in p-i-n (n-i-p) case are all confined in the outer shell, satisfying $Y_\ell(\lambda R)J_\ell(\lambda R_s) = Y_\ell(\lambda R_s)J_\ell(\lambda R)$. This yields complete charge separation. For general values of Δ, the spatial separation of electrons and holes can be qualitatively

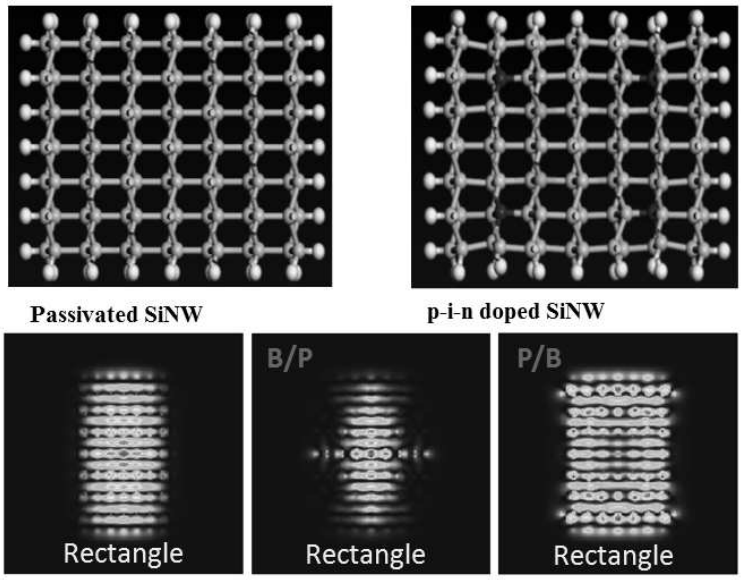

FIGURE 5. Top view of the H-passivated rectangular SiNW (top panels). The top-left panel is the pristine SiNW while the top right panel is the doped SiNW. The bottom panels are the charge density of the top of the valence band. The bottom left, center and right panels are for pristine, p-i-n doped and n-i-p doped SiNW.

determined through the solution of Eq. (1) with realistic parameters. For practical designs of solar cells, the intrinsic shell layer is important in preventing the tunneling of electrons and holes [5].

2.3. **Application on a doped silicon nanowire.** In order to test the reliability of the models presented above, we study the confinement effect in rectangular doped (p-i-n doping) silicon nanowires (SiNWs). It has been shown that technology that involves both p- and n-type doping, outperforms devices based on pure p- or n-type technology with a key characteristic of reduced static power consumption. Recent experimental work by Tian and co-workers [5] demonstrated the synthesis of multishell structured coaxial silicon nanowire that can be utilized as solar cells and nanoelectronic power sources. The solar cells involve the assembly of nanoscale "p-i-n" diodes, in which an intrinsic silicon shell is layered between p-type core and n-type outer shell that accommodate positive and negative charged carriers, respectively. The multishell sets up an electric field between the p- and n-layers, with the intrinsic component serving as a resistor. Consequently, the photogenerated electrons and holes in the intrinsic inner shell swept into the n-shell and p-core, respectively.

The SiNWs studied were oriented along the [112] direction. They were constructed from diamond structure and passivated with H atoms to eliminate the surface states. In order to compare NWs sizes, we represent them by a radius of a cylinder with the same surface area as the nanowires. The sizes of the nanowire was 9.97 Å.

Depicted in Fig. 5 is the ball-and-stick model of the prototype NW studied. The n and p doping were made by replacing some silicon atoms by P and B atoms. For each nanowire, we did a p-doping near the core and an n-doping near the edge and a n-doping at the core and a p-doping at the shell. The rectangular NW had 96 Si atoms and 42 H atoms. Our first-principles calculations were based on DFT with local density approximation (LDA) as implemented in DMol3. The calculation was done using an all-electrons potential with double numerical plus polarization (DNP) as the basis set. A 7 supercell was used to eliminate the interaction with neighboring wires. The energy was allowed to converge up to 2×105 eV. Nanowires were optimized using the Monkhorst sampling of $1 \times 1 \times 6$ k-point grid.

In Figure 5, we plotted the change density for the top of the valence band for the pristine nanowire as well as the doped SiNW. As it can be seen the pristine nanowire has states that are mostly localized in the core. When the core was doped with B and the shell with P, the states became more confined towards the core as in the case of the central well. On the other side, when the doping was reversed, we observe a reverse in the confinement effect: the charge became localized in the nanowire's shell. This is a prototype of a particle with a central barrier.

3. CONCLUSION

An analytical approach to the effective mass method has been developed for heterostructured cylindrical quantum wire systems. The model involves a potential well/barrier reminiscent of the band offset effect, and an infinite barrier height at the edge of the nanowire. We have studied the confinement effect in one dimension and two dimensional systems. For each case we derived a secular equation needed to solve the particle in the box problem. We presented the charge density for different level of confinement. It was shown that a central barrier confines charges near the shell while a central well confines states in the core. We also presented a model for a p-i-n/n-i-p doped nanowire and presented how charges are localized in this particular case. It is shown that the SINWs follow the model presented.

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