Calculation of the Band Properties of a Quantum Dot Intermediate Band Solar Cell with Centrally Located Hydrogenic Impurities

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To Rebecca,

who showed me how to ask Questions;

To Irving,

who showed me how to begin to answer Them.
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# TABLE OF CONTENTS

**DEDICATION** ............................................... iii

**ACKNOWLEDGEMENTS** ........................................ iv

**LIST OF TABLES** ............................................ vii

**LIST OF FIGURES** ........................................... viii

**SUMMARY** ................................................... ix

**CHAPTER I - ORIGIN AND HISTORY OF THE PROBLEM** .... 1

  1.1 Efficiency Limits of Homojunction Solar Cells .......... 1

  1.2 Ultra-High Efficiency Approaches .......................... 2

  1.3 Theoretical Basis for Intermediate Band Solar Cells ....... 3

  1.4 Review of Quantum Dot implementation of the Intermediate Band Solar Cell 5

  1.5 Review of Quantum Dot Technology .......................... 6

    1.5.1 The Early History of Epitaxially Grown Quantum Dot Semiconductor Heterojunction .......................... 6

    1.5.2 Quantum Dots Solar Cells Fabricated by Molecular Beam Epitaxy .......................... 9

    1.5.3 Recapitulation of Quantum Dot Technology ................ 14

  1.6 Recapitulation of the Origin and History .................. 14

**CHAPTER II - PHYSICAL INTERPRETATION OF HOW QUANTUM DOTS MAY IMPLEMENT AN INTERMEDIATE BAND SOLAR CELL** ........... 16

  2.1 The Role of a Confining Potential in a QD-IBSC ............ 17

    2.1.1 The Bound States within a Confining Potential ............ 17

    2.1.2 Allowed Energy Levels within a Single Quantum Dot ........ 19

  2.2 Optimum Placement of the Three Relevant Bands ............ 20

  2.3 Rules of Thumb for Predicting the Band Locations from the Energy Levels ............ 23

  2.4 The Importance of a Band as Opposed to an Impurity Level .......... 24

  2.5 The Role of the Impurity ............................... 24

  2.6 Recapitulation of Physical Interpretation ................. 25
CHAPTER III - MODELING THE OFFSET BETWEEN THE CONDUCTION BAND AND THE INTERMEDIATE BAND

3.1 Calculating the Energies of the Stationary States ........................................... 26
  3.1.1 The Hamiltonian of the System ................................................................. 27
  3.1.2 Selecting the Laguerre-based Basis ......................................................... 27
  3.1.3 The Hamiltonian in the Laguerre Basis ...................................................... 28
  3.1.4 Obtaining the Ground State ................................................................. 29
  3.1.5 Obtaining the Excited States ................................................................. 32
3.2 Requirements for the Acceptable Placement of the Electron Energy Levels .. 32
3.3 An Example with Al_{0.42}Ga_{0.58}As Barriers ............................................ 37
  3.3.1 Obtaining the Values of the Electron Effective Mass and the Dielectric Constant ......................................................... 37
  3.3.2 Discussion of the Results for Al_{0.42}Ga_{0.58}As Barriers ......................... 37
3.4 Chapter Recapitulation ................................................................. 40

CHAPTER IV - SELECTING A MATERIAL SYSTEM FOR AN OPTIMIZED QUANTUM DOT INTERMEDIATE BAND SOLAR CELL

4.1 Heterojunction Material Requirements for an Optimized QD-IBSC ........................................... 42
4.2 An Algorithm to Select the Heterojunction Materials ............................................ 44
4.3 Band Offsets Versus Lattice Constants from the Literature ........................................... 45
  4.3.1 Consideration of PBEVLC obtained from Levinshtein et al ........................................... 46
  4.3.2 Consideration of PBEVLC constructed by Tiwari and Frank ........................................... 48
  4.3.3 Consideration of PBEVLC constructed by Vurgaftman and Meyer ........................................... 49
4.4 Recapitulation of Selecting a Material System ........................................... 50

CHAPTER V - CONCLUSIONS ................................................................. 54

APPENDIX A — DERIVATION OF FINAL RELATION ........................................... 55

APPENDIX B — QUANTUM DOT HETEROSTRUCTURES PREVIOUSLY REPORTED ........................................................................... 63

APPENDIX C — MATLAB CODE TO CALCULATE ENERGY LEVELS ........................................... 64

REFERENCES ................................................................. 83
LIST OF TABLES

Table 1  Some heterojunctions on GaAs substrate .............................. 63
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Band diagram of a quantum dot intermediate band solar cell</td>
<td>4</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Hypothetical confining potential created by a quantum dot heterojunction’s conduction band offset and a centrally located hydrogenic impurity (1/r).</td>
<td>18</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Hypothetical confining potential created by a quantum dot heterojunction’s valence band offset.</td>
<td>18</td>
</tr>
<tr>
<td>Figure 4</td>
<td>The number of allowed hole states in Al$<em>{0.42}$Ga$</em>{0.58}$As with various potential depths.</td>
<td>20</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Band Diagram of an intermediate band solar cell</td>
<td>21</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Efficiency limit for an intermediate band solar cell</td>
<td>23</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Three examples to reinforce the concept of an “acceptable grouping of electron states”</td>
<td>34</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Electron levels in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 750 meV.</td>
<td>38</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Electron levels in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 1250 meV.</td>
<td>39</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Close-up of electron levels in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 1250 meV.</td>
<td>40</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Band edges versus lattice constant of various III-V materials obtained from Levinshstein.</td>
<td>47</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Electron levels in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 0.97 meV.</td>
<td>48</td>
</tr>
<tr>
<td>Figure 13</td>
<td>Interpretation of how the energy levels in the InAs/Al$<em>{0.42}$Ga$</em>{0.58}$As quantum dot heterojunction will form into bands when the quantum dots are ordered in a periodic array.</td>
<td>51</td>
</tr>
<tr>
<td>Figure 14</td>
<td>Band edges versus lattice constant of various III-V materials constructed by Tiwari and Frank.</td>
<td>52</td>
</tr>
<tr>
<td>Figure 15</td>
<td>Selecting the material system from the Tiwari and Frank construction.</td>
<td>52</td>
</tr>
<tr>
<td>Figure 16</td>
<td>Valence band edges versus lattice constant of various III-V materials constructed by Vurgaftman and Meyer.</td>
<td>53</td>
</tr>
<tr>
<td>Figure 17</td>
<td>Conduction band edges versus lattice constant of various III-V materials constructed by Vurgaftman and Meyer.</td>
<td>53</td>
</tr>
</tbody>
</table>
SUMMARY

The objective of this thesis is to examine the use of quantum dots in order to implement an intermediate band solar cell (IBSC). This thesis presents a quantum dot intermediate band solar cell (QD-IBSC) whose bandgaps realize the offsets necessary to optimize the conversion efficiency. The conceptual framework of the intermediate band solar cell provides a route to overcome the inherent efficiency limits of single junction solar cells. There are two components of the IBSC framework that are of particular importance to the work given herein: the existence of material with a valence band, conduction band, and an intermediate band; and that the intermediate band be metallic. In the quantum dot implementation of an IBSC, the intermediate band (IB) is created by a three dimensional periodic array of quantum dots enveloped by a semiconductor material. For each energy level available for a bound electron inside of a given quantum dot, a periodic array of the given quantum dot will produce a miniband within the previously forbidden band gap. If there is only one bound energy level in the quantum dot, this may become the intermediate band. If there are more than one allowed energy levels then there exists conditions that still allow for a single intermediate band. In either case, without doping the semiconductor material, the Fermi level is not guaranteed to lie within the IB, and therefore the IB is not guaranteed to be metallic. If the Fermi level lies inside the IB, the probability of creating photogenerated carriers is optimized. This thesis examines the use of $n$-type dopants to both ensure an IB and to center the Fermi energy within the IB. The specific form of the $n$-type dopants are single hydrogenic impurities centered within each quantum dot. In the case of a quantum dot with a single ionized impurity the Fermi level corresponds with the ground state energy level of a bound electron.

The Schrödinger equation is needed in order to calculate the energy levels in a quantum dot with an impurity because the potential energy varies appreciably over distances shorter than the wavelength of the electrons [1]. In calculating the energies of the stationary states
of an electron, the potential of the Hamiltonian is comprised of two parts: an electrostatic potential resulting from the introduction of the hydrogenic impurity, and a step function resulting from the conduction band offsets of the quantum dot heterojunction. The variational method is used to approximate the stationary states and their energies. The trial wave function that is used in the variational method is a linear combination of the hydrogenic wave functions. A constrained gradient descent algorithm is employed to search over the space of the free parameters in order to minimize the upper bound that is guaranteed by the variational method. Now that the major physical principals have been given the structure of the thesis itself will be given.

The following chapters of this thesis are arranged in the following manner. The first chapter of this thesis describes the motivation for developing the intermediate band solar cell. It then gives more details regarding the quantum dot implementation of the intermediate band solar cell. Chapter one continues by reviewing some early accomplishments in the epitaxial growth of quantum dot heterostructures. Finally, chapter one reviews some research done with epitaxial quantum dot heterostructures by the photovoltaic community. The second chapter of the thesis reviews some physical phenomena relating to the framework of the quantum dot implementation of the intermediate band solar cell. These phenomena are: the relationship between a confining potential and bound stationary states is given; the relationship between the band offsets of an IBSC, the solar geometry with respect to the solar cell, and the efficiency limits of the IBSC; the relationship between the stationary energy level(s) in a single quantum dot and the bands formed by a periodic array of quantum dots; and the role of an impurity in the QD-IBSC. The third chapter models the band offset between the conduction band and intermediate band of the QD-IBSC. The approximate energies of radially symmetric stationary states are calculated for an electron in a quantum dot as a function of the quantum dot radius. A set of requirements is then presented which place constraints upon the energy levels in order that the levels be suitable for the formation of an IBSC. Two examples are provided which show the energy levels for different values of the conduction band offset between the barrier material and the quantum dot material. It is shown that for a suitably large conduction band offset there exists an
interval of quantum dot radii whereby the energy levels meet the requirements and thus may form an IBSC. The fourth chapter of this thesis presents an algorithm for selecting a material system for a quantum dot heterojunction with which to fabricate a QD-IBSC. A focus is placed on the selection of heterojunction whose quantum dot material and barrier material offer a negligible valence band offset. Following these three chapters are three appendix. The first is the derivation of an important equation first given in chapter three. The second is a table of various quantum dot heterostructures that have been previously fabricated and studied. The final appendix contains the MATLAB code that was used to calculate the energy levels.
CHAPTER I

ORIGIN AND HISTORY OF THE PROBLEM

This chapter details approaches to exceeding the Shockley-Queisser limit of single junction solar cells. One of these approaches, the intermediate band solar cell (IBSC), is discussed in detail; especially as regards to the quantum dot implementation of the intermediate band solar cell (QD-IBSC). Some early literature regarding the microscopic structure and electronic properties of epitaxially grown quantum dots is then reviewed. Finally, research with epitaxially grown quantum dots applied to solar cells is reviewed.

1.1 Efficiency Limits of Homojunction Solar Cells

From purely thermodynamic considerations, the most ideal solar energy converter can convert concentrated sunlight into useful energy with an efficiency of 86.8 % [2]. For an idealized single junction solar cell, the thermodynamic efficiency limit, often referred to as the Shockley-Queisser limit, is 30.1 % under one-sun operation [3] and 40.7 % under maximum solar concentration [4]. Single junction silicon solar cells, with their band gaps slightly below the optimum value and their substantial degree of non-radiative recombination, are approaching the theoretical efficiency limit of 29.8 % [5]. For example, one-sun silicon solar cells have reached efficiencies of 24.5 % [6], and concentrator silicon solar cells have reached 26.8 % at 96 suns [7]. GaAs cells have a slightly higher efficiency potential because the band gap of GaAs is marginally closer to the optimum value for a one-band gap device and also because GaAs has lower Auger recombination. GaAs solar cells have been fabricated with an efficiency of 25.1 % as early as 1990 [8]. The extensive research on single junction solar cells has achieved efficiencies over 80 % of the theoretical efficiency limit under one sun concentration.

In order to achieve higher efficiencies than what is available from a single pn junction, solar cells have been physically stacked in tandem. Tandems consist of multiple stacks of
individual pn junctions, each made from a material with a distinct band gap. Tandem cells have two advantages over cells with a single pn junction: they are able to harvest a greater proportion of the energy of the incoming broadband solar flux and they may deliver the corresponding current at a higher voltage. Tandems contain pn junctions with a wide range of band gaps, thus a photon whose energy is too low to be absorbed by a optimally designed single band gap solar cell is more likely to be by the tandem element with a low band gap. In traditional single junction solar cells, high-energy photons lose much of their energy as heat waste due to the fact that the photogenerated carriers through phonon relaxation lose a large portion of the energy. In general, with tandems, a high-energy photon is absorbed by a band gap closer to the photon energy, thus less heat waste is produced. Tandems are said to have a higher degree of absorption selectivity than a traditional cell.

Under maximum concentration, the efficiency for tandems approaches the thermodynamic limit of 86.8 % as the number of cells in the stack increases to infinity and the concentration is increased to its maximum limit of 46050 suns [5]. Three stack tandems have a limiting conversion efficiency of 49.3 % under 1 Sun and 63.8 % under maximum concentration [2]. Triple-junction solar cells have reached 32.0 % under one Sun and 35.2 % at 150 Suns [9]. Despite these improved efficiencies relative to single pn junction efficiencies, it becomes increasingly difficult to make tandems with a large number of materials. This stems from the fact that, in practice, there is a limitation in lattice-matched materials with the appropriate band gaps.

1.2 Ultra-High Efficiency Approaches

There are only a few directions that provide a path to increase the efficiency above the Shockley-Queisser limit. These include producing cells that introduce more than two light generated carrier populations, producing cells that regularly yield more than one photogenerated carrier from an incoming photon, and producing cells that reshape the incoming spectrum so that more of the energy contained in the broadband incident light may be utilized by the cell in carrier generation. Within each of these directions there are many
approaches, of which tandems are but one. These approaches also include hot carrier solar cells [10], impact ionization solar cells [11], multiband solar cells [12], impurity level solar cells [13], intermediate level solar cells [14], quantum well solar cells [15], thermophotovoltaic [16, 17], and thermophotonic solar cells [18, 19]. This thesis is concerned with an ultra-high efficiency approach named the intermediate band solar cell. The conceptual framework of the intermediate band solar cell is reviewed in the next section.

1.3 Theoretical Basis for Intermediate Band Solar Cells

Luque et al first presented the notion of increasing the efficiency of solar cells by photon induced transitions at intermediate levels in 1997 [14]. The intermediate band solar cell (IBSC) has the potential of achieving 63.1% efficiency under maximum concentrated sunlight. This efficiency was calculated as occurring when the energy gap between the valence band and the conduction band was approximately 1.93 eV and when either the energy gap between the valence band and intermediate band or the conduction band and intermediate band was approximately 0.70 eV.

The optimum efficiency of the IBSC relies on a material with three bands: a valence band (VB), an intermediate band (IB) and a conduction band. In addition, in order to achieve high efficiency, the Fermi level of the material must be located within the intermediate band (see figure 1). Under these conditions there will exist 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. Relative to a material with two bands whose gap is equal in value to the widest band gap of the intermediate band solar, \( E_C - E_V \) in figure 1, the intermediate band solar cell will show an increase in photocurrent. Photon absorption is converted into photocurrent that is extracted at a voltage limited by the widest band gap of the material, \( E_C - E_V \) in figure 1.

Initially, Luque et al mention the possibility of constructing an IBSC by lone pair bands, low dimensional superlattices, and impurities [14]. For more information about

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1In their 1997 paper, Luque et al referred to this solar cell as an intermediate level solar cell or an intermediate band solar cell. The former terminology has since been abandoned in favor of the latter.
these techniques see [20]. Later, the possible fabrication of the ISBC was extended and refined. The three main avenues of investigation are: engineering the intermediate band through quantum dot technology; synthesizing an intermediate band material through a novel bulk material; and creating a localized absorber layer within a highly porous large band gap semiconductor [21]. Of these three, engineering the IB material via quantum dot technology is the most promising for an initial demonstration of the operating principles of the IBSC [21]. With respect to the second method, it is proposed to create a bulk GaAsTi material. Focus is now being given to the chemical stability of the compound, the prediction of electrical and optical properties, and methods of synthesis. With respect to the third method, TiO$_2$ and PbS are candidates for the porous material and absorbing material respectively. Following the work of Honsberg et al on multiple energy level solar cells [22], the potential role of impact ionization as an up-converting mechanism that may augment various non-idealities of fabricated intermediate band solar cells has been demonstrated [23].

In this section the framework of the intermediate band solar cell has been presented. In order to demonstrate the operating principles of the IBSC quantum dot technology is deemed promising. The following section of this chapter discusses some of the research made into the QD-IBSC.

**Figure 1:** Band diagram of a quantum dot intermediate band solar cell.
1.4 Review of Quantum Dot implementation of the Intermediate Band Solar Cell

This section states why quantum dots, rather than other low-dimensional structures, are deemed capable of forming an IBSC. In addition, the order of magnitude of the quantum dots radii and the inter-dot spacing are given. Lastly, three papers are discussed that offer routes to a metallic intermediate band.

Luque et al first present the framework of the intermediate band solar cell in 1997 [14]. The first major work proposing the quantum dot implementation of an IBSC was presented in 2000 [24]. In this work, Martí et al state that quantum dots, as opposed other low-dimensional structures, are necessary in order to implement an IBSC. They conclude that quantum dots are the only low dimensional structures with the possibility of intraband transitions which are theoretically dominated by radiative recombination. They state that other low-dimensional structures, such as quantum wires or quantum wells, to readily allow electrons to thermalize to the intermediate band.

Using standard quantum mechanical calculations and averaged empirical data for the InGaAs/AlGaAs system Martí et al obtain a relationship between the quantum dot radius and the potential depth of the conduction band offset for a system with only one bound electron state [24]. They conclude that the dot size ought to be about 40 Angstroms. Without coupling the intermediate energy levels exist only within the quantum dots [24]. This is not sufficient for the creation of an intermediate band, which is predicated upon an overlap between the various bound electron wave functions throughout the device. The tight binding method is used to calculate the relationship between the bandwidth of the intermediate band created by the quantum dots and the distance between the centers of adjacent dots. The authors state that inter-dot spacing ought to be around 100 Angstroms, yielding a 10 meV bandwidth [24]. Now that the scale of the quantum dots have been given, details of half-filling the quantum dots are presented.

The framework of the IBSC requires a half-full metallic intermediate band. There are various ideas regarding routes to half-fill the IB of a QD-IBSC [24, 25, 26]. It is proposed that the barrier material be nearly intrinsic and the quantum dot material be n-type [24].
This thesis goes into more depth regarding this proposed route. In addition, the use of modulation doping in the barrier region is suggested [25]. It is concluded that a metallic IB may be formed in the InGaAs/AlGaAs system with quantum dot radii of 39 Angstroms, and inter-dot spacing between 100 Angstroms and 600 Angstroms [24]. The necessary concentration of the modulation doping is concluded to be between $1 \times 10^{16}$ cm$^{-3}$ and $4 \times 10^{18}$ cm$^{-3}$ [24]. Cuadra et al discuss the possibility of implementing a QD-IBSC with type II broken bands [26]. The authors identify InAs/GaSb as possible materials with which to build such a heterojunction. One convenient aspect of the broken band route is that the formation of a metallic band may not require doping at all.

In this section we have reviewed some major accomplishments specific the quantum dot implementation of an intermediate band solar cell. In the following section, quantum dot technology is reviewed in order to assess if the technology has matured to a point where it may be used reliably to fabricate an IBSC.

1.5 Review of Quantum Dot Technology

It is proposed that quantum dot technology may be used to implement an intermediate band solar cell. In this section, a brief review of the history of epitaxial quantum dot technology is given. The major accomplishments which demonstrate the structural and electro-optical properties will be given. Such a review is important to the work of this thesis because it provides a basis with which evaluate the practical value of implementing the intermediate band solar cell with quantum dots. This section will also provide a review of the manners in which epitaxially grown quantum dots have been applied within the photovoltaic community. Such a review provides a base with which to view potential hazards particular to solar cells when utilizing quantum dot.

1.5.1 The Early History of Epitaxially Grown Quantum Dot Semiconductor Heterojunction

The history of epitaxially semiconductor material shows that is indeed possible to grow quantum dot heterojunctions. Further, as is prerequisite for the formation of an intermediate band material, the history shows that is indeed possible to create nearly periodic arrays
of quantum dots within a barrier material [27]. The quantum dot implementation of the intermediate band solar cells also requires some level of uniformity of the sizes of the quantum dots in a given sample. This is necessary so that the bands created by the overlapping wave function do not spread themselves through the previously forbidden bandgap. The literature shows that some measure of uniformity is possible [28, 27]. The literature also shows that it is possible to alter the growth process in order to tune the average radius size [27, 29, 30, 31, 32]. This is necessary within the framework of the QD-IBSC to tune the location of the intermediate band for high efficiency conversion.

Quantum dot heterostructures have been grown with many different material systems (see appendix B for more details). Quantum dots may be intentionally fabricated by lithographic techniques or by a self-organizing process. Bimberg outlines the various lithographic techniques: optical lithography and holography; X-ray lithography; electron and focused ion beam lithography, and scanning tunneling microscopy [33]. Self-organized defect free quantum dots are commonly fabricated by molecular beam epitaxy, metal-organic chemical vapor deposition or other epitaxial growth techniques [34, 35, 36, 37]. In these processes a two dimensional epilayer is grown upon a lattice. The lattice material and the epilayer material are purposely chosen to have different lattice constants. This being the case, there is considerable amount of strain energy that accumulates in the growth layer. As in all systems, the point of lowest potential energy is found; specifically, the 2 dimensional epilayer undergoes a relaxation process in which the epilayer material beads up into quantum dots.

As mentioned by Bimberg, Stranski and Krastanow first showed three-dimensional island formation from an initially two-dimensional heteroepitaxial layer [33]. Seifert et al explains the island formation by way of a model that includes a meta-stable epilayer under compression [38]. They offer a qualitative description of the epilayer growth and nucleation process leading to the growth of dots which takes into account energy of the system through time. In the first period of growth the elastic strain energy builds linearly with time as the deposition progresses. The authors state that at some point in time the critical wetting layer is reached and the stable two dimensional growth mode enters a into a metastable state. With continued deposition, a supercritically thick wetting layer builds
up, which means that the epilayer is potentially ready to undergo a transition towards a Stranski-Krastanow morphology. The next period of growth is a phase morphology that is comprised of a nucleation of the two-dimensional material into three-dimensional islands and the growth of these islands through strain relaxation.

Through the years, experimentation has provided empirical data with which to refine the self-organizing process. Moison et al give early evidence of the ability to have a large degree of spatial uniformity of self-organized quantum dots. They offer histograms of both dot height and half-base width that are measured from atomic force microscopy images. Moison et al also offer the probability distribution of the first nearest neighbor distance. In the same plot they cleverly show the distribution of a perfect QD lattice and the random Poisson law. The distributions that they measure fall between the two theoretical extremes and therefore indicate a considerable measure of order [27]. The work of Moison et al offer a feasibility study in constructing nearly perfect periodic arrays of quantum dots. There observation that the placement of the dots is somewhere between random and perfectly ordered is of utmost important with respect to fabricating an intermediate band solar cell, for nearly all the IBSC models assume that quantum dots may eventually be fabricated with near perfect periodicity.

Leonard et al show the uniformity of dots for various samples by plotting histograms of the dot sizes as measured from transmission electron microscopy images. The ratio of the standard deviation of the sizes to the mean value of the sizes is 1:10. The distribution in sizes is shown to follow a Gaussian distribution [28]. In 1999 Zundel et al offered a plot of the photoluminescence of a sample of GaAs with InP quantum dots measured at 8 K. The photoluminescence plot is flat save for one very sharp peak near 1.8 eV. This plot indicates clearly a uniform quantization of energy due to the three dimensional confinement of a quantum dot in potential barrier [39]. This observation also shows the feasibility of some day creating nearly perfectly periodic lattices.

In this subsection, several techniques that have been used to fabricate quantum dots have been listed. In addition, a model by Seifert et al, which illustrates a possible mechanisms for three-dimensional island formation, has been reviewed. Some early milestones in the
fabrication and measurement of epitaxial quantum dots have been provided. A literature review is also provided that shows that a significant amount of uniformity in quantum dot size and quantum dot placement may be obtained. Finally, the empirical work of Zundel is offered. His work shows that three dimensional energy confinement in quantum dots is presented. In relation to the work of this thesis, the literature prevented in this subsection offers encouragement that in the near future quantum dot technology may be used to fabricate an intermediate band solar cell.

1.5.2 Quantum Dots Solar Cells Fabricated by Molecular Beam Epitaxy

The quantum dot implementation of the intermediate band solar cell that is offered in this thesis will depend upon the controlled epitaxial growth of quantum dots within a barrier material. A properly designed and proficiently fabricated QD-IBSC ought to have an open circuit voltage is limited by the bandgap of the barrier material and a short circuit current greater than a sample consisting of the barrier material alone. Yet many in the photovoltaic community have fabricated solar cells with quantum dots. This subsection reviews there work in order to provide insight into the possible problems to be overcome in the quantum dot implementation of an IBSC.

Several groups in the photovoltaic community have produced experimental quantum dot solar cells with binary and ternary semiconductor materials [40, 29, 30, 31]. Aiguo et al report on self-assembling germanium dots on silicon grown using molecular beam epitaxy and the Stranski-Krastanov growth method [40]. They prepare samples with both 50 layers of stacked dots and 100 layers of stacked dots. Atomic force microscopy offers evidence of the formation of quantum dots in their samples. The images reveal a bimodal distribution of islands, domes, and pyramids whose heights and diameters averaged 17 nm and 81 nm respectively. Within the wavelengths of 1190 nm and 1450 nm, the external quantum efficiency (EQE) of the 100-layer stack is greater than the 50-layer stack that is greater than silicon device with no QD layers. The enhanced EQE in the infrared regime is attributed to the lower effective band gap of Ge with respect to Si. The increase in EQE with increasing layers is attributed to the number of confining layers that could
make more effective light absorption. The data shows that that the EQE in the infrared region (1190 nm and 1450 nm) decreases as the annealing temperature increases from 800 °C to 1020 °C. Data also indicates a complete loss of photoluminescence within the range of 800 meV and 900 meV. Alguno et al conclude that their results are indicative of the appearance of point defects within the islands, deformation of Ge dots with the Si spacer, or a disappearance of Ge dots as the overall material transforms to an inhomogeneous SiGe quantum well. With respect to fabricating a quantum dot intermediate band solar cell, the work of Alguno et al is encouraging. These researchers have shown that there is enhanced EQE in the infrared regime. It may be inferred from this data that a QD-IBSC may be able to photogenerate and collect electrons with photons whose energies cover a wide range of the solar spectrum, and thus offer improved conversion efficiency. Alguno et al do not mention if there is a deleterious effect in the other spectral regimes due to the quantum dots. Such additional empirical data is necessary in order to judge the extent to which an proficient QD-IBSC may be fabricated.

Konle et al report upon the fabrication of germanium QD on silicon for use in this film solar cells [29]. Molecular beam epitaxy to produce samples with Ge dot forming epilayers. The fabrication process is tuned so as to create samples with varied epilayer thickness. All photoluminescence measurements are recorded at 4 K. Intense photoluminescence at low photon energies (0.8 eV - 0.9 eV) only begins to appear when the Ge epilayer thickness increases to 6 monolayers. Konle et al report on Ge islands with lateral sizes around 80 nm and heights around 7 nm on the 4 monolayer surface Ge islands with lateral sizes around 205 nm and heights around 28 nm on the 6 and 8 monolayer Ge surfaces. The island densities are approximately $1 \cdot 10^9$ per square centimeter in both the 6 and 8 monolayer and [29]. Atomic force microscopy provides structural evidence of QD on the samples. The authors produce dot densities greater than $5 \cdot 10^9$ per square centimeter. Without surfactant-mediated growth high island densities can only be achieved with low growth temperatures, which result in low crystal quality [29]. High temperature growth, using Sb as a surfactant, allows the formation of dots with much higher densities and perfect crystal quality [29]. With the use of a Sb surfactant, Konle et al report densities of $1.8 \cdot 10^{11}$ per
square centimeter and $7.2 \cdot 10^{10}$ per square centimeter for a growth temperature of 630
$^o$ C and 670 $^o$ C respectively. Using the Sb surfactant sample grown at 700 $^o$C they study
the temperature dependence of photoluminescence measurements. The photoluminescence
signal from the Ge dots (centered near 0.81 eV) is observed at temperatures up to 270 K.
The current-voltage relation for one of their cells, under AM 1.5 radiation, shows a short
circuit current up to $26.6 \text{ A cm}^{-2}$ and an open circuit voltage of 433 mV. This is recorded
from a cell with ten layers of Ge dots grown at 700 $^o$C without Sb surfactant. The overall
result is poor with respect to a control device grown without Ge dots. In the control sample,
the short circuit current is $26.2 \text{ A cm}^{-2}$ and the open circuit voltage is 499 mV. With respect
to fabricating a quantum dot intermediate band solar cell, the work of Konle et al points
to some difficulties that lie ahead. In particular, the fact that there was no increase in
short-circuit current may indicate that crystal quality plays a role in obtaining an enhanced
photocurrent in an QD-IBSC. In addition, that the open-circuit voltage of the quantum
dot samples shows a 12 % reduction with respect to the control sample is alarming. The
theory of the IBSC is predicated upon the idea that the open circuit voltage will pinned
by the widest band gap material. The low value of the open circuit voltage is indicative of
rapid recombination rates. Rapid recombination rates is an issue in any device structure
with quantum dots and must be carefully examined.

The work of Konle et al is continued by Presting et al, who provide data of the photocur-
rent of SiGe solar cells compared to a Si reference. These researchers fabricated cells with
varying numbers of Ge layers. In all cases, the Ge layers were about 8 monolayers thick.
Presting states that their all their samples have the same tendency: a higher photocurrent
in the near infrared regime (0.88 micron) with a gradual drop as the photons become more
energetic. Specifically, the authors show that with increasing layers of Ge dots, there exists
an enhanced infrared response with respect to Si cells. It is worth noting that the authors
report fill factors of 69.6 % and 73 % for Si/Ge cells with 25 and 50 dot layers respectively.
These same samples yield overall average quantum efficiencies of 11.9 % and 11.8 % for
Si/Ge cells with 25 and 50 dot layers respectively. In conclusion, the authors state that
the high recombination and capture rates of the Ge dots combined with loss in open circuit
voltage prevent an overall efficiency increase [41]. It is inferred from the work of Konle et al that the efficacy of the QD implementation of the IBSC may depend upon the number of quantum dot layers.

The work of Kiravittaya et al show that the epitaxial growth temperatures effect the size of the quantum dots [30]. This fact will come to play in tuning the location of the IB in the QD-IBSC to optimize the conversion efficiency. Using molecular beam epitaxy at various growth temperatures, Kiravittaya et al at the University of Bangkok, have fabricated samples quantum dot materials on GaAs substrates with GaAs barriers [30]. Several variants were produced, these include: single monolayers of InAs dots; single monolayers of InGaAs dots; alternating layers of InAs and InGaAs dots (composite); and a stack of several layers of InGaAs/GaAs material grown on top of a stack of several layers of InAs/GaAs material (stacked). Kiravittaya et al state that the motivation for their work is that composite (InAs)(InGaAs) dots should give a wider spectral response and have the possibility for storing photogenerated carriers.

Atomic force microscopy and photoluminescence measurements show that dot sizes increased at higher growth temperatures [30]. These varying dot sizes produce shifts in the photoluminescence peaks (peaks centers migrate from 950 nm to 1100 nm). Kiravittaya et al note that at a growth temperature of 450 °C the typical dot had a diameter of 30 nm and a height of 5 nm. Similar results were obtained with InGaAs dots. With respect to the same temperature of growth the authors note that photoluminescence peak of In_{0.5}Ga_{0.5}/GaAs system found at shorter wavelengths as compared to InAs dots. The authors attribute this to an increase in the ground state energy within the InGaAs quantum dot. With these preliminary results the authors explore more complicated (In_{0.5}Ga_{0.5}As/GaAs)(InAs/GaAs) structures grown at 500 °C.

Photoluminescence data of the stacked system shows a broadened spectral response centered at 1100 nm [30]. The authors note that the spectral response may be tuned to better fit the solar spectrum. However, the composite structure did not display the broad spectral response. As a final point the authors provide analytic work illustrating the capacitive nature of the quantum dot heterostructures, which, they claim, is due to
Coulomb blockade. They comment that the capacitance is in the aF range.

The work of Kamprachum et al. show that the epitaxial growth rate and duration of etching effect the size of the quantum dots [30]. These facts will also come to play in tuning the location of the IB in the QD-IBSC to optimize the conversion efficiency. Kamprachum et al. have grown quantum dot material using molecular beam epitaxy [31]. They experiment with two schemes to create multi-stacked QD with graded dot sizes. The first scheme uses different growth rates to produce 1.8 monolayers of InAs self-assembling material. In the second scheme, different in situ etching times are varied while creating three layers of self assembling quantum dot material. The authors characterize the structures of many growth samples by atomic force microscopy and their optical properties are observed by photoluminescence. The authors present data showing that varying the growth rate changes dot size and dot density. Kamprachum et al. note that smaller dots, grown at high growth rates, show a blue shift compared with larger, more slowly grown, dots. The authors state that an advantage of the variable etching scheme is the controllability of quantum dot sizes without changing the dot density. Having performed these preliminary experiments the two schemes are employed to create stacked layers.

The first scheme uses different growth rates to produce 1.8 monolayers of InAs self-assembling material [31]. In three subsequent QD layers the growth rate is increased from 0.20 to 0.05 to 0.01 monolayers per second. In the second scheme different in situ etching times are varied while creating three layers of self-assembling quantum dot material. The first such layer is etched for 6 seconds, the next layer for 12 seconds, and the third for 24 seconds. The current voltage characteristic of a 0.06 cm² exposed area exhibits a short circuit current of 0.23 mA and an open circuit voltage of 0.23 V due to a 1000 W/m² light source. The spectral response is measured at different light intensities. Data shows two regions of response: a short wavelength region between 400 nm and 850 nm, and a long wavelength region between 1000 nm and 1800 nm. The authors conclude that the response in these two regions is due to the bulk GaAs and multistacked QD respectively.

In order to characterize the samples, both atomic force microscopy measurements and photoluminescence measurements are conducted. The theorized blue shift is observed for
samples with smaller dot sizes. Using both of the aforementioned MBE growth methods, these collaborators also fabricate multistacked samples; each subsequent layer having smaller dot sizes. Measurements of the room temperature photoluminescence, current-voltage characteristics, and spectral response are taken from the multistacked cells. The spectral response of the samples also shows the characteristic short wavelength response (based upon the GaAs band gap) and long wavelength response (based upon the InAs QD and GaAs bulk). The authors note an improvement in the current-voltage relation as compared to devices with a single layer of QD. These authors provide significant empirical results to illustrate quantum confinement in a photovoltaic application.

1.5.3 Recapitulation of Quantum Dot Technology

The literature shows that uniformity in quantum dot size may be achieved and that the concentration of quantum dots may be tuned. The success of the QD-IBSC are premised upon these facts. The literature also shows that the epitaxial growth process alters the physical dimensions of the quantum dots and the optoelectronic properties. This fact is indicative of the role that careful experimentation and fabrication will play in proving or disproving the concept of the QD-IBSC. The literature regarding solar cells implemented with quantum dots shows a trend of inferior conversion efficiency with respect to control solar cells without the quantum dots. With respect to fabricating a QD-IBSC, the challenges that are faced are to fabricate cells of sufficient crystalline quality so that an increased photocurrent may be observed and to advance the understanding of quantum dot heterojunctions so as to design a device without a decrease in open circuit voltage.

1.6 Recapitulation of the Origin and History

Single junction solar cells have inherent efficiency limits far below the thermodynamic limit. Several ultra high efficiency approaches were reviewed, especially the approach of fabricating an intermediate band solar cell. The major theoretical advances of the quantum dot implementation of the intermediate band solar cell were reviewed, especially as regards the advances of a barrier doped QD-IBSC. The broader quantum dot literature was reviewed in order to illustrate the feasibility of fabricating nearly periodic arrays of epitaxially grown
quantum dots and the possibility of tuning the quantum dot size. These are essential to the formation of an intermediate band within the previously forbidden band gap of a barrier material and to tuning the location of the intermediate band. The remainder of this thesis concentrates upon a quantum dot implementation of an intermediate band solar cell whose quantum dots are doped with centrally located hydrogenic impurities.
CHAPTER II

PHYSICAL INTERPRETATION OF HOW QUANTUMDOTS MAY IMPLEMENT AN INTERMEDIATE BAND
SOLAR CELL

The intermediate band solar cell has the potential of achieving 63.1 % efficiency under
maximum concentrated sunlight [14]. This efficiency relies upon 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 must be well within the
intermediate band. Quantum dot technology may be used to implement an IBSC [24]. The
quantum dot implementation of the IBSC requires a method to form an intermediate band,
the means to adjust the offset of the intermediate band, a means to calculate and adjust
the Fermi level.

An intermediate band may be formed by positioning uniformly shaped quantum dots
close enough and periodically enough so that their wave functions couple together. Evidence
is given in chapter one that some regularity in both inter-dot spacing and quantum dot size
is reported. In order that the intermediate band is metallic the Fermi level must be placed
with in it. In this thesis it is proposed to half-fill the doubly degenerate ground state with
the electron of an ionized donor impurity. Under such circumstances the Fermi level is equal
to the energy of the ground state. Evidence is given in chapter one that the fabrication
conditions may be used to alter the radii of the quantum dots. In chapter three it is
shown how to calculate the ground state energy of an electron within a quantum dot with
a centrally located hydrogenic impurity.

The goal of this chapter is to discuss physical phenomena pertaining to the quantum
dot implementation of an intermediate band solar cell. The role of a confining potential in
the formation of bound stationary states is discussed. A method to calculate the efficiency
limits of an intermediate band solar cell will be given. Hypotheses will be made as to how energy levels transform into bands within a periodic structure. A distinction will be made between an intermediate band and an impurity level. Finally the chapter discusses the role of impurities within the context of the quantum dot implementation of the intermediate band solar cell.

2.1 The Role of a Confining Potential in a QD-IBSC

The quantum dot implementation of the IBSC requires a method to form an intermediate band. It is proposed that the IB be formed by the overlap of the electron wave functions within a periodic array of quantum dots. Eigenenergies of the bound stationary states within a confining potential are the location of minibands formed by a periodic array of uniform confining potentials. In the case of a quantum dot within a barrier material, the minibands form within the previously forbidden bandgap of the barrier material considered alone. For this reason the role of the confining potentials in a QD-IBSC is to allow for the creation of energy levels, and hence miniband(s), within the previously forbidden bandgap. In the remainder of this section a discussion will be given regarding the existence of bound states within a confining potential and regarding the allowed energy levels within a single quantum dot.

2.1.1 The Bound States within a Confining Potential

In many instances, such as a 3-dimensional square well with an infinite potential depth, the discrete energy levels of the bound states may be derived in a closed form expression. In some circumstances, such as a 1-dimensional square well with an finite potential depth, a mathematical criteria for the existence of bound states within a confining potential can be formed with an expression that includes the depth and the width of the confining potential. In some instances, such as 3-dimensional spherical well with a finite potential depth, both the energy eigenvalues and the eigenfunctions of the state may not be solved in a closed form expression, yet may be obtained analytically. In some instances, it is not be relevant to calculate the eigenenergies nor the eigenfunctions. In this thesis two confining potentials, shown in figures 3 and 2, are considered: the first one derived from the quantum dot
heterojunction’s conduction band offset and the electrostatic potential; the second potential is derived from the quantum dot heterojunction’s valence band offset. The energy levels of an electron in the former confining will not be solved exactly, but rather, approximated in chapter three. The energy levels of the holes in the latter confining potential will not be solved for at all. In this case, it is sufficient to show the quantity of allowed hole states. This exercise will be performed in the next subsection.

**Figure 2:** Hypothetical confining potential created by a quantum dot heterojunction’s conduction band offset and a centrally located hydrogenic impurity (1/r).

**Figure 3:** Hypothetical confining potential created by a quantum dot heterojunction’s valence band offset.
2.1.2 Allowed Energy Levels within a Single Quantum Dot

The study of a single quantum dot can be found in many quantum mechanics texts [42]. They often appear under the heading radially symmetric, spherical quantum wells. In the case of the a quantum dot heterojunction’s valence band offset, the Hamiltonian takes the form of Bessel’s differential equation, whose solution’s are spherical Bessel functions. Once the particular heterojunction materials have been selected the magnitude of the potential, the effective mass, and the dielectric constant are known. The only parameter that adjusts the solutions to the differential equation is the radius of the quantum dot. The equation that relates the number of allowed energy levels to the radius of the quantum dot is:

\[ n_E = \text{ceil} \left( \frac{2 r_{QD} \sqrt{2 m_{e/f} V_{V_B} - \pi \hbar}}{2 \pi \hbar} \right), \tag{1} \]

where \( \text{ceil} \) indicates a rounding up of the argument to the nearest whole number, \( r_{QD} \) is the radius of the quantum dot, \( m_{e/f} \) is the effective mass of the bound particle, \( V_{V_B} \) is the potential depth of the quantum dot, and \( n_E \) is the number of bounded energy levels inside the quantum dot.

If neither the hole effective mass nor the dielectric constant varies appreciably between the QD material and the barrier material, equation 1 may be used to approximate the number of bound stationary hole states in the quantum dot created by a heterojunction’s valence band offset. For a given material system, the radius of the quantum dot, alone, adjusts how many allowed bound stationary states exist. As an example, consider a quantum dot within an Al_{0.42}Ga_{0.58}As barrier material. Allowing that the dielectric constant equals 11.7 and the hole effective mass is equal to 0.6150 \( \times \) 9.11 \( \times \) 10^{-34} kg, as is reported for the Al_{0.42}Ga_{0.58}As material, then equation 1 may be used to calculate the number of allowed hole states within the quantum dot as a function of the quantum dot radius. The results are shown below in figure 4 for various potential depths. As seen in figure 4, the number of holes increases for both an increase in the potential depth and an increase in the quantum dot radius. As the number of allowed states increases they eventually create a continuum of allowed energies for a confined hole.
Figure 4: The number of allowed hole states in Al$_{0.42}$Ga$_{0.58}$As with various potential depths

2.2 Optimum Placement of the Three Relevant Bands

In this section, a method is provided which allows for the calculation of the optimum efficiency of the intermediate band solar cell. These results will indicate what the relevant offsets ought be between the conduction band, intermediate band, and valence band in order to obtain optimal efficiency. The efficiency of photovoltaic conversion under black body illumination is

\[ w = \frac{V \cdot I(V)}{C f \sigma T_s^4}, \]

where \( V \) is the output voltage of the photovoltaic material; \( I \) is the net photogenerated current; \( C \) is a concentration factor; \( f \) is a dilution factor, \( T_s \) is the Kelvin temperature of the radiant source; and \( \sigma = \frac{(2\pi^5 k^4)}{(15c^2\hbar^3)} \) [2]. \( k \) is Boltzmann’s constant, \( c \) is the speed of light in vacuum; and \( \hbar \) is Plank’s constant. The efficiency limit will be found at maximum concentration; that is when \( C = 1/f \). In the remainder of this section the maximum concentration is assumed, that is \( C \cdot f = 1 \), except where otherwise stated.

The intermediate band solar cell is idealized in such a way that the output voltage, \( V \), is given as the difference between the quasi Fermi levels of the electrons in the conduction band and the holes in the valence band divided by the elementary charge \( q \).

\[ V = \frac{\mu_CI + \mu_IV = \mu_CV}{q}, \]

where \( \mu_CI, \mu_IV \), and \( \mu_CV \) are defined in figure 5.
The net photogenerated current is equal to the unit charge, $e$, multiplied by the net particle flux between the intermediate band solar cell and the Sun. From a black body or gray body source, which includes semiconductors and metals, the particle flux is given by the integral of the emission spectrum over the energy range of allowed emission:

$$N(E_{\text{low}}, E_{\text{high}}, T, \mu) = g \int_{E_{\text{low}}}^{E_{\text{high}}} \frac{E^2}{\exp \left( \frac{E - \mu}{kT} \right) - 1} \, dx,$$

where $E$ is the energy of an emitted photon, $\mu$ is the chemical potential of the emitted photon, and $g = (2\pi) / (c^2 h^3)$. The particle flux emitted from Sun which may be absorbed by a semiconductor of band gap, $E_G$, is given by:

$$N(E_g, E_\infty, T_S, 0) = g \int_{E_G}^{E_\infty} \frac{E^2}{\exp \left( \frac{E}{kT_S} \right) - 1} \, dx,$$

where $T_S$ is the Kelvin temperature of the Sun. Similarly, the particle flux emitted from semiconductor of band gap, $E_G$, is given by:

$$N(E_g, E_\infty, T_a, \mu) = g \int_{E_G}^{E_\infty} \frac{E^2}{\exp \left( \frac{E - \mu}{kT_a} \right) - 1} \, dx,$$

where $T_a$ is the Kelvin temperature of the semiconductor, and $\mu$ is the chemical potential of the photons. Therefore, the net particle flux between the Sun and a semiconductor with
a single band gap, $E_g$, under full concentration is given as:

$$N_{net} = N(E_g, E_{\infty}, T_S, 0) - N(E_g, E_{\infty}, T_a, \mu).$$  \hspace{1cm} (7)

In the case of the intermediate band solar cell, there are three interactions that affect net photon transfer between the semiconductor and the Sun: the first is due to net photons generated by absorption and recombination between the conduction band and valence band; the second is due to the net generated by absorption and recombination between the intermediate band and the conduction band; and the third is due to the net generated by absorption and recombination between the valence band and the conduction band. However, since there is no current extracted from the IB, the incoming and outgoing particle flux are equal. This may be expressed in mathematical terms as:

$$N(E_{CI}, E_{IV}, T_S, 0) - N(E_{CI}, E_{IV}, T_a, \mu_{CI}) = N(E_{IV}, E_G, T_S, 0) - N(E_{IV}, E_G, T_a, \mu_{IV}).$$  \hspace{1cm} (8)

Thus, the net particle flux between the IBSC and the Sun may be described by,

$$N_{net} = [N(E_G, \infty, T_S, 0) - N(E_G, \infty, T_a, \mu_{CV})]$$

$$+ [N(E_{CI}, E_{IV}, T_S, 0) - N(E_{CI}, E_{IV}, T_a, \mu_{CI})].$$  \hspace{1cm} (9)

where the various energies and chemical potentials are shown in figure 5 [14].

Using an equation equivalent to equation (9), Luque has calculated the values of the band gap (between the conduction band and valence band) that yield the optimum conversion efficiencies as a function of the band gap between the valence band and the intermediate band [14]. He has done this for a Sun at 6000 K and a solar cell at 300 K. The graphical results from Luque are shown in the upper trace of figure 6 [14]. The figure indicates that the highest possible conversion efficiency, 63.1 %, is found when the band gap between the conduction band and valence band is approximately 1.93 eV, the band gap between the intermediate band and valence band is approximately 0.70 eV, and the band gap between the intermediate band and valence band is approximately 1.23 eV. Due to symmetry considerations, there is another permutation that offers the same efficiency: when the band gap between the intermediate band and valence band is approximately 1.23 eV, and the band
gap between the intermediate band and valence band is approximately 0.70 eV. In a subsequent paper, Luque et al clarified that for optimum efficiency, \( E_G = 1.95 \), \( E_I = 0.71 \) eV or \( E_I = 1.24 \) eV, and \( E_C = 1.24 \) eV or \( E_C = 0.71 \) eV; where \( E_G = E_C + E_I \) [43]. This thesis presents a quantum dot intermediate band whose band gaps realize the energy levels necessary in order to optimize the conversion efficiency.

![Efficiency graph](image)

**Figure 6:** Efficiency limit for an intermediate band solar cell (upper trace). This plot is reproduced from Luque’s 1997 IBSC paper [14].

### 2.3 Rules of Thumb for Predicting the Band Locations from the Energy Levels

Qualitatively, the Kronig-Penney model may be used to understand how a periodic array of quantum dots, all with identical bound electron energy levels, may form a band within the crystal. The periodicity of the crystal allows that a single allowed energy level in one quantum dot, viewed in isolation, becomes \( N \) closely spaced allowed energy levels centered around the single energy level (where \( N \) is the number of quantum dots). As the number of periodically arrayed quantum dots increases, the discrete spacing of the allowed energy levels blur into a continuum, hence forming a band.

In the case where more than one bound electron level exists within a single quantum dot
it is possible that two distinct bands will form or that the bands will merge in a periodic array of such quantum dots. There are two rules of thumb that will be used within this thesis to interpret the energy levels of the bound stationary states. Firstly, if two energy levels are within $4 kT$ ($\approx 100$ meV) of each other, then a single band will be formed whose width will be at least $4 kT$. Secondly, if two energy levels are separated by at least $20 kT$ ($\approx 500$ meV), then two distinct bands will be formed separated from each other by less than $20 kT$.

2.4 The Importance of a Band as Opposed to an Impurity Level

The derivation offered in section 2.2 of this chapter presumes the existence of three bands: a conduction band, a valence band, and a metallic intermediate band. In the quantum dot implementation of the IBSC, the intermediate band appears in the previously forbidden band gap of the bulk material. It need be stressed, that the phenomena under discussion is not equivalent to the discussion of defect levels within the band gap. Electrons within the intermediate band have non-localized wave functions. Such non-localization allows direct transitions between the carrier population (e.g. IB $\rightarrow$ VB, CB $\rightarrow$ IB), hence allowing radiative recombination to be the dominant recombination process. Further, such non-localization augments transport throughout the IBSC material. With a band, as opposed to defect levels, the channeling of photoexcited carriers is augmented via the coupling between the electrons' wave functions within in the various quantum dots. Defect levels tend to cause non-radiative recombination and also greatly diminish carrier lifetimes.

2.5 The Role of the Impurity

Without doping either the barrier or the dot, the Fermi level will remain midway between the barrier's conduction and valence bands. Depending upon the offset of the intermediate band the likelihood of transitions to and from the intermediate band may be relatively low. The low likelihood of transition may be remedied by aligning the Fermi level within the intermediate band.

In this thesis n-type dopants are inserted into the quantum dots in order to adjust Fermi
level. It will be assumed that a single ionized hydrogenic impurity is placed at the center of each quantum dot. The effect of the donor electrons is to occupy the ground state energy eigenvalues inside the dot. Due to the spin of the electron the ground state energy is two-fold degenerate. Therefore the effect of the impurity is to half-fill the ground state energy. Because the ground state energy will be half full, the ground state energy, by definition of the Fermi energy, becomes the Fermi energy.

2.6 Recapitulation of Physical Interpretation

This chapter details how quantum dots may be used to create energy levels within the previously forbidden bandgap of a barrier material. The selective creation of energy levels within a quantum dot may boost the ability to photogenerate carriers. Along this vein, an example has been given that shows how to approximate the number of bound stationary hole states within a heterojunction’s valence band offset. This chapter also details a method for calculating the efficiency of an intermediate band solar cell given the band offsets between the conduction band and valence band, the conduction band and the intermediate band, and the intermediate band and the valence band. The absolute maximum solar energy conversion efficiency, 63 % occurs when the band gap between the conduction band and valence band is 1.95 eV and when the band gap between the valence band and the intermediate band or the conduction band and the intermediate band is 0.71 eV. A qualitative discussion of how a band is formed from a periodic lattice follows is provided. Two rules of thumb are offered as regards to the transformation of energy levels into bands. If the energy between two successive energy levels is greater than 500 meV, two distinct bands are formed. The differences between an intermediate band and an impurity level are stressed in this chapter. The major point is that the wave functions of impurities are localized whereas the wave functions are non-localized. Finally, the role of the donor impurity is to set the Fermi level within the conduction band. In this following chapter of this thesis, an n-type hydrogenic donor impurity is placed at the center of the quantum dot and it is shown how to calculate the energy levels of the radially symetric states.
CHAPTER III

MODELING THE OFFSET BETWEEN THE
CONDUCTION BAND AND THE INTERMEDIATE
BAND

This chapter presents a method to approximate the band offset between the conduction band and the intermediate band of a quantum dot intermediate band solar cell with centrally located hydrogenic impurities within the quantum dots. The offset between the conduction band and intermediate band is found by calculating the energies of the radially symmetric stationary electron states within a quantum dot with a hydrogenic impurity. In order to perform such calculations it is necessary to obtain empirical values of the effective mass of the electron, the dielectric constant of the material confining the bound particle, the potential depth of the confining potential, and the radius of the quantum dot. Based upon the rules of thumb presented in section 2.3 of chapter two, the possible arrangement of the energy levels are limited if they are to form an IBSC. This chapter enumerates the various acceptable arrangements of the energy levels. In order to do this, the concept of “acceptable groupings of electrons states” is defined. Finally, an example of such calculations is presented for quantum dots in AlGaAs barriers, along with an interpretation of the results.

3.1 Calculating the Energies of the Stationary States

In this section a derivation is provided that shows how to calculate the energy levels of the radially symmetric stationary states of an electron within a quantum dot with a hydrogenic impurity. The energy of the \( n^{th} \) radially symmetric state, \( E_{n,0} \), is calculated by obtaining the expected value of the Hamiltonian with the eigenket \( |R_{n,0}\rangle \). For the case of a quantum dot with a centrally located hydrogenic impurity, the potential energy is radially symmetric, therefore, only the radial portion of the Hamiltonian will be considered. Mathematically,
the expected value of the energy of the $n^{th}$ radially symmetric stationary state, $E_{n,0}$, is given as:

$$\langle E_{n,0} \rangle = \langle R_{n,0} | H | R_{n,0} \rangle,$$  \hspace{1cm} (10)

where $H$ is the radial portion of the Hamiltonian.

### 3.1.1 The Hamiltonian of the System

The Hamiltonian of the system under consideration is given as:

$$H = H_o - V_o.$$  \hspace{1cm} (11)

The component $H_o$ in equation 11 is the Hamiltonian of the hydrogenic system explicitly described as follows:

$$H_o = -\frac{\hbar^2}{2m_{e\text{ff}}} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m_{e\text{ff}}} \frac{2}{r} \frac{\partial}{\partial r} + \frac{\hbar^2}{2m_{e\text{ff}}} \frac{l(l+1)}{r^2} - \frac{q^2}{4\pi \kappa \varepsilon_o r};$$  \hspace{1cm} (12)

where $\hbar$ is Planck’s constant, $m_{e\text{ff}}$ is the empirical effective mass of an electron within the lattice, $r$ is the radius whose origin lays at the center of the quantum dot, $l$ is the angular quantum number, $q$ is the elementary charge of an electron, $\kappa$ is the empirical effective mass of the lattice, and $\varepsilon_o$ is the permittivity of free space. The remainder of this thesis is only concerned only with the radially symmetric stationary states. Such states have their angular quantum number, $l$, set to zero. The component $V_o$ in equation 11 is the idealized potential profile of a heterojunction. Specifically,

$$V_o = 0 \quad \text{when } r \geq r_{QD},$$

$$V_o = V_{CB} \quad \text{when } r < r_{QD};$$  \hspace{1cm} (13)

where $r_{QD}$ is the radius of the quantum dot and $V_{CB}$ is the positively valued conduction band offset of the quantum dot heterojunction.

### 3.1.2 Selecting the Laguerre-based Basis

The eigenfunctions of the hydrogenic portion of the Hamiltonian, labeled $H_o$, given in equation (11) are known [44]. This orthonormal basis, referred to in the remainder of this thesis as the hydrogenic basis or the Laguerre-based basis, is used in concert with
the variational method to construct several radially symmetric stationary states of the single electron system. The orthonormal hydrogenic basis is constructed with Laguerre polynomials as follows:

\[ R_{j,0}^L = 2a^{-3/2} j^{-5/2} \exp \left( -\frac{r}{ja} \right) \frac{L_{j-1}^{1}}{L_{j-1}^{1}} \left( \frac{2r}{ja} \right) \]  

(14)

In the hydrogenic model \( j \) is the principle quantum number, in this work \( j \) is an index into the hydrogenic basis set. The variable \( a \) is the effective Bohr radius of the hydrogenic portion of the Hamiltonian, \( \mathcal{H}_o \), and is given as:

\[ a = \frac{4\pi \kappa \epsilon_o \hbar^2}{m_e j f q^2}, \]  

(15)

and \( L_{n-1}^1 \) are associated Laguerre functions, which are defined as follows:

\[ L_{n-1}^1 \left( \frac{2r}{ja} \right) = \sum_{k=0}^{n-1} \frac{(-1)^k (u+n-1)!}{(n-1-k)! (u+k)!} \left( \frac{2r}{ja} \right)^k \]  

(16)

The set of wave functions given in equation (14) define an orthonormal basis with respect to the dot product given by:

\[ \langle f | g \rangle = \int_0^\infty r^2 f^*(r) g(r) dr. \]  

(17)

### 3.1.3 The Hamiltonian in the Laguerre Basis

The \( n^{th} \) radially symmetric stationary eigenket, \( |R_{n,0}\rangle \), may be approximated by a finite number, \( J \), of Laguerre-based basis elements:

\[ R_{n,0} \approx \sum_{j=1}^{J} \alpha_j^n R_{j,0}^L. \]  

(18)

However, in order to satisfy the physical mandate that the probability of finding the electron somewhere in space is unity, the norm of \( R_{n,0} \) must be equal to unity. Exploiting the fact that the basis set is an orthonormal basis, a norm of unity is ensured so long as the set of coefficient \( \{\alpha_j^n\} \) meets the following constraint:

\[ \sum_{j=1}^{J} \left( \alpha_j^n \right)^2 = 1. \]  

(19)
The expected value of the Hamiltonian may be expressed in the Laguerre basis by plugging the expression for the Hamiltonian given in equation (11), and the expression for the eigenket in the Laguerre basis given in equation (14) into equation (10). After suitable manipulations, which are given explicitly in appendix A, the following quadratic form is obtained which may approximate the radially symmetric eigenenergies.

\[
\langle E_{n,0} \rangle = \langle R_{n,0} | \mathcal{H} | R_{n,0} \rangle \approx \mathbf{\alpha}^{\dagger} \mathbf{Q} \mathbf{\alpha};
\]

where \( \mathbf{\alpha} \) is a column vector of length \( J \) that holds the values of the coefficients \( \alpha_1^n, \alpha_2^n, \ldots, \alpha_J^n \); and \( \mathbf{Q} \) is a \( J \times J \) matrix given by equation (55) of appendix A. As regards to the calculations performed in this thesis, \( J \) is set to fourteen. \( J \) is set to fourteen because this value is found to offer a good compromise between computational accuracy and computational processing time. The variational method is employed with equation (20) once \( \mathbf{Q} \) is constituted.

3.1.4 Obtaining the Ground State

An approximation to the ground state is expressible as a linear combination of elements from the hydrogenic basis given in equation (14). The approximation to the ground state energy is given as a quadratic form with respect to the array of coefficients \( \mathbf{\alpha} \). The most accurate approximation to the ground state energy obtainable by this quadratic form occurs when the elements of \( \mathbf{\alpha} \) are valued so that the quadratic form obtains its minimum value. The values of the elements of \( \mathbf{\alpha} \) are, of course, constrained by equation (19).

**Quadratic Form for the Ground State Energy** When the exact form of the ground state ket, \( |R_{1,0}\rangle \), is known the expected value of ground state energy, \( \langle E_{1,0} \rangle \), may be expressed as follows:

\[
\langle E_{1,0} \rangle = \langle R_{1,0} | \mathcal{H} | R_{1,0} \rangle.
\]

In the case where the exact form of the ground state is not known, an approximate ground state energy, \( \langle \widetilde{E}_{1,0} \rangle \), may be obtained with a normalized wave function which approximates the ground state. In this thesis, the ground state wave function is approximated as a linear
combination of the hydrogenic wave functions as follows:

\[ |R_{1,0}\rangle \approx \sum_{j=1}^{J} \alpha_{j}^{1}|R_{j,0}^{L}\rangle. \]  

(22)

It is shown in appendix A that using an approximate ground state wave function of this form that an approximate ground state energy, \( \langle E_{1,0} \rangle \), may be written in a quadratic form as follows:

\[ \langle E_{1,0} \rangle = \overline{\alpha^{T} Q \alpha}. \]  

(23)

Up until now, it has not been stated how to find the values of the coefficients \( \{\alpha_{j}\} \) that best approximate the ground state wave function, and hence the ground state energy. The variational method provides a means to do so. Any approximation to the ground state energy, \( \langle E_{1,0} \rangle \), calculated by the variational method will be greater than or equal to the exact ground state energy [44]. This is expressed mathematically as:

\[ \langle E_{1,0} \rangle \leq \langle \overline{E_{1,0}} \rangle. \]  

(24)

An approximation to the ground state energy, and hence to the ground state eigenfunction, is more precise as the number of terms in the linear combination, \( J \), is increased. Additionally, for any given value of \( J \), the most accurate approximation occurs when the set of coefficients contained in the vector \( \overline{\alpha} \) is adjusted so that equation (23) takes its minimum value. Such being the case, the ground state is approximated as follows:

\[ \langle E_{1,0} \rangle \approx \min_{\|\overline{\alpha}\|=1} \left\{ \overline{\alpha^{T} Q \overline{\alpha}} \right\}. \]  

(25)

The above equation should be read as follows. The expected energy of the ground state is approximately equal to the minimum value obtainable by the bracketed expression subject to the single constraint that the sum of squares of the coefficients \( \alpha_{1}, \alpha_{2}, \ldots, \alpha_{J} \) is equal to unity. The next paragraph shows how the gradient descent method may be used to obtain the approximate ground state. The next paragraph shows how the gradient descent method may be used to obtain the approximate ground state.

**Minimizing the Quadratic Form of the Ground State Energy** The gradient descent method is suited to minimizing quadratic forms such as the one given in equation (25). The
reason for this is that the update equation of the gradient descent method relies upon
the derivative of the expression being minimized. In the case where the expression to be
minimized is a quadratic form, the derivative is expressed simply and compactly. For a
column vector $x$ of length $p$ and a $p \times p$ square matrix $B$, the derivative of the quadratic
form $x' B x$ is given as $B x$. Thus with respect to equation (25), the gradient descent method
provides the following update equation for the vector $\alpha^i$ [45]:

$$\overline{\alpha^{(y+1)}} = (I - \mu Q) \overline{\alpha^{(y)}};$$

(26)

where $I$ is an identity matrix of rank $J$, $\mu$ is the update step size, and the superscripts $y + 1$
and $y$ indicate that the column vector which represents the ground state has been updated
$y + 1$ and $y$ times respectively. Due to the constraint given in equation (19) the update
must be normalized as follows:

$$\overline{\alpha^{(y+2)}} = \frac{\overline{\alpha^{(y+1)}}}{\|\overline{\alpha^{(y+1)}}\|};$$

(27)

where $\|\overline{\alpha^{(y+1)}}\|$ is the norm of the vector $\overline{\alpha^{(y+1)}}$.

The vector $\overline{\alpha^i}$ is updated until the dot product of subsequent vectors $\overline{\alpha^{(p)}}$ and $\overline{\alpha^{(p+1)}}$
passes above a threshold and the relative errors of subsequent values of $\langle \overline{E_{1,0}}^{(p)} \rangle$ and
$\langle \overline{E_{1,0}}^{(p+1)} \rangle$ passes below a given threshold. With respect to the former threshold, the value
0.999 is used in obtaining the results in this thesis. With respect to the latter threshold, the value
$5 \times 10^{-9}$ is used in obtaining the results in this thesis. The values of these thresholds were selected in a process of trial and error. The step size, $\mu$, is not constant
throughout the execution of the gradient descent. Through trial and error it is found that
the rate of convergence in calculating the energy levels is considerably increased by both
increasing and decreasing the step size. Readers are encouraged to view the MATLAB code
provided in appendix C in order to view the exact details of the computer algorithm; such
as how step size $\mu$ is altered throughout the gradient descent. Once the ground state has
been approximated, the variational method provides for the approximation of the radially
symmetric excited states. Details regarding the use of the variational method to calculate
these excited states are presented in the following subsection.
3.1.5 Obtaining the Excited States

The variational method allows for an approximation to the excited states. The method of obtaining them is very similar to the method of obtaining the ground state. To obtain the $n^{th}$ state, the Hamiltonian is again minimized. As always the minimization is constrained by the fact that the norm of the vector $\vec{\alpha}^n$ must be unity. In addition to this constraint the vector which approximates the $n^{th}$ state, $\vec{\alpha}^n$, must be orthonormal to all the vectors $\vec{\alpha}^1$, $\vec{\alpha}^2$, $\ldots$, $\vec{\alpha}^{n-1}$. In the case of obtaining, for example, the $n^{th}$ state, the minimization may be written as:

$$\langle E_{n,0} \rangle \approx \min_{\|\vec{\alpha}^n\| = 1} \left\{ \alpha^m \cdot Q \vec{\alpha}^n \right\}.$$ (28)

Therefore, the update equation for $\vec{\alpha}^n$ is similar to that of the update equation for $\vec{\alpha}^1$. The difference is that after the initial update, given in equation 26, the portions of $\vec{\alpha}^m(y+1)$ that are not orthogonal to $\vec{\alpha}^1$, $\vec{\alpha}^2$, $\ldots$, and $\vec{\alpha}^{n-1}$ are subtracted from $\vec{\alpha}^m(y+1)$ to create $\vec{\alpha}^m(y+2)$. The vector $\vec{\alpha}^m(y+2)$ is then normalized to create $\vec{\alpha}^m(y+3)$. For more details about the exact algorithm that is used to calculate the excited states, please see the MATLAB code provided appendix C.

3.2 Requirements for the Acceptable Placement of the Electron Energy Levels

The previous section presents a method to approximate the radially symmetric electron states in a confining potential created by the quantum dot heterojunction’s conduction band offset and the electrostatic potential of the ionized impurity. In chapter two, a physical interpretation is provided for how these energy levels may transform into bands when the quantum dots are organized in periodic arrays. Further, chapter two presents two rules of thumb regarding how energy levels will transform into bands. The first rule of thumb states
that energy levels within 100 meV of each other will merge into a single miniband. The
second rule of thumb states that energy levels separated from each other by more than
500 meV will certainly form distinct minibands. Additionally, chapter two discusses the
theory of the intermediate band solar cell. This theory mandates the existence of only
three bands: a valence band, an intermediate band, and a conduction band. It is therefore
imperative that each and every electron energy level merge into one of these three bands.

Based upon the band requirements of an IBSC and the manner in which minibands
are interpreted to form a set of requirements regarding the positions of the energy may be
stated. These requirements will be put forward in two tiers. First will come requirements for
the energy levels to be aggregated into what are called acceptable groups of electron states
(AGES). AGES will be defined in the following paragraph. Second will come requirements
placed upon groups of AGES so that they transform and merge into the required valence
band, intermediate band, or conduction band.

Acceptable Grouping of Electron States  This paragraph provides the definition of
“acceptable grouping of electron states” (AGES). Several examples are provided in figure
7 that show various configurations of electron energy levels. Some of the configurations
meet the requirements of AGES, while others do not. Discussion of these examples assist
in reinforcing the definition of AGES. An acceptable grouping of electron states (AGES) is
defined as follows:

- An AGES is comprised of an arbitrary number of bound electron states.

- The first member of an AGES must be located more than 500 meV above a bound
electron state below it (if one exists).

- The last member of an AGES must be located more than 500 meV below a bound
electron state above it (if one exists).

- All electron states that exist at energies between the first element of an AGES and
the last element of the same AGES must be within 100 meV of its nearest neighbor.
Now that the concept of “acceptable grouping of electron states” has been defined, several examples are provided to reinforce the concept. Shown in figure 7 are three hypothetical energy spectra for an electron in a quantum dot. Example A shows all the bound electron levels forming into three AGES. Although not shown explicitly, within each AGES the energy difference between a given level and its nearest neighbor is less than 100 meV. Example A shows that one or more energy levels may be present within a single AGES. Example B shows a situation where some bound electron levels do not group within an AGES while others do. In example B there exist two energy levels that are spaced too far apart from one another to join together into a single AGES and are too close to one another to form into two distinct AGES. Example C is similar to example B, except that the location of the energy levels are permuted. In the following paragraph restrictions are placed upon the number of AGES and their locations, so as to conform with the requirements of the IBSC.

\[\text{AGES # 1} \quad > 500 \text{ meV} \]
\[\text{AGES # 2} \quad < 500 \text{ meV} \]
\[\text{AGES # 3} \quad > 100 \text{ meV} \]

\[\text{AGES # 1} \quad > 500 \text{ meV} \]
\[\text{AGES # 2} \quad < 500 \text{ meV} \]
\[\text{AGES # 3} \quad > 100 \text{ meV} \]

\[\text{AGES # 1} \quad > 500 \text{ meV} \]
\[\text{AGES # 2} \quad < 500 \text{ meV} \]
\[\text{AGES # 3} \quad > 100 \text{ meV} \]

**Figure 7:** Three examples to reinforce the concept of an “acceptable grouping of electron states.” Example A shows all the bound electron levels forming into three AGES. Although not shown explicitly, within each AGES the energy difference between a given level and its nearest neighbor is less than 100 meV. Example A shows that AGES can have one or more energy levels within an single AGES. Example B shows a situation where some bound electron levels do not group within an AGES while others do. In example B there exist two energy levels that are spaced too far apart from one another to join together into a single AGES and are too close to one another to form into two distinct AGES. Example C is similar to example B, except that the location of the energy levels are permuted.
Restrictions placed upon the AGES so as to create an IBSC  
In the previous paragraph the concept of AGES was defined and reinforced by example. This paragraph considers the existence of several AGES and their relationship to the formation of an IBSC. The theory of the IBSC requires three bands: a valence band, an intermediate band and a conduction band. In a quantum dot implementation of an IBSC the bandgap of the barrier material, $E_{G,B}$, provides an upper limit to the bandgap between the conduction band and valence band of the QD-IBSC, $E_{CV}$. The intermediate band is located between the conduction band and valence band. Similar to the interpretation of how energy levels may merge with each other to form a single miniband, in the interpretation offered in this thesis, an AGES may merge with the conduction band of the QD-IBSC if it has an element within 100 meV of the conduction band of the barrier material. Analogously, an AGES may merge with the valence band of the QD-IBSC if it has an element within 100 meV of the valence band of the barrier material. Therefore in order to meet the requirements of the IBSC there are three possible permutations for satisfying the requirements of the IBSC theory:

1. **The case where there are more than three AGES**
   
   This scenario is unacceptable as it will lead to more than one intermediate band.

2. **The case where there are three AGES**
   
   - The AGES whose elements have the greatest average energy, AGES$_1$, must have its member with greatest energy within 100 meV of the conduction band of the barrier material.
   
   - The AGES whose elements have the lowest average energy, AGES$_3$, must have its member with lowest energy within 100 meV of the valence and of the barrier material.
   
   - THE AGES whose elements have the second greatest average energy, AGES$_2$, must have its member with greatest energy more than 500 meV below the lowest energy member of AGES$_1$; and its member with least energy more than 500 meV above the member of AGES$_3$ with greatest energy.
3. The case where there are two AGES

(a) possibility number one:

- The AGES whose elements have the greatest average energy must have its member with greatest energy within 100 meV of the conduction band edge of the barrier material.
- The element with the lowest energy in the remaining AGES must have its energy more than 500 meV from the valence band edge of the barrier material.

(b) possibility number two:

- The AGES whose elements have the lowest average energy must have its member with lowest energy within 100 meV of the valence band edge of the barrier material.
- The element with the greatest energy in the remaining AGES must have its energy more than 500 meV from the conduction band edge of the barrier material.

4. The case where there is one AGES

The element with the greatest energy must have its energy more than 500 meV below the conduction band edge of the barrier material and the element with the lowest energy must have its energy more than 500 meV above the valence band edge of the barrier material.

**Bandgap Narrowing**

Some of the items listed in the preceding paragraph lead to bandgap narrowing. By this it is meant that the band-gap between the QD-IBSC conduction band and QD-IBSC valence band, $E_{CV}$ will be less than the bandgap of the barrier material, $E_{G,B}$. This is due to the fact that one or more of the AGES merge with the valence band edge or conduction band edge of the barrier material. Hence the valence band edge of the barrier material.

---

1While the physics may be the same, in this thesis the term “bandgap narrowing” does not refer to a doping induced bandgap narrowing.
QD-IBSC is shifted to a higher energy and/or the conduction band edge of the QD-IBSC is shifted to a lower energy. With the respect to the list in the previous paragraph, bandgap narrowing will occur if the energy levels are in accord with items 2, 3a, and 3b.

3.3 An Example with $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$ Barriers

A goal of this thesis is to determine whether a quantum dot heterojunction with a centrally located hydrogenic impurity may be used to create an intermediate band solar cell. The previous section of this chapter provides a complete list of the possible arrangements of the energy levels so as to realize a QD-IBSC. In this section the results of calculating the approximate energy level for two hypothetical heterojunctions with AlGaAs barriers are presented. It will be seen that one of these hypothetical heterojunctions is in accord with item 3a of the enumeration given on page 35 of the previous section.

3.3.1 Obtaining the Values of the Electron Effective Mass and the Dielectric Constant

In both examples with AlGaAs barriers presented below the effective mass is given as the empirical value found for $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$; namely the effective mass is $0.098 \times 9.11 \times 10^{-31}$ kg [46]. The dielectric constant is similarly obtained and is given as 11.7 [46]. 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 specific values of the conduction band offset are selected in light of the fact that the band offset between the conduction band and intermediate must be either 0.71 eV or 1.24 eV for the optimum efficiency of an IBSC. Thus the first selected potential depth is meant to accommodate the placement of an energy level at 0.71 eV; and the second selected potential depth is meant to accommodate the placement of an energy level at both 0.71 eV and 1.24 eV. The energy levels of the first ten radially symmetric states are shown in figures 8 and 9.

3.3.2 Discussion of the Results for $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$ Barriers

Figures 8 and 9 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 sixth eigenstate, there is a range of quantum dot radii for which the eigenenergy is greater than zero; thus the eigenstate is no longer bound within the confining potential. However, as theorized in appendix A, and as shown in figures 8 and 9, the sixth and seventh radially symmetric eigenstates are bounded at a suitable large quantum dot radius. Specifically, their eigenenergies asymptotically approaches \( \frac{\hbar^2}{2m_{_0}a^2} \) J and \( \frac{\hbar^2}{2m_{_0}a^2} \) J respectively as \( r_{QD} \) goes towards infinity.

\[
\kappa = 11.7; \quad m_{_{eff}} = 0.098 \times 9.11 \times 10^{-31} \text{ kg}; \quad V_{CB} = 0.75 \text{ eV}; \quad l = 0
\]

\[\text{Figure 8:}\] Energies of the first ten radially symmetric electron states in a quantum dot with a centrally located hydrogenic impurity. \( V_{CB} \) is 750 meV.

With respect to the energy levels plotted in figures 8 and 9 intervals of quantum dot radii \([r_{QD,A} r_{QD,B}]\) are sought that present AGES that are in accord with an item enumerated in the list on page 35. For the example with \( V_{CB} \) equal to 750 meV, there is no interval where the energy levels are arranged in accord with any of the enumerations. As shown in figure 10, for the example with \( V_{CB} \) equal to 1250 meV, there is an interval which is in accord with one of the enumerations. Specifically, for \( r_{QD} = [7.6 \text{ nm}, 9.3 \text{ nm}] \) the energy levels group into two AGES and the AGES are in accord with item 3a. Therefore, according to the interpretation initially offered in chapter two and expanded in this chapter, for the
Figure 9: Energies of the first ten radially symmetric electron states in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 1250 meV.

case when the conduction band offset is 1250 meV and the quantum dot radius is between 7.6 nm and 9.3 nm, the excited states will form a single band which will be part of the conduction band and an intermediate band will occur at an offset between 500 meV and 620 meV below the conduction band edge.

Band Gap Shrinkage at the Conduction Band  In these examples, the barrier material is $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$. The band gap of this material, $E_{G,B}$, is measured to be approximately 1.9 eV [46]. For the example with the conduction band offset of 1250 meV there is an interval of quantum dot radii that will create an intermediate band. Yet, within this interval there are several energy levels that merge with the valence band edge of the barrier material. Therefore the bandgap between the conduction band and valence, $E_{CV}$, of the QD-IBSC will be less than 1.9 eV. Consider in figure 10 the case when the quantum dot radius is 9.3 nm. In this case all of the radially symmetric excited bound states are interpreted to create a single miniband near 0 eV. This is precisely the location of the conduction band.
Figure 10: Energies of the first ten radially symmetric electron states in a quantum dot with a centrally located hydrogenic impurity. $V_{CB}$ is 1.25 eV. This close-up shows that there exists an interval of quantum dot radii where an intermediate band may be formed. This interval exists between $r_{QD} = [7.6 \, \text{nm}, 9.3 \, \text{nm}]$. Within this interval, all the energy levels fit into exactly two AGES. Furthermore, the two AGES satisfy case 3a on page 36.

edge of the barrier material when considered alone. Hence, for this specific case the conduction band edge will shrink by approximately 140 meV. In general it is concluded that for a QD-IBSC with a centrally located hydrogenic impurity the conduction band edge will appear closer to the valence band edge than is indicated by the empirical data of the barrier material alone.

3.4 Chapter Recapitulation

In this chapter I calculate the radially symmetric energy levels in a quantum dot with a centrally located hydrogenic impurity. I provided two example of such calculations with Al$_{0.42}$Ga$_{0.58}$As barriers. The results indicate that there are quantum dot radii such that it is possible to obtain a ground state energy well separated from the energies of the excited states and such that the excited states are grouped closely to one another. Based upon these
results it is concluded that, within the framework offered in chapter two and expanded upon in this chapter, an intermediate band may be created with \( \text{Al}_{0.42}\text{Ga}0.58\text{As} \) barriers if the quantum dot radii are between 7.6 nm and 9.3 nm and the quantum dots have centrally located hydrogenic impurities.
CHAPTER IV

SELECTING A MATERIAL SYSTEM FOR AN OPTIMIZED QUANTUM DOT INTERMEDIATE BAND SOLAR CELL

The goal of this chapter is to select a material system for an optimally designed QD-IBSC with centrally located hydrogenic impurities within each quantum dot. In order to yield optimum energy conversion the band gap between the conduction band edge and valence band edge, $E_{CV}$, must be 1.95 eV, and the bandgap between the conduction band edge and intermediate band edge, $E_{CI}$, must be either 0.71 eV or 1.24 eV. In order to accomplish this goal a set of requirements is enumerated regarding the barrier material and quantum dot material. In addition, an algorithm is presented that utilizes plots of the band edges versus lattice constants in order to select a binary substrate, a ternary barrier material, and a ternary quantum dot material. Band edge plots are examined from three distinct sources. There is variability in each of these works due to the complexity of measuring the offsets. Yet, for a first pass of achieving the goal there is sufficient agreement with which to select material systems for further review.

4.1 Heterojunction Material Requirements for an Optimized QD-IBSC

This section enumerates the requirements in selecting a substrate, a barrier material and a quantum dot material for an optimized QD-IBSC with centrally located hydrogenic impurities.

1. Selection of a barrier material

   (a) **Barrier material with a band gap greater than 1.95 eV**

   According to the theory of the IBSC, the band gap, $E_{CV}$ ought be 1.95 eV for
optimum conversion efficiency [25]. It is useful to select a barrier material with a bandgap greater than 1.95 eV in order to compensate for electron levels just below the conduction band edge or hole levels just above the valence band edge.

(b) **Barrier material lattice matched with a binary substrate**

Quantum dot technology provides a near term proof of concept regarding the theory of the IBSC. In order to facilitate the speedy development of the technology the barrier material ought be lattice matched to a binary material. Lattice matching the barrier material with the substrate provides superior crystal quality because surface defects are minimized. Binary materials of good crystalline quality, such as GaAs, can be readily purchased and they therefore provide an path to implementing a QD-IBSC.

2. Selection of a quantum dot material

(a) **Quantum dot material whose valence band edge is located at the valence band edge of the barrier material**

The output voltage of an the QD-IBSC will be limited by the bandgap of the barrier material. In order to maintain as high an output voltage as possible, it is necessary to avoid narrowing of the bandgap, $E_{CV}$. While it may not be possible to avoid shrinking near the conduction band edge, due to the effect of the dopants, it is possible to avoid shrinking at the valence band edge. Therefore the material selected for the quantum dot heterojunction ought to provide a non-positive valence band offset, $V_{VB}$.

(b) **Quantum dot material whose conduction band edge is located more than 1.25 eV below the conduction band edge of the barrier material**

According to the theory of the IBSC, the band gap, $E_{CI}$ may be 0.71 eV or 1.24 eV for optimum conversion efficiency [43]. In chapter three the electron energy levels are calculated for a quantum dot heterojunction whose material parameters are taken from $\text{Al}_{0.42}\text{Ga}_{0.58}\text{As}$ and with a conduction band offset,
$V_{CB}$, equal to 1.25 eV. It is concluded that a valence band offset of 1.25 eV meets the requirements laid down on page 35 of chapter three for the formation of a distinct intermediate band. However, in the example presented with $V_{CB} = 1.25$ eV, within the range of acceptable quantum dot radii, the maximum energy difference between the ground state and first excited state is 620 meV. This falls short of the required 0.71 eV for optimal conversion efficiency. Therefore, a quantum dot material ought to be selected so that the conduction band offset, $V_{CB}$, is of greater than 1.25 eV.

(c) **Quantum dot material offers a lattice mismatch with respect to the barrier material**

Lattice mismatch introduces surface strain which is essential to the formation of self-organized quantum dots [38]. Many quantum dot heterojunction have been fabricates with a range of lattice mismatch. The necessary lattice mismatch between the quantum dot material and the barrier material is of order a few percent.

### 4.2 An Algorithm to Select the Heterojunction Materials

In the previous section, requirements are given for the selection a quantum dot heterojunction that may yield an optimized QD-IBSC. Within these requirements both enumerations 1b and 2c refer to the necessity of lattice matching and lattice mismatch respectively. In what follows in this section, an algorithm is presented that utilizes plots of the band edges versus lattice constants (PBEVLC) in order to meet the requirements given in section 4.1. Such plots may be viewed in figures 11, 14, 16, and 17 of this thesis. In addition, plot 15 shows the results of using this algorithm on the Tiwari PBEVCL.

1. On a PBEVLC draw a vertical, line ≠ 1 from the conduction band edge of a material to the valence band edge of the same material which simultaneously satisfies enumerations 1a and 1b of the requirements given in section 4.1. This line demarcates a suitable barrier material.
2. Draw a horizontal line, line # 2, which intersects the endpoint of line # 1 at the valence band edge.

3. Draw a horizontal line, line # 3, which intersects the endpoint of line # 1 at the conduction band edge.

4. Draw vertical lines, # 4a, # 4b, # 4c, etcetera, at each point where there exists an intersection between line # 2 and a valence band edge. These lines demarcate potentially suitable quantum dot materials.

5. Draw horizontal lines, # 5a, # 5b, # 5c, etcetera, at each point where lines # 4a, # 4b, # 4c, etcetera cross the conduction band edges of the corresponding material.

6. Measure the difference in energy between line # 3 and each of lines # 5a, # 5b, # 5c. These measurements represent the conduction band offsets of the suitable barrier material with the potentially suitable quantum dot materials.

7. Refine the list of potentially suitable quantum dot materials by discarding those materials whose measured conduction band offset is less than 1.25 eV.

In this section an algorithm is presented that facilitates the selection of materials for the QD-IBSC heterojunctions. In the next section, PBEVLC from three distinct sources are reviewed in order to uncover materials for an optimally designed QD-IBSC.

### 4.3 Band Offsets Versus Lattice Constants from the Literature

In this section plots of band offsets versus lattice constants are presented from the literature. In fact, three distinct PBEVLC are presented: one constructed from date obtained in Levinstein *et al* [46], a second constructed by Tiwari and Frank [47], and third constructed by Vurgaftman *et al* [48]. Each of these PBEVLC is reviewed in order to uncover heterojunction materials that meet the requirements given in section 4.1.
4.3.1 Consideration of PBEVLC obtained from Levinshtein et al

In this subsection, a PBEVLC is presented which has been constructed from the data compiled by Levinshtein et al [46]. Here forth this PBEVLC will be referred to as the Levinshtein PBEVLC and it is shown in figure 11. The Levinshtein PBEVLC does not present any material systems that satisfy the requirements given in section 4.1. Regardless of this fact, the information compiled by Levinshtein et al is used in an example to calculate the band offset of a sub-optimally designed QD-IBSC. Two x’s appear in figure 11 that demarcate the barrier material used in the example: Al$_{0.42}$Ga$_{0.58}$As; and two x’s appear in figure 11 that demarcate the quantum dot material used in the example: InAs. According to the information compiled by Levinshtein et al, the conduction band offset of this system is 0.97 eV, the valence band offset is 0.62 eV, the bandgap of the barrier material is 1.95, and the bandgap of the quantum dot material is 0.36 eV.

**Electron Energy Levels within the Confining Potential** In this paragraph the approximate band offsets of an QD-IBSC composed of InAs/Al$_{0.42}$Ga$_{0.58}$As quantum dot heterojunction is presented. According to the data obtained from Levinshtein et al, the conduction band offset of this system is 0.97 eV and the valence band offset is 0.62 eV. According to information obtained from Levinshtein, the effective mass of electrons in an InAs and Al$_{0.42}$Ga$_{0.58}$As is $0.023 \times 9.11 \times 10^{-31}$ kg and $0.098 \times 9.11 \times 10^{-31}$ kg respectively. Similarly, the static dielectric constants 15.2 and 11.7 respectively. For this demonstration, these values are averaged and hence the dielectric constant, $\kappa$, is equal to 13.4 and the electron effective mass, $m_{eff}$, is equal to $0.06 \times 9.11 \times 10^{-31}$ kg. Figure 12 plots a close up of the energy levels of the electron in the confining potential caused by the conduction band offset and the centrally located hydrogenic impurity. The results contained in figure 12 show an interval of quantum dot radii whereby the configuration of the energy levels satisfy the requirements presented on page 35 of chapter three. This interval begins when the quantum dot radius is 18.0 nm and ends when the quantum dot radius is 18.8 nm. The energy separation between the ground state and first excited state is 500 meV and 520 meV at the start and end of the interval respectively.
Figure 11: Plot of the conduction band edges and valence band edges versus lattice constant of various III-V materials and their alloys. The four x’s mark the selected conduction band edges and valence band edges of the barrier material (Al_{0.42}Ga_{0.58}As) and quantum dot material (InAs). These materials are used to demonstrate the technique derived herein for obtaining the band offsets of QD-IBSC. The conduction band offset of this system is 0.97 eV, the valence band offset is 0.62 eV, the bandgap of the barrier material is 1.95, and the bandgap of the quantum dot material is 0.36 eV. This plots is constructed from information compiled in [46].

Hole Energy Levels within the Confining Potential  Equation (1) of chapter two predicts that there are approximately six bound hole states within the valence band offset of the InAs/Al_{0.42}Ga_{0.58} quantum dot heterojunction. In rough terms, for the valence band offset of 620 meV, this amounts to one hole level per 100 meV.

Interpreting the Band Offsets from the Energy Levels  In the previous paragraphs the approximate hole levels and electron levels in a single InAs/Al_{0.42}Ga_{0.58} quantum dot heterojunction were calculated using information compiled in [46]. This paragraph provides an interpretation of the bands formed by these energy levels. This interpretation relies on the rules of thumb provided in section 2.3 of chapter two. The band offsets obtained from this interpretation are shown in figure 13. To begin with, it is concluded that the bandgap, $E_{CV}$ will be approximately equal to 1.1 eV. This value is obtained by subtracting the band
Figure 12: The approximate energies of the first ten radially symmetric electron states within the confining potential of the conduction band offset of the InAs/Al\textsubscript{0.12}Ga\textsubscript{0.88}As system and an electrostatic potential created by an ionized centrally located donor.

gap shrinkage at both the valence band edge and conduction band edge from the 1.9 eV band gap of the barrier material. The bandgap shrinkage at the conduction band edge results from the energy levels of the excited electron states and is of order 200 meV. The bandgap shrinkage at the valence band edge results from the energy levels of the allowed hole states and is of order 600 meV.

4.3.2 Consideration of PBEVLC constructed by Tiwari and Frank

In this subsection, materials for a quantum dot heterojunction will be selected from the work of Tiwari and Frank. The algorithm offered in section 4.2 is applied to the PBEVLC that these researches have compiled. Figure 14 is a duplicate of the original PBEVLC offered by Tiwari and Frank and figure 15 shows the line constructions necessitated by the algorithm superimposed upon their original PBEVLC. The vertical line labeled “# 1” in figure 15 shows that there exists some molar fraction \( x_o \) such that Al\textsubscript{\( x_o \)}Ga\textsubscript{1-\( x_o \)}As will have a band gap of 1.95 eV and be well lattice matched to a GaAs binary substrate. This figure
indicates that the valence band edges of five ternary materials cross vertical line “# 2”. Hence, there are five ternary materials which offer a non-positive valence band offset with respect to Al$_{x_o}$Ga$_{1-x_o}$As; these are: AlPbSb, InAlAs, AlAsSb, InPbAs, and InPSb. After completing the remainder of the algorithm, the following conclusions are made. There does not appear to be any material system that strictly satisfies the algorithm. However, if one were to relax the requirement of step 7 of the algorithm, namely that the necessary conduction band offset be of order 1.0 eV, then there are some mole fractions, $x_o$ and $y_o$, such that In$_{y_o}$P$_{1-y_o}$As/Al$_{x_o}$Ga$_{1-x_o}$As/GaAs is uncovered as a candidate material for a nearly optimized QD-IBSC. Using the PBEVLC of Tiwari and Frank, the approximate valence band offset of this system is negligible, the approximate conduction band offset of this material system is 1 eV, the lattice mismatch between the GaAs substrate and the Al$_{x_o}$Ga$_{1-x_o}$As barrier is negligible, and the lattice mismatch of the In$_{y_o}$P$_{1-y_o}$As quantum dot material and Al$_{x_o}$Ga$_{1-x_o}$As barrier material is 4.8 %. From previous examples, a conduction band offset on the order of 1 eV should be sufficient to produce an offset between the conduction band and intermediate band of the order 400 meV. It is concluded from this subsection that there is a possible material system with which to fabricate a near optimum quantum dot implementation of an intermediate band solar cell. In the next subsection an PBEVLC constructed by Vurgaftman and Meyer is considered.

4.3.3 Consideration of PBEVLC constructed by Vurgaftman and Meyer

In this subsection, data collected by Vurgaftman and Meyer is used in exactly the same manner as above [18]. Figures 16 and 17 show the PBEVLC for the valence band edges and conduction band edges respectively. The results of applying the algorithm of section to these figures indicate that the material system which comes closest to being optimal for a DQ-IBSC is that of Al$_{y}$In$_{1-y}$As/Al$_{x}$Ga$_{1-x}$As/GaAs ($0 < x < 1$, $0.48 < y < 1$). The next best alternative is the Al$_{y}$In$_{1-y}$P/Al$_{x}$Ga$_{1-x}$As/GaAs ($0 < x < 1$, $0 < y < 0.52$) system. The energy offsets and lattice matching for this system obtained by the Vurgaftman PBEVLC are approximately the same as those already mentioned when discussing the Tiwari PBEVLC.
4.4 Recapitulation of Selecting a Material System

In this chapter I have presented material requirements for an optimized QD-IBSC with hydrogenic impurities located at the center of each quantum dot. An algorithm has been proposed which utilizes plots of the valence band edges and conduction band edges versus lattice constant of semiconductor materials in order to satisfy these requirements. I have constructed such a plot from data compiled by Levinshhtein et al and have used such a plot to calculate the band offsets of the InAs/Al$_{0.42}$Ga$_{0.58}$As system. A similar plot constructed by Tiwari and Frank has been evaluated as has a plot from Vurgaftman and Meyer. These two plots indicate that a near optimum QD-IBSC may be fabricated with InPAs quantum dots and AlGaAs barriers grown on GaAs substrates.
Figure 13: Interpretation of how the energy levels in the InAs/Al_{0.42}Ga_{0.58}As quantum dot heterojunction will form into bands when the quantum dots are ordered in a periodic array. Shown on the left are: the valence band offset, $E_{VB}$; conduction band offset, $E_{CB}$; the bandgap of the barrier material, $E_{G,B}$; the bandgap of the quantum dot material, $E_{G,QD}$; the energy of the ground state electron, $E_{1,0}$; the levels that the excited electron is able to occupy within the confining potential formed by the electrostatic potential and the conduction band offset; the quantum dot diameter, $d_{QD}$; and the levels that the hole is able to occupy within the confining potential formed by the valence band offset. On the right hand side is an interpretation of these results. Shown on the right are: the expected bandgap between the valence band and the intermediate band, $E_{IV}$; the expected bandgap between the valence band and the conduction band, $E_{CV}$; the expected bandgap between the conduction band and the intermediate band, $E_{CI}$; and expected amount of band shrinking. The dashed lines indicate the conduction band edge and valence band edge that would be expected in the absence of band shrinking. Shortening of the bandgap at the conduction band edge is due to closely packed bound electron states. Shortening of the bandgap at the valence band edge is due to hole levels permitted with the confining potential caused by the heterojunction’s valence band offset. An intermediate band is formed by the ground state electron level due to the fact that this energy level is well separated from the excited levels.
**Figure 14:** The conduction band edge and valence band edge energies as a function of lattice constant for various semiconductor heterojunctions. This figure is taken from Tiwari and Frank [47].

**Figure 15:** This figure illustrates the technique given in section 4.2 of this chapter. Overlaid on band edge versus lattice constant constructed by Tiwari and Frank are the lines called for by the algorithm. This figure shows that a near optimum quantum dot heterojunction may be fabricated with InPAs quantum dots and AlGaAs barriers grown on GaAs substrates.
Figure 16: “Valence band offset as a function of lattice constant. The offsets for binaries and lattice-matched ternaries are indicated by points, offset variations with composition for lattice-mismatched ternaries (not including strain effects) are given by dashed curves, and the VBO ranges for quaternary alloys lattice matched to a particular substrate material (GaAs, InP, InAs, or GaSb) are given by the vertical solid lines,” [48].

Figure 17: “Conduction band offsets corresponding to the VBOs in [figure 16]. The various points and curves have the same meaning as in that figure,” [48].
CHAPTER V

CONCLUSIONS

This thesis models a quantum dot intermediate band with n-type hydrogenic impurities located at the center of each quantum dot. In order to approximate the location of intermediate band the electron energy levels are calculated within a potential with two components: the step-like potential caused by the quantum dot heterojunction’s conduction band offset, and the electrostatic, \((1/r)\), potential of the n-type impurity. The results indicate that for a suitable large conduction band offset, of the order 1.2 eV, there exists an interval of quantum dot radii that may yield electron levels suitable to the formation of an IBSC. However, within this interval, bandgap narrowing is theorized to occur because there exists energy levels very close to the conduction band edge. In addition, the hole levels are evaluated for the case where there exists valence band offset. These hole levels are theorized to narrow the bandgap at the valence band edge. Based upon this work an algorithm is formulated which allows for selecting the material system with which to design a QD-IBSC. This algorithm relies on plots of the band edges of semiconductor materials plotted against the lattice constants of the materials.

This thesis has advanced the state of knowledge regarding the quantum dot implementation of an intermediate band solar cell. This thesis demonstrates the use of the variational method with Laguerre-based wave functions in calculating the electron energy levels confined within the quantum dot. This thesis presents a novel material system, InPAs quantum dots enveloped in AlGaAs barriers grown on GaAs substrates, with which to implement a QD-IBSC. This novel material system is selected based upon a refined set of design rules which are introduced in this thesis. One key design rule that is introduced is the selection of a quantum dot/barrier pair which offers a negligible valence band offset. With such a design rule the existence of hole levels is avoided, thus reducing the bandgap narrowing at the valence band edge and the existence of minibands below the intermediate band.
APPENDIX A

DERIVATION OF FINAL RELATION

One of the major achievements of this thesis is the presentation of a means to approximate the band offset between the conduction band and intermediate band of a quantum dot solar cell with a centrally located ionized hydrogenic impurity. The band offset is interpreted, as per the discussion in chapter two of this thesis, from the eigenenergies of the radially symmetric stationary electron states. This appendix presents a means in which to approximate the energy levels of the radially symmetric eigenstates. The results obtained in this appendix are used in chapter three, in conjunction with the variational method, in order to illustrate the band offset between the conduction band and intermediate band of several hypothetically doped quantum dot heterojunctions.

The expected value of the energy of the $n^{th}$ such state, $E_{n,0}$, is given as follows:

$$\langle E_{n,0} \rangle = \langle R_{n,0} | \mathcal{H} | R_{n,0} \rangle;$$

where $\mathcal{H}$ is the Hamiltonian of the system given in chapter three, and $| R_{n,0} \rangle$ is the $n^{th}$ radially symmetric eigenket. In the case, where the exact representation of the eigenket $| R_{n,0} \rangle$ is unknown, as is the case of the confined electron in the quantum dot with impurity, the eigenket may be represented as a linear combination of basis functions. In the hydrogenic basis, the $n^{th}$ radially symmetric state is approximated as follows:

$$R_{n,0} \approx \sum_{j=1}^{J} \alpha_j^n R_{j,0}^{L};$$

where $R_{j,0}^{L}$ is the $j^{th}$ radially symmetric hydrogenic eigenfunction and $J$ is a positive integer. In order that the approximation to the wave function is physically realistic, the sum of the squares of all the coefficients $\alpha_1, \alpha_2, \ldots, \alpha_n$ must be unity. Thus the approximate expected value is rewritten as:

$$\langle E_{n,0} \rangle \approx \sum_{j'=1}^{J} \sum_{j''=1}^{J} \alpha_{j'}^n \alpha_{j''}^n \left\langle R_{j',0}^{L} | \mathcal{H} | R_{j'',0}^{L} \right\rangle,$$  

(31)
Chapter three of this thesis describes the Hamiltonian in terms of the hydrogenic Hamiltonian, \( \mathcal{H}_o \) and a perturbation \( V_o \). Equation (31) is thus rewritten as:

\[
\langle E_{n,0} \rangle \approx \sum_{j=1}^{J} \sum_{j'}^{J} \alpha_j^n \alpha_{j'}^n \alpha_j \langle R_{j,0}^L | \mathcal{H}_o | R_{j',0}^L \rangle - \sum_{j=1}^{J} \sum_{j'=1}^{J} \alpha_j^n \alpha_{j'}^n \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle. \tag{32}
\]

Equation (32) may be simplified because the exact values of the left hand terms in equation (32) are known [44]. In mathematical language the left hand terms may be expressed as follows.

\[
\sum_{j=1}^{J} \sum_{j'=1}^{J} \alpha_j^n \alpha_{j'}^n \langle R_{j,0}^L | \mathcal{H}_o | R_{j',0}^L \rangle = \sum_{j=1}^{J} \langle E_j^L |, a \rangle = -\frac{\hbar^2}{2m_e} \sum_{j=1}^{J} \left( \frac{\alpha_j^n}{j} \right)^2; \tag{33}\]

where \( m_e \) is the effective mass of the electron and \( a \) is the Bohr radius defined in equation (15) of chapter three. Thus equation (32) is rewritten as follows:

\[
\langle E_{n,0} \rangle \approx -\frac{\hbar^2}{2m_e} \sum_{j=1}^{J} \left( \frac{\alpha_j^n}{j} \right)^2 - \sum_{j=1}^{J} \sum_{j'=1}^{J} \alpha_j^n \alpha_{j'}^n \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle. \tag{34}\]

The next section of this appendix will derive, step-by-step an expression for the expected value of \( \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle \).

### A.1 An Expression for \( \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle \)

In this section the expected value \( \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle \) will be simplified. Equation (17) of chapter three defines how to write the expected value in terms of an integral. Therefore, \( \langle R_{j,0}^L | V_o | R_{j',0}^L \rangle \) may be rewritten as follows:

\[
\langle R_{j,0}^L | V_o | R_{j',0}^L \rangle = \int_0^\infty r^2 R_{j,0}^L V_o R_{j',0}^L \, dr. \tag{35}\]

Equation (13) of chapter three defines \( V_o \) and using this information, equation (35) is rewritten as:

\[
\langle R_{j,0}^L | V_o | R_{j',0}^L \rangle = \int_0^{r_{Q,0}} r^2 R_{j,0}^L V_o C R_{j',0}^L \, dr. \tag{36}\]

Additionally, the Laguerre-based hydrogenic wave functions have also been defined in chapter three. Using this definition equation (36) is rewritten as:

\[
\langle R_{j,0}^L | V_o | R_{j',0}^L \rangle = \frac{4a^{-3}V_o}{(j + j')^3/2} \int_0^{r_{Q,0}} r^2 \exp \left( -r \left( \frac{j + j'}{j a} \right) \right) L_{j-1}^1 \left( \frac{2r}{j a} \right) L_{j',-1}^1 \left( \frac{2r}{j' a} \right) \, dr. \tag{37}\]
Equation (16) of chapter three defines the Laguerre polynomials. Plugging this definition into equation (37) the expectation value is written as:

\[
\langle R_{j',0}^L | V_0 | R_{j'',0}^L \rangle = \frac{4 a^{-3} V_{CB}}{(j' + j'')^{5/2}} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \frac{(-1)^{k' + k''} (j'')!}{(j' - 1 - k'!)(1 + k'!)(j'' - 1 - k''!)(1 + k''!)k''!} \\
\times \left( \frac{2}{a} \right)^{k' + k''} \int_0^{r_QD} r^{2 + k' + k''} \exp \left( \frac{-r}{j'a} \right) \, dr.
\]

(38)

After integrating equation (38) the following form is obtained.

\[
\langle R_{j',0}^L | V_0 | R_{j'',0}^L \rangle = \frac{4 a^{-3} V_{CB}}{(j' + j'')^{5/2}} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \frac{(-1)^{k' + k''} (j'')!}{(j' - 1 - k'!)(1 + k'!)(j'' - 1 - k''!)(1 + k''!)k''!} \\
\times \left( \frac{2}{a} \right)^{k' + k''} \left( j'+k'\right) \left( j''+k''\right) \left( 2 + k' + k''! \right) \left( \frac{j' j'' a}{j' + j''} \right)^{(3+k' + k'')} \\
\times \left[ 1 - \exp \left( \frac{-r_QD (j' + j'')}{j' a} \right) \sum_{z=0}^{\infty} \frac{1}{z!} \left( \frac{r_QD (j' + j'')}{j' a} \right)^z \right].
\]

(39)

Equation (39) may be simplified into the following expression.

\[
\langle R_{j',0}^L | V_0 | R_{j'',0}^L \rangle = 4 V_{CB} \sqrt{j' j''} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \left\{ \left( \frac{j'}{j' - 1 - k'} \right) \left( \frac{j''}{j'' - 1 - k''} \right) \\
\times j' k' \, j'' k'' \left( \frac{-2}{j' + j''} \right)^{(k' + k'')!} \left( 2 + k' + k''! \right) \left( 1 + k'!k''! \right) \\
\times \left[ 1 - \exp \left( \frac{-r_QD (j' + j'')}{j' a} \right) \sum_{z=0}^{\infty} \frac{1}{z!} \left( \frac{r_QD (j' + j'')}{j' a} \right)^z \right]\right\}
\]

(40)
Next, for reasons not quite obvious at first, equation (40) is rewritten in the following form.

\[
\left\langle R_{j''}^{L} | V_{o} | R_{j'}^{L} \right\rangle = 4 V_{CB} \sum_{j' = 0}^{j'} \sum_{k' = 0}^{j'} \left\{ \frac{(-2)}{j' + j''} \left( \frac{2 + k' + k''}{k'! k''!} \right) \cdot \left( j' - 1 - k' \right) \left( j'' - 1 - k'' \right) \right\} 
\]

\[
-4 V_{CB} \sum_{j' = 0}^{j'} \sum_{k' = 0}^{j'} \left\{ \frac{(-2)}{j' + j''} \left( \frac{2 + k' + k''}{k'! k''!} \right) \cdot \left( j' - 1 - k' \right) \left( j'' - 1 - k'' \right) \right\} 
\]

\[
\times \exp \left( -r_{QD} \left( j' + j'' \right) \right) \sum_{z = 0}^{2 + k' + k''} \frac{1}{z!} \left( \frac{r_{QD} (j' + j'')}{j' j'' a} \right)^{z} 
\]

According to equation (13) of chapter three, if \( r_{QD} \) were set equal to zero, then \( V_{o} \) is equal to zero for all values of \( r \). This is written in mathematical terms as:

\[
\left\langle R_{j''}^{L} | V_{o} | R_{j'}^{L} \right\rangle |_{r_{QD} = 0} = 0. 
\]

In this case, the Hamiltonian \( \mathcal{H} \) reduces to \( \mathcal{H}_{o} \). Therefore, the expectation value

\[
\left\langle R_{j''}^{L} | V_{o} | R_{j'}^{L} \right\rangle 
\]

need be equal to zero. In substituting zero for \( r_{QD} \) in equation (41) all of the exponential terms go to unity and the only polynomial terms that are nonzero are those of zero order. The following result is found.

\[
\left\langle R_{j''}^{L} | V_{o} | R_{j'}^{L} \right\rangle |_{r_{QD} = 0} = 4 V_{CB} \sum_{j' = 0}^{j'} \sum_{k' = 0}^{j'} \left\{ \frac{(-2)}{j' + j''} \left( \frac{2 + k' + k''}{k'! k''!} \right) \cdot \left( j' - 1 - k' \right) \left( j'' - 1 - k'' \right) \right\} 
\]

\[
-4 V_{CB} \sum_{j' = 0}^{j'} \sum_{k' = 0}^{j'} \left\{ \frac{(-2)}{j' + j''} \left( \frac{2 + k' + k''}{k'! k''!} \right) \cdot \left( j' - 1 - k' \right) \left( j'' - 1 - k'' \right) \right\} 
\]

\[
\times \exp \left( -r_{QD} \left( j' + j'' \right) \right) \sum_{z = 0}^{2 + k' + k''} \frac{1}{z!} \left( \frac{r_{QD} (j' + j'')}{j' j'' a} \right)^{z} 
\]

\[
= 0. 
\]

Equation (43) is in accord with the reasoning provided above. Similarly, if \( r_{QD} \) is allowed to go towards infinity, \( V_{o} \) is a constant equal to \( V_{CB} \). Thus the constant, \( V_{CB} \) may
be removed from the expectation value and what remains is the product of two orthonormal functions. The result, written in mathematical language is that:

\[
\left\langle R_{j',0}^L \left| V_o \right| R_{j'',0}^L \right\rangle_{r_{QD} \to \infty} = V_{CB} \delta_{j',j''}.
\]  

(44)

Allowing \(r_{QD}\) to go towards infinity all the exponential terms in equation (41) decay towards zero and because the exponential terms dominate over the polynomial terms the following is found:

\[
\left\langle R_{j',0}^L \left| V_o \right| R_{j'',0}^L \right\rangle_{r_{QD} \to \infty} = 4 V_{CB} \frac{\sqrt{j'} \sqrt{j''} \sqrt{j' + j''}}{(j' + j'')^3} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \left\{ \left( \frac{j'}{j' + j''} \right)^{j - 1 - k'} \left( \frac{j''}{j' + j''} \right)^{j'' - 1 - k''} \right. \\
\times \left. \left( \frac{2 + k' + k''}{k! k''!} \right) \right\}
\]  

(45)

Hence, comparing equation (44) and (45) the following relationship is found.

\[
\delta_{j',j''} = 4 \frac{\sqrt{j'} \sqrt{j''} \sqrt{j' + j''}}{(j' + j'')^3} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \left\{ \left( \frac{j'}{j' + j''} \right)^{j - 1 - k'} \left( \frac{j''}{j' + j''} \right)^{j'' - 1 - k''} \right. \\
\times \left. \left( \frac{2 + k' + k''}{k! k''!} \right) \right\}
\]  

(46)

Substituting the result obtained in equation (46) into equation (41), and rearranging slightly, the following formula is obtained.

\[
\left\langle R_{j',0}^L \left| V_o \right| R_{j'',0}^L \right\rangle = V_{CB} \delta_{j',j''}
\]  

\[
- V_{CB} \exp \left( \frac{-r_{QD} (j' + j'')}{j' + j''} \right) \sum_{z=0}^{2} \frac{1}{z!} \left( \frac{r_{QD} (j' + j'')}{j' + j''} \right)^z \delta_{j',j''}
\]

\[
- 4 V_{CB} \frac{\sqrt{j'} \sqrt{j''} \sqrt{j' + j''}}{(j' + j'')^3} \sum_{k' = 0}^{j' - 1} \sum_{k'' = 0}^{j'' - 1} \left\{ \left( \frac{j'}{j' + j''} \right)^{j - 1 - k'} \left( \frac{j''}{j' + j''} \right)^{j'' - 1 - k''} \right. \\
\times \left. \left( \frac{2 + k' + k''}{k! k''!} \right) \right\}
\]  

(47)

\[
\times \exp \left( \frac{-r_{QD} (j' + j'')}{j' + j''} \right) \sum_{z=0}^{2} \frac{1}{z!} \left( \frac{r_{QD} (j' + j'')}{j' + j''} \right)^z \}
\]
A.2 Writing the Equation in a Quadratic Form

Equation (34) can be rewritten in a quadratic form in terms of a column vector \( \overrightarrow{\alpha} \) of length \( J \) and \( J \times J \) square matrices \( \mathcal{U} \) and \( \mathcal{R} \) as follows.

\[
\langle E_{n,0} \rangle \approx \overrightarrow{\alpha}^\top \mathcal{U} \overrightarrow{\alpha} - \overrightarrow{\alpha}^\top \mathcal{R} \overrightarrow{\alpha};
\]  

(48)

where the \( j', j'' \) matrix elements of \( \mathcal{U} \) and \( \mathcal{R} \) are given as follows.

\[
\mathcal{U}_{j', j''} = -\frac{\hbar^2}{2m_{\text{eff}} a^2} \left( \frac{1}{\jmath} \right)^2 \delta_{j', j''},
\]  

(49)

and

\[
\mathcal{R}_{j', j''} = \langle R^{j'}_{j',0} | V_n | R^{j''}_{j'',0} \rangle.
\]  

(50)

In light of equation (47), the matrix \( \mathcal{R} \) may be separated into three \( J \times J \) square matrices as follows.

\[
\mathcal{R} = V_{CB} \mathcal{I} + \mathcal{V} + \mathcal{W};
\]  

(51)

where \( \mathcal{I} \) is an identity matrix, and the \( j', j'' \) matrix elements of \( \mathcal{V} \) and \( \mathcal{W} \) are given as follows.

\[
\mathcal{V}_{j', j''} = -V_{CB} \exp \left( \frac{-r_{QD} \left( j' + j'' \right)}{j' \ j'' a} \right) \sum_{z=0}^{2} \frac{1}{z!} \left( \frac{r_{QD} \left( j' + j'' \right)}{j' \ j'' a} \right)^z \delta_{j', j''}, \text{ and}
\]  

(52)

\[
\mathcal{W}_{j', j''} = -4 V_{CB} \sqrt{j' \ j''} \sum_{k'=0}^{j'} \sum_{k''=0}^{j''} \left\{ \left( j' - 1 - k' \right) \left( j'' - 1 - k'' \right) \right\}
\]  

\[
\times j' k' j'' k'' \left( \frac{-2}{j' \ j''} \right) \left( \frac{2 + k' + k''}{k'! k''!} \right) \times \exp \left( \frac{-r_{QD} \left( j' + j'' \right)}{j' \ j'' a} \right) \sum_{z=3}^{2+k'+k''} \frac{1}{z!} \left( \frac{r_{QD} \left( j' + j'' \right)}{j' \ j'' a} \right)^z \};
\]  

(53)

where \( k' \) and \( k'' \) are indices.

Thus, using the definitions provided above, equation (48) may be rewritten as:

\[
\langle E_{n,0} \rangle \approx \overrightarrow{\alpha}^\top \left[ V_{CB} \mathcal{I} + \mathcal{U} + \mathcal{V} + \mathcal{W} \right] \overrightarrow{\alpha};
\]  

(54)

Finally let us define a new matrix, \( Q \) as follows:

\[
Q = V_{CB} \mathcal{I} + \mathcal{U} + \mathcal{V} + \mathcal{W}.
\]  

(55)
It is possible to calculate the radially symmetric states in this manner for any value of \( r_{QD} \). Yet, there are two values of \( r_{QD} \) which significantly simplify the matrix \( \mathcal{Q} \). In these cases, which are discussed in the following section, the energy eigenvalues are obtained in a closed form.

### A.3 Observations Regarding the Position of the Energy Levels for Two Special Cases

Equation (54) may be simplified when \( r_{QD} = 0 \) and in the limit as \( r_{QD} \to \infty \). Such simplifications are useful because they provide for situations with which to check the results of calculations. We begin by showing the simplification for when \( r_{QD} = 0 \) and then for the limit as \( r_{QD} \to \infty \).

**Energy Levels when \( r_{QD} = 0 \)** When the radius of the quantum dot is equal to zero, the matrix \( \mathcal{V} \) defined in equation (52) becomes the identity matrix. This is because \( \exp(0) = 1 \); and \( 0^k = 0 \) when \( k = 1, 2, 3, \ldots \) yet \( 0^k = 1 \) when \( k = 0 \). Furthermore, when \( r_{QD} = 0 \) the matrix \( \mathcal{W} \) defined in equation (53) becomes a zero matrix. This is again due to the fact that its elements depend upon a polynomial in \( r_{QD} \). Thus the following expression may be derived:

\[
\langle E_{n,\alpha} \rangle |_{r_{QD}=0} \approx \alpha^2 \mathcal{U} \alpha^2. \quad (56)
\]

Therefore when the quantum dot radius is zero, the energy eigenvalues are the scaled eigenvalues of \( \mathcal{U} \). Because \( \mathcal{U} \) is a diagonal matrix its eigenvalues are already known. In fact, they are expressible in a closed-form expression. Thus for the case when \( r_{QD} = 0 \) the energy eigenvalues of the radially symmetric electron states are given exactly as:

\[
\langle E_{n,\alpha} \rangle |_{r_{QD}=0} = -\frac{\hbar^2}{2m_{e f f} a^2 n^2}. \quad (57)
\]

These energy values are in fact the known levels for the hydrogenic Hamiltonian \( \mathcal{H}_o \).

**Energy Levels as \( r_{QD} \to \infty \)** In the limit as the radius of the quantum dot goes to infinity, both of the matrices \( \mathcal{V} \) and \( \mathcal{W} \) defined in equations (52) and (53) become zero matrices. This is because \( \lim_{r_{QD} \to \infty} \left\{ \exp(-r_{QD}) \times \sum_{j=0}^{J} \alpha_j \cdot r_{QD}^j \right\} = 0 \) Thus for this case,
the energy eigenvalues of the radially symmetric electron states are given exactly as:

$$\langle E_{n,0} \rangle \left|_{m_r Q_D \to \infty} = -V_{CB} - \frac{\hbar^2}{2m_{eff} a^2 n^2}. \right. \tag{58}$$

These energy values are in fact the known levels for the hydrogenic Hamiltonian $H_o$ with an additive constant equal to the conduction band offset of the heterojunction. In chapter three, the results of calculating the first ten radially symmetric allowed electron states are given for several materials. The observations made in this subsection are in accordance with the results of the calculations.

### A.4 Summary

In this appendix it is shown, step by step, how to arrive at an explicit approximation (equation 54) for the energies of the radially symmetric stationary states of an electron with respect to the Hamiltonian given in equation (11) of chapter three. The results of this chapter may be used to calculate energy levels for various quantum dot heterojunctions. Using the interpretation of the energy levels presented in chapter two, the band offset between the conduction band and intermediate band of a QD-IBSC with a centrally located donor impurity may found.
<table>
<thead>
<tr>
<th>Table 1: Some heterostructures on GaAs substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOVPE - metalorganic vapor phase epitaxy</td>
</tr>
<tr>
<td>MBE - molecular beam epitaxy</td>
</tr>
<tr>
<td>FET - Field Effect Transistor</td>
</tr>
<tr>
<td>CL - cathode luminescence</td>
</tr>
<tr>
<td>MOCVD - metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>TTM  - transmission electron microscopy</td>
</tr>
<tr>
<td>DLTS - deep level transient spectroscopy</td>
</tr>
<tr>
<td>AFM - atomic force microscopy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Technique</th>
<th>GaAs</th>
<th>InGaAs</th>
<th>InAlAs</th>
<th>InP</th>
<th>InGaAsP</th>
<th>InGaP</th>
<th>InGaAsP</th>
<th>GaSb</th>
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<tr>
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</tr>
</tbody>
</table>

PREVIOUSLY REPORTED
APPENDIX C

MATLAB CODE TO CALCULATE ENERGY LEVELS

C.1 calculateEnergyLevels.m

close all
pause(3)
clear all
pause(3)
c1c

H_BAR = 1.05457e-34; % Joules*sec
EPS0 = 8.85419e-12; % Cb^-2/N/m^-2
E = -1.60218e-19; %Cb
KAPPA = 11.7043; % [1]
EPS = KAPPA * EPS0; % Cb^-2/N/m^-2
ME = 0.0979*9.10939e-31; % kg

% R_Over_A = [0:0.20:5],[6:1:25];
% r_over_a = R_Over_A(1);
J = 14;

V_DOT = 1.25*abs(E); % given in Joules // should be positive
A = 4*pi*EPS/ME*(H_BAR/E)^2; % meters
RY = E^-2/2/(4*pi*EPS)/A; % given in Joules

BEGIN = 1;
END = 52;
REL_ERR = 5e-9;
%REL_ERR = 1;

doSteepedDescent = 1;
if doSteepedDescent == 1;
for PP = BEGIN:END,
PP
cd matrices/w
eval(sprintf('load w_%.d',PP))
cd ..../..
eval(sprintf('r_over_a = r_%.d',PP));
eval(sprintf('M3 = abs(V_DUT)*w_%.d',PP));
eval(sprintf('clear w_%.d w_%.d',PP,PP))
M1 = zeros(J,J);
for j = 1:J,
M1(j,j) = -(H_BAR/j/A) - 2/2/ME;  \% given in Joules
end
M2 = zeros(J,J);
for j = 1:J;
M2(j,j) = abs(V_DUT)*exp(-2*r_over_a/j)*1+(1+r_over_a/j)*2*r_over_a/j;
end
clear j
Q = M1+M2+M3;
clear M1 M2 M3
Q = Q/2+Q'/2;
Q = eval(Q);

%%% CALCULATE THE GROUND STATE ENERGY
%% AT A GIVEN QUANTUM DOT RADIUS

eigenstate = 1;
mu = 100/2/(abs(V_DOT)+RY);
dex = 1;
al(1:j, dex) = 0;
if PP == 1,
al(1) = 1;
else
save allTemp
save parametersTemp PP eigenstate
clear all
load parametersTemp
cd energyData
eval(sprintf('load radius_%d', PP-1))
cd ..
eval(sprintf('al = A_%d;', eigenstate))
eval(sprintf('mu = abs(1000/E_%d);', eigenstate))
save parametersTemp al mu
clear all
load allTemp
load parametersTemp
end
al(:, dex) = al(:, dex)/norm(al(:, dex));
Ex(dex) = al(:, dex)'*Q*al(:, dex);
if isa(Ex, 'sym'),
   Ex = eval(Ex);
end
flag1 = 0;
numPasses = 1;
while flag1 == 0,
al(:,dex+1) = (eye(J)-2*mu*Q)*al(:,dex);
al(:,dex+1) = al(:,dex+1)/norm(al(:,dex+1));
Ex(dex+1) = al(:,dex+1)'*Q*al(:,dex+1);
if Ex(dex+1)-Ex(dex) > 0
    mu = mu/1.5;
dex = dex - 1;
elseif abs(2*(Ex(dex+1)-Ex(dex))/(Ex(dex+1)+Ex(dex))) < REL_ERR & ( abs(al(:,dex)'*al(:,dex+1)) > .999),
    flag1 = 1;
elseif rem(dex,50) == 0,
    mu = abs(1000/Ex(length(Ex)));
end
dex = dex + 1;
umPasses = numPasses + 1;
end
E_i = -V_DOT+Ex(length(Ex));
A_i = al(:,length(Ex));
clear Ex

%%% CALCULATE THE ENERGY
%%% SOME EXCITED STATES
for eigenstate = 2:10,
dex = 1;
al(1:J,dex) = 0;
save allTemp
save parametersTemp PP eigenstate
clear all
load parametersTemp
cd energyData
eval(sprintf('load radius_%d',PP))
cd ..
eval(sprintf('al = A_\%d;', eigenstate))
eval(sprintf('mu = abs(1000/E_\%d);', eigenstate))
save parametersTemp al mu
clear all
load allTemp
load parametersTemp
for q = 1:eigenstate-1,
x = sprintf('\(al(:,dex) - (\text{transpose}(al(:,dex))\text{A}_\%d)\text{A}_\%d)/\text{norm}(\text{al(:,dex) - (\text{transpose}(al(:,dex))\text{A}_\%d)\text{A}_\%d});\)', q, q, q, q)
al(:,dex) = eval(x)
end
Ex(dex) = al(:,dex)’*Q*al(:,dex);
flag1 = 0;
while flag1 == 0,
al(:,dex+1) = (eye(J)-2*mu*Q)*al(:,dex);
for q = 1:eigenstate-1,
x = sprintf('\(al(:,dex+1) - (\text{transpose}(al(:,dex+1))\text{A}_\%d)\text{A}_\%d)/\text{norm}(\text{al(:,dex+1) - (\text{transpose}(al(:,dex+1))\text{A}_\%d)\text{A}_\%d});\)', q, q, q, q)
al(:,dex+1) = eval(xx)
end
Ex(dex+1) = al(:,dex+1)’*Q*al(:,dex+1);
if Ex(dex+1)-Ex(dex) > 0
    mu = mu/1.5;
dex = dex - 1;
elseif abs(2*(Ex(dex+1)-Ex(dex))/(Ex(dex+1)+Ex(dex))) < REL_ERR & ( abs(al(:,dex)’*al(:,dex+1)) > .999),
    flag1 = 1;
elseif rem(dex,50) == 0,
    mu = abs(1000/Ex(length(Ex)));
end
dex = dex + 1;
end
eval(sprintf('E%d = -V\_DOT\_Ex(length(Ex));',eigenstate))
eval(sprintf('A%d = a1(:,length(Ex));',eigenstate))
cd energyData
save tempEnergyData
cd ..
clear Ex
end

cd energyData
eval(sprintf('save radius_%d r\_over\_a E\_1 E\_2 E\_3 E\_4 E\_5 E\_6 E\_7 E\_8 E\_9 E\_10\',PP))
eval(sprintf('save radius_%d A\_1 A\_2 A\_3 A\_4 A\_5 A\_6 A\_7 A\_8 A\_9 A\_10 -append\',PP))
cd ..
clear al mu j k flag1 dex M1 M2 M3 Q Ex
eval(sprintf('clear r_%d\',PP))
clear E\_1 E\_2 E\_3 E\_4 E\_5 E\_6 E\_7 E\_8 E\_9 E\_10 A\_1 A\_2 A\_3 A\_4 A\_5 A\_6 A\_7 A\_8 A\_9 A\_10
end

clearPlot = 1;
figure
if clearPlot == 1,
for PP = 1:END,
cd energyData
eval(sprintf('load radius_%d\',PP))
cd ..
ra(PP) = r\_over\_a;
E1(PP) = E\_1/abs(E);
E2(PP) = E\_2/abs(E);
E3(PP) = E\_3/abs(E);
E4(P) = E_4/abs(E);
E5(P) = E_5/abs(E);
E6(P) = E_6/abs(E);
E7(P) = E_7/abs(E);
E8(P) = E_8/abs(E);
E9(P) = E_9/abs(E);
E10(P) = E_10/abs(E);
end
r = ra*A;
plot(r,E1,r,E2,r,E3,r,E4,r,E5,r,E6,r,E7,r,E8,r,E9,r,E10)
xlabel('quantum dot radius [m]')
ylabel('energy [eV]')
title('\kappa = 11.7; \mu_{eff} = 0.098\times10^{-31} \text{ kg}; \ W_{CB} = 1.25 \text{ eV}; \ \text{i} = 0')
end

C.2 construct_w_matrices.m

clear all
R_Over_A = [[0:0.2:5],[6:1:25]];
R_over_a = R_Over_A(1);

J = 14;

%Phi is not a function of r_over_a ??

constructPhi = 0;
if constructPhi == 1,
    for j = 1:J,
for k = 1:J, 
    [j,k]
    Phi = makePhiMatrix(j,k);
    eval(sprintf('Phi%d%d = Phi;\n',j,k))
if ~exist('matrices\Phi'),
    mkdir('matrices\Phi')
    eval(sprintf('save matrices\Phi\Phi%d%d',j,k))
else
    eval(sprintf('save matrices\Phi\Phi%d%d',j,k))
end
end
else
    %load it
end

constructw = 1;
if constructw == 0,
    %then do nothing
elseif constructw == 1,
    for PP = 2:2,
      r_over_a = R_Over_A(PP);
      [r_over_a]
      for j = 1:J,
        for k = 1:J,
          constructTheta = 1;
%Theta is a function of r_over_a
if constructTheta == 1,
    sum = zeros(j+k-1,1);
    Theta = zeros(j,k);
    eval(sprintf('Theta%d%d = zeros(j,k);',j,k))
for che = 2:j+k;
    sumtemp = 1;
    z = che;
    while z > 3,
        sumtemp = vpa(sumtemp * vpa(1 + r_over_a*(j+k)/z/j/k, 100),100);
        z = z-1;
    end
    sumtemp = vpa(sumtemp/6*(r_over_a*(j+k)/j/k)^3,100);
    if che >= 3
        sum(che-1) = sumtemp;
    end
    for p = 1:che-1,
        if p <= j & che-p <= k,
            eval(sprintf('Theta%d%d(p,che-p) = sum(che-1);',j,k))
        end
    end
end
clear sum che z Theta sumtemp p
end
eval(sprintf('load matrices\Phi\Phi%d%d',j,k))
eval(sprintf('W%d%d = Phi%d%d .* Theta%d%d;',j,k,j,k,j,k,k,k,k))
\[ w(j,k) = \exp(-r_{over\,a}(j+k)/j/k) \sum \left( \text{eval(sprintf('W%d%d,j,k))}) \right) \]

\[ \text{eval(sprintf('clear Phi%d%d Theta%d%d W%d%d',j,k,j,k,j,k))} \]

C.3 makePhiMatrix.m

function Phi = makePhiMatrix(j,k)

for p = 0:j-1,
    for q = 0:k-1,
        % get the first numerator and denominator
        if (j-1-p) > (1+p)
            num = 1;
            for ii = j-p:j
                num = num*ii;
            end
            temp = gcd(num,factorial(1+p));
        end
num1 = num/temp;
den1 = factorial(1+p)/temp;
%bin2 = num/den
else
    num = 1;
    for ii = (2+p):j
        num = num*ii;
    end
    temp = gcd(num,factorial(j-1-p));
    num1 = num/temp;
    den1 = factorial(j-1-p)/temp;
    %bin2 = num/den
end
%get the second numerator and denominator
if (k-1-q) > (1+q)
    num = 1;
    for ii = k-q:k
        num = num*ii;
    end
    temp = gcd(num,factorial(1+q));
    num2 = num/temp;
    den2 = factorial(1+q)/temp;
    %bin2 = num/den
else
    num = 1;
    for ii = (2+q):k
num = num*ii;
end
temp = gcd(num,factorial(k-1-q));
num2 = num/temp;
den2 = factorial(k-1-q)/temp;
%bin2 = num/den
end
% get the third numerator and denominator
if (p) > (q)
    num = 1;
    for ii = (p+1):(2+p+q),
        num = num*ii;
    end
temp = gcd(num,factorial(q));
num3 = num/temp;
den3 = factorial(q)/temp;
%bin2 = num/den
else
    num = 1;
    for ii = (q+1):(2+p+q),
        num = num*ii;
    end
temp = gcd(num,factorial(p));
num3 = num/temp;
den3 = factorial(p)/temp;
%bin2 = num/den
end

% get the rest with as much precision as possible;
num4 = k^p;
num5 = j^q;
num6 = 2^(p+q+2);

% now begin to divide out the (j+k)^(3+p+q) from any single numerator

den6 = 1;

z = p+q+3;
flagA = 0;
while z > 0 & flagA == 0,
    if z == 9 & j == 8 & k == 13 & p == 3 & q == 11
        disp('')
    end
[endnum1x, num2x, num3x, num4x, num5y, num6x, den6x] = DivideOut_00(num1, num2, num3, num4, num5, num6, den6, j+k, p+q);
if isempty(find(([num1x, num2x, num3x, num4x, num5y, num6x] ~= [num1, num2, num3, num4, num5, num6]) == 1)),
    flagA = 1;
    den6 = den6*(j+k)^z;
    z = 0;
else
    num1 = num1x;
    num2 = num2x;
    num3 = num3x;
    num4 = num4x;
    num5 = num5x;
    num6 = num6x;
    den6 = den6x;
\[ z = z - 1; \]
end
end
NUM(p+1,q+1) = ((-1)^{(p+q)}) \times \text{num1} \times \text{num2} \times \text{num3} \times \text{num4} \times \text{num5} \times \text{num6};
DEN(p+1,q+1) = \text{den1} \times \text{den2} \times \text{den3} \times \text{den6};
eval(\text{sprintf}('\Phi(p+1,q+1) = \text{vpa(NUM(p+1,q+1)/DEN(p+1,q+1),100);'}',j,k))
end
end

\textbf{C.4 \textit{DivideOut.m}}

\begin{verbatim}
function [n1,n2,n3,n4,n5,n6,denA] = DivideOut_00(n1,n2,n3,n4,n5,n6,denA,base,ex)

%clear temp
combo = nchoosek([1 2 3 4 5 6],1);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
eval(\text{sprintf}('div(m) = gcd(n%d,(base));',combo(m)))
end
if ~isempty(find((div ~= 1 & div > 0)),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA\times base/div(dex);
eval(\text{sprintf}('n\text{temp} = n%d/div(dex);',combo(dex,1)));
if round(denAtemp) == denAtemp \& round(n\text{temp}) == n\text{temp},
denA = denAtemp;
\end{verbatim}
eval(sprintf('n\%d = ntemp;\', combo(dex,1)))
for dex2 = 2:1,
  eval(sprintf('n\%d = 1;\',combo(dex,dex2)))
end
return
end
end

combo = nchoosek([1 2 3 4 5 6],2);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
  eval(sprintf('div(m) = gcd(n\%d*n\%d,(base));\',combo(m,1),combo(m,2)))
end
if isempty(find((div ~= 1 & div > 0))),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA*base/div(dex);
else
    eval(sprintf('ntemp = n\%d*n\%d/div(dex);\',combo(dex,1),combo(dex,2)));
if round(denAtemp) == denAtemp & round(ntemp) == ntemp,
denA = denAtemp;
    eval(sprintf('n\%d = ntemp;\', combo(dex,1)))
for dex2 = 2:2,
  eval(sprintf('n\%d = 1;\',combo(dex,dex2)))
end
return
combo = nchoosek([1 2 3 4 5 6],3);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
eval(sprintf('div(m) = gcd(n%d*n%d*n%d,(base));',combo(m,1),combo(m,2),combo(m,3)))
end
if isempty(find((div == 1 & div > 0))),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA*base/div(dex);
eval(sprintf('ntemp = n%d*n%d*n%d/div(dex);',combo(dex,1),combo(dex,2),combo(dex,3)))
if round(denAtemp) == denAtemp & round(ntemp) == ntemp,
denA = denAtemp;
eval(sprintf('n%d = ntemp;', combo(dex,1)))
for dex2 = 2:3,
eval(sprintf('n%d = 1;',combo(dex,dex2)))
end
return
end
end

combo = nchoosek([1 2 3 4 5 6],4);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
    eval(sprintf('div(m) = gcd(n%d*n%d*n%d*n%d,(base));','combo(m,1),combo(m,2),combo(m,3),combo(m,4)))
end
if isempty(find((div ~= 1 & div > 0))),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA*base/div(dex);
eval(sprintf('ntemp = n%d*n%d*n%d/n%d/div(dex);','combo(dex,1),combo(dex,2),combo(dex,3),combo(dex,4)))
if round(denAtemp) == denAtemp & round(ntemp) == ntemp,
denA = denAtemp;
eval(sprintf('n%d = ntemp;','combo(dex,1)))
for dex2 = 2:4,
eval(sprintf('n%d = 1;','combo(dex,dex2)))
end
return
end
end

combo = nchoosek([1 2 3 4 5 6],5);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
    eval(sprintf('div(m) = gcd(n%d*n%d*n%d*n%d*(base));','combo(m,1),combo(m,2),combo(m,3),combo(m,4),combo(m,5)))
end
if isempty(find((div ~= 1 & div > 0))),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA*base/div(dex);
eval(sprintf('ntemp = n%d*n%d*n%d*n%d*%d/div(div);',combo(dex,1),combo(dex,2),combo(dex,3),combo(dex,4),combo(dex,5)));
if round(denAtemp) == denAtemp & round(ntemp) == ntemp,
denA = denAtemp;
eval(sprintf('n%d = ntemp;', combo(dex,1)))
for dex2 = 2:5,
eval(sprintf('n%d = 1;',combo(dex,dex2)))
end
return
end
end

combo = nchoosek([1 2 3 4 5 6],6);
[M,N] = size(combo);
div = ones(M,1);
for m = 1:M,
x = sprintf('gcd(n%d*n%d*n%d*n%d*n%d*n%d,(base));',combo(m,1),combo(m,2),combo(m,3),combo(m,4),combo(m,5),combo(m,6))
div(m) = eval(x)
end
if ~isempty(find((div ~= 1 & div > 0))),
dex = find(div == max(div));
dex = dex(1);
denAtemp = denA*base/div(dex);
x =
sprintf('%d*%d*%d*%d*%d/div(dex);',combo(dex,1),combo(dex,2),combo(dex,3),combo(dex,4),combo(dex,5),combo(dex,6));
ntemp = eval(x);
if round(denAtemp) == denAtemp & round(ntemp) == ntemp,
denA = denAtemp;
end
val(sprintf('%d = ntemp;', combo(dex,1)))
for dex2 = 2:6,
val(sprintf('%d = 1;',combo(dex,dex2)))
end
return
end
end

denA = denA*base;
REFERENCES


