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แคดเมียมซีลีไนด์ (CdSe) ด้วยระเบียบวิธีกึ่งเอ็มพีริคัล
Electronic Structure Calculation of CdSe Quantum Dots by
Semi-Empirical method

โดย
นายกมล สุวรรณรัตน์

รายงานนี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร

ปริญญาวิทยาศาสตรบัณฑิต

ภาควิชาเคมี คณะวิทยาศาสตร์

จุฬาลงกรณ์มหาวิทยาลัย

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Electronic Structure Calculation of CdSe Quantum Dots by
Semi-empirical method



by

Mr. Kamon Suwannarat

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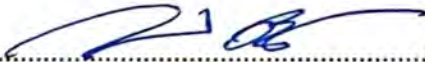
By Mr. Kamon Suwannarat

Field of Study Chemistry


Project Advisor Dr. Nattapong Paiboonvorachat

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Bachelor's Degree

Project Committee


.....Chairman
(Associate Professor Viwat Vchirawongkwin, Ph.D.)

N. Paiboonvorachat.
.....Project Advisor
(Nattapong Paiboonvorachat, Ph.D.)


.....Examiner
(Assistant Professor Boosayarat Tomapatanaget, Ph.D.)

This report has been endorsed by Head of Chemistry Department

.....
(Associated Professor Vudhichai Parasuk, Ph.D.)

Head of Chemistry Department

Date..... Month..... Year.....

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ชื่อโครงการ การคำนวณโครงสร้างเชิงอิเล็กทรอนิกส์ของควอนตัมดอทชนิดแคดเมียมซีลีไนด์ (CdSe)
ด้วยระเบียบวิธีกึ่งเอ็มพีริคัล

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ชื่ออาจารย์ที่ปรึกษา อาจารย์ ดร.ณัฐพงศ์ ไพบูลย์วรชาติ

ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2558

บทคัดย่อ

การวิจัยครั้งนี้มีวัตถุประสงค์เพื่อเขียนและพัฒนาโปรแกรมการคำนวณโครงสร้าง เชิงอิเล็กทรอนิกส์ของควอนตัมดอทชนิดแคดเมียมซีลีไนด์ (CdSe) และศึกษาผลของรูปร่างและขนาดต่างๆของควอนตัมดอท เนื่องจาก ควอนตัมดอทของแคดเมียมซีลีไนด์มีสมบัติทางแสงที่มีการนำไปใช้ประโยชน์อย่างมากมาทางด้าน การแพทย์ โดยเฉพาะทางด้านการพิมพ์ภาพทางชีวภาพและการวินิจฉัยโรค สมบัติทางแสงของควอนตัมดอท นั้นถูกอธิบายได้โดยโครงสร้างเชิงอิเล็กทรอนิกส์ของควอนตัมดอท ทั้งนี้จึงสนใจการคำนวณโครงสร้างเชิงอิเล็ก- ตรอน ของควอนตัมดอทด้วยแบบจำลอง tight-binding จากผลการคำนวณสามารถสรุปได้ว่า ความกว้าง ของช่องว่างระหว่างแถบพลังงาน (energy band gap) มีขนาดเล็กลง เมื่อควอนตัมดอทชนิดแคดเมียม ซีลีไนด์ในรูปร่างทั้ง 3 แบบ มีขนาดใหญ่ขึ้น ซึ่งสอดคล้องกับทฤษฎี แต่ค่าที่ได้จากการคำนวณนี้ยังไม่ตรงกับ ข้อมูลจากการทดลอง เนื่องจากในแบบจำลองที่ใช้ศึกษานั้นไม่ได้พิจารณาถึงอันตรกิริยาระหว่างอิเล็กตรอน

คำสำคัญ: แคดเมียมซีลีไนด์, ควอนตัมดอท, แบบจำลอง tight-binding

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Chapter 1 Introduction

1.1 Quantum Dots

Nanomaterial is substance with at least one dimension less than 100 nanometres. It can be in the nanoscale in one dimension (e.g. surface films), two dimensions (e.g. strands or fibres), or three dimensions (e.g. particles). Nanomaterials play an important role in many fields such as advanced materials, pharmaceuticals and medicals [1]. Due to a variety of applications including many efforts from the governments of many countries [2], nanomaterials have become a major interdisciplinary area of research recently. Nanomaterials are commonly used in daily life, e.g. cosmetics, textile, electronics. One important class of nanomaterials is quantum dots, which have many unique properties and show an interesting phenomenon.

Quantum dots are nanoscale semiconductor materials which are composed of elements in Periodic Groups II-VI, III-V, or IV-VI that tightly confine either electrons or electron-holes in all three spatial dimensions [2]. Among many unique properties of quantum dots, optical properties are the most commonly interesting properties for the applications of quantum dots. For example, in medical bio-imaging and disease detection application, in Figure 1.1, quantum dots can be set to any arbitrary emission spectra to allow labelling and observation of the biological processes [3].

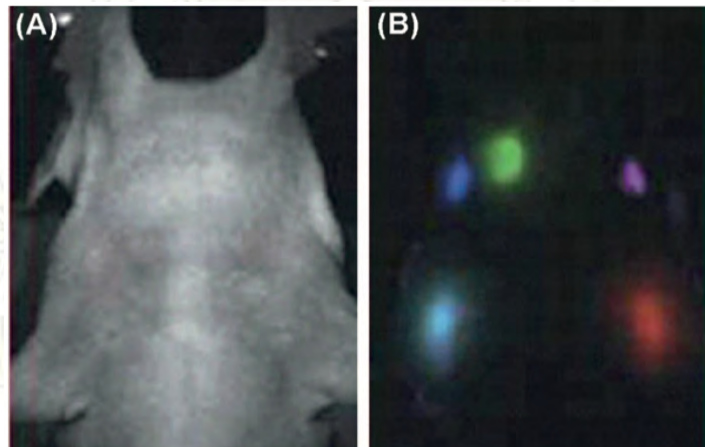


Figure 1.1 Detection of lymphatic system with five-colour spectrally unmixed QDs. (a) Auto fluorescence image of mouse (b) Fluorescence image of draining lymph nodes after spectral unmixing [3].

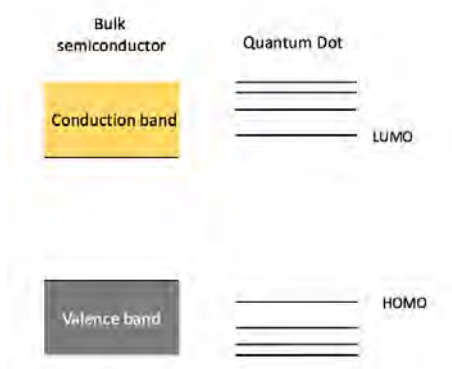


Figure 1.2 Energy level of bulk Semiconductor and Quantum Dot.

In crystalline inorganic solids, atomic orbitals overlap to give nearly continuous electronic energy levels (bands), two of which are primarily concerned in the electronic and optical processes, *i.e.* conduction and valence bands separated by a band gap [4]. The levels in quantum dots are however more discretised and the band gap is determined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [5] as shown in Figure 1.2.

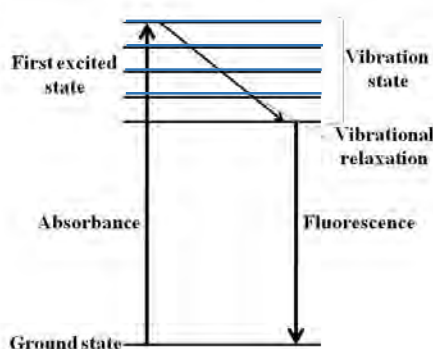


Figure 1.3 The fluorescence energy diagram [6].

On exposure to the electromagnetic radiation, a molecule can absorb the energy. After the molecule absorbs a photon, an electron is excited to a higher electronic state, typically also at an excited vibrational state. As a result, the fluorescence emission is occurred during the relaxation from the excited state to the ground state as shown in Figure 1.3. The energy of the photon emitted from the first electronically excited state approximately corresponds to the HOMO-LUMO energy gap.

Regarding the optical properties of quantum dots, CdSe is one of the major research interests which many researchers are concentrating on developing controlled synthesis of CdSe nanomaterials. [7] Due to its wide band gap with high quantum yield [8] and have various applications such as quantum-dots-synthesized solar cells [9], photoelectronic applications [10], and quantum dot light-emitting devices (QD-LEDs). [11] Therefore, we first study the electronic structure of CdSe as will be discussed next.

1.2 Electronic Structure Calculation of Quantum Dots

In quantum mechanics, there are 2 approaches for electronic structure calculation, that is, *ab initio* and semi-empirical method.

(i) *Ab initio* methods have high accuracy, based on many different quantum-chemical methods that solve the Schrödinger equation with the electronic Hamiltonian. *Ab initio* methods are used to understand the electronic structure and related properties especially bandgap variation with size. From previous reported, Tamura *et al.* studied the excitation energy transfers in a semiconductor nanocrystals using a $(\text{CdSe})_8$ cluster and a rhodamine cation as a simplified model. In this study, the GAMESS code [12] is employed for *ab initio* calculation. [13]

When the system becomes larger, *ab initio* method will require high computational resources (memory and time). *Ab initio* methods can only be used in the calculation in small system (tens of atoms). [14]

(ii) Semi-empirical methods are commonly used for the electronic structure calculation of nanocrystals, because these methods employ empirical parameters obtained from the experimental data. As semi-empirical method provides a means to study large systems (hundreds of atoms) [15], this method is commonly used to study the electronic structure of quantum dots. Previously reported, Leung *et al.* studied the electronic fine structure in CdSe nanocrystals incorporating electron-hole and spin-orbit interactions with tight binding model. [16]

One of the computationally powerful model in semi-empirical methods for the investigation of quantum dots energies is the tight-binding model. It has existed for many years as a convenient model for the description of electronic structure in molecule or solid. [17]

1.3 Project Objective

The project objectives are to design and develop a program to calculate the electronic structure of CdSe quantum dots by semi-empirical method and to study the effect of different shapes and sizes of small CdSe crystallites on their optical properties.

Chapter 2 Quantum Dots

2.1 Cadmium Selenide Quantum Dots with Zinc Blende Structure

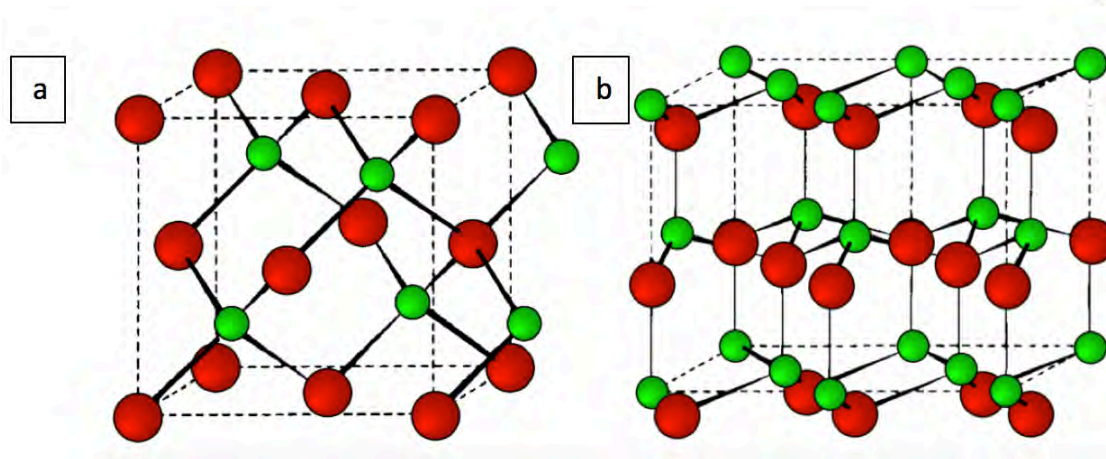


Figure 2.1 Unit cell of CdSe with (a) zinc blende structure, and (b) wurtzite structure [18]. Cadmium atoms are shown in green, selenide atoms are shown in red.

CdSe quantum dots mainly exist in two different forms as shown in Figure 2.1: hexagonal wurtzite and cubic zinc blende structure. The wurtzite structure is more thermodynamically stable, compared to the zinc blende structure [19] at above $95\pm 5^\circ\text{C}$ with a small difference in energy between these two forms. Even though the zinc blende structure is more stable at room temperature, the wurtzite form is more commonly found [20]. This is because the traditional synthesis of CdSe quantum dots usually is usually conducted at the temperature higher than 300°C , at which the wurtzite structure is preferred. [21] So, there were many studies of the crystalline structures of CdSe quantum dots with wurtzite structure. Besides, zinc blende structure is rarely reported [22] and the CdSe quantum dots with zinc blende structure become more interested recently. In addition, in the first step of program development, we started with the zinc blende structure seeing that cubic structure is easier to set up.

According to Figure 2.1 (a), zinc blende CdSe quantum dots structure can be described by the Face-Centred Cubic (FCC) of Se^{2-} ions with Cd^{2+} ions occupying one half of tetrahedral holes. [23] Based on the structure of zinc blende CdSe quantum dots, the structure can be constructed by our C++ program, the confining it to various shapes and sizes.

According to the face-centred cubic from Bravais lattice, the structure has lattice points on the faces and corners of the cube. These lattice points are first set up in a large size (width of $7-8a$; a is lattice constant) in the program. Next, the structure of these lattice points to be in required any shapes and sizes in these following cases:

(i) For spheres;

The centre of the structure containing lattice points is first calculated. With an input r (radius of the desired sphere), the distance value from the centre to each lattice point must be no more than r value.

(ii) For cubes;

With an input w (width of desired cube), all x , y and z values of each lattice point must be no more than the value of w .

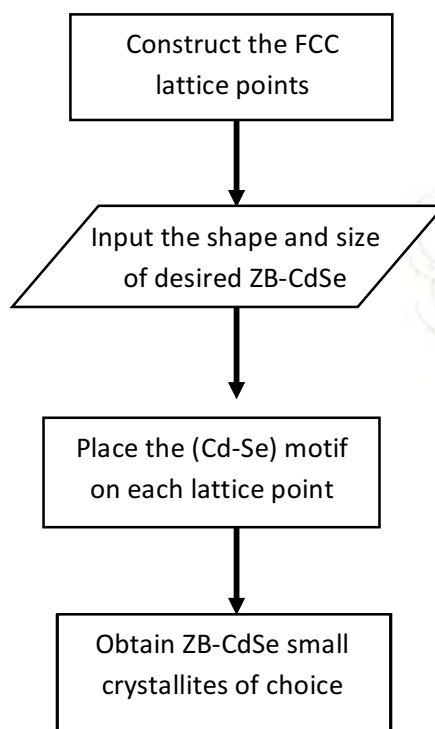
(iii) For lamina;

With an input w (width of desired lamina), all x and y values of each lattice point must be no more than w value with fixed z at $0.5a$ and a .

So these lattice points which are agreed with the condition in each shape and size is collected. Then, each lattice point is replaced by the motif: Se^{2-} at $(0,0,0)$; Cd^{2+} at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. [24] Until here, we can get the zinc blende CdSe structure from the program. From this structure, it can be noticed that number of Se^{2-} ions and Cd^{2+} ions are equal which will be discussed in the next section.

The flow chart of CdSe quantum dots with zinc blende structure is shown below and the code is shown in the Appendix.

Flow Chart of C++ Program: Part 1



2.2 Electronic Structure Calculation of Zinc Blende CdSe Quantum Dots

In the electronic structure calculation of nanocrystals, tight-binding method is primarily used with the basis states of localised orbitals. [25] Tight-binding model considers the hopping interactions between nearest neighbours with no consideration of electron-electron interactions. This model demands low amount of computational resources, compared to other models, and is simple and very fast in computation. [26] So, in order to study large and complicated systems, such as quantum dots, the tight-binding model is suitable in this study.

In order to calculate the electronic structure of CdSe quantum dots with tight-binding model, the basis is firstly defined. Due to tight-binding model is useful for the description of the complicated valence band structure. [15] Based on the band structure result from literature [13], the valence band is originated from the p orbital of anion, while conduction band arise from s orbital from cation.

In this electronic structure calculation program, we chose the sp tight-binding basis with the use of $4p$ orbital from Se^{2-} and $5s$ orbital from Cd^{2+} . Then the electronic structure can be calculated by these following steps.

2.2.1 Construct and solve the Hamiltonian

From the zinc blende structure of CdSe shown in Figure 2.1 (a), considering the interactions in the structure within tight-binding model, which consist of orbital energies and hopping integrals of nearest neighbour and next-nearest neighbour in this version. Therefore, tight-binding Hamiltonian is given by:

$$\hat{H} = \sum_i \varepsilon_i \hat{n}_i + \sum_{\langle\langle ij \rangle\rangle\sigma} t_{ij} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma})$$

where \hat{H} – Hamiltonian operator, \hat{n}_i – number operator ($\hat{n}_i = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$).

Consider the tight-binding Hamiltonian, the creation and annihilation operators $\hat{c}_{i\sigma}^\dagger$ and $\hat{c}_{j\sigma}$ creates and removes the electron at site i and j with spin σ , respectively. ε_i is the orbital energy at site i . t_{ij} is the hopping integral between sites i and j . [27] In this system which is described by only s and p orbitals, there are two orbital energies ε_p and ε_s , and three hopping integrals t_{sp} , t_{pp} and t_{ss} . Tight-binding parameters are obtained from previous reported [15] as shown in Table 2.1.

Parameters	TB
ε_p	-1.2738
ε_s	3.6697
t_{sp}	1.1396
t_{pp}	0.1587
t_{ss}	-0.1608

Table 2.1: Tight-binding parameters (in eV) for zinc blende CdSe.

Using the model and parameters defined above, we can construct the Hamiltonian matrices in two different forms. First, the Hamiltonian is constructed in the state or configuration basis, where the electronic states can directly be obtained by performing an Exact Diagonalisation (ED) on the matrix. Alternatively, the Hamiltonian can be constructed in the atomic orbital basis, in which the matrix can be solved by Hückel Molecular Orbital (HMO) method in order to obtain the HMOs and corresponding energies. The matrices in both methods can be solved by routines available from previous work by Dr. Nattapong Paiboonvorachat. [28]

2.2.1.1 Exact Diagonalisation

In the use of orbital energies (ε_i) and hopping integral (t_{ij}) parameters from sp basis of tight-binding model in CdSe with zinc blende structure, we can consider these interactions and construct the Hamiltonian matrix of electronic states with the element of tight-binding parameters. This obtained Hamiltonian matrix is a really huge matrix. In order to solve this Hamiltonian matrix, it is diagonalised by exact diagonalisation which is required to diagonalise in every electronic states. This consumes highly computational resources.

Since the Hamiltonian matrix is sparse, so it can be diagonalised by Conjugate Gradient Routine for a specific number of low-lying states instead of all states to reduce the use of computer resources. So we can obtain the electronic states.

As a result of the Hamiltonian matrix which is constructed from electronic state is so huge and exact diagonalisation program is solving the Hamiltonian matrix state by state, thus exact diagonalisation program can only calculate the electronic structure of CdSe quantum dots in a very few small sizes. Thus the Hückel Molecular Orbital Program is used in this study in order to calculate the electronic structure of CdSe quantum dots in many shapes and large sizes.

The preliminary condition of calculation by using these two programs is to confirm the precision of the results in a small structure. Due to complicated coding problem which is cannot completed in this year. Thus Hückel Molecular Orbital Program is firstly used in order to solve the Hamiltonian matrix.

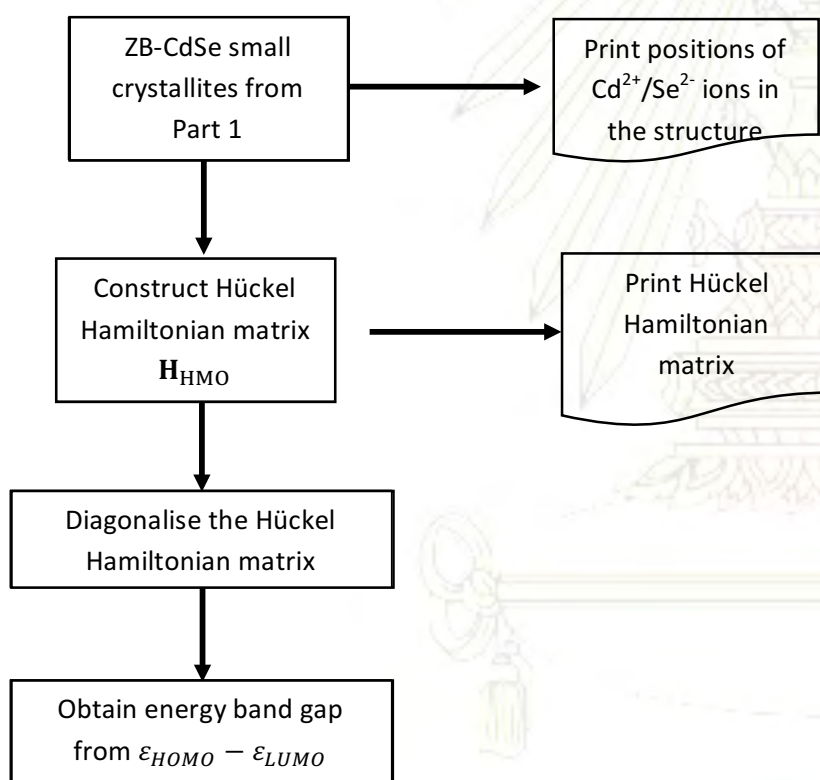
2.2.1.2 Hückel Molecular Orbital (HMO)

In the use of orbital energy and hopping integral parameters from sp basis, it can be constructed the $N \times N$ Hamiltonian matrix of basis atomic orbitals. The Hamiltonian matrix can be diagonalised and give the molecular orbital energies of CdSe quantum dots. Because of the Hamiltonian matrix which is constructed in the atomic orbital band is simpler and

smaller, then HMO Program can be diagonalised this Hamiltonian matrix providing the results of many sizes and shapes of CdSe quantum dots.

From HMO program, we cannot calculate in every structure but only CdSe structure with a balance charge would be work. According to the previous section, the number of Se^{2-} and Cd^{2+} are the same which is already balanced charge. When the charge is balance, molecular orbitals are half-filled as all electrons are in the HOMO and other lower energy MOs (valence band) with empty other higher MOs including LUMO (conduction band). From the results of molecular orbital energies from HMO program, band gap energy is determined by the difference between HOMO and the LUMO. So the calculated energy band gap can represent the electronic energy gap for fluorescence.

Flow Chart of C++ Program: Part 2



Chapter 3 The study of shape and size effect of small CdSe crystallites

In this study, we have described how to calculate the electronic structure of zinc blende CdSe quantum dots by semi-empirical method with using tight-binding model in the previous section. Now we compare results of the calculation of HOMO-LUMO gap energy in three shapes of small CdSe crystallites with first obtained structure are shown below.

3.1 CdSe small crystallites with zinc blende structure in many shapes

From the obtained CdSe with zinc blende structure by our C++ program, they are shown below:

(i) Sphere

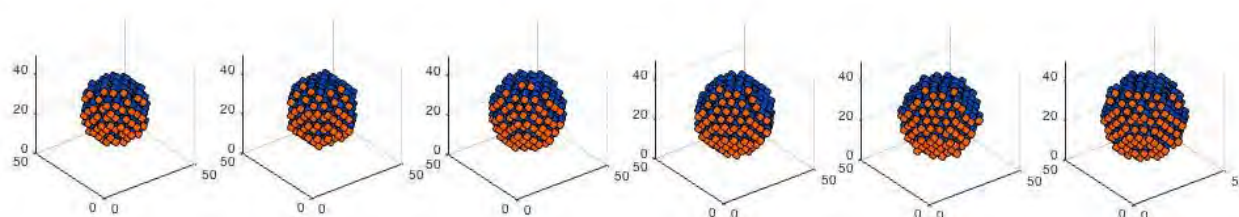


Figure 3.1 Spherical ZB-CdSe small crystallites with the diameters of 28.647, 29.902, 31.126, 33.386, 33.526, and 35.604 Å.

(ii) Cube

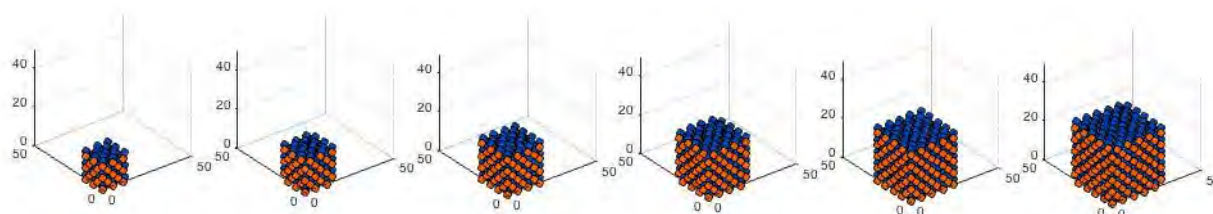


Figure 3.2 Cubic ZB-CdSe small crystallites with the widths of 16.671, 16.705, 19.7015, 22.7325, 25.7635, 28.7945 Å.

(iii) Lamina

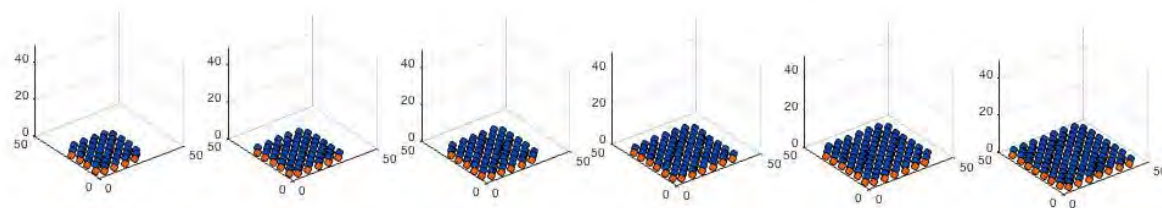


Figure 3.3 Laminal ZB-CdSe small crystallites with 1.856 Å thickness and the widths of 25.764, 28.795, 31.826, 34.857, 37.888, 40.919 Å.

3.2 Effect of Shape

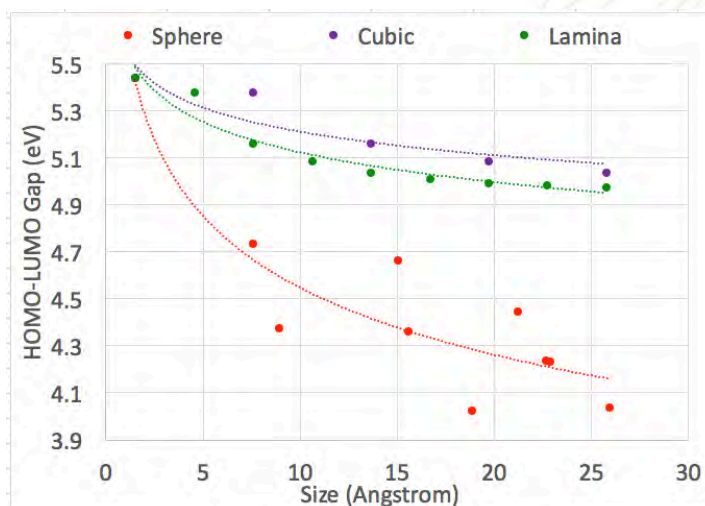


Figure 3.4 Size-dependencies of HOMO-LUMO gap energies for spheres, cubes, and lamina.

In general, the band gap values of spheres are smaller than the band gap values of cubes. [8] The calculated band gap energies of spherical and cubic shapes of CdSe small crystalline are in good agreement to the previous calculation report. [29] In Figure 3.4, there is a significant difference in the band gap values for the spheres, cubes, and lamina. For the larger sizes of spheres, the band gaps of spheres are below 4.76 eV, while the energy seems to converge around 4.95 eV for cubes and lamina.

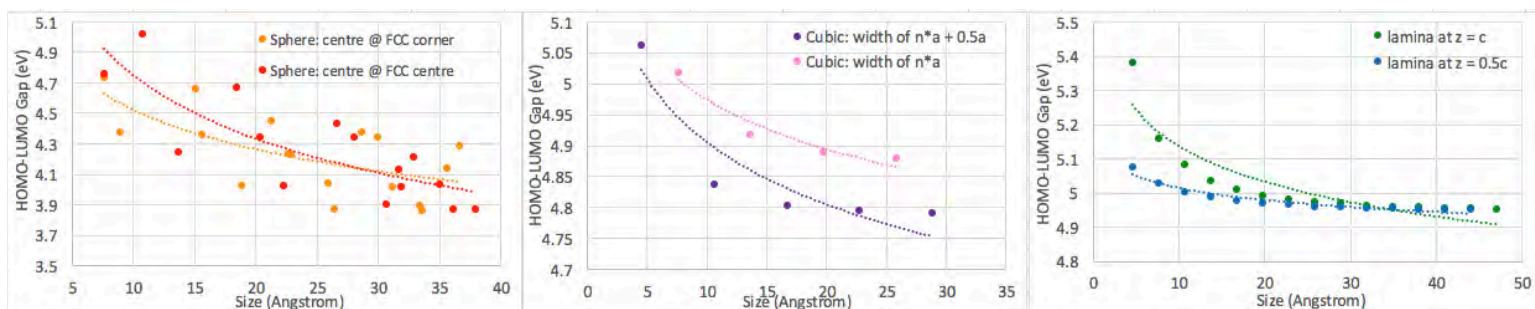


Figure 3.5 Size-dependencies of HOMO-LUMO gap energies for (a) spheres, (b) cubes, (c) lamina.

From the results of band gap energy values of zinc blende CdSe crystallites with spherical shape in Figure 3.5 (a), the calculated band gap is difference from the experimental values of approximately 1 eV from previous report. [6] Despite the absence of experimental value for optical spectra of cubic and lamina, these could be useful for future study.

There are 2 trends in each shape because of the obtained shape are slightly different into two structure. For sphere in Figure 3.5 (a), (i) the centre of sphere is at the FCC centre (red line) and (ii) the centre of sphere is at the FCC corner (orange line). For cubic in Figure 3.5 (b), (i) the widths of cubic are roughly equal to integral multiples of lattice constant plus one half of lattice constant (purple line) and (ii) the widths of cubic are roughly equal to integrals multiples of lattice constant (pink line). For lamina in Figure 3.5 (c), (i) lamina is at $z = c$ (or a , lattice constant) (green line) and (ii) lamina is at $z = 0.5c$ (or a , lattice constant) (blue line).

At a small size of quantum dots there is significant difference in value for each structure. When quantum dots size become larger, the HOMO-LUMO gap tends to approximately the same value as quantum dots lie between the discrete atomic and continuous bulk materials. [11] When a quantum dot is enlarged in size as shown in Figure 3.5, the HOMO-LUMO gap shifts to smaller values as the bulk phase properties. With size increasing, the HOMO-LUMO gap is converged to the band gap value of bulk CdSe (from previous report, bulk band gap for CdSe is 1.74 eV).

3.3 Effect of Size

The calculated energy band gap for different size in the spheres, cubes, and lamina shapes are plotted in Figure 9. The size dependencies of HOMO-LUMO gap is influenced by the term in proportional to $1/d^2$, which agrees with the particle-in-a-box model, whose energy levels are shown below:

$$E = \frac{n^2 h^2}{8mR^2}$$

where E – energy of levels, R – size of the box [11]

From the above equation, band gap energy depends on reciprocal of square of size of quantum dots which we plot this relationship in Figure 3.6.

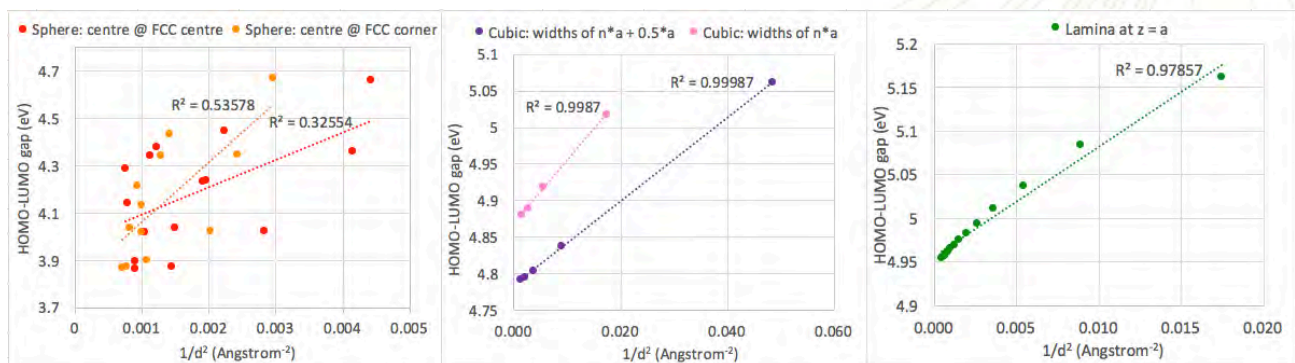


Figure 3.6 Reverse square of size VS HOMO-LUMO gap energies of (a) spheres, (b) cubes, (c) lamina.

From Figure 3.6, we present effect of the various sizes in 3 shapes (spheres, cubes, and lamina). In the case of cubes and lamina as shown in Figure 3.6 (b) and Figure 3.6 (c), the coefficient of determination (R^2) is approximately equal to 0.999 and 0.978 for cubes and lamina, respectively. It becomes clear that the calculated HOMO-LUMO gap is in a good linear relationship with inverse square of size, which agrees well with the particle-in-a-box model. While the results for sphere in Figure 3.6 (a) are not so good in correlation. We believe that some of the obtained zinc blende CdSe quantum dots structure may not really be spherical in shape because they are not exact spherical shape with cubic characters in some spherical shapes as shown is Figure 3.1 (a) and (b).

In setting up the spherical shape of CdSe with zinc blende structure in the C++ program, a sphere of FCC lattice points at any diameter is first obtained. Then Cd-Se motif is placed to the structure in order to assure the equal amount of Cd^{2+} and Se^{2-} ions in the structure instead of getting small spherical shape from a large CdSe with zinc blende structure. So some diameters of desired sphere shape do not give an exact spherical shape.

CdSe zinc blende structure with a diameter of 29.902 Å is depicted in Figure 3.1 (b) which has more cubic character compared to the 28.647 Å diameter structure as shown in Figure 3.1 (a). As a result, the effect of sizes in the case of spheres cannot directly be compared to the theory.

In addition, the structures are constructed from the simple geometric structure by C++ program. The obtained structures are not a good representative of the actual CdSe QDs structure. Thus, the C++ program can be improved to include the geometry optimisation in the future research.



Chapter 4 Conclusion

In this study, tight-binding model with sp basis have been applied to the calculations of electronic structure of Cadmium Selenide quantum dots with zinc blende structure to study of the effect of shape and size. The advantage of this approach is the use of theoretical with electronic structure parameters that effectively reduce the amount of computational resources required.

Zinc blende CdSe structure in many shapes and sizes is first set up in the C++ programming based on the concept of crystal structure. Then the Hamiltonian matrix is constructed in the tight-binding model which only takes into account orbital energies and hopping integrals between nearest neighbour and next nearest neighbour. So, the electron-electron interactions are not included in this model.

The constructed Hamiltonian matrix need to be diagonalised in the HMO program to obtain the HOMO-LUMO gap. In fact, the result from HMO Program need to be confirmed by the result from exact diagonalisation which is now under coding problem.

According the previous calculation report, there is a good agreement that the calculated band gap value of spheres is smaller than the band gap values of cubes with a significant difference values of band gap for these three shapes.

The results of band gap energy do not fit to experimental data because the tight-binding model does not include the electron-electron interactions. While the results provide a good trend of the relationship between energy and size of quantum dots, agreed with the particle-in-a-box model.

From this work, we can construct CdSe with zinc blende structure by our C++ program. The Hamiltonian matrix which is constructed by using sp tight-binding is diagonalised by HMO program to obtain the band gap. Even if the calculated HOMO-LUMO gaps, which corresponds to the fluorescence of quantum dots, are still far from the experimental value. These results provide a good agreement to the particle-in-a-box model, where the result for sphere cannot directly be compared to the theory.

Suggestion for future research

There are many ways to improve in the future research:

1. This project uses tight-binding model with minimal sp basis, so to use a higher basis, i.e. sp^3s^* , sp^3ds^* , will give more accurate valence and conduction bands. [30]

2. Tight-binding model does not include the electron-electron interactions. So to use other model with electron-electron interaction and long-range interaction would give a better result.

3. The C++ program for the structure construction is still not give a good representative of actual CdSe structure. Thus the C++ program needs to be able to construct CdSe structure with more accuracy.

4. Consider other geometric structure of CdSe quantum dots by set up wurtzite CdSe structure.



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Appendix A

```

//
// main.cpp
// CdSe Spherical Shape
//
// Created by Kamon Suwannarat on 4/6/2559 BE.
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//

#include <iostream>
#include <fstream>
#include <math.h>
#include <iomanip>
#include <string>
#include <locale>
#include <sstream>
using namespace std;

int i,j;

/* Distance function */
double dist(double x1,double y1, double z1,double x2,double y2, double z2){
    double d;
    d= sqrt(pow(x1-x2,2)+pow(y1-y2,2)+pow(z1-z2,2));
    return d;
}

/* Start up from size of unit cell at a = 6.062 b = 6.062 c = 6.062 angstroms T = Anion F =
Cation */
int main(int argc, const char * argv[]) {
    ofstream Hout;
    ofstream Coord;

    const double a = 6.062; //const double a = 6.062 A; parameter
    const double b = 6.062;
    const double c = 6.062;
    const int Lattice = 4;

    //Ion Objects
    struct IonStructure{
    public:
        bool type;
        double posx;
        double posy;
        double posz;
    };

```

```

//lonStructure lon[IniAtom];
bool prelon[Lattice] = {true,true,true,true};
double prea[Lattice] = {0.0*a,0.5*a,0.5*a,0.0*a};
double preb[Lattice] = {0.0*b,0.0*b,0.5*b,0.5*b};
double prec[Lattice] = {0.0*c,0.5*c,0.0*c,0.5*c};

int m;
cout << "Please enter your structure size" << "\t";
cin >> m; // m is number of unit cell in each axis of box
int q = m * m * m; // dimension of box
int TotalAtom = 4 * q;
//Big m
lonStructure lon2[TotalAtom];

for (i = 0; i < Lattice; i++) {
    lon2[i].type = prelon[i];
    lon2[i].posx = prea[i];
    lon2[i].posy = preb[i];
    lon2[i].posz = prec[i];
}
for(i = 0; i < m; i++){
    for(j = 0; j < 4 ; j++){
        lon2[4*i+j].type = lon2[j].type;
        lon2[4*i+j].posx = lon2[j].posx + i*a;
        lon2[4*i+j].posy = lon2[j].posy;
        lon2[4*i+j].posz = lon2[j].posz;
    }
}
for(i = 1; i < m; i++){
    for(j = 0; j < 4*m ; j++){
        lon2[4*m*i+j].type = lon2[j].type;
        lon2[4*m*i+j].posx = lon2[j].posx;
        lon2[4*m*i+j].posy = lon2[j].posy + i*b;
        lon2[4*m*i+j].posz = lon2[j].posz;
    }
}
for(i = 1; i < m; i++){
    for(j = 0; j < 4*m*m ; j++){
        lon2[4*m*m*i+j].type = lon2[j].type;
        lon2[4*m*m*i+j].posx = lon2[j].posx;
        lon2[4*m*m*i+j].posy = lon2[j].posy;
        lon2[4*m*m*i+j].posz = lon2[j].posz + i*c;
    }
}

//Built new spherical lon
//cout << "New Spherical Shape" << endl; // Select only atoms in spherical shape with

```



radius r

```

bool lon3[TotalAtom]; //necessary ion lon3[TotalAtom] from lon2;
// d is diameter of spherical shape
double d;
cout << "Enter diameter of spherical QD (Angstrom) :" << "\t";
cin >> d ;
cout << "d " << d << endl;

// Calculate D(distance) between each atom to centre
double centrex = 0.5*(double)m*a;
double centrey = 0.5*(double)m*b;
double centrez = 0.5*(double)m*c;
cout << centrex << " " << centrey << " " << centrez << endl;

//cout << "radius " << endl;
for (i = 0; i < TotalAtom; i++) {
    //cout << "Order : " << i+1 << "\t";
    double r = dist(lon2[i].posx, lon2[i].posy, lon2[i].posz, centrex, centrey, centrez);

    //cout << D << " ";
    if (r <= 0.5*d) {
        lon3[i] = true; // when distance from center to atom no more than radius,
NewShape[i] = 1
    }
    else {
        lon3[i] = false; // when distance from center to atom more than radius, NewShape[i]
= 0
    }
    cout << "i " << i << " " << " x " << lon2[i].posx << " y " << lon2[i].posy << " x " <<
lon2[i].posz << " distance " << r << " check " << lon3[i] << endl;
}

int counter = 0;
for (i = 0; i < TotalAtom; i++) {
    //cout << "lon3[" << i << "]" << lon3[i] << endl;
    if (lon3[i] == true) {
        counter = counter + 1;
    }else continue;
}

//ion in new spherical shape
int AllNumber = 2*counter;
lonStructure lon4[AllNumber];
int number = 0;
for (i = 0; i < TotalAtom ; i++) {
    if (lon3[i] == true) {
        lon4[number] = lon2[i];
    }
}

```

```

lon4[number+1].type = false;
lon4[number+1].posx = lon4[number].posx + 0.25*a;
lon4[number+1].posy = lon4[number].posy + 0.25*b;
lon4[number+1].posz = lon4[number].posz + 0.25*c;
number = number + 2;
}else continue;
}

ostringstream convert, convert1, convert2;
string filename, nocubic, diameter, NoH;
convert << AllNumber;
NoH = convert.str();
convert1 << m;
nocubic = convert1.str();
convert2 << d;
diameter = convert2.str();
filename = nocubic + "_" + diameter + "_" + NoH + ".txt";
Hout.open(filename);
filename = "Coord" + nocubic + "_" + diameter + "_" + NoH + ".txt";
Coord.open(filename);

// Print Coordinate of Ions and type of Ions
Coord << "Se" << endl;
for (int i = 0; i < AllNumber; i = i+2) {
    //Coor << lon4[i].type << "\t";
    Coord << lon4[i].posx << "\t";
    Coord << lon4[i].posy << "\t";
    Coord << lon4[i].posz << endl;
}
Coord << endl;
Coord << endl;
Coord << "Cd" << endl;
for (int i = 1; i < AllNumber; i = i+2) {
    //Coor << lon4[i].type << "\t";
    Coord << lon4[i].posx << "\t";
    Coord << lon4[i].posy << "\t";
    Coord << lon4[i].posz << endl;
}

cout << "Hamiltonian size is : " << AllNumber << endl;
Hout << AllNumber << endl;
Hout << endl;

// Hamiltonian matrix of the cubic structure
double H[AllNumber][AllNumber]; // tb[][] is Tight-binding integrals for initial cubic cell

```



```

for (i = 0; i < AllNumber; i=i+2) {
  for (j = 0; j < AllNumber; j=j+2) {
    if (i==j) {
      H[i][j] = -1.2738; // when i = j and i&j are even number, H is ep = -1.2738
      //cout << "ptest-1:" <<tb[i][j] << endl ;
    }
  }
}
for (i = 1; i < AllNumber; i=i+2) {
  for (j = 1; j < AllNumber; j=j+2) {
    if (i==j) {
      H[i][j] = 3.6697; // when i = j and i&j are odd number, H is es = 3.6697
      //cout << "stest1:" <<tb[i][j] << endl ;
    }
  }
}
for (i = 0; i < AllNumber; i++) {
  for (j = i+1; j < AllNumber; j++) {
    double pos = dist(lon4[i].posx, lon4[i].posy, lon4[i].posz, lon4[j].posx, lon4[j].posy,
lon4[j].posz);
    if (pos > 0 && pos < 5.0) {
      if (lon4[i].type + lon4[j].type == 2) {
        H[i][j] = 0.1587; // when atoms are both Se(1)(lonm[i]+lonm[j]=2), H is tpp =
0.1587
        //cout << "tpptest-2:" <<tb[i][j] << endl;
      }
      else if (lon4[i].type + lon4[j].type == 0) {
        H[i][j] = -0.1608; // when atoms are both Cd(0)(lonm[i]+lonm[j]=0), H is tss =-
0.1608
        //cout << "tsstest2:" <<tb[i][j] << endl;
      }
      else if (lon4[i].type + lon4[j].type == 1) {
        H[i][j] = 1.1396; // when atoms are Cd(0) and Se(1)(lonm[i]+lonm[j]=1), H is tsp
=1.1396
        //cout << "tsptest5:" <<tb[i][j] << endl;
      }
    }
  }
  else{
    H[i][j] = 0.0; // when bond order further than 2 bonds, there is no interactions, H is
0
    //cout << "0test:" <<tb[i][j] << endl;
  }
}
}
for (i = 1; i < AllNumber; i++) {
  for (j = 0; j < i; j++) {
    H[i][j] = H[j][i];

```

```
    }  
  }  
  
  //Print Hamiltonian Matrix of the cubic structure  
  //cout << "*****" << endl;  
  //cout << "New Hamiltonian" << endl;  
  for (i = 0; i < AllNumber; i++) {  
    for (j = 0; j < AllNumber-1; j++){  
      //cout << fixed << setw(20) << setprecision(15) << H[i][j] << "\t";  
      Hout << fixed << setw(20) << setprecision(15) << H[i][j];  
    }  
    //cout << fixed << setw(20) << setprecision(15) << H[i][AllNumber-1] << endl;  
    Hout << fixed << setw(20) << setprecision(15) << H[i][AllNumber-1] << endl;  
  }  
  
  return 0;  
}
```



Curriculum Vitae

Mr. Kamon Suwannarat was born on May 16, 1994 in Nakhon Si Thammarat, Thailand. In 2011, he graduated from the Mathematics-Science program from Benjamarachutit School, Nakhon Si Thammarat, Thailand. Since 2012, he was admitted to a Bachelor's degree program in Chemistry, Faculty of Science, Chulalongkorn University and would complete the program in 2016. His address is 274, Moo. 5, Prik, Thungyai, Nakhon Si Thammarat 80240.

