

Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) calculations of fundamental optoelectronic properties of CdSe Quantum Dots.

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Total Amount Requested: \$10,050 (Travel: \$1,550, Salary: \$7,000, Equipment: \$1,500)

Project Description:

Past Results and Present Proposal

We have focused our initial DFT calculations on CdSe clusters. They are well studied experimentally and the results of our calculations can be readily compared to the existing data and thus we can also verify the robustness of our approach. We have previously used DFT and TDDFT to perform calculations on CdSe quantum dots with attached ligands. We have obtained results on $\text{Cd}_{10}\text{Se}_4(\text{X})_{12}(\text{L})_{12}$, $\text{Cd}_{20}\text{Se}_{10}(\text{X})_{20}(\text{L})_{20}$, $\text{Cd}_{35}\text{Se}_{20}(\text{X})_{30}(\text{L})_{30}$, and $\text{Cd}_{56}\text{Se}_{35}(\text{X})_{42}(\text{L})_{42}$ ($\text{X}=\text{OH}$, $\text{L}=\text{NH}_3$). TDDFT of the four clusters show absorption peaks centered at 4.59 eV, 4.00 eV, 3.54 eV and 3.44 eV, respectively. We previously reported that the results for $\text{Cd}_{35}\text{Se}_{20}(\text{X})_{30}(\text{L})_{30}$, and $\text{Cd}_{56}\text{Se}_{35}(\text{X})_{42}(\text{L})_{42}$ compare relatively well with reported experimental data of 3.54 eV and 3.26 eV for similar sized clusters. The cores of the optimized structures maintain the tetrahedral structures of the starting geometries to a large degree, also supported by experimental pair distribution function (pdf) structure data. Some of the data from our past efforts are summarized in Figure 1 below.

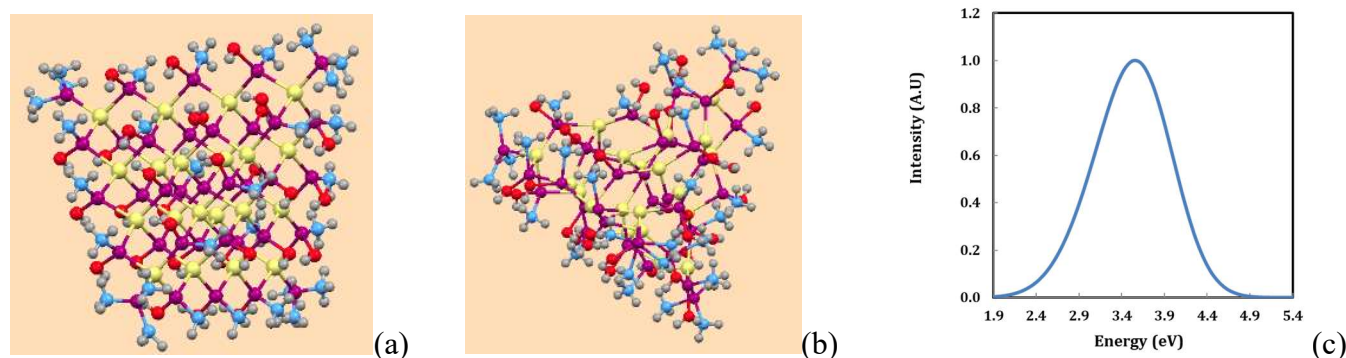


Figure 1. (a) Input structure of $\text{Cd}_{35}\text{Se}_{20}(\text{X})_{30}(\text{L})_{30}$, (b) DFT optimized structure of $\text{Cd}_{35}\text{Se}_{20}(\text{X})_{30}(\text{L})_{30}$, (c) TDDFT absorption peak for $\text{Cd}_{35}\text{Se}_{20}(\text{X})_{30}(\text{L})_{30}$ showing the corresponding energy of 3.54 eV.

Obtaining the ground state structure for the larger cluster of interest, $\text{Cd}_{84}\text{Se}_{56}(\text{X})_{56}(\text{L})_{56}$, remains a challenge. However, TDDFT of an intermediate structure of substantially lower energy shows an absorption peak at 3.18 eV, compared to the experimental value of 3.04 eV. This work seeks to fully optimize the larger, $\text{Cd}_{84}\text{Se}_{56}(\text{X})_{56}(\text{L})_{56}$, and to probe its electronic properties via TDDFT.

Pedagogical Measurable Goals and Impact on Teaching at Lincoln University

For the past 10 years or so, I have taught MAT313 (Numerical Analysis). Numerical Methods introduces students to modern computational algorithms for the numerical solution of a variety of applied mathematics problems. Density Functional Theory (DFT) is a multi-faceted comprehensive tool which probes whether a given material system is stable or not by minimizing the system's geometrical energy. Although the full features of the calculations involved can be quite complex, certain global aspects of the approach can be incorporated in undergraduate courses such MAT313, and indeed also in another course the Department of Mathematical Sciences seeks to revive, MAT212 (Mathematical Modeling).

The pedagogical thrust of my research is also evidenced by the fact that I have brought along two of our students who were Engineering Science majors to my summer research projects at Brookhaven National Laboratory on Long Island New York. I also managed to recruit a very smart and hardworking Computer Science major from Cheyney University the following summer. His contribution to the project was pivotal.

Timeline

Summer 2021 – Beginning of May: Recruitment and Orientation of Student Assistant

Summer 2021 – End of May: Train Student Assistant in the use of IQmol and Mercury to construct input files for calculations

Summer 2021 – Mid June: Resume submission of the Gaussian scripts on the CFN super cluster

Summer 2021 – July: Continue submission of the Gaussian scripts on the CFN super cluster

Summer 2021 – August: Hold consultative zoom conference calls with CFN collaborator. These meetings will also include the student assistant

Fall 2021 – Start to work on manuscript, including compiling previous data

Fall 2021 – Start preparing inclusion of student assistant assignment into MAT313

Spring 2020 – January to February: Begin preparation of conference proceedings presentation focusing on aspects of the work done under the Faculty Development Grant with student assistant/collaborator.

Summative Assessment of Success of Project:

By the end of summer, we hope to have achieved complete optimization of the $\text{Cd}_{84}\text{Se}_{56}(\text{X})_{56}(\text{L})_{56}$ quantum dot. At that time, a comprehensive report of the work done will be produced. We will also commence preparation of a conference proceeding presentation. Parallel work in the Fall of 2021 will focus on incorporating the results of optimizing $\text{Cd}_{84}\text{Se}_{56}(\text{X})_{56}(\text{L})_{56}$ into the existing results of the smaller quantum dots as we prepare the larger complete journal article to be published in the journal *Nanotechnology*.

The experience working with the student assistant will also inform how and which parts of the assignments that he or she accomplishes can be used as projects for MAT313. Ultimately, assessment of the success of the project will be the submission of the results for publication as a journal article.

Conference Proceedings and Journal Publication

The final results of the research will be presented at the Materials Research Society (MRS) either in Fall Meeting which will be held November 28 – December 3, 2021 in Boston, Massachusetts, or the Spring 2022 Meeting which will be held May 8-13, 2022 in Honolulu, Hawai'i. The overall outcome of the project accumulated over the past few summers will be published as a journal article in *Nanotechnology*, a journal published by IOP (Institute of Physics) Publishing (<https://iopscience.iop.org/journal/>). The intent to submit our work has already been communicated to the publisher by myself and my collaborator at the Center for Functional Nanomaterials (CFN) at BNL.

Appendix:

Density Functional Theory

Density Functional Theory is a quantum chemical-mechanical protocol that seeks to find solutions to Schrödinger's equation, the most fundamental of equations which describes the behavior of atoms and molecules at the quantum level. For any materials system, determining its ground-state energy is fundamental to ultimately understanding its properties. The overall total energy of the system depends on the energy of its constituent parts, the mechanics of its molecules, atoms and their electrons. Specifically, the collection of molecules, atoms and their electrons in a system determines the energy of the system through their mechanics and locations, which leads to the development of the structure-property-function relationship for any given material. One form of Schrödinger's equation which describes multiple electrons interacting with multiple nuclei of the atoms is (1):

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(r_i) + \sum_{i=1}^N \sum_{j < i} U(r_i, r_j) \right] \psi = E\psi. \quad 1$$

The first term in the brackets of equation 1 above defines the kinetic energy of each electron, the second term defines the interaction energy between each electron and the collection of atomic nuclei, and the last term defines the interaction energy between different electrons. The electronic wave function is, ψ , which is in actuality a function of each of the spatial coordinates of the N electrons so that $\psi = \psi(\vec{r}_1, \dots, \vec{r}_N)$. E is the ground-state energy of the electrons. Since the number of electrons N is considerable larger than the number of nuclei in a material, the calculations for solving Schrödinger's equation for multi-component systems is quite daunting. For example, the full wave function for a cadmium selenide molecule, CdSe, is a 246-dimensional function (3 dimensions for each of the 82 electrons). In practice, we cannot directly observe the wave function for any particular coordinates of a system, but we can measure the probability that the N electrons are at a particular set of coordinates, $\vec{r}_1, \dots, \vec{r}_N$. A quantity related to this probability is the density of electrons at a particular position in space, $n(\vec{r})$, given by (1):

$$n(\vec{r}) = 2 \sum_i \psi_i^*(\vec{r}) \psi_i(\vec{r}). \quad 2$$

In equation 2, $\psi^*(\vec{r})$ is the complex conjugate of the wave function $\psi(\vec{r})$ since the wave function is a complex quantity. As previously alluded to, $\psi^*(\vec{r})\psi(\vec{r})$ is the probability that an electron with wave function $\psi(\vec{r})$ is located at position, $\vec{r}$.

Density functional theory (DFT) is entirely based on two theorems which were proved by Kohn and Hohenberg (2) and a set of subsequent equations derived by Kohn and Sham (3). The first theorem states that (2): *The ground-state energy from Schrödinger's equation is a unique **functional** of the electron density.* The theorem is significant because it states that the ground-state energy E is a function, a **functional**, of the electron density, $n(\vec{r})$. The second theorem states that (2): *The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solutions of the Schrödinger equation.* That means if we know the "real" functional form, then we can minimize the energy from the functional by varying the electron density until we find the more descriptive electron density, the target electron density. DFT as it is based on these theorems is a powerful tool because it means instead of finding the $3N$ dimensional wave function solution to Schrödinger's equation, we can find the electron density which is a function of only three spatial variables. The actual task and process of finding the target electron density was demonstrated by Kohn and Sham when they showed that it can be accomplished through an approach that solves a set of equations in which each equation

deals with a single electron. Their approach led to an algorithm in DFT that solves the set of equations in a *self-consistent* iterative manner (3).

Budget

The bulk of the funds provided towards supplies will go to purchasing a laptop with a reasonable fast CPU dedicated to the use with the Ubuntu Linux operating system. Presently, we have identified a laptop available from (<https://laptopwithlinux.com/product/clevo-nh77dpq/>). At the cost of **\$1,500.00**, it is a 17.3-inch FHD LED 60Hz Clevo NH77DPQ with 10th generation Intel Core i7 processor and NVIDIA GeForce RTX3060 capable of heavier graphics applications. With up to 64GB of DDR4 working memory and fast NVMe PCIe SSDs, this Clevo laptop makes the best choice for running multiple virtual machines (VMs).

References:

1. D. S. Sholl and J. A. Steckel, *Density Functional Theory – A Practical Introduction*, John Wiley & Sons, Hoboken, New Jersey, 2009.
2. P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, 136, Issue 3B, 864-871.
3. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, 140, Issue 4A, 1133-1138.