Background

A number of years ago, I decided to broaden my scope of research by doing computational materials science. This proposal represents ongoing efforts to not only perfect my computational skills in ab initio methods of materials science, but also to understand every theoretical aspect of the CdSe materials systems.

The attached abstract captures the details of the history of the project. In summary, we have previously benchmarked our Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations by performing calculations on CdSe quantum dots (QDs) of different sizes with attached ligands. Geometry optimization was successfully done at the PBE1PBE level of theory in a Gaussian 16 environment on five different sized nanocrystals which are: $Cd_{10}Se_4(X)_{12}(L)_{12}$, $Cd_{20}Se_{10}(X)_{20}(L)_{20}$, $Cd_{35}Se_{20}(X)_{30}(L)_{30}$, $Cd_{56}Se_{35}(X)_{42}(L)_{42}$, and $Cd_{84}Se_{56}(X)_{56}(L)_{56}$ (X=OH, L=NH_3).

TDDFT calculations of the five clusters show first excitations at 3.78 eV, 3.43 eV, 3.24 eV, 3.04 eV and 2.77 eV respectively. These data are summarized in Table 1 (see appendix). When compared with published experimental data for similar sized clusters, the energies for $Cd_{35}Se_{20}(X)_{30}(L)_{30}$, $Cd_{56}Se_{35}(X)_{42}(L)_{42}$, and $Cd_{84}Se_{56}(X)_{56}(L)_{56}$ are systematically lower by an average of 0.26 eV. We believe this level of discrepancy is within reasonable margins of error for DFT calculations and therefore validates our approach to DFT.

We also calculated absorption spectra from TDDFT of the five optimized clusters mentioned above and the results are shown in Figure 1 (see appendix). Cluster size dependent red-shifting is clearly observed as expected. This is another significant result, which provides evidence about the robustness of our calculations.

Although visual inspection of the structures of the optimized nanocrystal nanoclusters show that the tetrahedral cores of the as-built input structures remain, nevertheless there are significant deformations and distortions in the final structures. More importantly, and in most cases, there is systematic rearrangement in which some of the surface Cd atoms are moved to the interior of the nanoclusters and the inner Se atoms are pushed to the surface.
The example of these distortions can be seen in Figure 2 (see appendix) below showing the before and after structures of $Cd_{10}Se_4(X)_{12}(L)_{12}$, $Cd_{20}Se_{10}(X)_{20}(L)_{20}$, and $Cd_{35}Se_{20}(X)_{30}(L)_{30}$. The as-built input model structures cut from bulk Wurtzite CdSe before ligands are attached show clean symmetric tetrahedral clusters with terminal Cd atoms, with the corner Cd atoms of the tetrahedra prominently visible. On the other hand, optimized nanoclusters from which the ligands are stripped clearly show distortions as shown in Figure 3 (see appendix). Importantly, the corner Cd atoms bonds are bend almost being pushed into the core and bring the inner Se atoms to the surface. This has the effect of making the cores spherical, away from the original trigonal pyramidal crystals.

Project Proposal

This proposal seeks to explore in detail the reasons why DFT optimization causes the distortions mentioned earlier. Specifically, the project will focus on $Cd_{10}Se_4(X)_{12}(L)_{12}$, $Cd_{20}Se_{10}(X)_{20}(L)_{20}$, and $Cd_{35}Se_{20}(X)_{30}(L)_{30}$, to investigate why the as-built input structures cut from bulk Wurtzite CdSe having clean symmetric tetrahedral clusters clearly show distortions in which the corner Cd atoms bonds are bend so as to be pushed into the core and bring the inner Se atoms to the surface. It is apparent that these distortions have the effect of making the cores spherical, away from the original trigonal pyramidal crystals. The question we seek to answer is whether these distortions are truly systematic consequences of doing DFT, and if so, why they happen.

Measurable goals and objectives of the project:

We will built different types of input structures of the three different sized CdSe nanoclsuters by varying the terminating atoms between Cd and Se and observe the output structures upon geometry optimization. Careful analysis of the input/output structures will be made, as well as paying attention to the impact of the location of attached ligands.

As mentioned in the abstract, we have previously used the commercial Gaussian 16 software with licensing access obtained through a grant. Although Gaussian 16 is , we seek to use freely available academic and free open source software (FOSS) most of which implement DFT in terms of the all-electron full-potential linearized augmented-plane-wave (LAPW) method, such as, FLEUR (MIT based free plane-wave method), ELK (VASP like free version) , DMol3 (free version), Yambo, and NWChem.

The timeframe for the project:

We believe that the defined scope of the project will yield reportable results that address the question that has been posed by the end of summer 2025.

How the project will enhance teaching and research at Lincoln:

I have previously engaged students from Lincoln University and Cheney University to participate in the project as a way of enhancing their chemistry, computer science, and engineering science training.

How the outcome of the project will be measured:

We believe the outcome of the project will speak for itself in the sense that a clear correlation between the input and output structures will have been established as a result of DFT optimization.

How, when, where, and with whom the project's outcome will be shared:

A report will be generated at the end of the research activities and shared with the responsible committee as per stipulated deliverables and expectations of the FRDC.