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DR. MOSES HAIMBODI

Thursday, March 30
12:30p.m.-1:30p.m.

Geometric Optimization of CdSe Molecular Clusters using DFT

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Who I Am?

Moses W. Haimbodi

2005-Present: Lincoln University

Chair & Associate Professor, Mathematical Sciences -
Lincoln University Pennsylvania

Education:

PhD, Materials Science & Engineering
University of Delaware, Delaware
MS, Materials Science & Engineering
Marquette University, Wisconsin
BA, Physics
Saint Olaf College, Minnesota

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I. Background – Research Interests

II. Laboratory vs Theory

III. DFT – Method

IV. CdSe as Model System

V. Implementation of DFT

VI. Results and Comparison to Experiments/Other work

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Areas of Interest and Expertise:

Interests:

Electronic materials, especially for solar cells
Computational Materials Science
Protein Dynamics

Expertise*:*

High vacuum systems, including a PVD system for deposition of thin I-III-VI materials for PV applications, and characterization thereof.
UV-Vis Spectrometry, Scanning Electron Microscope (SEM) with EDS
Transmission Electron Microscopy (TEM), Atomic Force Microscope (AFM), X-ray Diffractometer (XRD), Optical Spectrophotometry
Atomic Absorption Spectroscopy (AAS), Auger Electron Spectroscopy (AES)
X-ray Photoelectron Spectroscopy (XPS), Scanning Tunneling Microscopy (STM), Ellipsometry, Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR); Differential Scanning Calorimetry (DSC), Secondary Ion Mass Spectroscopy (SIMS)

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Electronic Materials

ASMA Haseeb, University of Malaya, Kuala Lumpur, Malaysia, Elsevier 2016

1. Semiconductors
2. Magnetic Materials and Superconductors
3. Optoelectronic and Photonic Materials
4. Piezoelectric, Ferroelectric and Thermoelectric Materials
5. Polymeric Materials and Flexible Electronics
6. Sensors, Actuators and Micro Electro Mechanical Systems (MEMS)
7. Electronic Materials for Energy Applications
8. Microelectronic Fabrication and Device Materials
9. Synthesis and Characterization of Electronic Materials
10. Theory, Modeling and Simulation of Electronic Materials

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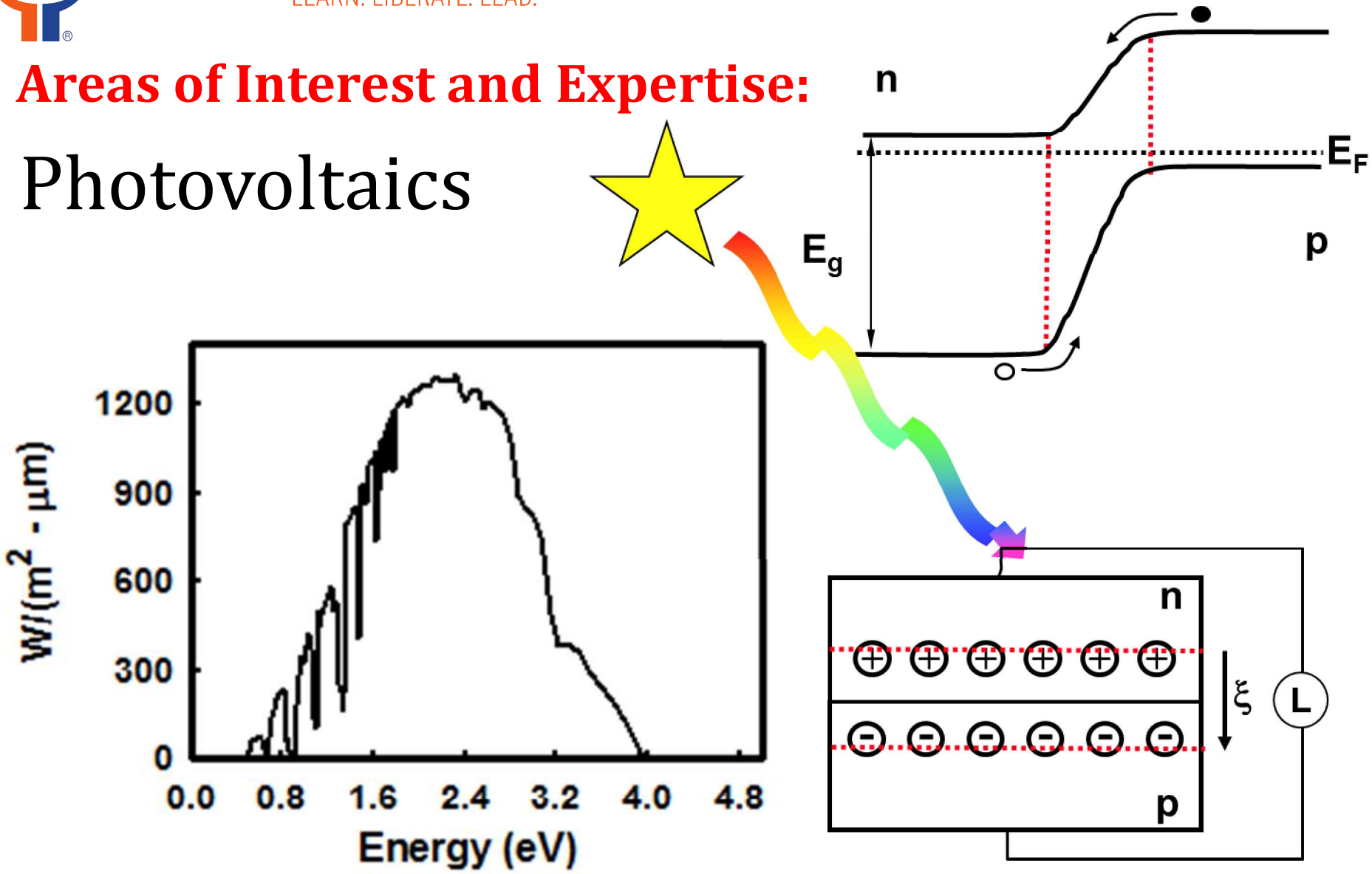
Areas of Interest and Expertise:

Photovoltaics



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Areas of Interest and Expertise:

Photovoltaics

Maximize J_{sc}

- Significant to ***efficiently*** absorb as ***much*** of the incident light
  - High Absorption coefficient, α (cm^{-1})
  - Small band gap, E_g (eV)
  - High minority carrier life time, τ (s) and mobility, μ (cm^2/V-s)

Maximize V_{oc}

- Increase E_g
- Significant to reduce J_o

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Electronic Functional Materials

Structure

Properties

FUNCTION

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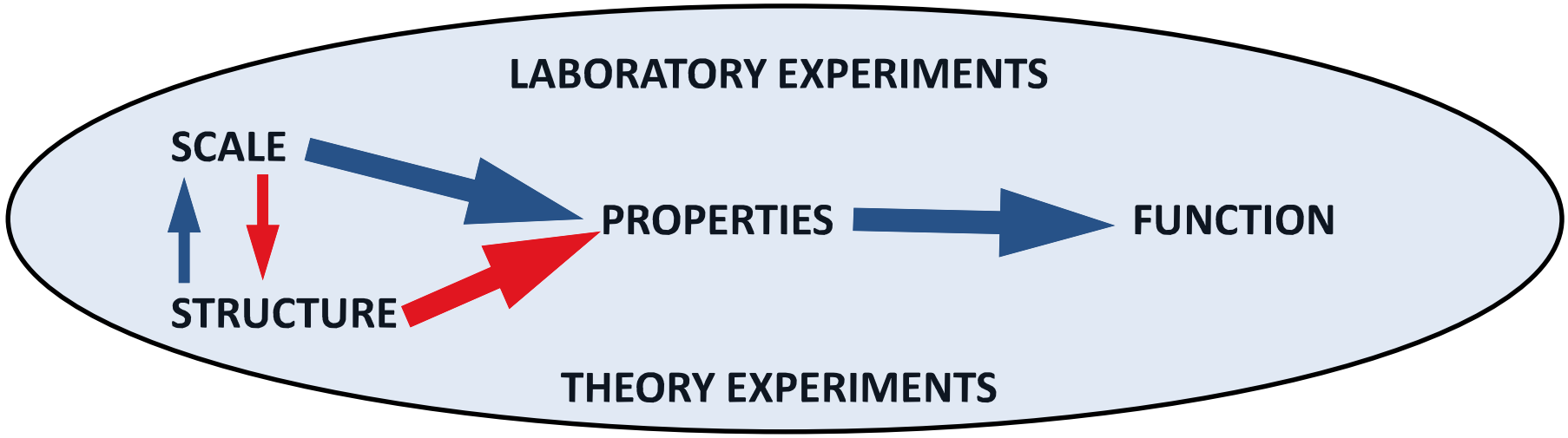
Density Functional Theory of CdSe Nano-clusters

ELECTRONIC FUNCTIONAL MATERIALS



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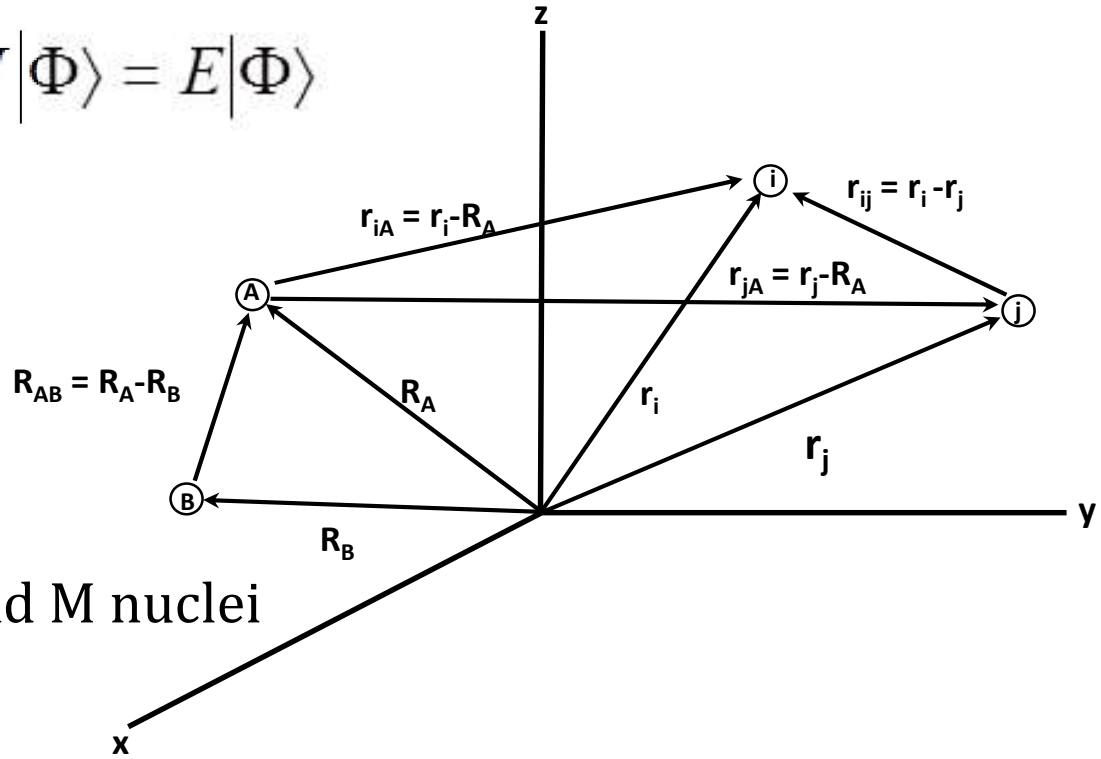
Density Functional Theory of CdSe Nano-clusters

Density Functional Theory

Schrödinger's Equation $H|\Phi\rangle = E|\Phi\rangle$



Hamiltonian for N electrons and M nuclei

$$H = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}$$

Density Functional Theory of CdSe Nano-clusters

Density Functional Theory

Hohenberg and Kohn Theorems:

1. The ground-state energy from Schrödinger's equation is a unique *functional* of the electron density.
2. The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.

⇒ one-to-one mapping between ground-state wave function and the ground-state electron density $E\left[n(\vec{r})\right]$

Density Functional Theory of CdSe Nano-clusters

Density Functional Theory

In terms of the single-electron wave function

$$E[\{\psi_i\}] = E_{known}[\{\psi_i\}] + E_{XC}[\{\psi_i\}]$$

$$E_{known}[\{\psi_i\}] = -\frac{\hbar^2}{m}\sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(\vec{r}) n(\vec{r}) d^3r + \frac{e^2}{2}\iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r d^3r' + E_{ion}$$

Kohn-Sham Equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \qquad n(\vec{r}) = 2\sum_i \psi_i^*(\vec{r})\psi_i(\vec{r})$$

a. **Define an initial, trial electron density, n(r)**
b. **Solve the KS equations using the trial electron density to find the single-particle wave functions**
c. **Calculate the electron density defined by the KS single-particle wave functions from (b), $n_{KS}(r)$**
d. **Compare the calculated electron density, $n_{KS}(r)$, with the initial trial electron density, n(r). If same, then this is the ground-state electron density. If not, update n(r) – somehow!**

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Density Functional Theory of CdSe Nano-clusters

Density Functional Theory

$V(\vec{r})$ defines the interaction between an electron and the collection of atomic nuclei

$$V_H(\vec{r}) = e^2 \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r'$$ Hartree potential: single electron – total electron density repulsion

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}(\vec{r})}{\delta n(\vec{r})}$$ Exchange-Correlation Potential ← finding this very difficult!

3N dimensions! → 3 dimensions!

"The development of functionals that more faithfully represent nature remains one of the most important areas of active research in the quantum chemistry community" – **David S. Sholl & Janice A. Steckel, Density Functional Theory, Wiley, 2009.**

$$V_{XC}(\vec{r}) = V_{XC}^{electron\ gas}[n(\vec{r})]$$

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Kohn–Sham (KS) Density Functional Theory (DFT)

- **Hohenberg–Kohn Theorem I**

The total energy can be calculated from a universal functional of the density.

Existence theorem

- **Hohenberg–Kohn Theorem II**

The correct density minimizes the energy functional.

Variational principle.

- **Kohn–Sham Theorem**

For each density exists a system of non-interacting particles in a local external potential with the same density.

Orbital picture.

Jürg Hutter, Department of Chemistry, University of Zurich

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Density Functional Theory of CdSe Nano-clusters

Density Functional Theory

Environment – Gaussian 16

Method:

Functional – PBE1PBE

The 1998 modified gradient-corrected correlation functional of Perdew, Burke and Ernzerhof.

Basis Sets:

LANL2DZ(Los Alamos National Laboratory 2 Double-Zeta) for Cd, and Se

3-21G for N,O, and H

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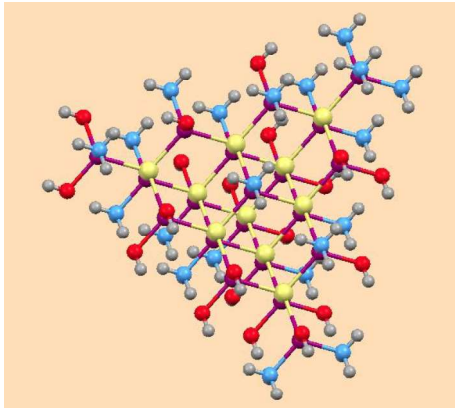
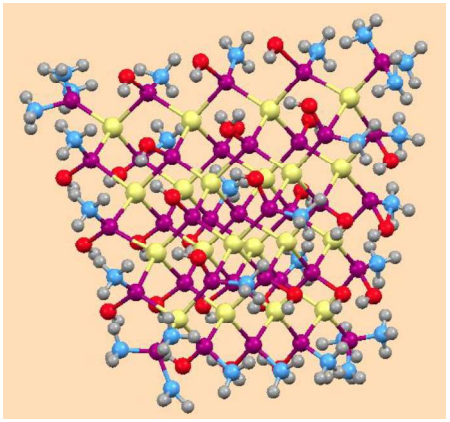
Density Functional Theory of CdSe Nano-clusters

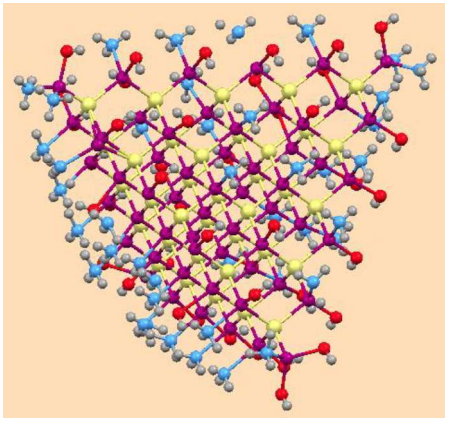
Input CdSe Structures/Geometries



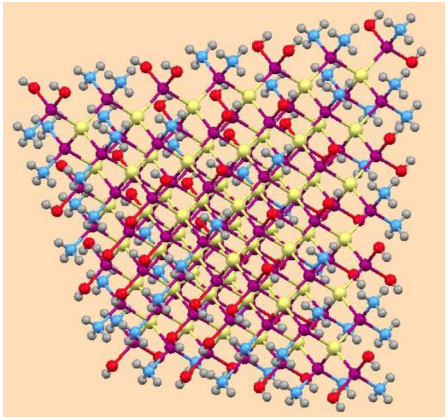
$Cd_{20}Se_{10}(OH)_{20}(NH_3)_{20}$



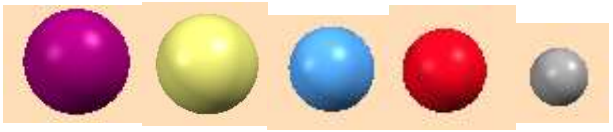
$Cd_{35}Se_{20}(OH)_{30}(NH_3)_{30}$



$Cd_{56}Se_{35}(OH)_{42}(NH_3)_{42}$



$Cd_{84}Se_{56}(OH)_{56}(NH_3)_{56}$



Cd Se N O H

Ligands:

-OH

NH_3

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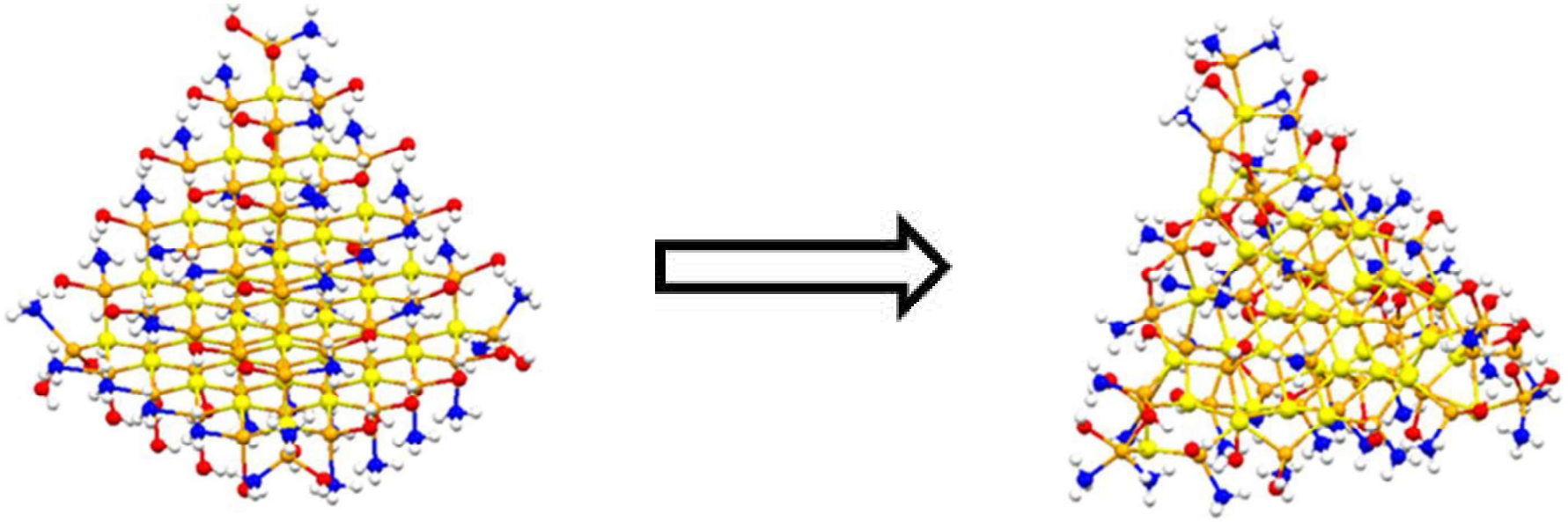
Visualization of the $Cd_{56}Se_{35}(NH_3)_{42}(OH)_{42}$ cluster before (left) and after optimization (right). There is some distortion on the surface ligands after optimization, but the core retains some of the tetrahedral configuration of the input structure. The spheres represent: Cd (light brown), Se (yellow), N (blue), O (red), and H (white).

Gaussian 16
PBE0
LANL2DZ



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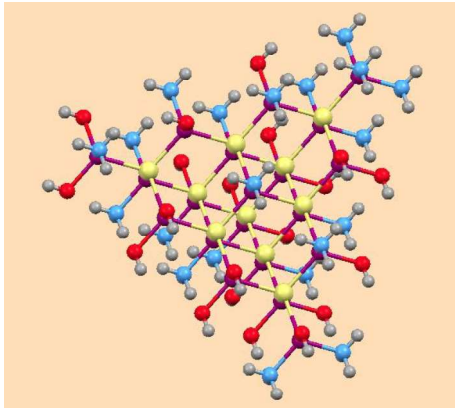
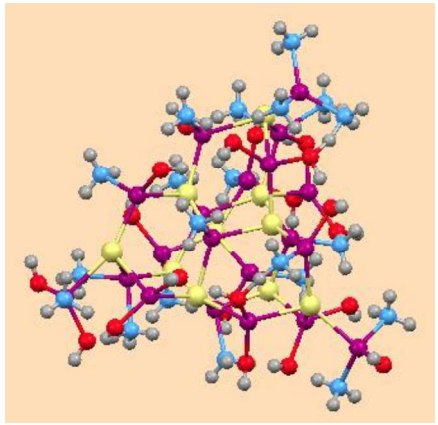
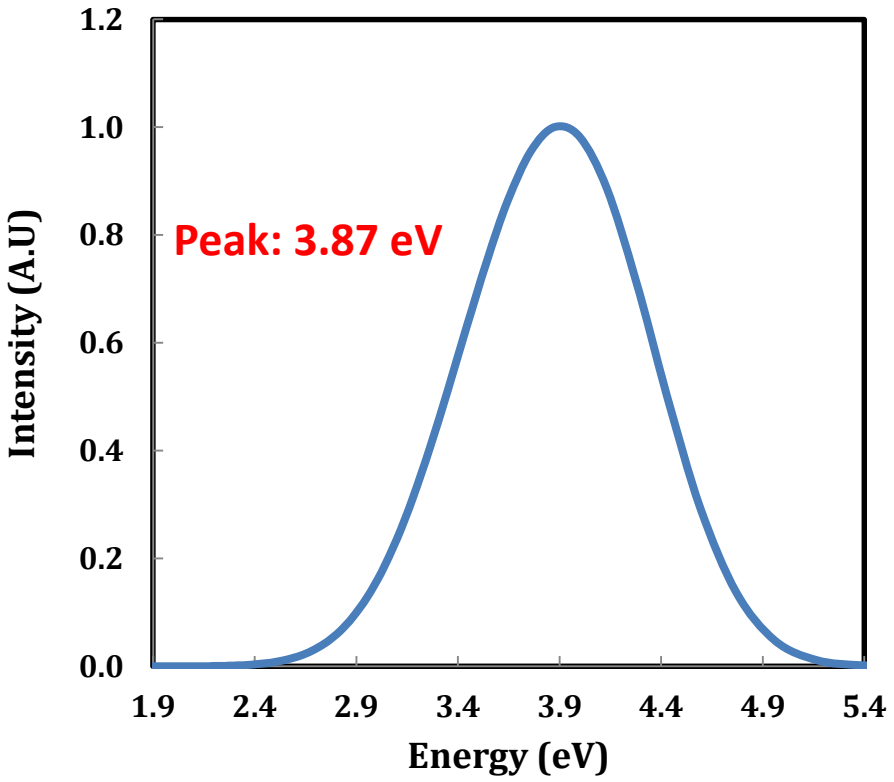
Density Functional Theory of CdSe Nano-clusters

Optimized Structures: $Cd_{20}Se_{10}(OH)_{20}(NH_3)_{20}$





Absorption from TDDFT with 40 transition states



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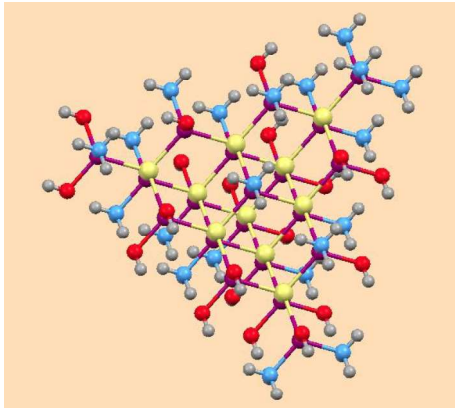

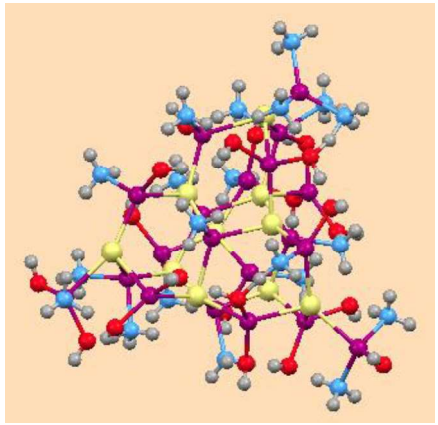

Time Dependent DTF:

The output files from Gaussian excited states calculations report the excitation energies and oscillator strength for each excited state:

Excited State 1: Singlet-?Sym 5.4863 eV
284.45 nm f=0.0002 <S**2>=0.000
20 -> 22 0.49950
21 -> 23 0.49950

$$\varepsilon_i(\tilde{\nu}) = \frac{\sqrt{\pi}\cdot e^2\cdot N}{1000\cdot \ln(10)\cdot c^2\cdot m_e}\,\frac{f_i}{\sigma}\,\exp\left[-\left(\frac{\tilde{\nu}-\tilde{\nu}_i}{\sigma}\right)^2\right]$$

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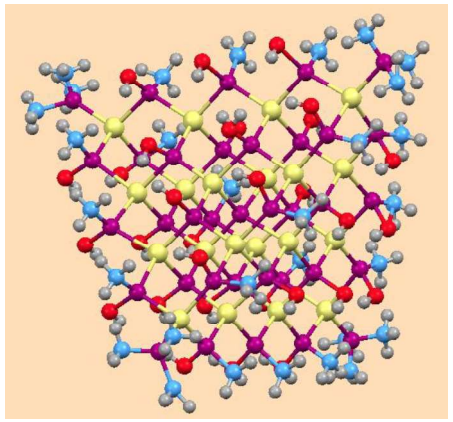

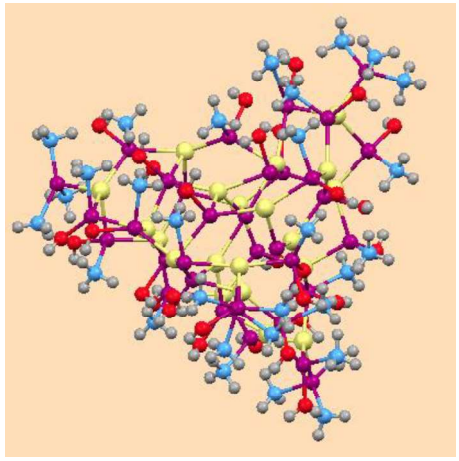

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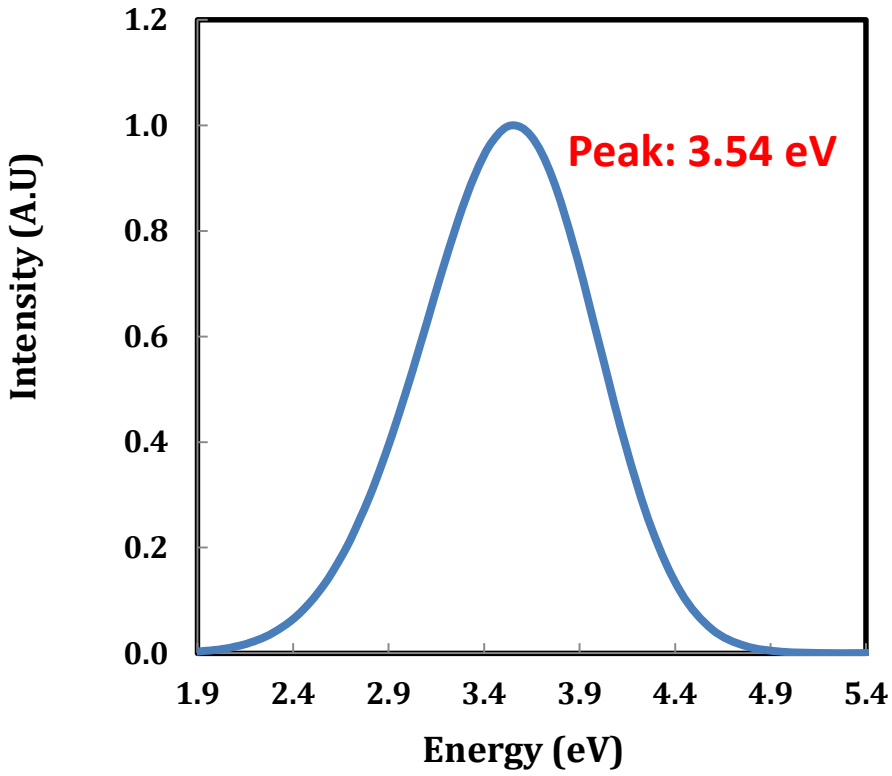

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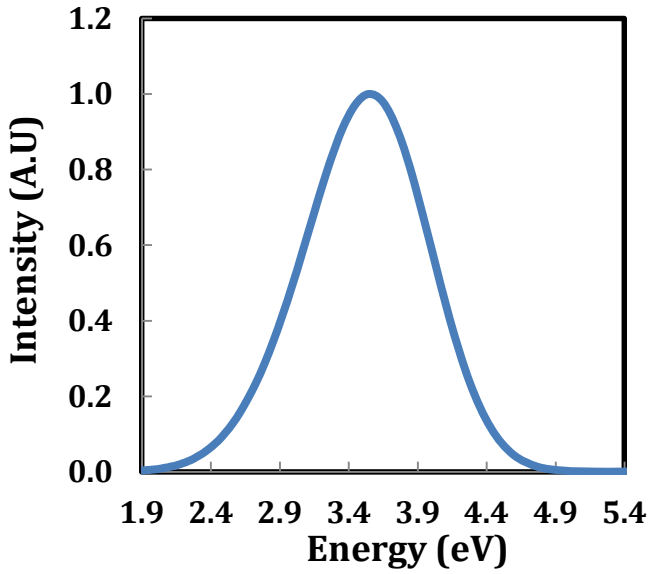
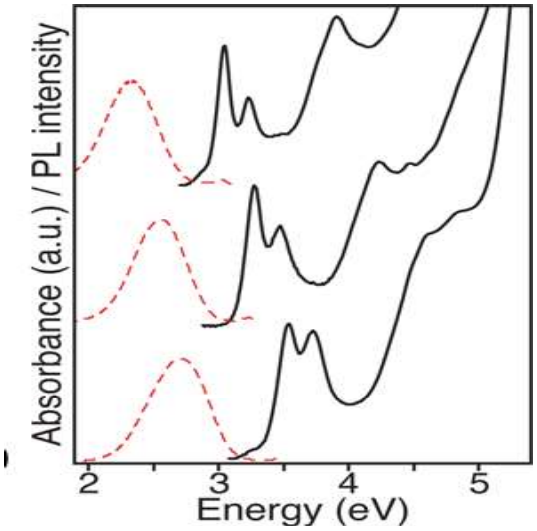
Density Functional Theory of CdSe Nano-clusters

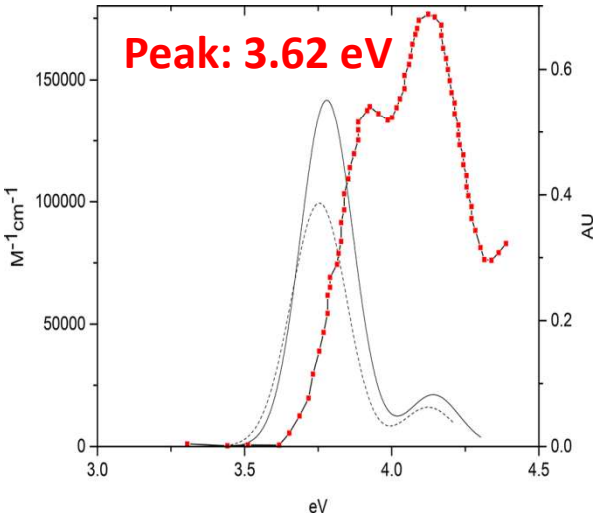
Optimized Structures: $Cd_{35}Se_{20}(OH)_{30}(NH_3)_{30}$

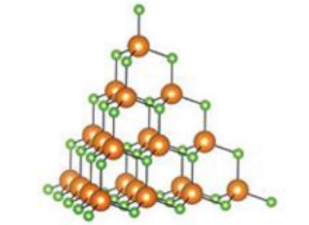
Peak: 3.54 eV



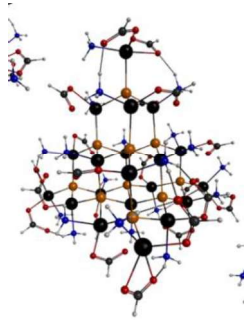


Peak: 3.62 eV





J. Phys. Chem. A 2018, 122, 6704–6712
Nguyen et al.



J. Am. Chem. Soc. 2014, 136, 10645–10653
Beecher et al.

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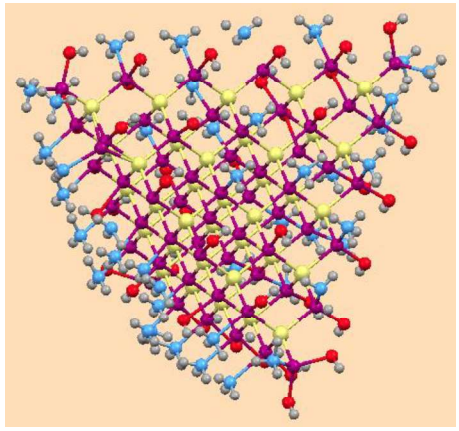
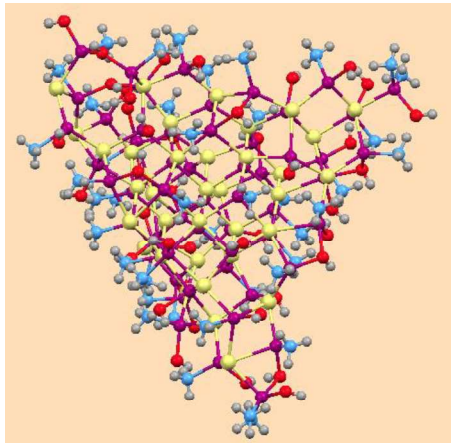
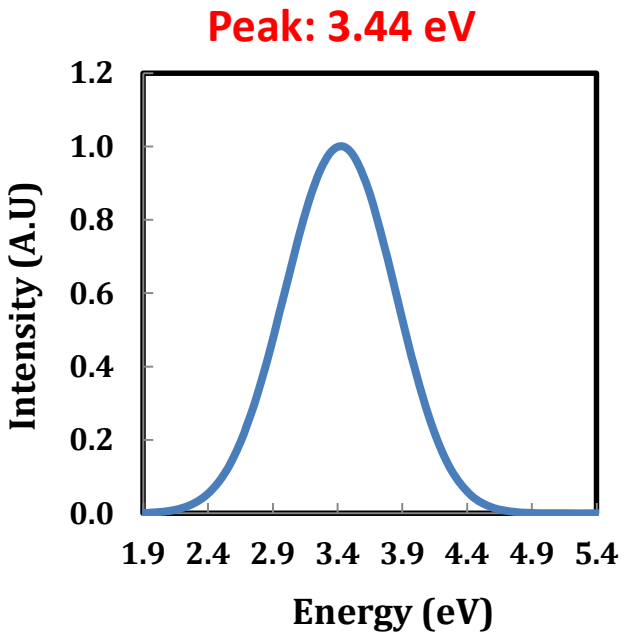
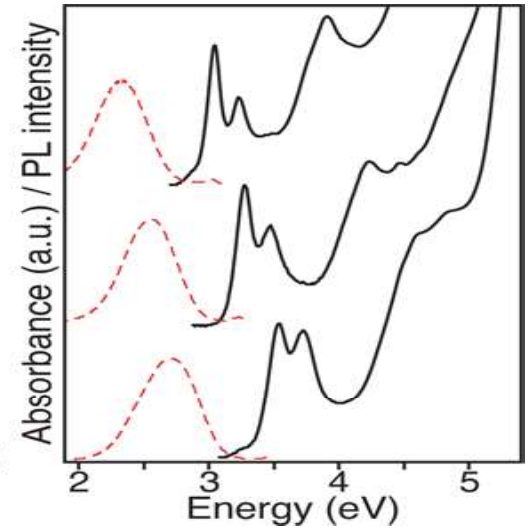
Density Functional Theory of CdSe Nano-clusters

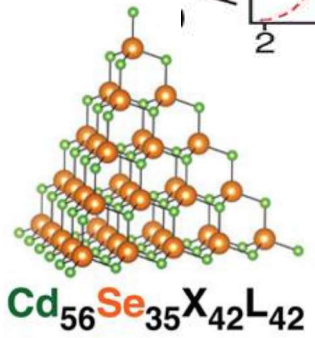
Optimized Structures: $Cd_{56}Se_{35}(OH)_{42}(NH_3)_{42}$











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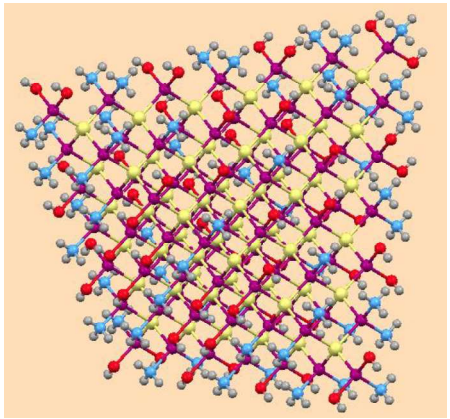
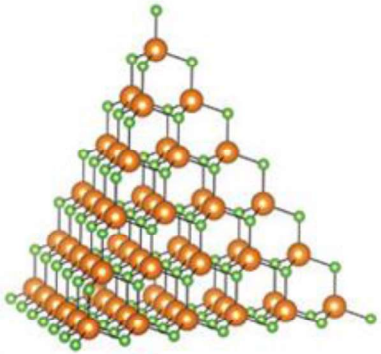
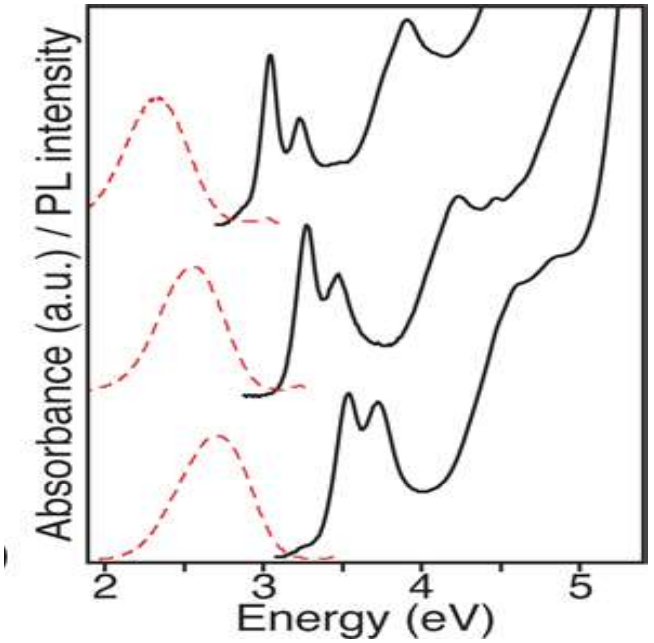
Density Functional Theory of CdSe Nano-clusters

Continuing CHALLENGE! Complete Optimization of $Cd_{84}Se_{56}(OH)_{56}(NH_3)_{56}$







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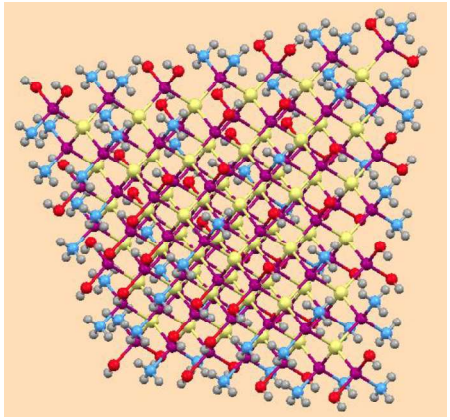

Exhausted linear combination of localized basis function approach: Gaussian 16

Implementing linear combination of plane wave (PW) approach: VASP & Elk LAPW

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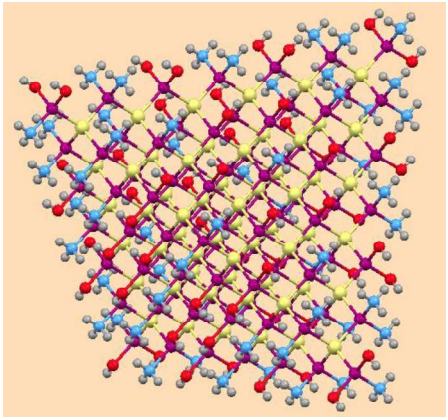

Elk LAPW Code:

"Elk is an all-electron full-potential linearized augmented-plane wave (FP-LAPW) code with many advanced features, and which has been in development for eight years. It is released under the GNU General Public License (GPL)"