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Simulations of CdSe Quantum Dots

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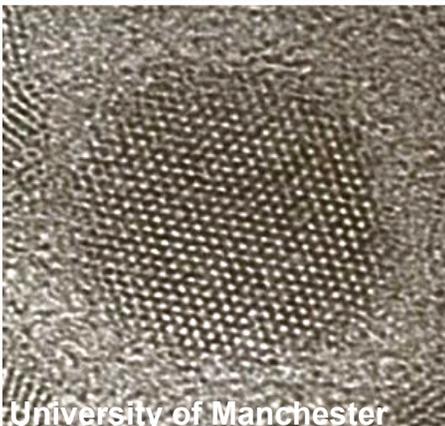
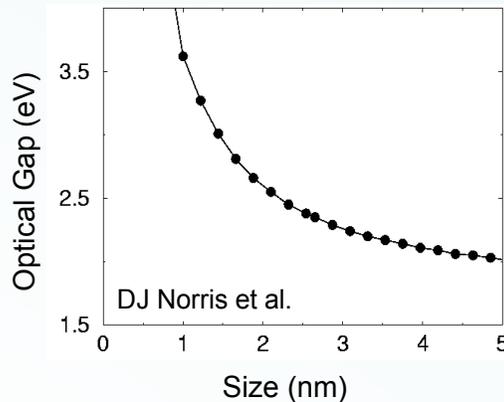
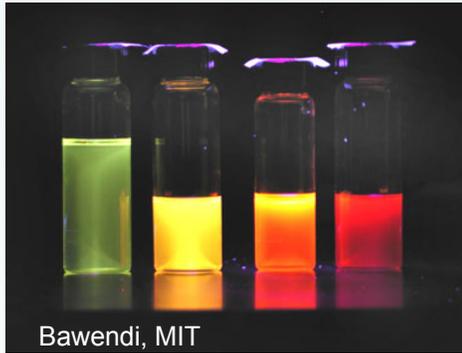
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Structural, Electronic, and Optical Properties of CdSe Nanocrystals: First-Principles Computations

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Optical Properties of CdSe Quantum Dots

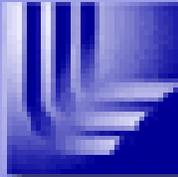


Remarkable Optical Properties

- CdSe Qdots have robust optical emission
- High Quantum Yields
- Predictable size dependence
- Insensitive to Surface Passivation

Questions

- What is the atomic structure?
(Surface can't be imaged in TEM)
- Why is the gap insensitive to passivation?
- Where are the nature of the band edge states?
- What is the origin of observed sub-gap emission?

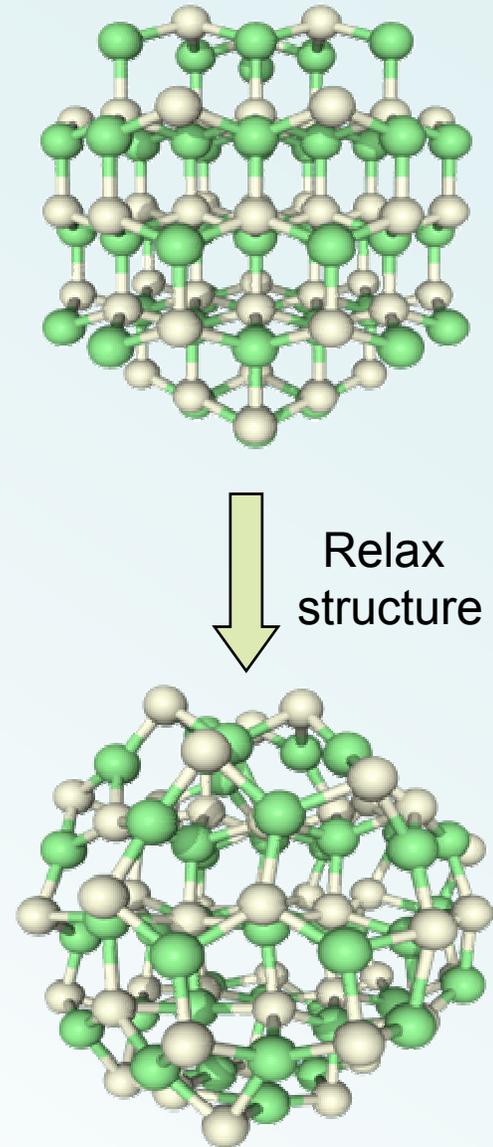


Previous Theoretical Investigations

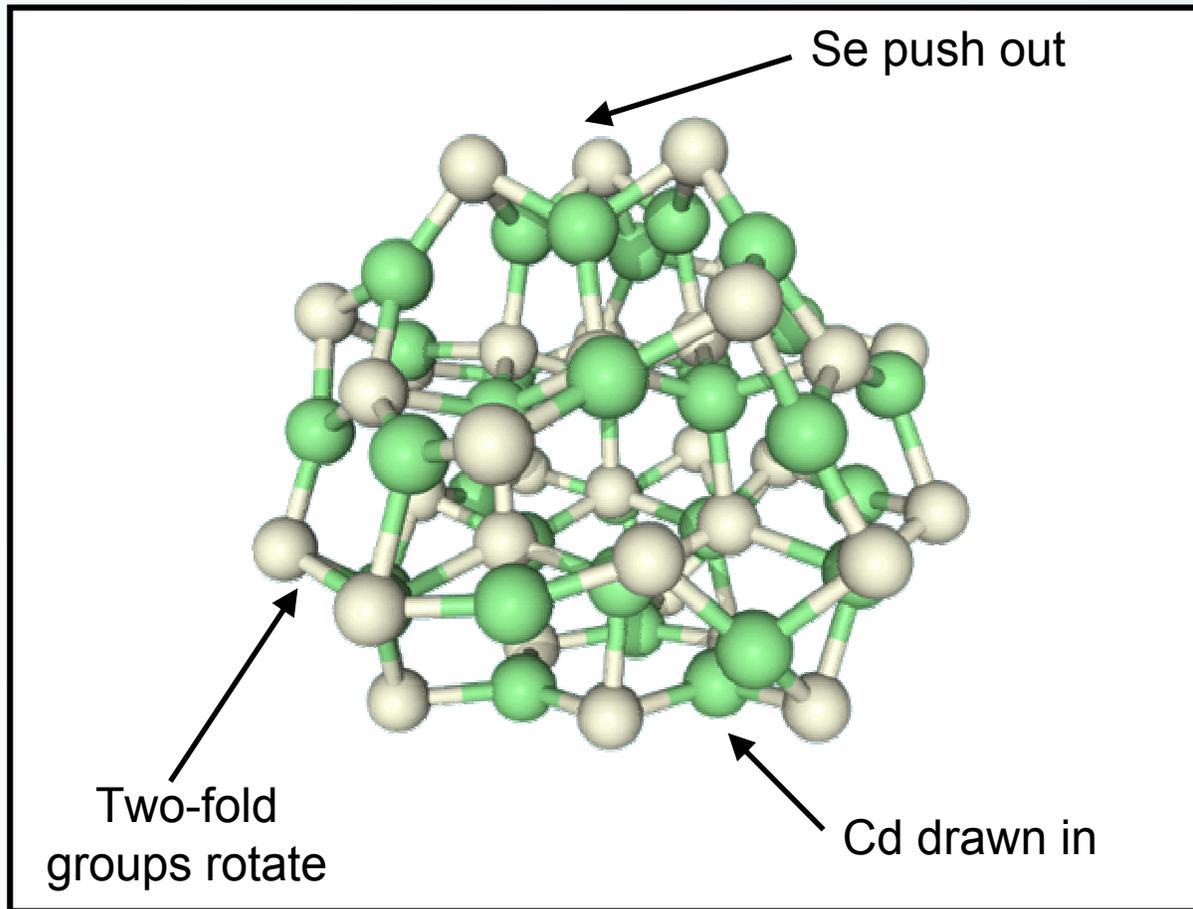
- **Effective Mass Calculations:**
A. Efros et al. Phys. Rev. B (1996)
- **Empirical Pseudopotentials:**
L.W. Wang and A. Zunger Phys. Rev. B (1996)
- **Empirical Tight Binding:**
P. Lippens and M. Lanoo, Phys. Rev. B (1990)
S. Pokrant and K.B. Whaley, Eur. Phys. Journ. (1999)
- **Density Functional Theory:**
C. Troparevsky *et al.* J. Chem. Phys. (2003)
P. Deglmann and R. Ahlrichs J. Chem. Phys. (2002)

Calculation Methods

- Atomistic description of Qdots
- *Ab-Initio* Density Functional Theory (GP Code, F. Gygi, LLNL)
- LDA and GGA(PBE) exchange-correlation functionals
- 18 Cd *s*, *p* and *d* valence electrons (not partial core correction)
- Semi local projection operators (not Kleinman Bylander)
- 35 Ry cutoff (50 Ry convergence checks)

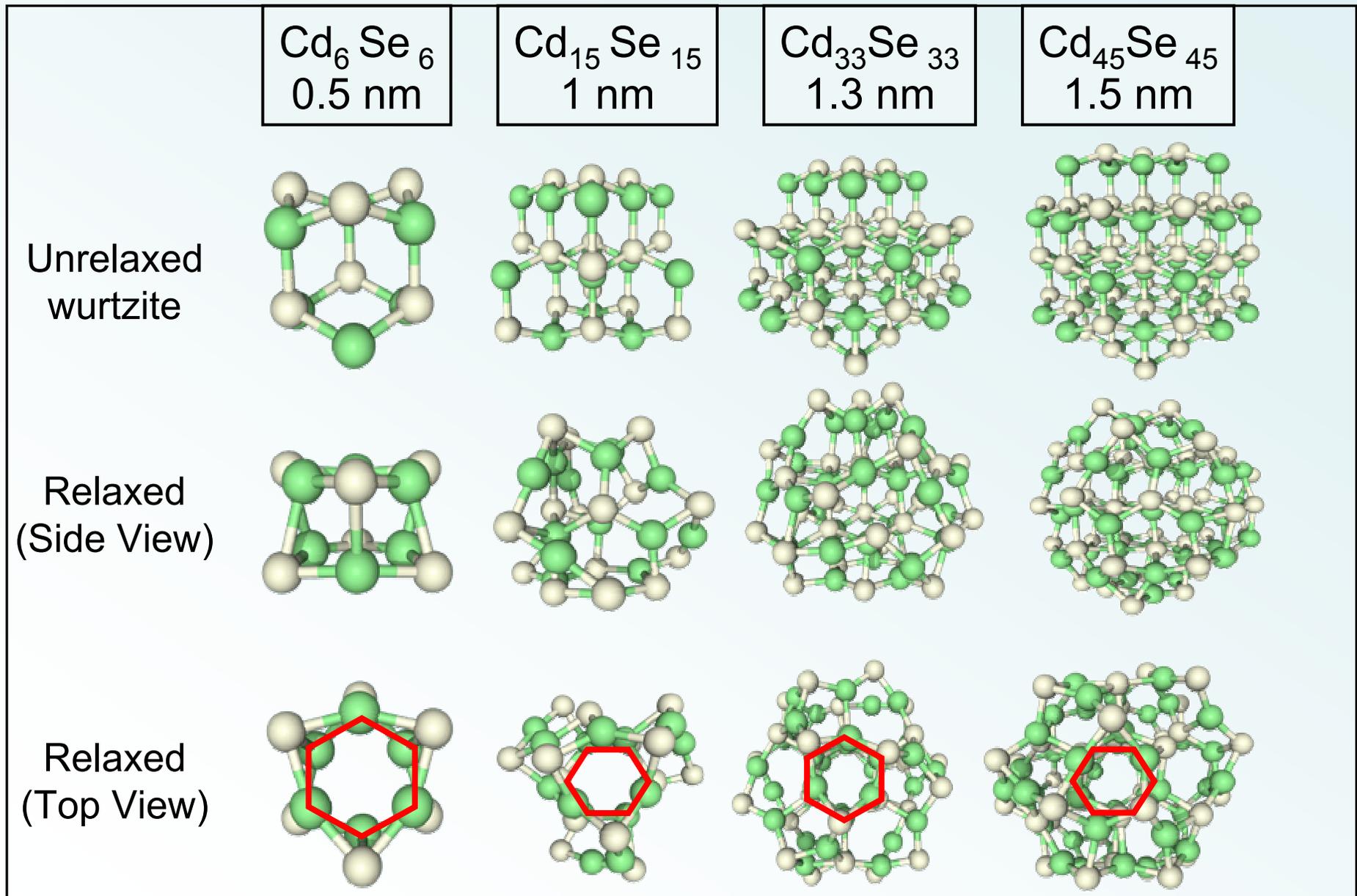


Relaxation of a 1.3 nm CdSe Q-Dot

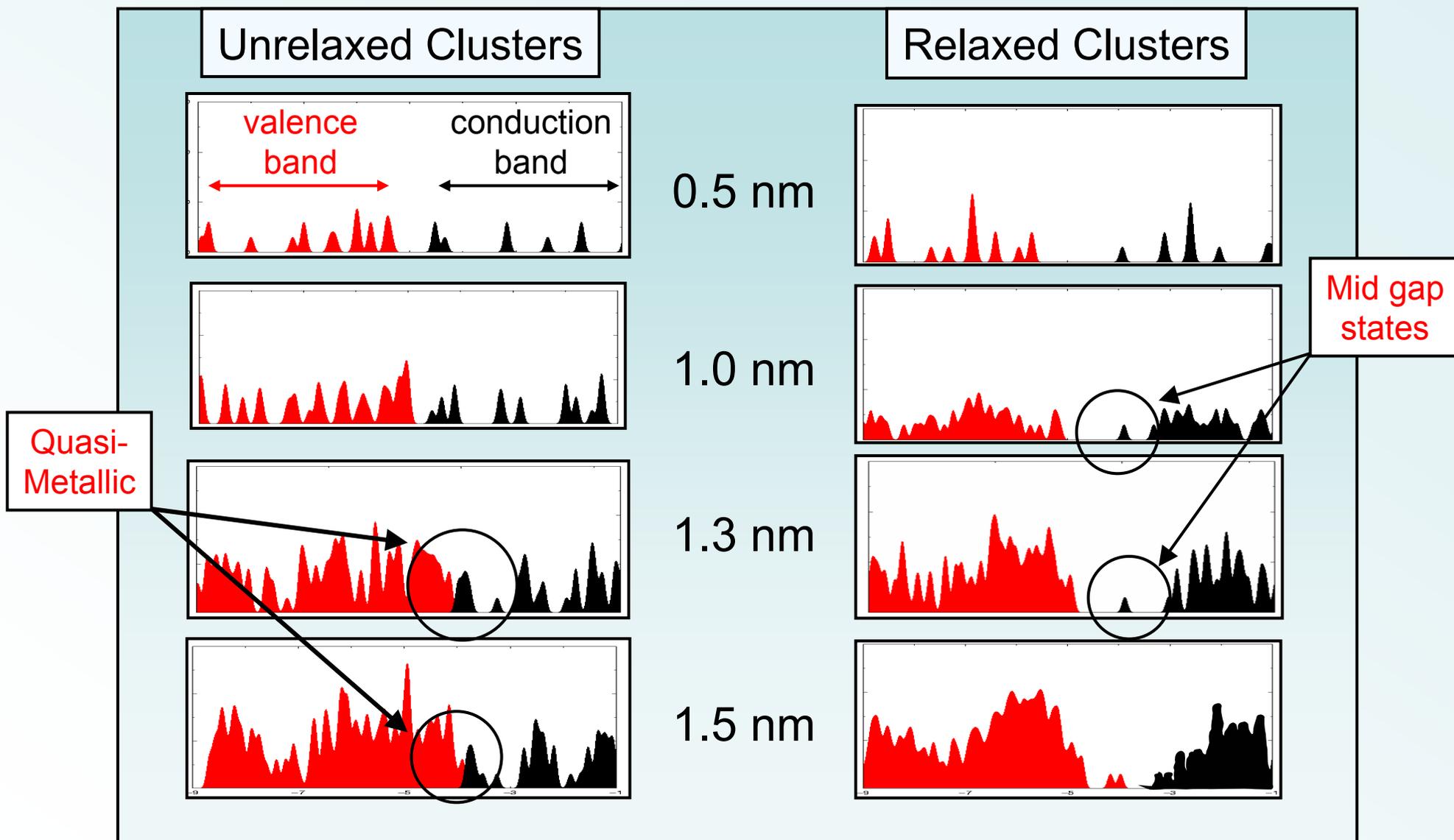


- Structure relaxes at zero temperature
- Cd atoms are drawn into the surface
- Se atoms push out from the surface
- Two-fold coordinated Cd atoms rotate round

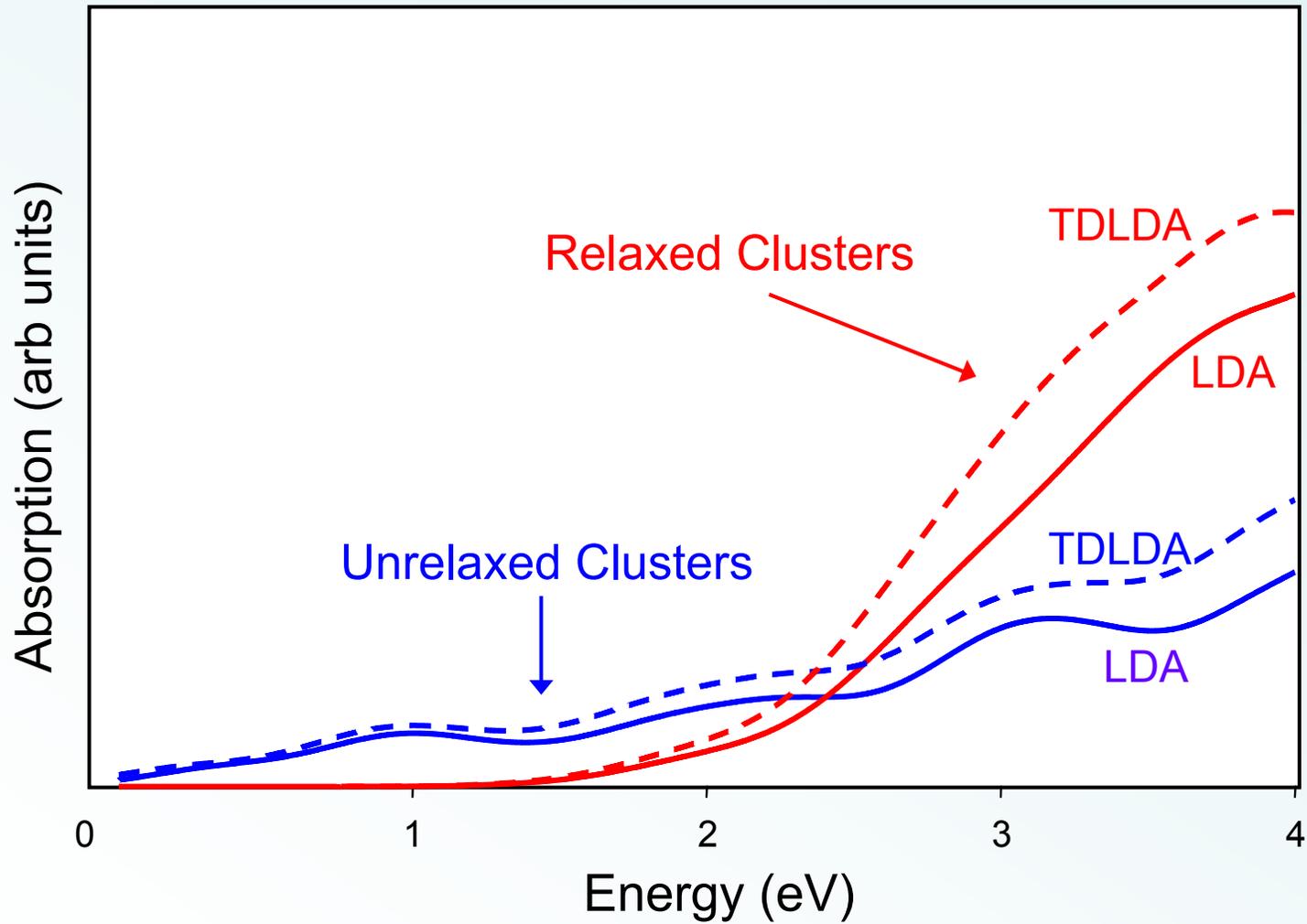
Relaxed CdSe Structures



Electronic Density of States

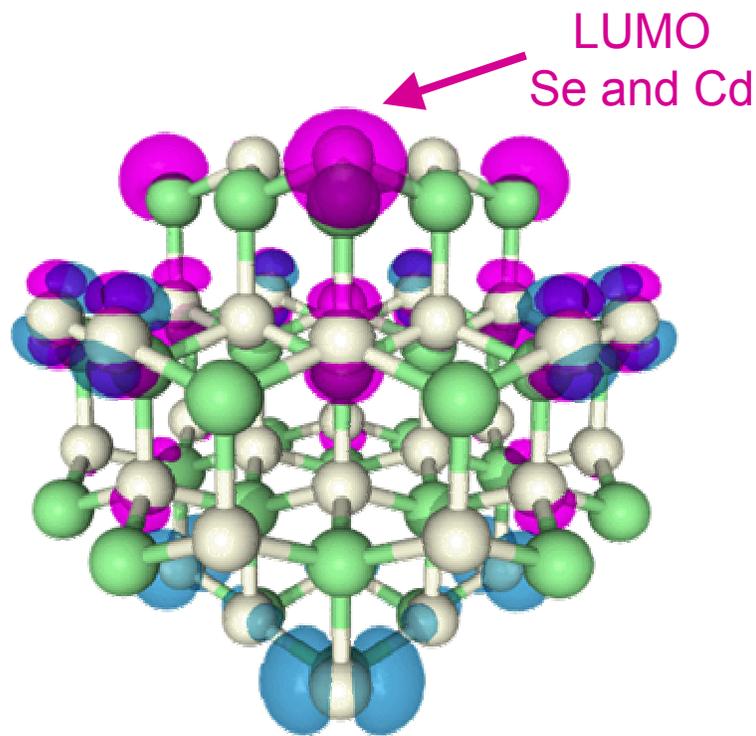


Predicted Absorption Spectra

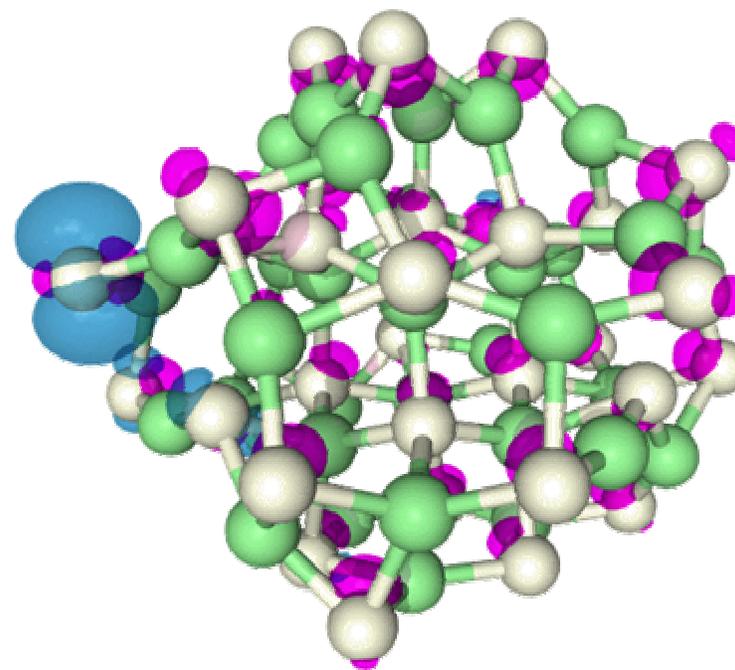


Nature of the Band Edge States

Unrelaxed Structure



Relaxed Structure



HOMO
Se Dangling bond

Conclusions

- Accurate DFT calculations including s , p and d valence electrons are required to accurately predict the electronic structure of CdSe quantum dots.
- Bulk derived wurtzite structures are unstable even at zero temperature.
- Structural relaxations, “heal” the surface opening an optical gap.
- Structural imperfections at the surface can generate mid gap states.