LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-CONF-203007

Simulations of CdSe Quantum Dots

A. Puzder, A. Williamson, F. Gygi, G. Galli

March 18, 2004

APS
Montreal, Canada
March 22, 2004 through March 26, 2004

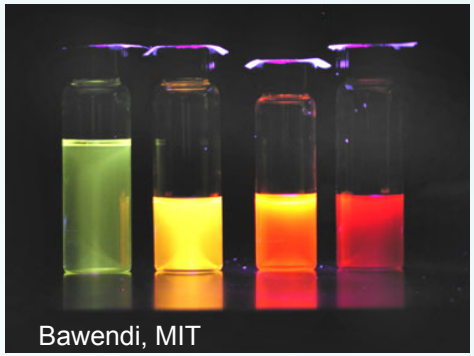
Structural, Electronic, and Optical Properties of CdSe Nanocrystals: First-Principles Computations

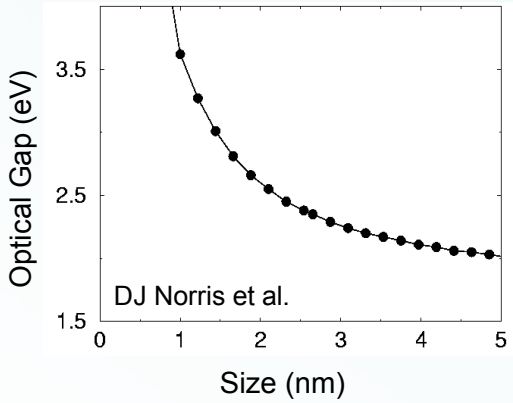
Aaron Puzder, **Andrew Williamson**
Francois Gygi and Giulia Galli

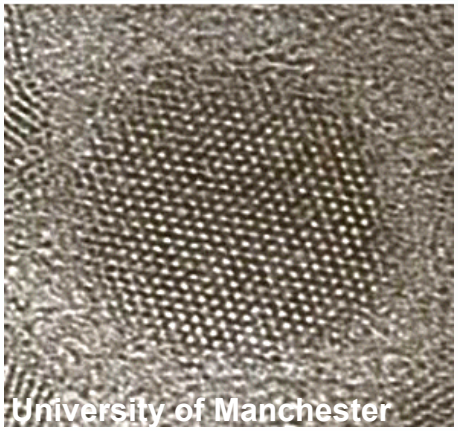
Quantum Simulations Group
Lawrence Livermore National Laboratory

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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

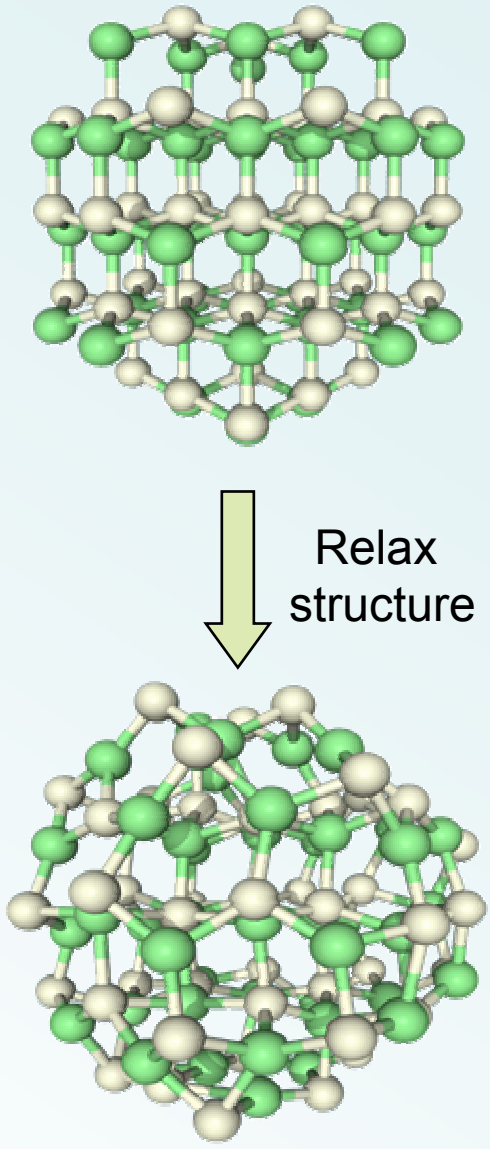
- What is the atomic structure?
  (Surface can't be imaged in TEM)
- Why is the gap insensitive to passivation?
- Where are the nature of the band edge states?
- What is the origin of observed sub-gap emission?

Previous Theoretical Investigations

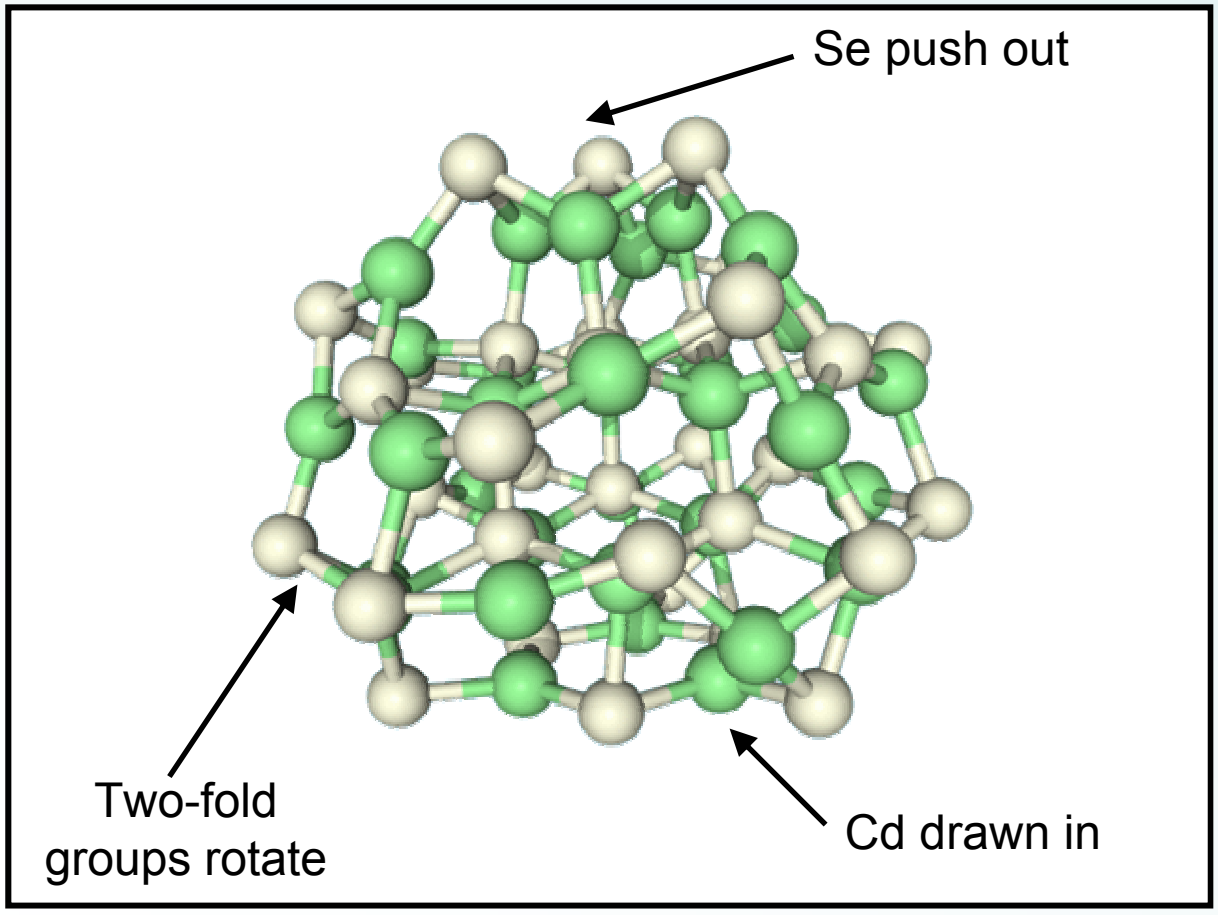
- Effective Mass Calculations:
  A. Efros et al. Phys. Rev. B (1996)
- Empirical Pseudopotentials:
  L.W. Wang and A. Zunger Phys. Rev. B (1996)
- Empirical Tight Binding:
  P. Lippens and M. Lanoo, Phys. Rev. B (1990)
  S. Pokrant and K.B. Whaley, Eur. Phys. Journ. (1999)
- Density Functional Theory: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

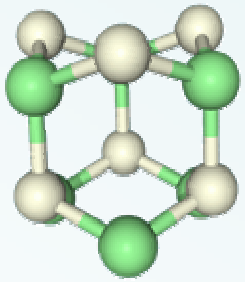
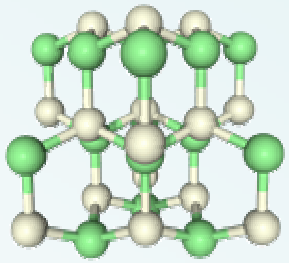
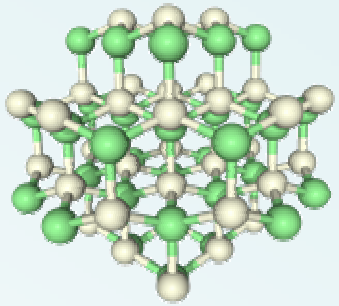
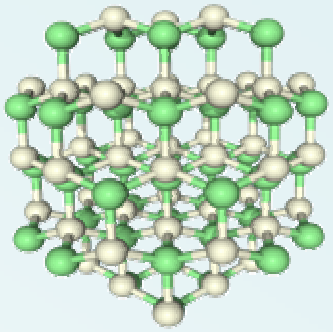
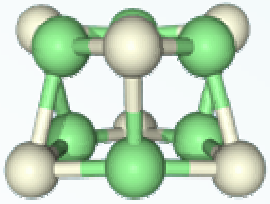
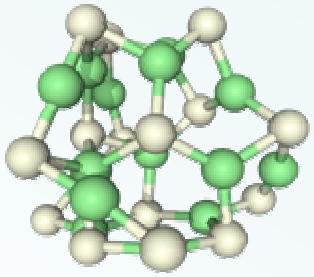
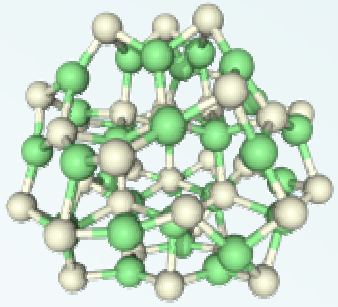
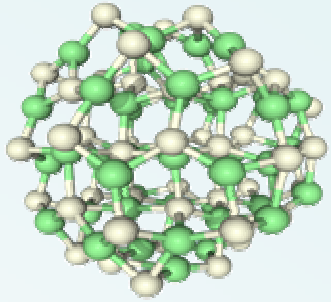
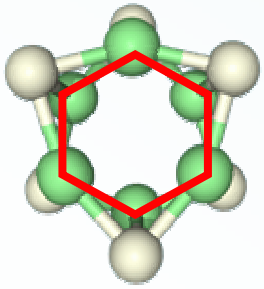
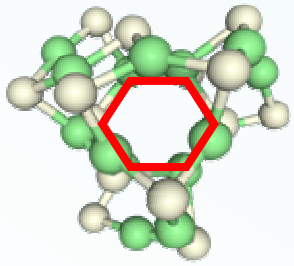
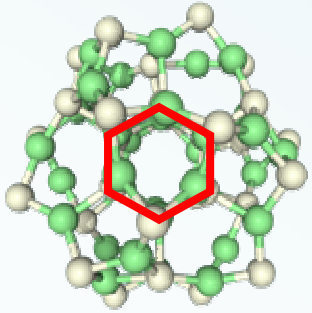
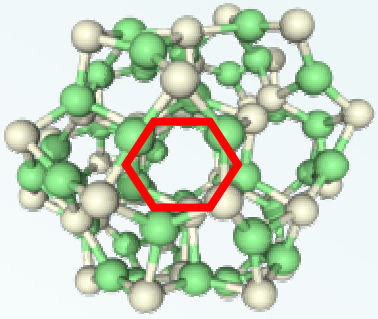


Relaxation of a 1.3 nm CdSe Q-Dot

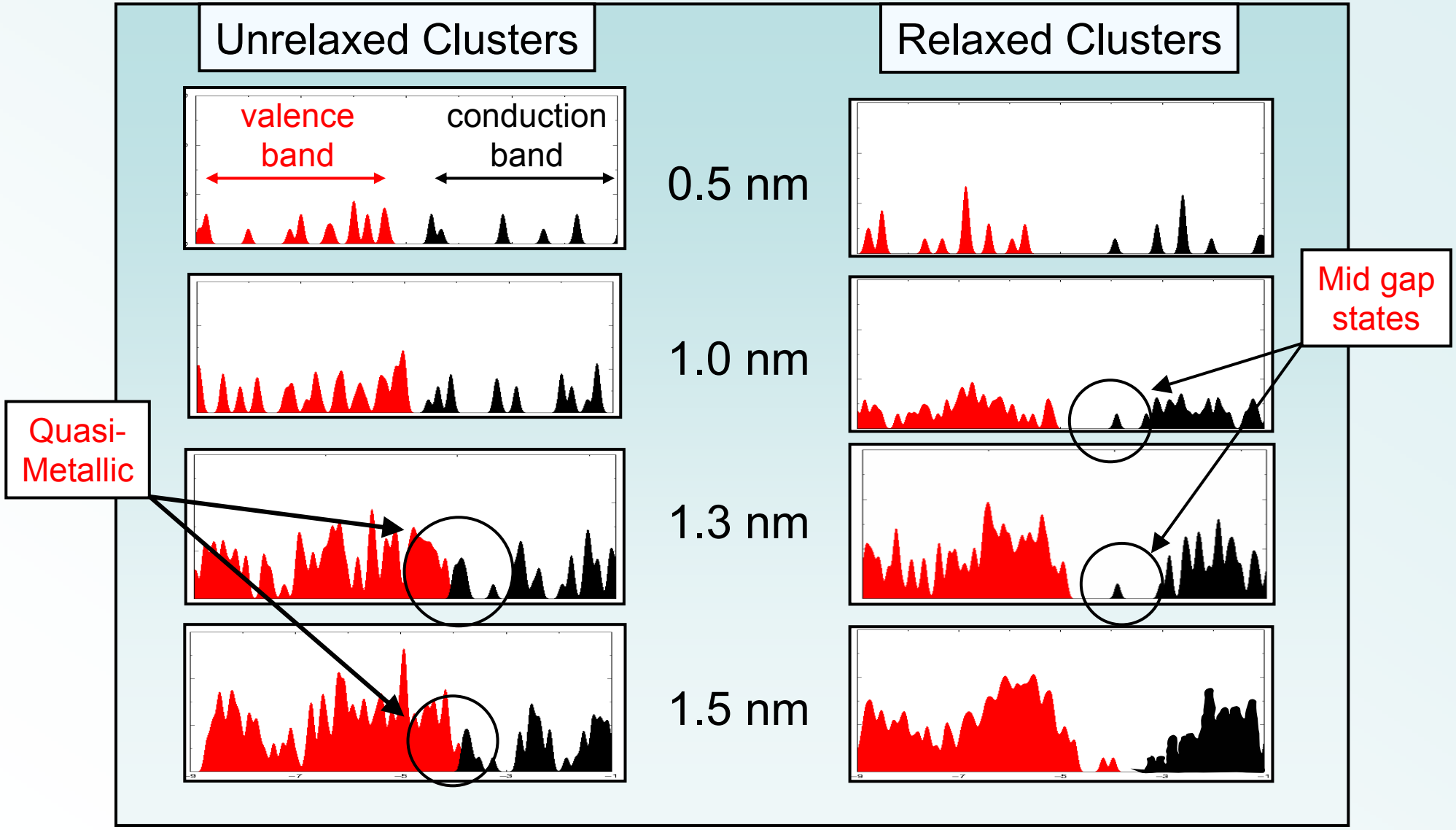


- Structure relaxes at zero temperature
- Cd atoms are drawn into the surface
- Se atoms push out from the surface
- Two-fold coordinated Cd atoms rotate round

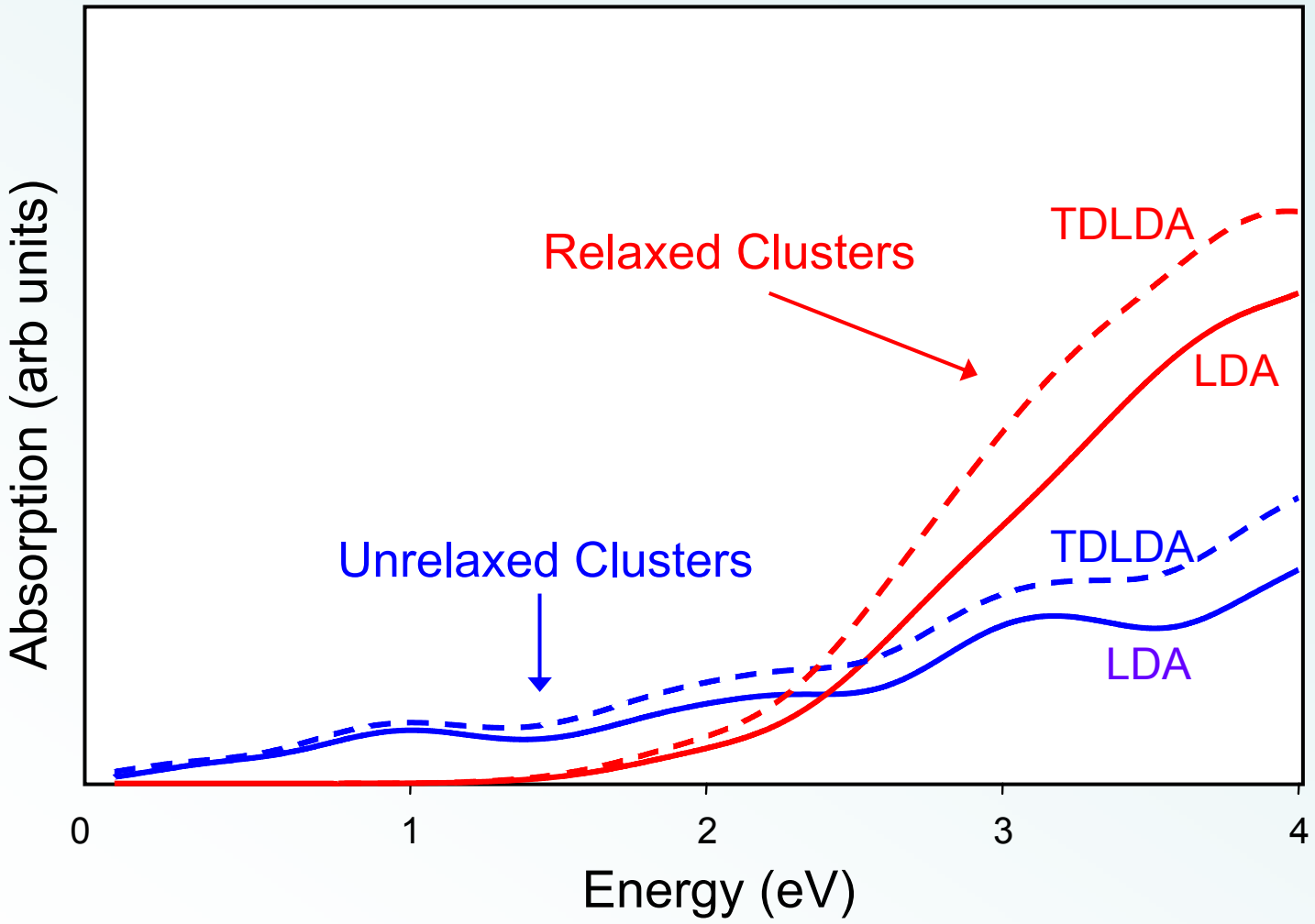
Relaxed CdSe Structures

	Cd_6Se_6 0.5 nm	$Cd_{15}Se_{15}$ 1 nm	$Cd_{33}Se_{33}$ 1.3 nm	$Cd_{45}Se_{45}$ 1.5 nm
Unrelaxed wurtzite				
Relaxed (Side View)				
Relaxed (Top View)				

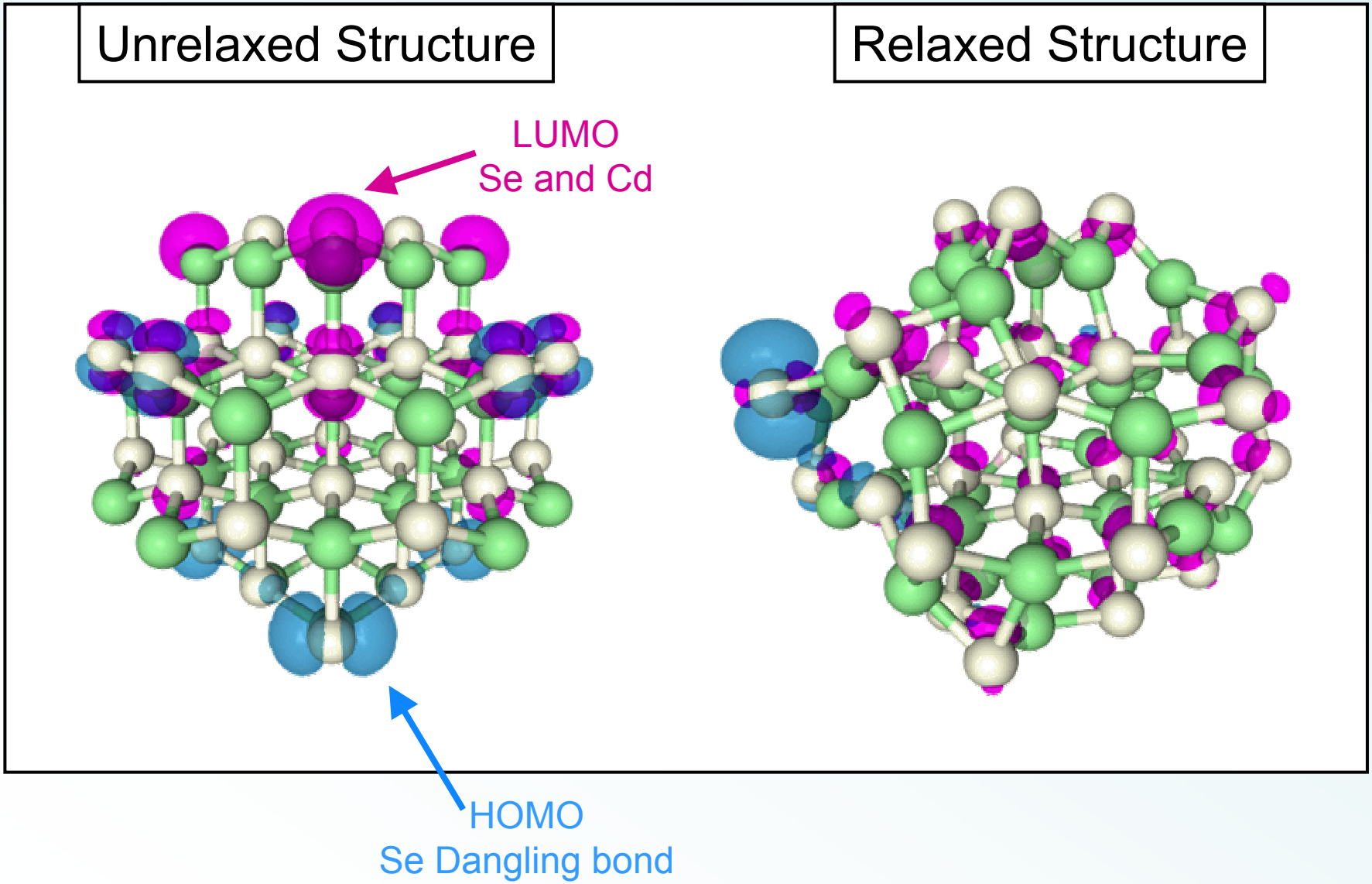
Electronic Density of States



Predicted Absorption Spectra



Nature of the Band Edge States



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.

Preprint: A. Puzder, A. Williamson, F. Gygi and G. Galli, *Self-Healing of CdSe Quantum Dots*