Casting Light on Fundamentals with Cutting Edge Research
Fundamentals

Molecular Orbitals
Not Only Paramagnetism of Molecular Oxygen

Particle-in-a-Box
Beyond Dye Molecules

Hydrogen Atom Expanded
Spherical Waves on Small Clusters
Introduction: Band Gap in Group IV — The Semiconductor Group — depends on size of atoms in semiconductor.
Band Gap in Group IV Semiconductors.
Moving Out from Group IV, Band Gap Increases with Increasing Electronegativity Difference.

We shall focus on the II-VI semiconductors, primarily CdS.
Band Gap in Binary II-VI Semiconductors.
Small Clusters:

Why Miniaturize?
  Speed
  Cost

Ultimately
  Too Small to be a Solid
  Too Big to be a Molecule

Quantum Dots
Why Miniaturize?

Speed
Cost

If Aircraft had advanced at the same rate as electronic components, i.e. fallen in cost and increased speed,

Boston → LA
would now cost $20
and take 10 min!!!
Optical Properties:

CdS Bulk Material - a Lemon-Yellow, opaque solid.

Quantum Cluster:
Transparent, Colorless Solution
Fluorescent in Blue-Green

PbS - Bulk is a Sooty, Black Solid.
Quantum Cluster:
Transparent, Red Solution
Fluorescent in the Green.
CdS is a Zinc Blend Structure

FCC lattice of $S^{2-}$ with every other tetrahedral hole occupied by the smaller $Cd^{2+}$ ions.
Cluster: $13 \ S^{2-}$

Cluster $55 \ S^{2-}$
In these small clusters, quantum effects begin to be important: they are too big to be molecules, too small to be solids. Typical cluster has about 1,000 atoms, about 1/3-1/2 are on the surface. There are corner atoms and flat atoms. The chemistry of these are interesting too. Our focus today is the optical properties. In particular, the band gap is larger than the corresponding solid. How can we understand this? Simple model: missing states.
Semiconductor  Few  Many Missing States
Next more sophisticated, introductory or physical chemistry model, a particle-in-a-box model:
\[ \Delta E = \frac{(2n + 1)\hbar^2}{8m_e L^2} \]

\( m_e \) mass of electron
\( L = \text{Box Length} \)
Finally:
Model as an “atom”
coulombic potential with heavier
hole localized in cluster center

CdS hole mass $\sim 4\times$ electron mass. bulk exciton diameter 60Å


parabolic potential:
\[ E_{n,\ell} = \hbar \omega_0 (2n + |\ell| + 1) \]
In presence of magnetic field, $\pm \ell$ split, electrons shuffle

Acknowledgments

Assistance:
Steve Baldelli
Cheryl Schnitzer
Danielle Simonelli

Students:
Chemistry 016 (Materials Chemistry)
Chemistry 032/034 (Physical)

Financial
National Science Foundation
PEW Charitable Trust
Question: How do you synthesize these small clusters?

Three Methods:

1. Polymer Method: 4% polyvinyl alcohol solution, polyvinyl alcohol is 124,000-186,000 molecular weight. Heat water to ~80°C, stir vigorously, add PVA slowly. Continue to maintain 80°C with stirring for a couple of hours. Solution should be nearly clear. Use for PbS clusters. Makes large clusters.

Polyvinyl alcohol surrounding water.

Used for CdS, makes smaller clusters.

Instructions for these two on attachment.
3. Dendrimer Method:
Makes smallest clusters, ~2-4 nm diameter.

Dendrimer Source: Aldrich

Generation 0 PAMAM Dendrimer:
Generation 1 PAMAM Dendrimer

Larger ones have increasingly more amines.