From an Atom to a Solid

Photoemission spectra of negative copper clusters versus number of atoms in the cluster. The highest energy peak corresponds to the lowest unoccupied energy level of neutral Cu.

Typically, there are two regimes:

1) For $<10^2$ atoms per cluster, the energy levels change rapidly when adding a single atom (e.g. due to spin pairing).

2) For $>10^2$ atoms per cluster, the energy levels change continuously (e.g. due to the electric charging energy (next slide)).
Energy Levels of Cu Clusters vs. Cluster Radius R

\[ \Delta E = (E_\infty - E_R) \propto \frac{1}{R} \]  
(charged sphere)

FIG. 2. Electron affinities and 3d-band-energy onsets of copper clusters as a function of \( 1/R \)
The Band Gap of Silicon Nanoclusters

3 nm: Gap begins to change
Band Structure of Silicon Nanoclusters

![Graphs showing valence and conduction band shifts as a function of diameter (nm)]

Energy (eV) vs. Diameter (nm)

- **Valence Band**
- **Conduction Band**

**Bulk Band Gap** = 1.1 eV
Increase of the Band Gap in Small Nanoclusters by Quantum Confinement

![Diagram showing the increase of band gap due to quantum confinement.](image)
Size Dependent Band Gap in CdSe Nanocrystals

CdSe Quantum Dots (Bawendi Group)

Photo by Felice Frankel
The Band Gap of CdSe Nanocrystals

Photon Energy vs. Wavelength:

\[ h\nu (\text{eV}) = \frac{1240}{\lambda (\text{nm})} \]
Beating the size distribution of quantum dots
Quantum dots formed by thin spots in GaAs layers

Figure 24 Toward spectroscopy of a single nano object. The energy levels in an array of self-assembled semiconductor quantum dots are probed by laser spectroscopy. The size distribution of the dots smears the spectra into broad peaks. Using a small aperture reduces the number of dots that are sampled and thereby leads to sharper spectra. The ultimate goal is a spectrum from a single quantum dot. The spectrum of such an "artificial atom" consists of a characteristic pattern of \( \delta \)-functions. [From Gammon et al., Appl. Phys. Lett. 67, 2391 (1995).]
Termination of nanocrystals

Critical for their electronic behavior

H-terminated Si nanocrystal:
Electrons stay inside,
passivation, long lifetime

Oxygen atom at the surface:
Electrons drawn to the oxygen

Fluorine at the surface:
Complex behavior

From Giulia Galli’s group
Single Electron Transistor

A single electron $e^-$ tunnels in two steps from source to drain through the dot.

The dot replaces the channel of a normal transistor (below).
Nanoparticle attracted electrostatically to the gap between source and drain electrodes. The gate is underneath.

Designs for Single Electron Transistors

Large (≈ μm) for operation at liquid He temperature

Small (10 nm) for operation around room temperature

The quantum-dot structure studied at Delft and NTT in Japan is fabricated in the shape of a round pillar. The source and drain are doped semiconductor layers that conduct electricity, and are separated from the quantum dot by tunnel barriers 10 nm thick. When a negative voltage is applied to the metal side gate around the pillar, it reduces the diameter of the dot from about 500 nm to zero, causing electrons to leave the dot one at a time.
Quantum Dots as Artificial Atoms in Two Dimensions

* The elements of this Periodic Table are named after team members from NTT and Delft.

Filling electron shells in 2D
Magnetic Clusters

Fig. 3. View of the $V_{15}$ cluster. A disordered water molecule is trapped in the central cavity of the cluster but not shown. The filled circles represent the arsenic atoms, and the small empty circles, the oxygen atoms. The large circles are vanadium atoms, and those defining the six membered rings are hatched.

Fig. 4. Structure of the $Fe_8$ cluster. The cross-hatched circles are the metal atoms, the hatched circles are the oxygen atoms, and the empty circles represent, in order of decreasing size, nitrogen and carbon atoms.

Fig. 5. View of the ring structure of the $Fe_{10}$ cluster, where the dotted circles represent the iron atoms and the empty circles are, in order of decreasing size, chlorine, oxygen, and carbon.

“Ferric Wheel”
Magnetic Nanoclusters in Biology

FIGURE 7. (a) Pictorial view of the assembly of the apoferritin quaternary structures into the complete protein shell which contains the magnetic material. (From reference [36].) (b) An atomic force microscope image of the antiferromagnetic protein. (See color plate.)
The Holy Grail of Catalysis: Reactions at a Specific Nanoparticle

Want this image chemically resolved.

Have chemical resolution in microspectroscopy via X-ray absorption but insufficient spatial resolution.

Fischer-Tropsch process converts coal to fuel using an iron catalyst.


Di and Schlögl
The Oxygen Evolving Complex

Instead of rare metals with 5d or 4d electrons, such as Pt, Rh, Ru, one finds plentiful 3d transition metals in bio-catalysts: Mn, Fe.

Nature does it by necessity. Can we do that in artificial photosynthesis?
Biocatalysts = Enzymes

Most biocatalysts consist of a protein with a small metal cluster at the active site.

The active $\text{Fe}_6\text{Mo}$ center of nitrogenase,
Nature’s efficient way of fixing nitrogen.