Magic numbers in nature: Quantum shell structure in large metal clusters

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Solving the Schrödinger Equation

- Assume each electron feels a spherical potential $V(r)$ (rather crude: ignores electron interactions, ...)
- We want to solve

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) - E\right]\psi(\mathbf{r}) = 0$$

- Guess wave function of the product form $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$
- Plug into differential equation and use separation of variables to solve it.

Emergence of quantum numbers

An example using a simple atomic model

Counting solutions

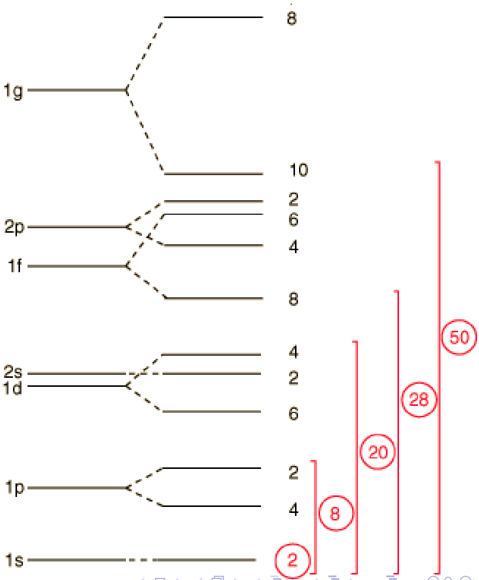
- Separated solutions:

$$\begin{aligned} R_n(r) &= \langle \text{depends on } V(r) \rangle, \\ \Theta_l(\theta)\Phi_m(\phi) &= Y_{lm}(\theta,\phi), \end{aligned} \quad \begin{cases} n = 1, 2, 3, \ldots \\ l = 0, 1, \ldots, n-1 \\ m = -l, \ldots, +l \end{cases}$$

- Each value of n yields one shell, occupations being determined by (l, m) combination count (and spin multiplicity)
- n'th shell : $N_n = 2\sum_{l=0}^{n-1}(2l+1) \rightarrow 2, 8, 18\ldots$
- Closed-shell configurations correspond to noble gases. This determines the periodic table! (almost)

Nuclear shells

- Assume each nucleon feels a spherical potential
- Turns out that energies split due to "spin-orbit interactions", resulting in different energies and occupations
- Magic numbers 2, 8, 20, 28, 50, 82, 126
- Numbers apply to proton and neutron counts separately, making "doubly magic numbers" possible.



Examples of clusters

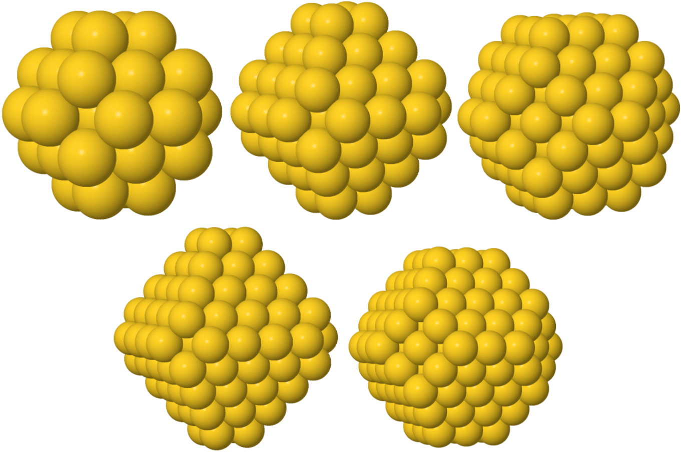


Figure: Different truncated octahedral gold clusters. Atom counts 38, 79, 116, 140, 201.

Cluster structures

Packing of atoms

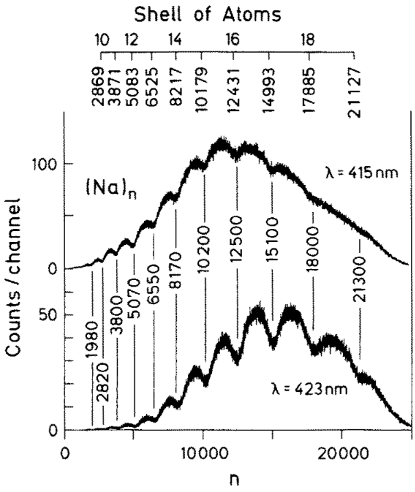
- Clearly, clusters can be constructed by adding layers of atoms
- A complete layer, or atomic shell, generally means a low energy. This is readily observed for large clusters
- As we shall see later, rather more interesting things happen in metals, related to electronic shells

Mass spectroscopy technique

- Clusters condensate from vapours of constituent atoms
- Hit clusters with ionizing radiation
- Accelerate clusters in electric fields, measure time of flight to determine charge per mass
- Stable structures are difficult to ionize, so these will appear as dips in the resulting mass spectrum

Mass spectrum for Na clusters

- Minima correspond precisely to closed atomic shells of specific lattice structures.
- Source: T. P. Martin et al. Z. Phys. D - Atoms, Molecules and Clusters 19, 25-29 (1991)



Two types of shell structure

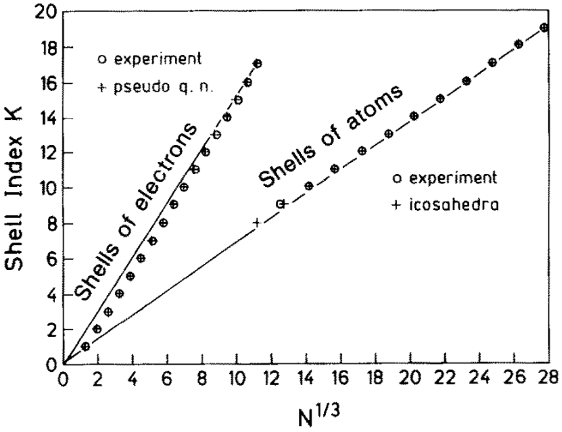
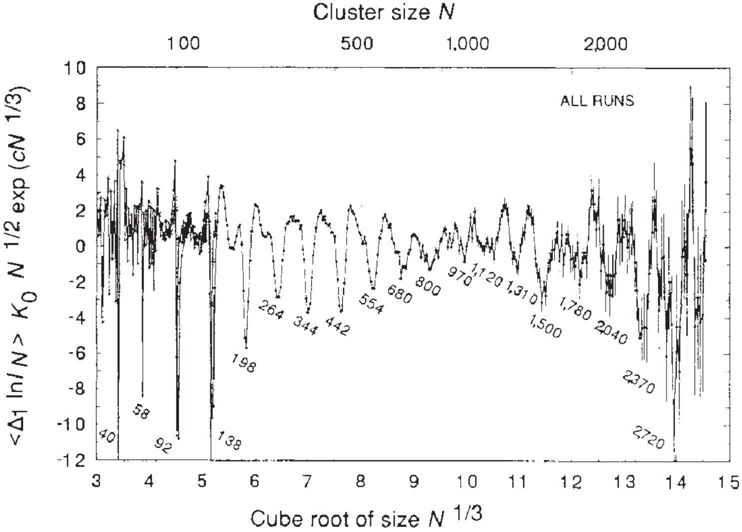


Figure: New set of magic numbers appearing for smaller clusters. T. P. Martin et al. Z. Phys. D - Atoms, Molecules and Clusters 19, 25-29 (1991), Springer

Measurement of magic numbers and beat mode

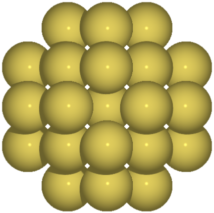


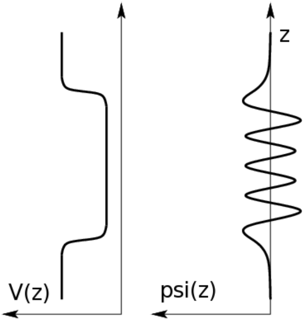
Pseudopotential principles

Valence and core electrons

- The core electrons of an atom do not participate in chemical bonding, while valence electrons are chemically active.
- Physical and chemical properties can generally be described by considering just the valence electrons.
- The nuclear and core electron charges form a hazy background charge, giving rise to a smooth “effective potential” felt by the valence electrons

Metal cluster, potential and wavefunction





- Constant effective potential (metallic cluster)
- Fast wave function oscillation compared to cluster scale
- Like an isolated atom, but quantum numbers are larger

Mathematical description

- Balian and Bloch have described spherical systems under cluster-like assumptions (large domain, low-wavelength oscillations) in terms of a "multiple reflection expansion".
- Effectively, electronic states are ascribed periodic paths of length L, reflecting at the points $r_0, r_1, \ldots$ on the boundary, and states are described by a complex wave number k such that

$$e^{\mathrm{i}kL} = e^{\mathrm{i}k_r L} e^{-k_i L}, \quad k_r \gg k_i$$

- The parameter k_i acts as a damping, so short paths are favoured.
- See R. Balian, C. Bloch: Ann. Phys **69**, 76-160 (1972).

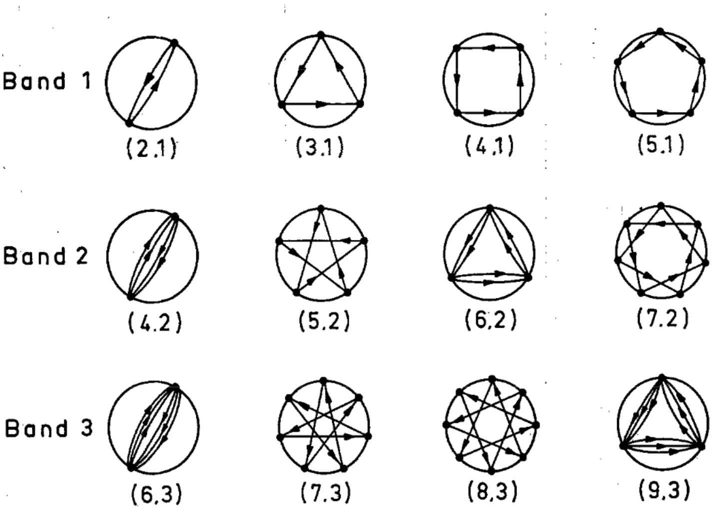


Figure: Polygonal solutions and quantum numbers (p, t) being the number of sides and revolutions around the center

Explanation of beat mode

- J. Pedersen et al. suggest the observed beat mode is described by

$$\cos k_{\triangle} n + \cos k_{\square} n = 2\cos\left(\frac{k_{\triangle}+k_{\square}}{2} b\right)\cos\left(\frac{k_{\triangle}-k_{\square}}{2} n\right)$$

- This agrees with the theoretical description, which predicts that dominating triangular and square modes produce beat modes

Concluding remarks

What has been said so far

- Quantum numbers and magic numbers emerge from simple models
- Cluster stability depends on completeness of atomic shells
- Also, electronic shell structures are observed for metal clusters up to a several thousand atoms
- Electrons are predicted to follow triangular and square orbits, explaining properties of measured mass distributions

Ongoing work

- Chemical, notably catalytic, properties of clusters have considerable interest
- DFT calculations on gold and platinum clusters in progress