Electronic Structure of Metal Clusters, Shells, Supershells and all that

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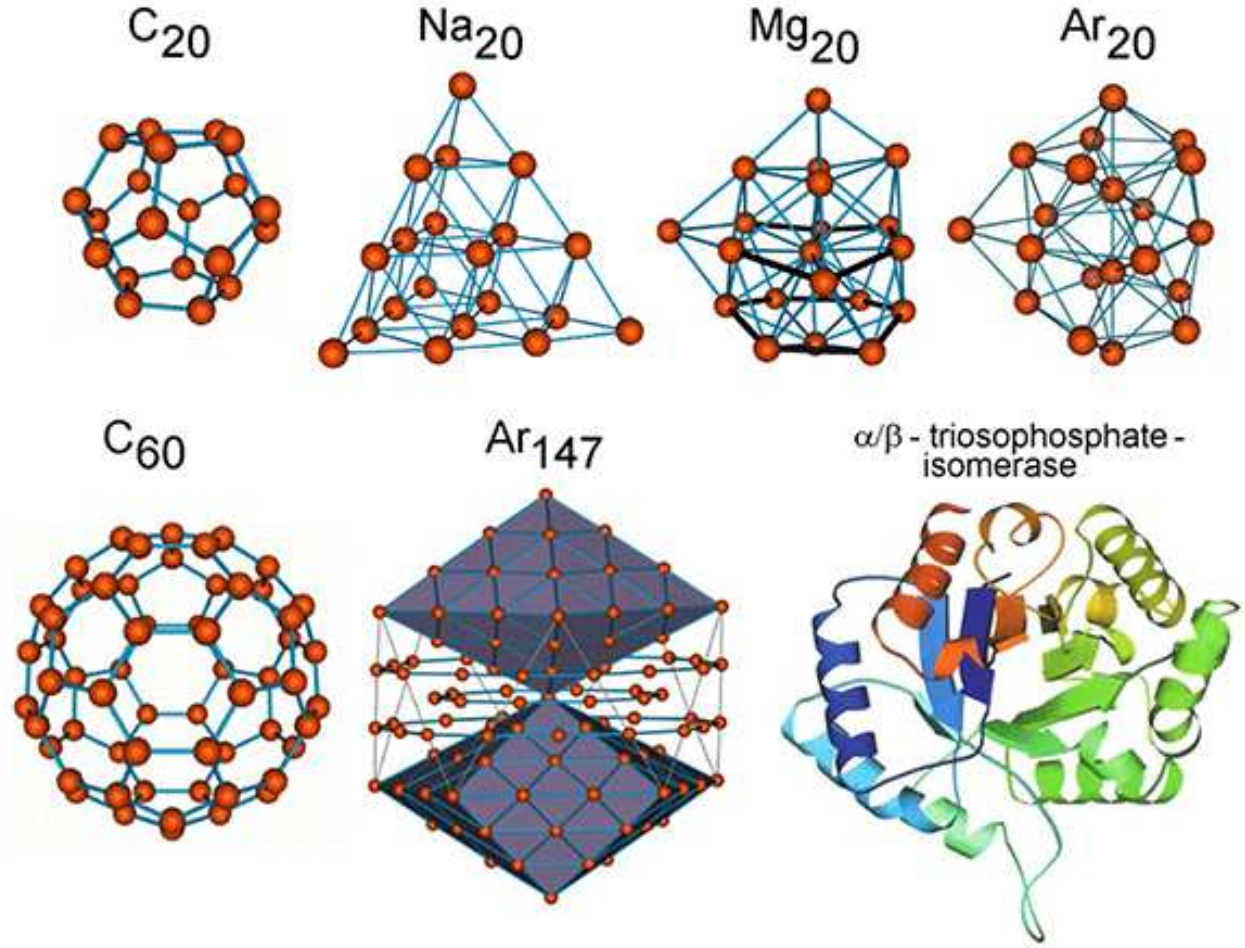
Contents of lectures:

1. Metal clusters: Phenomenology, electronic properties
2. The many body problem: An elementary introduction
3. Semiclassics: Quantum mechanics with classical orbits

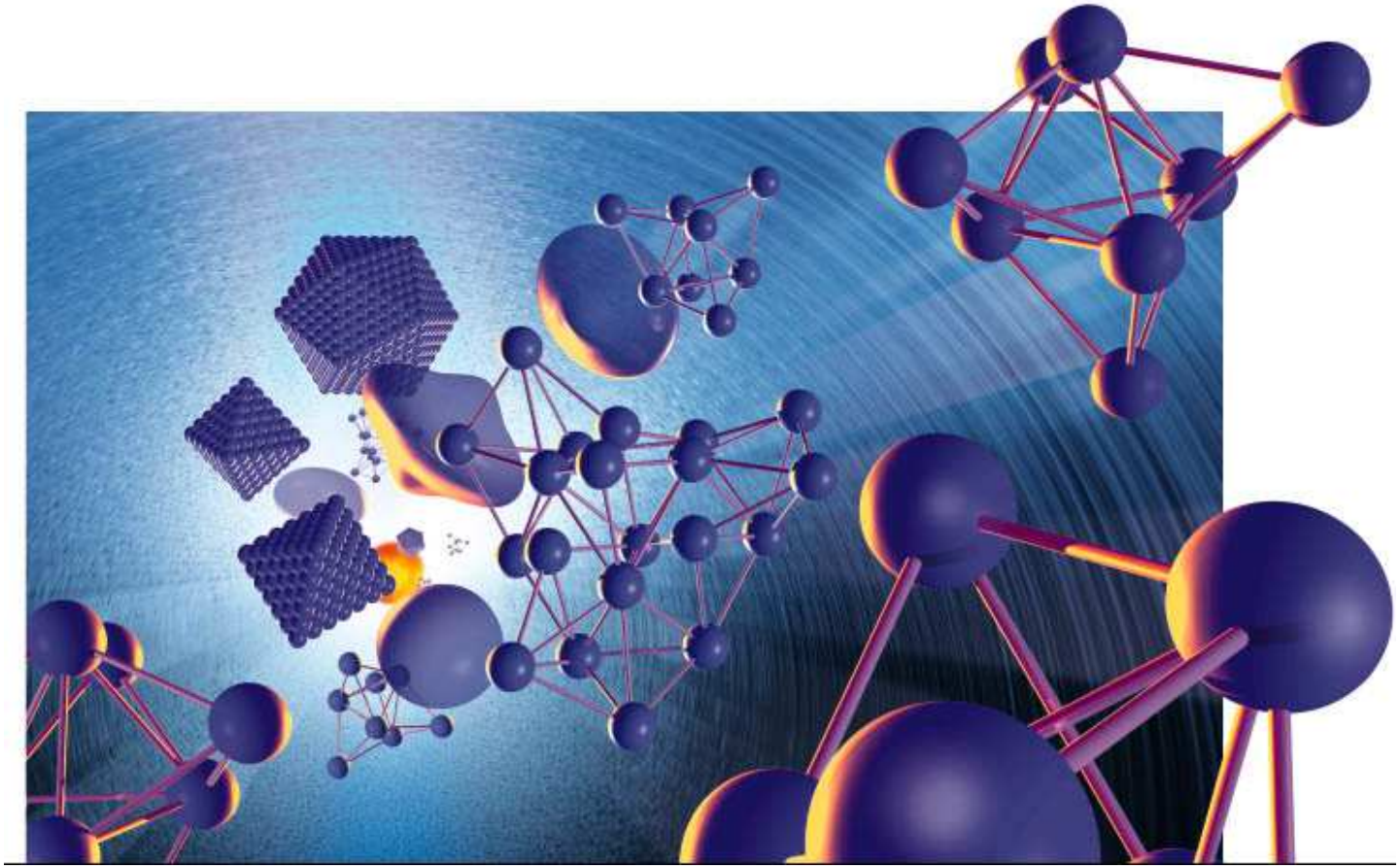
We start with **1. Metal clusters**

Atomic clusters



You may use any number of atoms of any kind to form a cluster!

Metal clusters



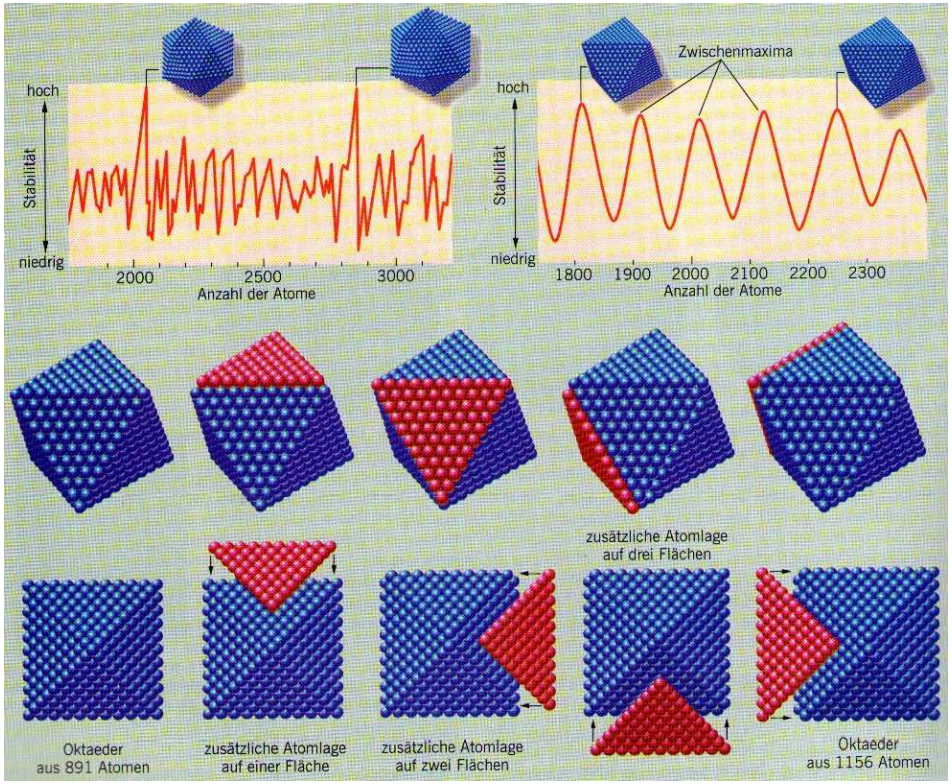
These are molecules consisting of a few or many - even thousands of - **metal atoms**. Their shapes depend on their number N and on their temperature.

[from: M.B., "Scientific American" 1997]

Cold, large metal clusters

Large cold clusters form densely packed **geometrical polyhedra** (T. P. Martin et al., 1991).

Na: Icosahedra (upper left) Al: Octahedra (rest of figure)



"Magic numbers" N_m for ideal polyhedra:

Icosahedra (e.g. Na):

$N_m = \ldots, 2057, 2869, 3871, \ldots$

Octahedra (e.g. Al):

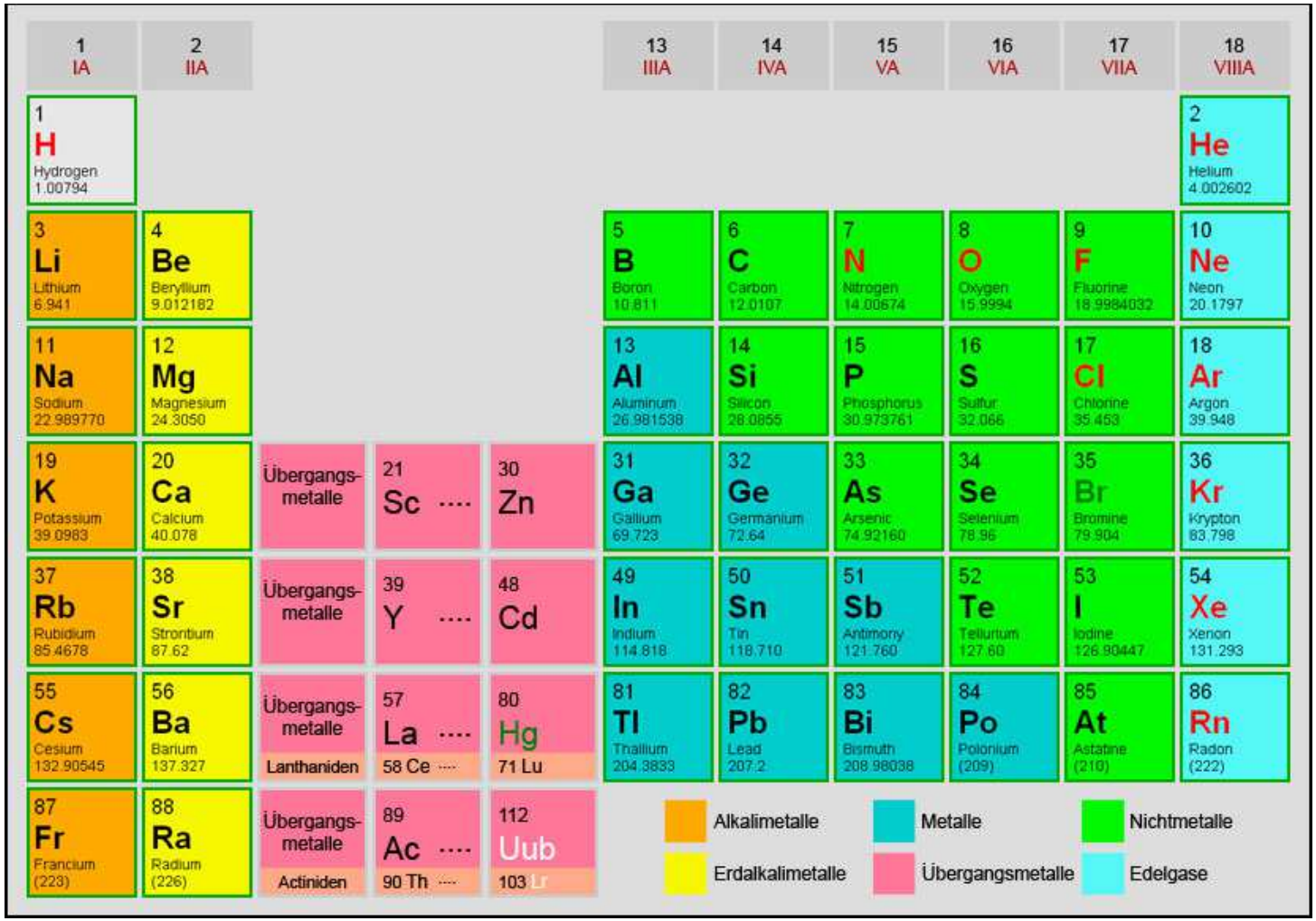
$N_m = \ldots, 1834, 2255, 2736, \ldots$

(adding single layers yields intermediate subshells)

(From: "Scientific American" 1997, after T.P. Martin, MPI Stuttgart)

$\Rightarrow$ The **ionic structure** determines forms and magic numbers N_m!

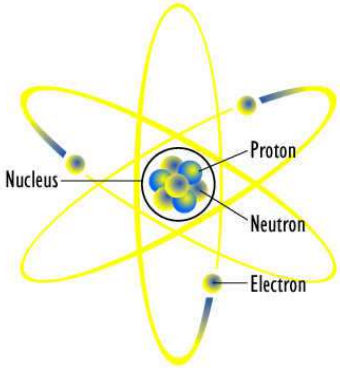
The periodic system of elements



Alkali metals ↑ ↑ other metals ↑ ↑ noble gases

The structure of an atom

Atom = Nucleus + Z Electrons:



Attention: The extension of the electron cloud is $\sim$ 10'000 times larger than that of the nucleus! The nucleus contains $>$ 99.9% of the total mass of the atom!

Nucleus = Z Protons (positively charged) + N Neutrons (neutral)
that is $Z + N = A$ "Nucleons" ($m_p \simeq m_n \simeq 1'836\, m_e$!)
The nucleons are bound together by the strong interaction ("nuclear forces").

The atoms are held together by the electromagnetic interaction ("Coulomb force") which dominates also molecluar physics and chemistry.

The **macroscopic world** is dominated by the gravitational interaction ("Newton's force") and the electromagnetic interaction.

The sodium (Na) atom

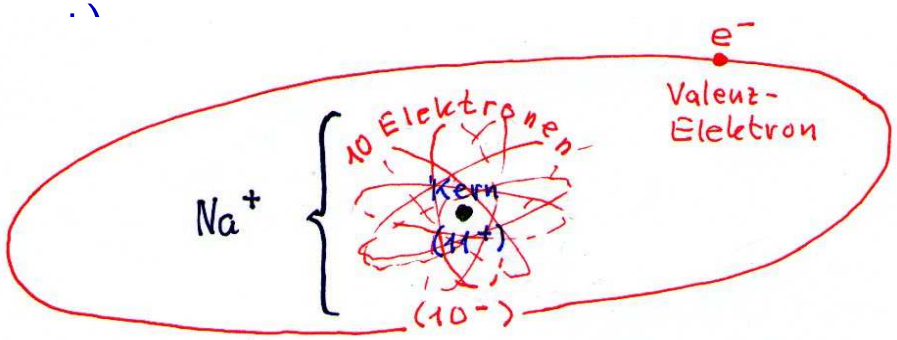
The neutral Na atom has $Z = 11 = 10 + 1$ electrons plus in the nucleus: Z=11 protons (+12 neutrons in the natural element).

$Z_m = 10 =$ a "magic number" corresponding to noble gas atoms with filled electronic shells. ($Z_m = 2, 10, 18, 36, \ldots$)

The 11th electron in Na is very weakly bound ("delocalised") and is called the "valence electron" (it makes the binding in NaCl and provides conduction in the Na metal).

Thus: $\boxed{\text{Na} \simeq \text{Na}^+ + \text{valence electron}}$ is a good approximation!

"Ion" Na^+ = nucleus (with Z=11 protons) + 10 electrons in filled shells (is rather com

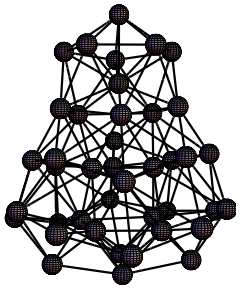


(Problem of "pseudopotential" felt by the valence electron!)

The Na_N cluster

A many body problem: N nuclei + $11N$ electrons = $12N$ particles.
We want to study N up to $\sim$ 10'000 $\Rightarrow$ **very hard to calculate!**

Simpler, using Na = (Na^+ + electron): $\Rightarrow$ only $2N$ particles:
N Na^+ ions are bound ("glued") together by N valence electrons.
But the calculation of their structure is still very difficult!



Structure of $(Na_{41})^+$
(obtained by Car-Parrinello molecular dynamics, DFT-KS-LDA and local pseudopotentials)
[S. Kümmel et al. (1998)]

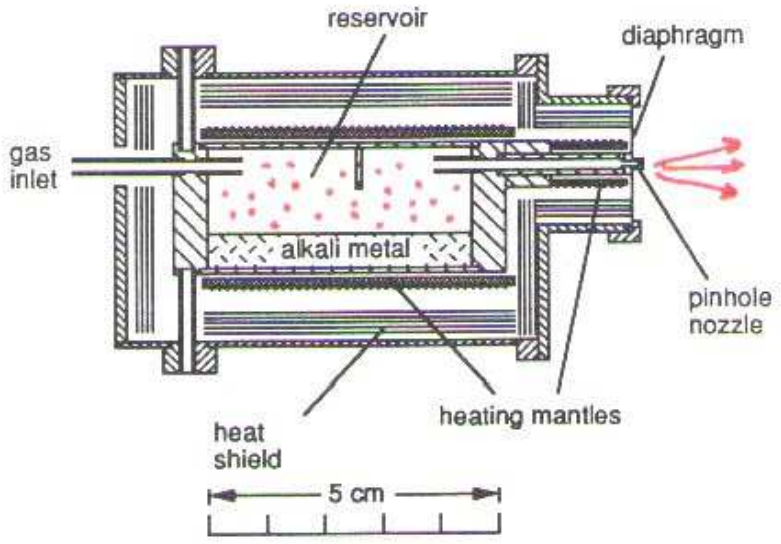
For hot clusters, we may use the **Jellium model**:

The N ions are replaced by an N-fold positively charged deformable dough (gelée, jellium), which is held together by the valence electrons.
$\Rightarrow$ "Mean field" calculation of N valence electrons in the potential of the jellium. Justification: delocalised valence electrons see only the **averaged** ionic structure. (Fermi wavelength $\gg$ inter-ionic distance.)

The only parameter: Wigner-Seitz radius $r_s \leftrightarrow$ average electronic density!

A cluster source: supersonic jet

Metal is heated in a pressure chambre and vaporised. A stream of He gas, entering from left, pushes the vapor towards right through a nozzle.

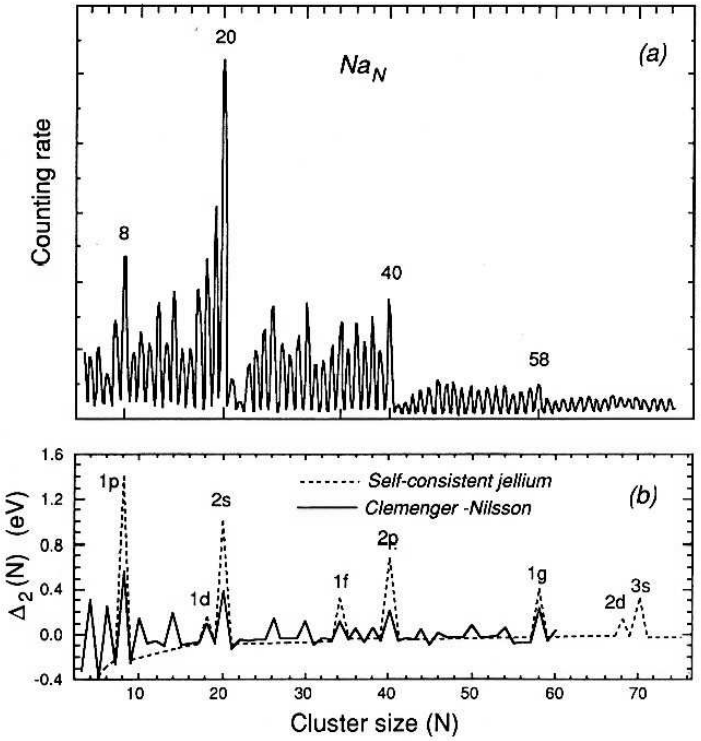


The metal vapor gets through the nozzle into a vacuum tube, where it condensates into (hot) clusters.

[from: W. de Heer, Rev. Mod. Phys. **65**, 611 (1993)]

The condensated clusters are ionised and their rate is counted as a function of the number N of atoms.

"Magic" clusters: filled shells of valence electrons



Experimental abundances of hot clusters (counting rate) shown against the number N of valence electrons in Na_N

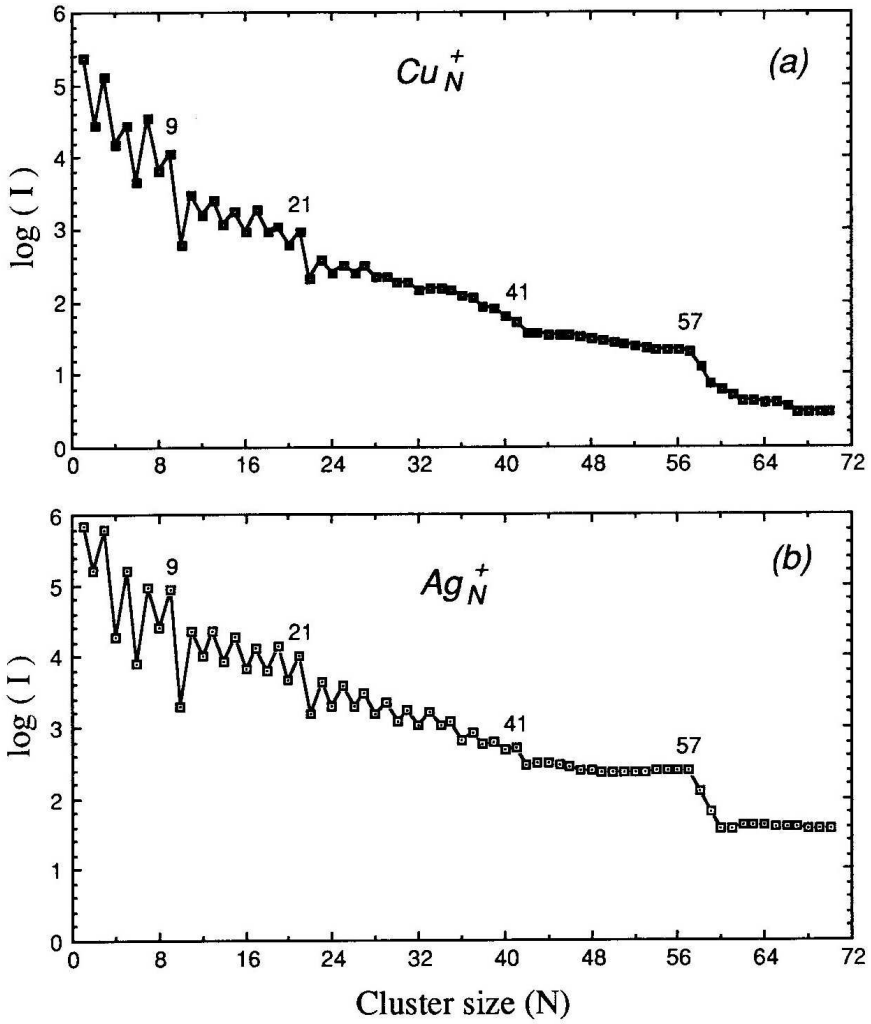
[W. Knight et al. (1984)]

Predicted abundances (gaps in calculated electron spectra)

[W. de Heer et al. (1984)]

The most abundant Na clusters have "magic numbers" N_m of valence electrons (also in ionised clusters!): $N_m = (2,)\ 8, 20, 40, 58$.
2, 8, 20, 40, 70 correspond to a **spherical** harmonic potential $V(r) = kr^2$.
(Minor maxima in between are explained by **deformed** clusters!)
But no peak is seen at $N = 70$. And how about larger clusters?

Magic numbers in charged clusters



Logarithmic experimental abundances

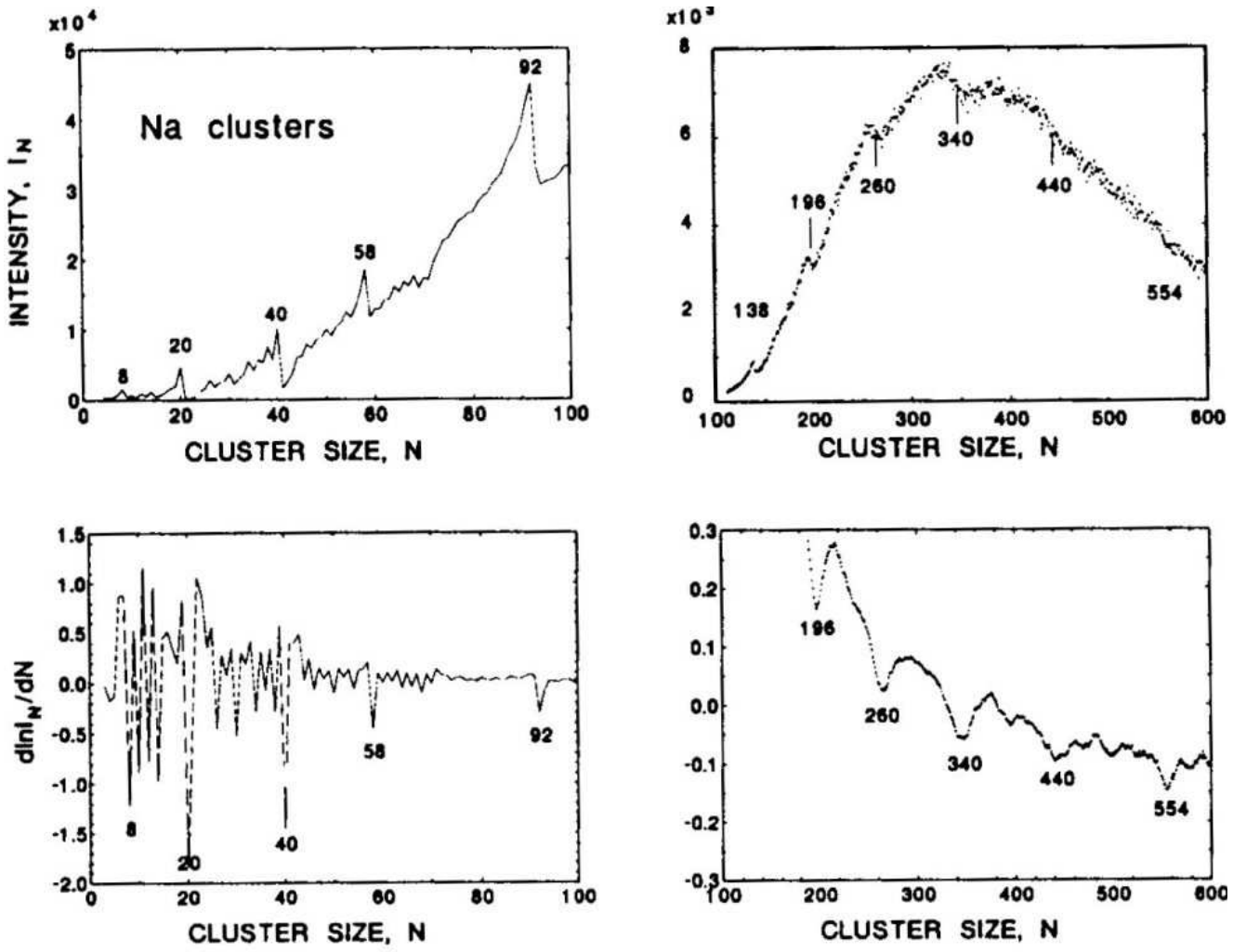
of charged cupper (Cu)

and silver (Ag) clusters

Note: N-1 is number of valence electrons!

[Katakuse et al. (1985)]

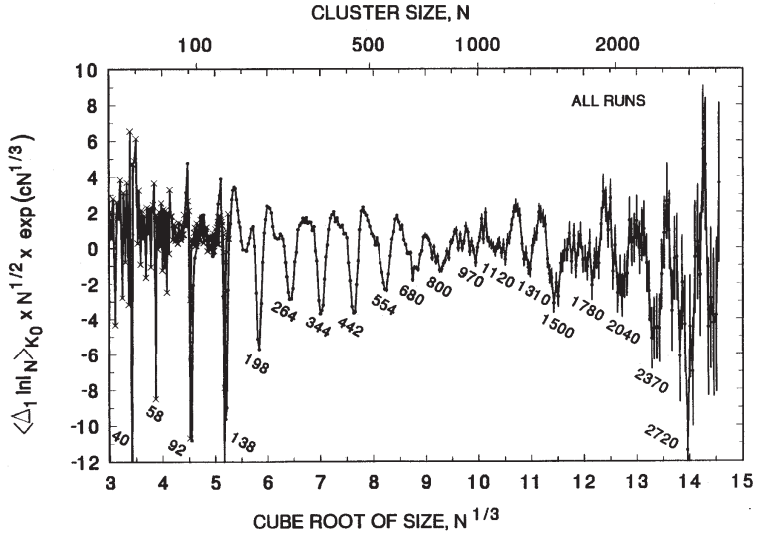
Larger magic numbers in Na clusters



Top: experimental abundances I_N, bottom: logarithmic differences $\mathrm{d}\ln I_N/\mathrm{d}N$

[Björnholm et al., NBI (1991)]

"Supershells": Beats in the shell structure



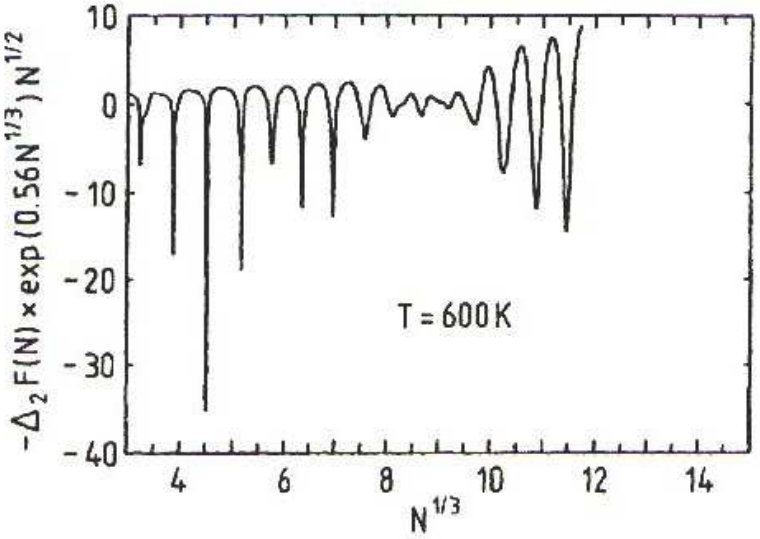
Experimental abundances of hot Na clusters (only oscillating part:)

Minima: stable clusters with N_m

New $N_m = 92, 138, 198, 264, \ldots$

Note: $N_m^{1/3}$ are **equidistant!**

[J. Pedersen et al., NBI (1991)]



Theory: using a selfconsistent quantum-mechanical mean field (Jellium model, DFT-KS-LDA) for a hot canonical ensemble (cf. Klavs Hansen's lecture)

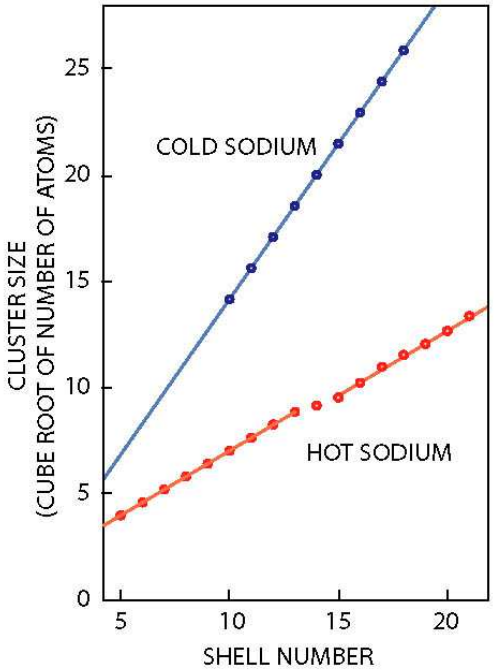
[O. Genzken and M.B., PRL (1991)], see also

[M.B., O.Genzken and K. Hansen, Z. Phys. D **21**, 65 (1991)]

Radii of "magic" clusters

The volume of a sphere is $V = \frac{4\pi}{3} R^3$ (R = radius). If V is proportional to N_m, we must have: $R_m = r_s N_m^{1/3}$ (r_s = Wigner-Seitz radius).

Plotting cubic roots $N_m^{1/3}$ for successive shell numbers m gives straight lines with slopes s: $N_m^{1/3} = s\, m$



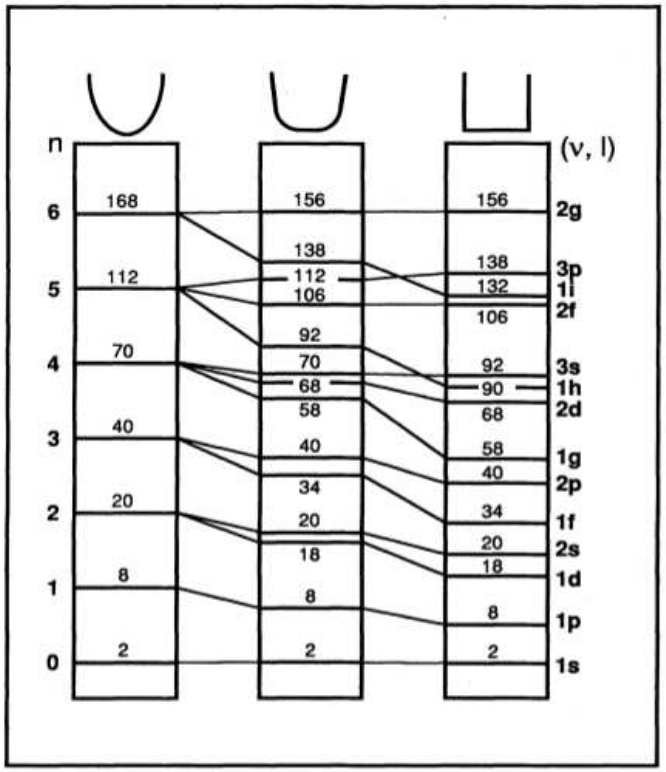
(above:) cold Na clusters:
ionic cores form perfect icosaedra
of N_m atoms (ions)
give slope $s = 1.49$

(below:) hot Na clusters:
N_m **valence electrons in spherical shells**
give slope $s = 0.61$ (dislocation at $m \simeq 14 - 15$ corresponds to beat minimum)
Experiment and theory (see below)
give the same slopes

s=0.61 for the electronic shell structure can be explained semiclassically using periodic orbits in a spherical cavity!

Shell closures for different radial potential forms

Shells in spherical potentials with different radial forms (schematic):



Left: harmonic oscillator

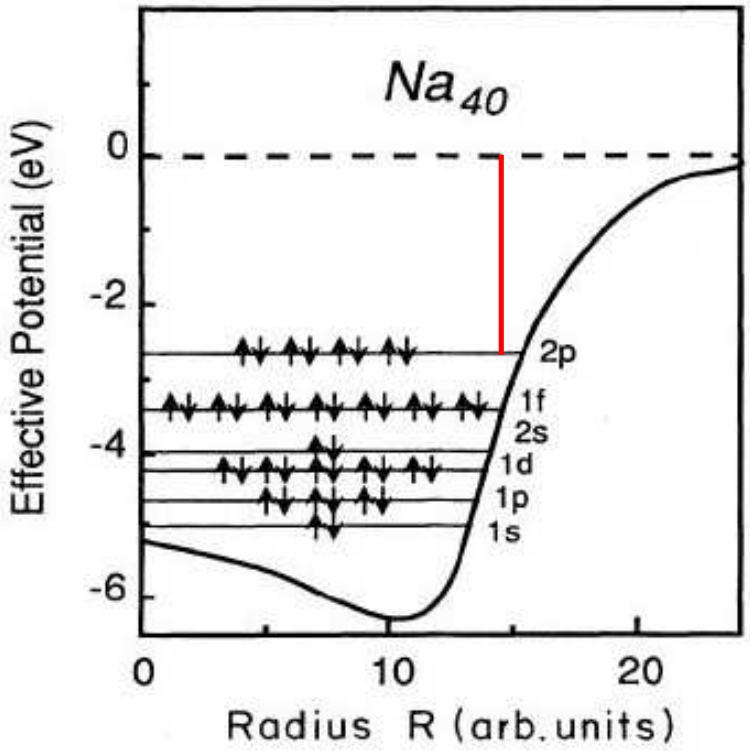
Right: square-well potential (spherical box) gives new $N_m = 58, 92, 138, \ldots$

Middle: intermediate case

Nature does not like sharp edges!

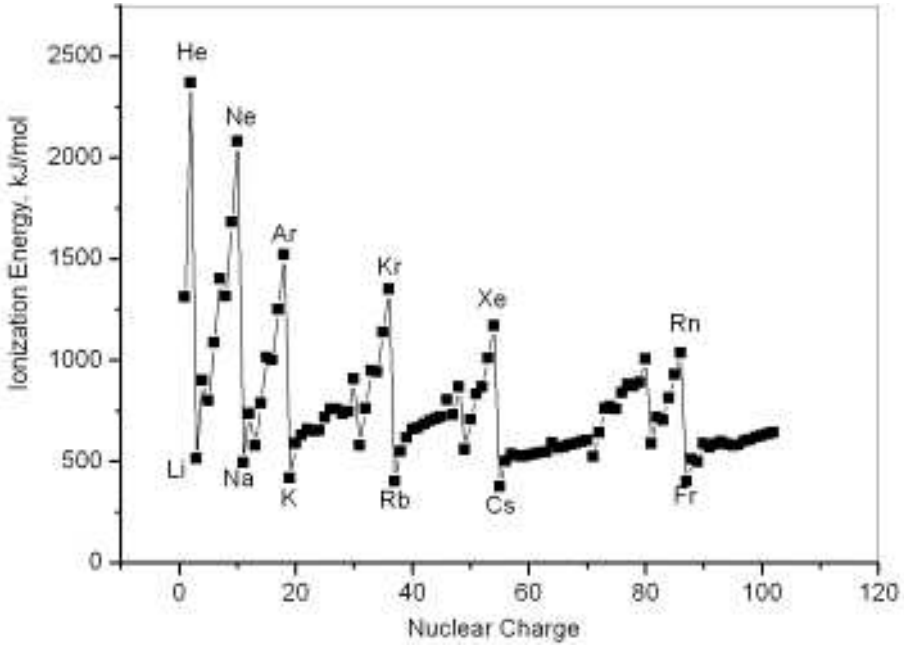
From the observed magic numbers N_m, the realistic potential for clusters with closed shells appears to be close to a (finite) spherical square well with slightly rounded corners.

Jellium potential of the valence electrons in Na_{40}

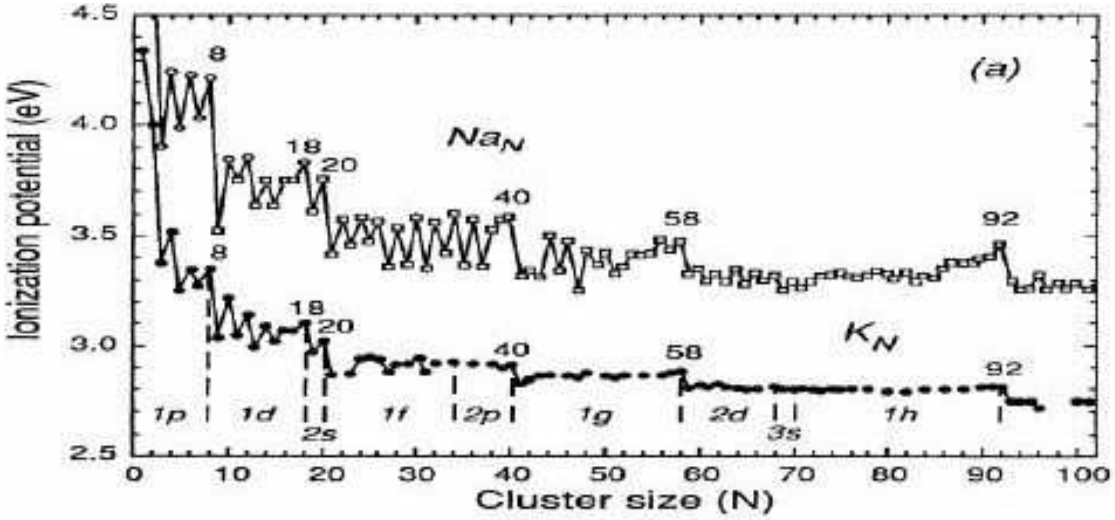


Can we "see" the levels of the electrons?
Yes, by photo-ionisation: shine (laser) light on the cluster and lift one of the electrons out of the potential!
From highest level: $\longrightarrow$ ionisation energy (or ionisation potential: IP)

Ionisation energies in atoms and clusters



atoms:
peaks correspond to filled atomic shells: He(2), Ne(10), Ar(18), Kr(38), ...



Alkali clusters:
magic numbers are $N_m = 2, 8, 20, 40, 58, 92, \ldots$

Ionisation potential (IP) vs. electron affinity (EA)

Let $E(N, Z)$ be the energy of a cluster with N atoms and Z valence electrons. ($N = Z$ corresponds to a neutral cluster.) We then define the **ionisation potential** IP and the **electron affinity** EA by:

$$\begin{aligned} \mathrm{IP} &= E(N, N-1) - E(N, N)\,, \\ \mathrm{EA} &= E(N, N) - E(N, N+1)\,. \end{aligned}$$

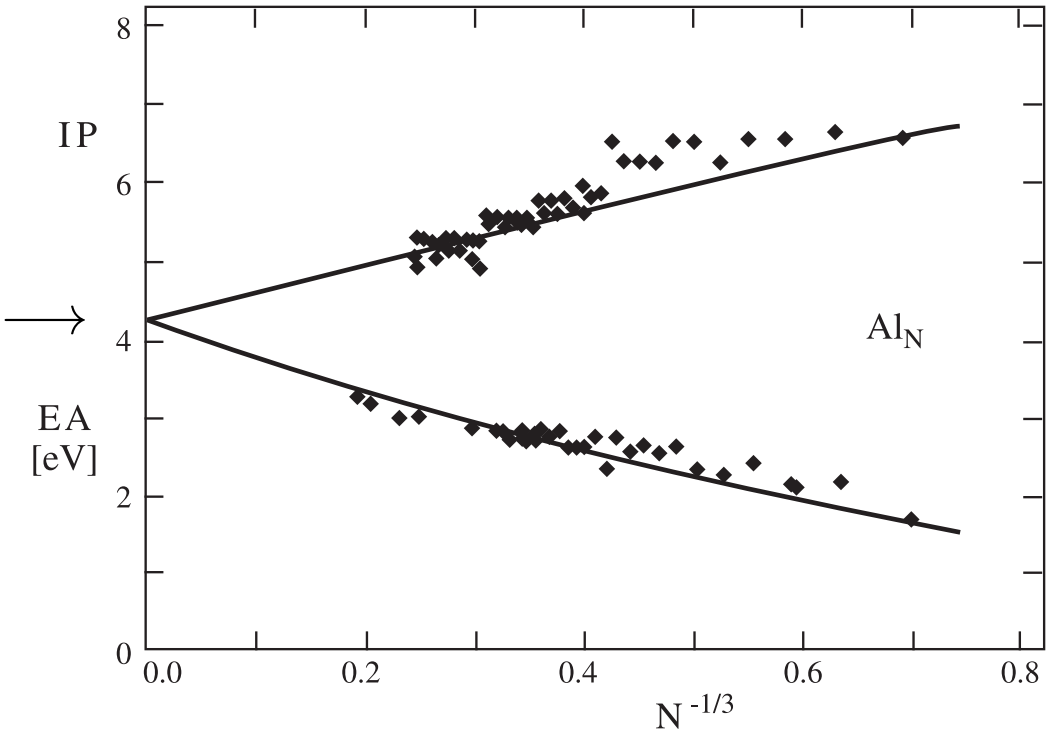
A liquid-drop model expansion in the inverse radius $1/R$ of a spherical cluster yields

$$\begin{aligned} \mathrm{IP}\,(R) &= W + \left(\frac{1}{2} - C\right)\frac{e^2}{R} + \mathcal{O}(R^{-2})\,, \\ \mathrm{EA}\,(R) &= W - \left(\frac{1}{2} + C\right)\frac{e^2}{R} + \mathcal{O}(R^{-2})\,, \end{aligned}$$

where W is the **work function** of the bulk metal, $\frac{e^2}{2R}$ the classical charging energy, and C a quantum-mechanical correction.

IP and EA of Aluminum clusters

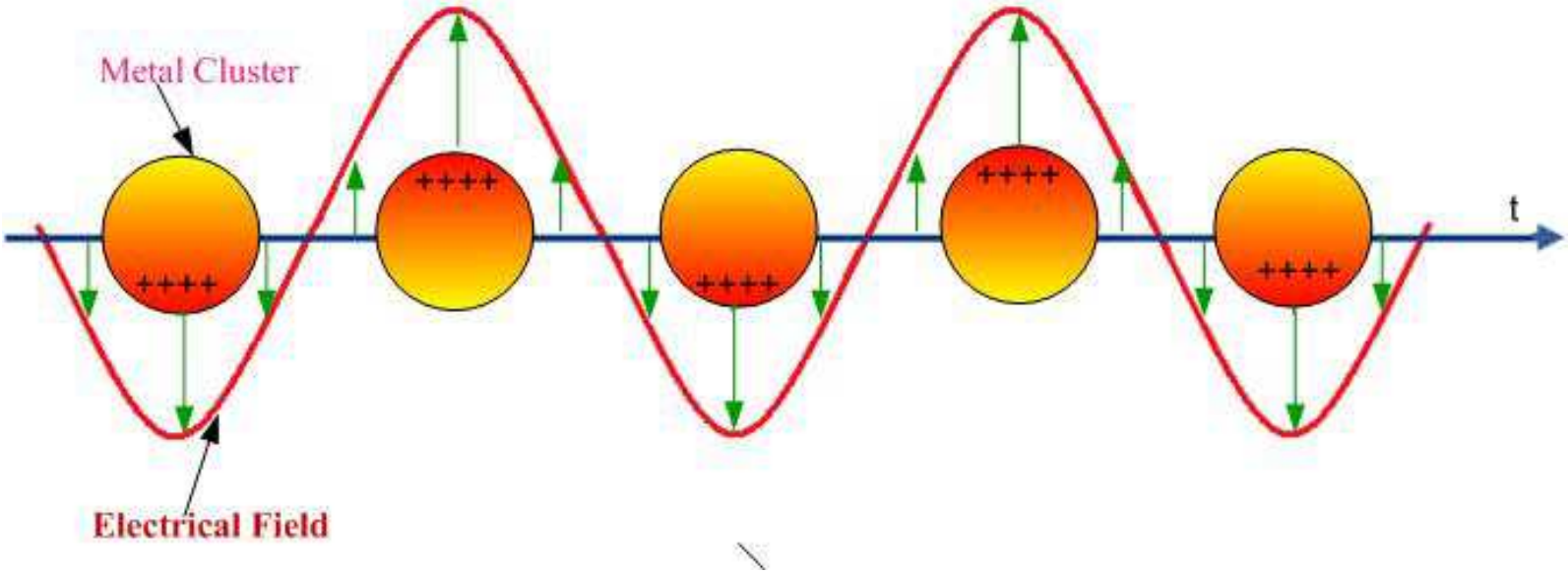
Work function $W \longrightarrow$



Diamonds: experimental results
Solid lines: semiclassical (ETF) jellium model calculations (vertically adjusted to the work function W to take into account the ionic structure)
[From: M. Seidl et al., J. Chem. Phys. (1991)]

Optic response: the Mie resonance

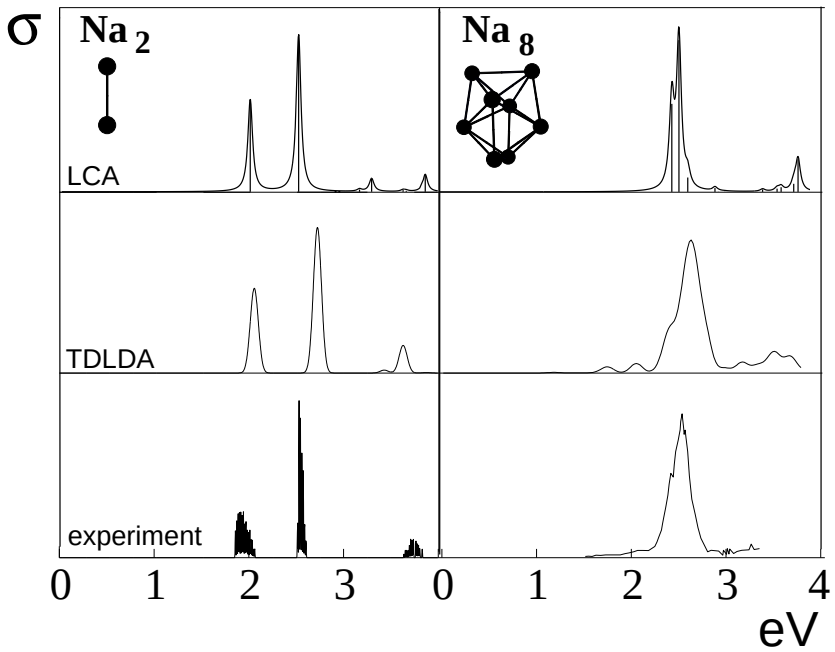
Shining light on a cluster excites a collective dipole oscillation of the valence electrons against the ionic cores:



In the photoabsorption cross section, this yields a resonance peak, called the Mie (dipole) resonance (or "Mie surface plasmon") after Mie's classical theory (1908) of charged spheres.

Dipole response in small Na clusters

Dipole absorption cross section for small Na clusters:



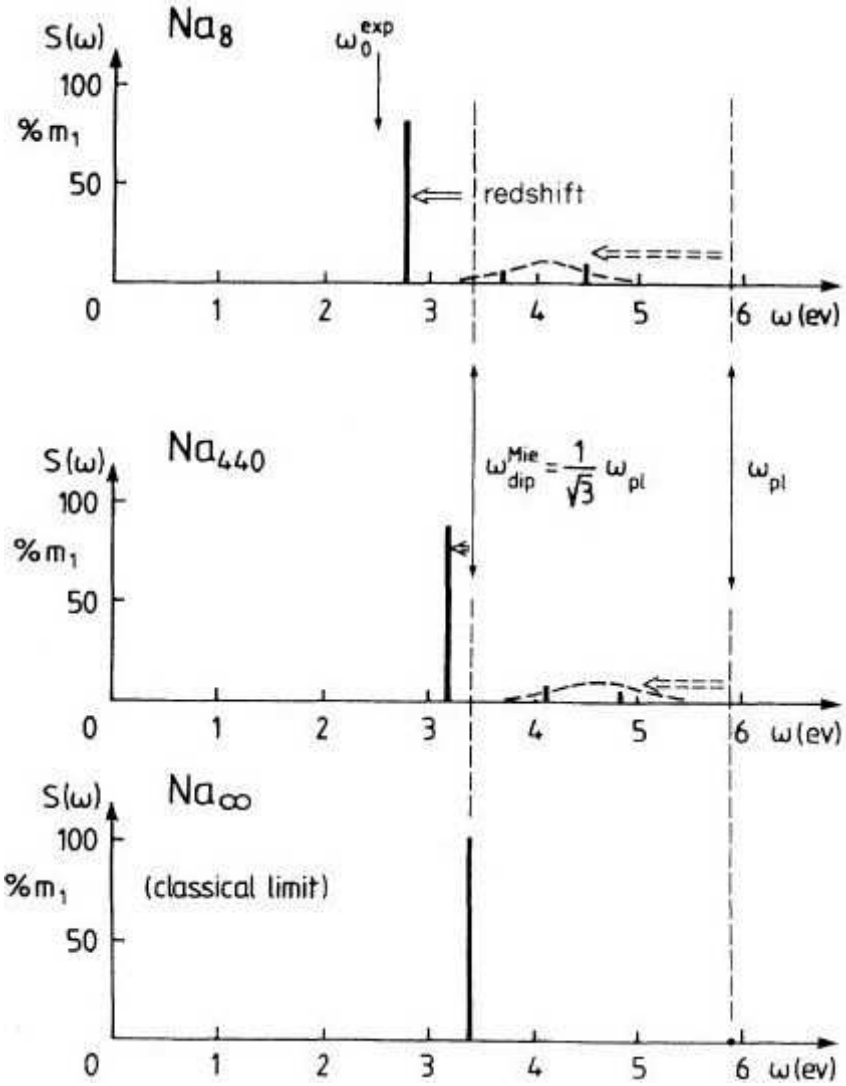
Top and middle: two versions of theory (semiclassical RPA, TDLDA)
[S. Kümmel, PhD thesis, Regensburg 2000]

Bottom: experimental cross section

In Na_2: single lines (isolated dipole transitions)

in Na_8: a clear resonance peak!

Size dependence of Mie resonance



[From: M.B., Rev. Mod. Phys. **65**, 677 (1993)]

In finite clusters, the Mie resonance is **red shifted** with respect to $\omega_{\rm dip}^{\rm Mie}$ due to finite size and quantum effects

The small peak at higher frequency is a (red-shifted) reminiscence of the bulk plasma frequency $\omega_{\rm pl}$ ("volume plasmon" coupled to the Mie surface plasmon)

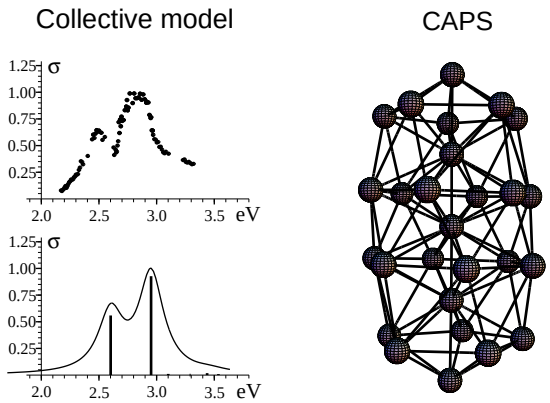
In the classical (very large) sphere:

$$\omega_{\rm dip}^{\rm Mie} = \left[\frac{Z\hbar^2 e^2}{mR^3}\right]^{1/2} = \frac{1}{\sqrt{3}}\,\omega_{\rm pl}$$

Splitting of dipole resonance in deformed clusters

In a spheroidally deformed cluster, there are two dipole modes:
1. along the symmetry axis, and 2. perpendicular to the symmetry axis!
(We have learned this from the giant dipole resonance in nuclei!)

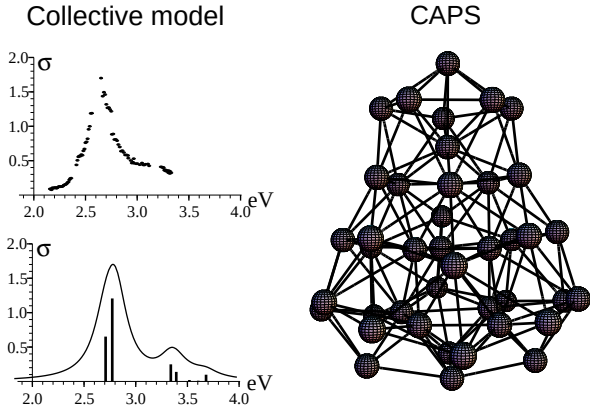
Na 27+



Left: dipole absorption cross section
(top: experiment, bottom: theory)
Right: structure from theory (DFT-KS-LDA)
[S. Kümmel et al., (1998)]

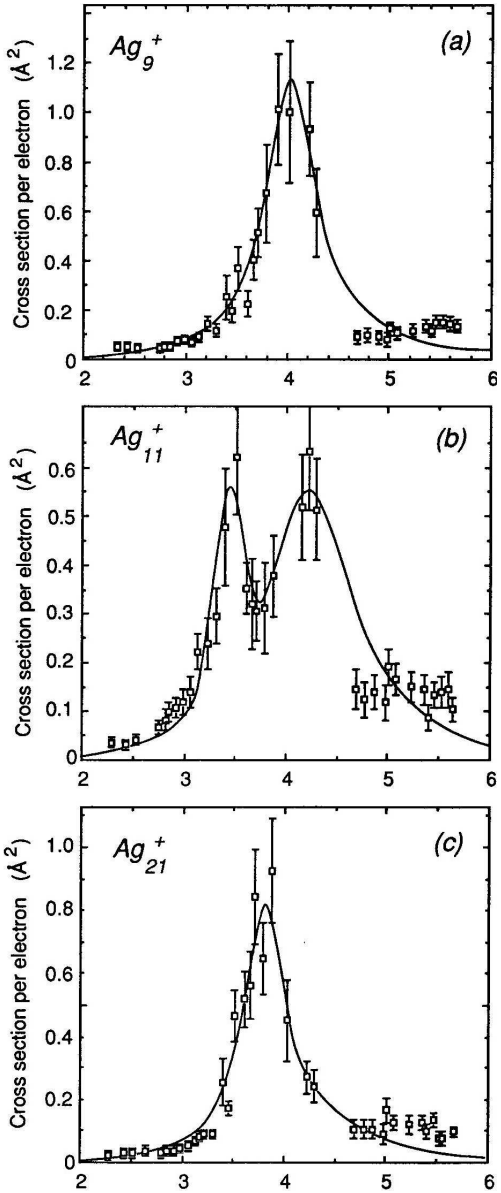
Na_{27}^{+} is spheroidally deformed
and shows two resonance peaks!

Na41+



Na_{41}^{+} has $N_m = 40$ valence electrons
and is (nearly) spherical!
(upper strength: "volume plasmon")

The Mie resonance in charged Ag clusters



Experimental dipole absorption cross section

[From: Tiggesbäumker et al. (1992)]

$N_m = 8$: spherical

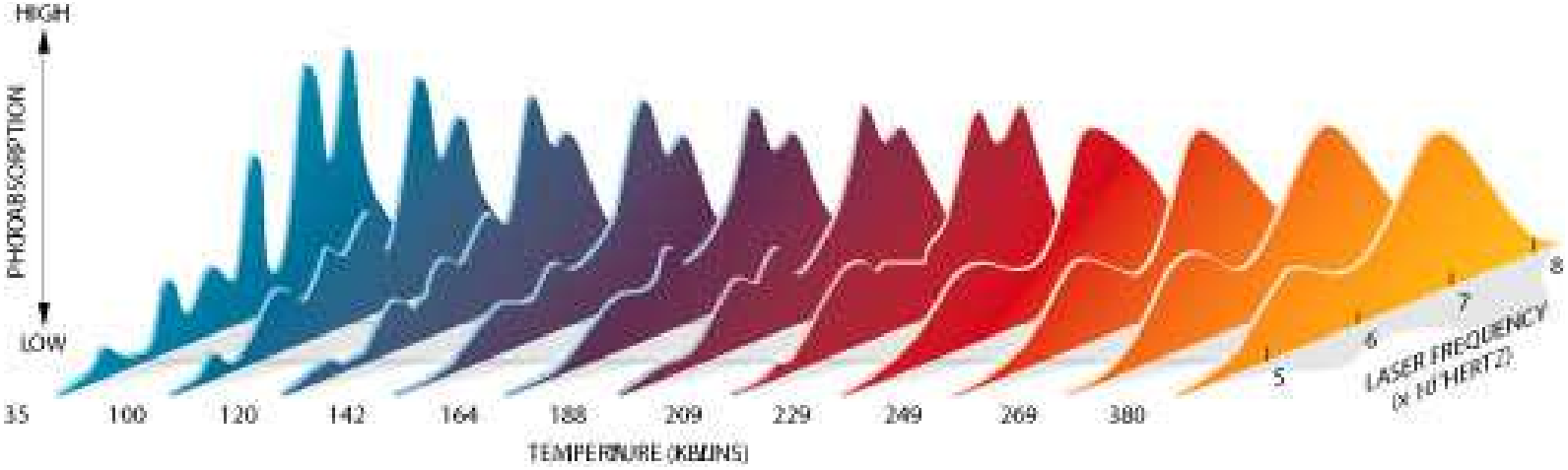
$N = 10$: deformed!

$N_m = 20$: spherical

(Solid lines: Lorentzian fits)

Transition from a cold to a hot cluster

Laser photoabsorption spectra of clusters embedded in a He gas, taken at increasing temperatures: [After H. Haberland et al., Freiburg]

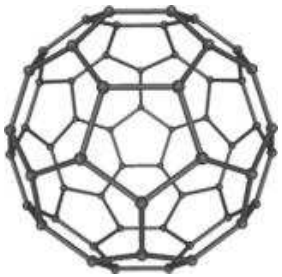


At low temperature (left, blue) we see the single lines (electronic levels) of the cluster (reflecting also the ionic structure).

At high temperature (right, yellow) we see the double-humped Mie resonance of a deformed cluster as described by the jellium model.

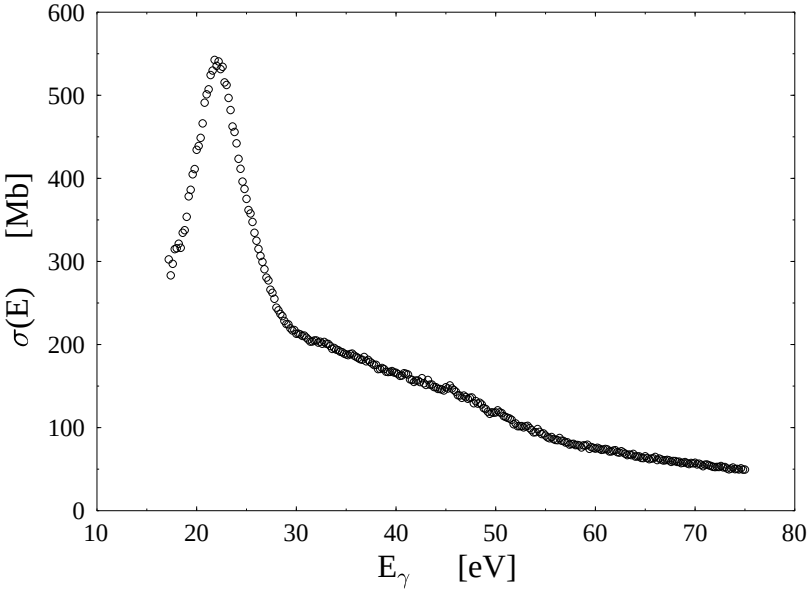
Mie plasmon in C_{60} clusters

The Buckminster fullerene ("buckey ball") C_{60}:



has 60 C atoms with
4 valence electrons each:
$\Rightarrow N = 240$ valence electrons oscillate against ionic cores!

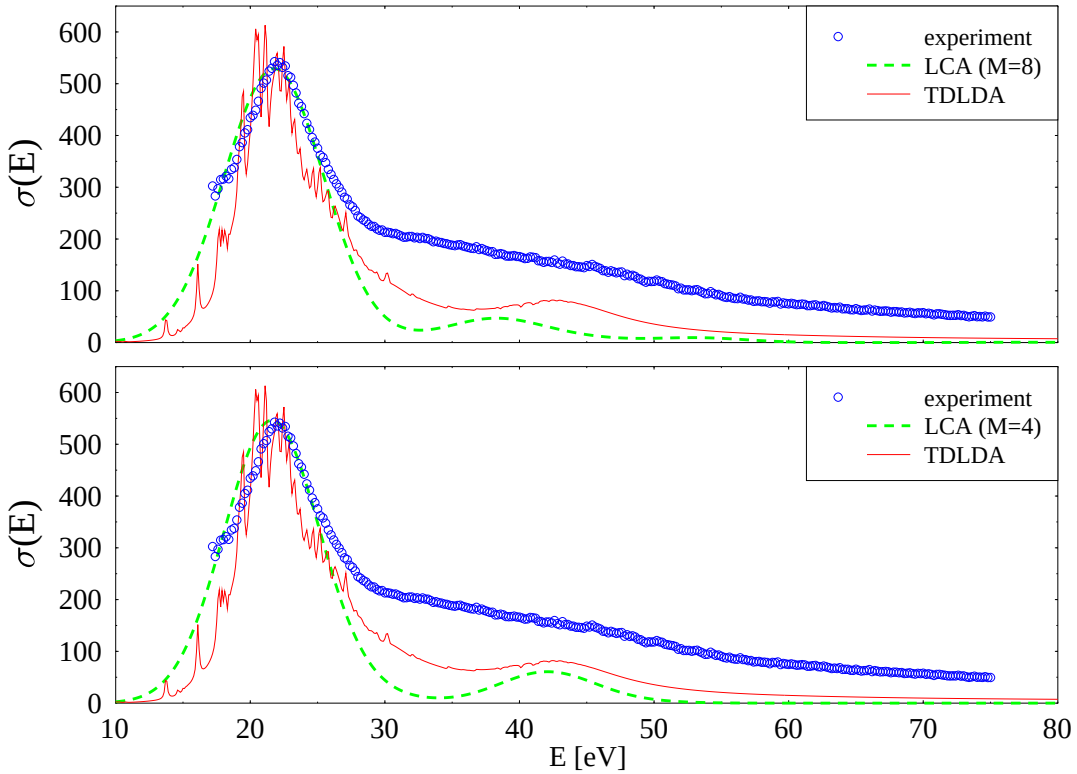
Experimental photoabsorption cross section:



[S.W.J. Scully et al. (2005)]

C_{60}: comparison with theory

Dipole absorption cross section of C_{60}: Experiment (o) versus theory: TDLDA ($\simeq$ quantum continuum RPA) [1] and
semiclassical RPA (LCA) [2] (two versions of couplings)
(both red shifted by 5.5 eV, heights adjusted)



Besides a strong Mie surface plasmon,

a volume plasmon (broad shoulder)

is seen!

[1] A. Rüdel et al., PRL (2002)

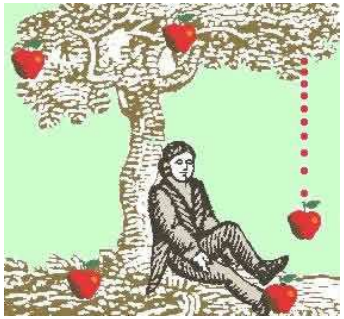
[2] K. Lamichhane et al., Int. J. Quant. Chem. (2011), ← coupling surface and volume plasmons

Contents of lectures:

1. Metal clusters: Phenomenology, electronic properties
2. The many body problem: An elementary introduction

We now go on with **2. The many body problem**

The one-body problem: Newton and the apple

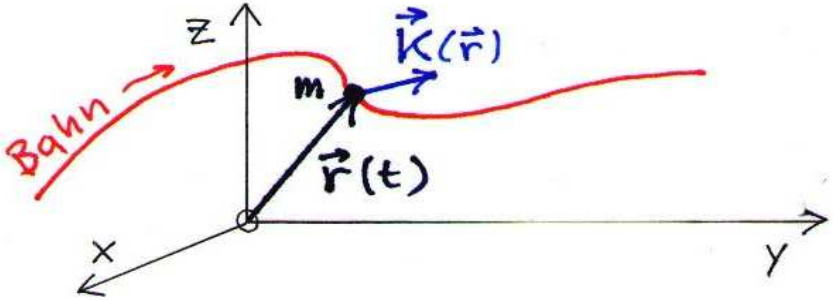


Newton's third axiom:

Force = mass × acceleration

$\vec{\mathbf{F}} = m\,\vec{\mathbf{a}} \quad (\vec{\mathbf{K}} = \text{Kraft})$

Mathematically: apple → point particle with mass m
Position of particle: $\vec{\mathbf{r}}$ (vector of three coordinates x, y, z)
Motion of particle along "trajectory" $\vec{\mathbf{r}}(t)$ (t = time)



If the force field $\vec{\mathbf{F}}(\vec{\mathbf{r}})$ is known at all positions $\vec{\mathbf{r}}$, the trajectory $\vec{\mathbf{r}}(t)$ of the particle can be determined using $\vec{\mathbf{F}}(\vec{\mathbf{r}}) = m\,\vec{\mathbf{a}} = m\,\ddot{\vec{\mathbf{r}}}(\mathbf{t})$
(i.e., solving the **"equations of motion"**)

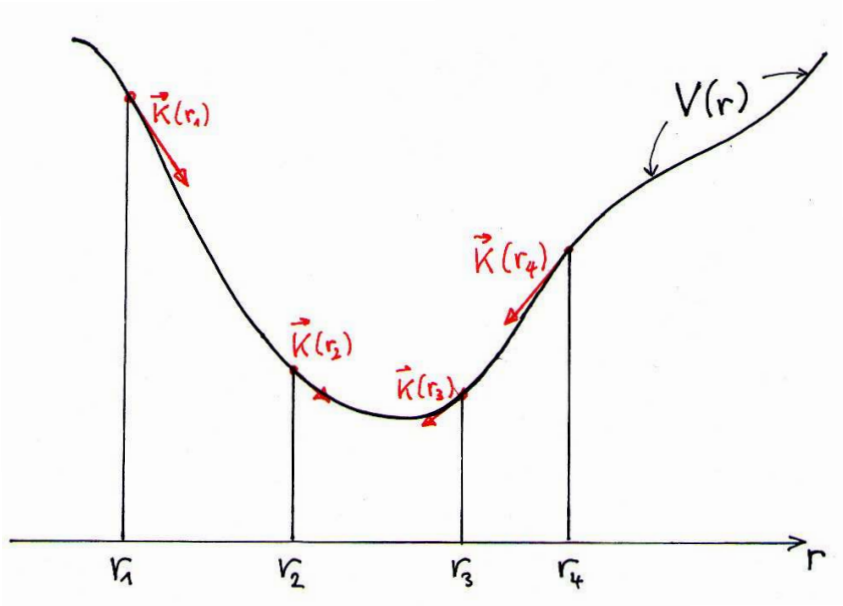
A particle in a potential $V(\vec{\mathbf{r}})$

Let $V(\vec{\mathbf{r}})$ be the potential energy (in short: "the potential") of a particle at $\vec{\mathbf{r}}$. Then the particle feels the force

$$\vec{\mathbf{K}}(\vec{\mathbf{r}}) = -\vec{\nabla} V(\vec{\mathbf{r}})$$

The vector $\vec{\nabla} V$ measures the (directed) local change ("gradient") of the potential

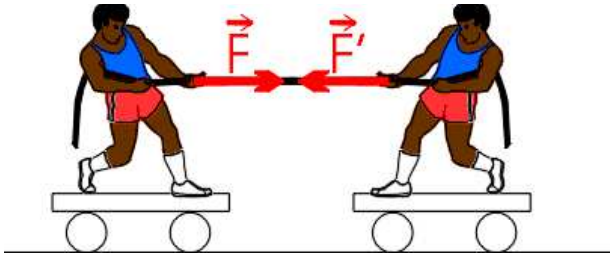
Illustration (1-dimensional):



$\vec{\mathbf{K}}(r_i)$ here equals the (negative) slope of the curve $V(r)$ at the positions r_i

The vector $-\vec{\nabla} V$ points in the direction of **steepest descent** (remember skiing!)

The two body problem

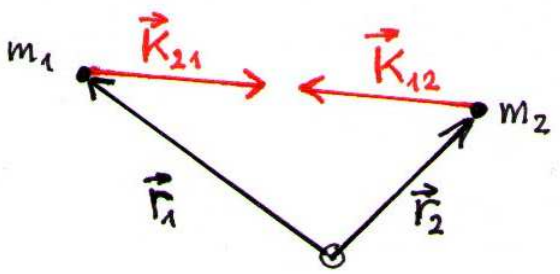


Newton's second axiom:

actio = reactio

$\vec{\mathbf{F}} = -\vec{\mathbf{F}}'$ ($\vec{\mathbf{F}}$ for "force" here: $\vec{\mathbf{K}}$ for "Kraft")

Mathematically: 2 point particles with masses m_1, m_2 at $\vec{\mathbf{r}}_1$, $\vec{\mathbf{r}}_2$:



$\vec{\mathbf{K}}_{12} = -\vec{\mathbf{K}}_{21}$
(forces in direction of the line m_1 - m_2)
(is true for all forces)

The gravitational force is inversely proportional to the square of the distance:

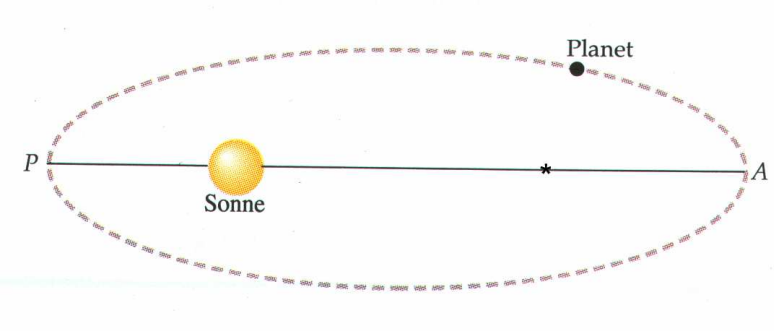
$$|\vec{\mathbf{K}}_{12}| = K_{12} = \gamma \frac{m_1 m_2}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|^2} \qquad \text{"gravitational law"}$$

γ = gravitation constant

Kepler's planet orbits

Newton showed: it follows from the gravitational law that two point masses move around each other on ellipses.
(Their centre of mass lies in one of the foci of the ellipse.)

⇒ This explained Kepler's elliptic planet orbits around the sun!



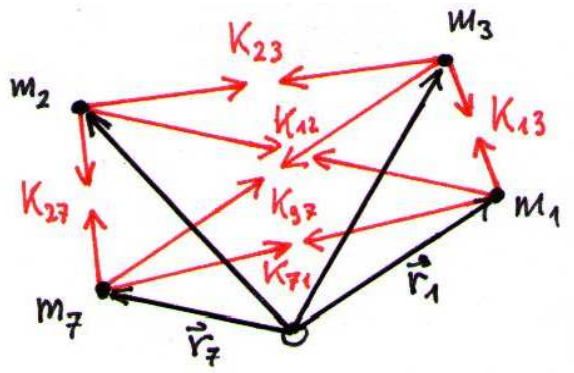
But only if one neglects the influence of all the other celestial bodies!

The two body problem (for any force that depends only on the absolute value of their distance) can be solved **exactly** in closed form (or, mathematically, in form of a converging series).

Today we say: The two body problem is "integrable".

The N body problem

Consider now N particles with masses $m_1, m_2, \ldots, m_N$ at the locations $\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, \ldots, \vec{\mathbf{r}}_N$:



This gives $\frac{1}{2}N(N-1)$ mutual pair forces K_{ij}!

We look for the solutions of the equations of motion for all orbits $\vec{\mathbf{r}}_i(t)$ $(i = 1, 2, \ldots, N)$, i.e. of $3N$ functions $x_i(t)$, $y_i(t)$, $z_i(t)$.

This can in general only be done numerically on large computers!

But the situation is even worse ...

A step towards chaos ...

Henri Poincaré recognized (ca. 1890) that for $N \geq 3$ the equations of motion for the $\vec{\mathbf{r}}_i(t)$ **in principle cannot be solved exactly** (i.e., there exist in general no converging series for the solutions)!

Today we say: The $N \geq 3$ body problem is (in general) "not integrable".

Poincaré found that unstable or even chaotic motion is possible in a non-integrable system.
He was the founder of chaos theory.

Don't panic: our solar system is quite regular ("almost integrable")!
(But one finds asteroids with chaotic orbits!)

There exist exceptionally integrable systems for $N \geq 3$.
(In these, chaos cannot emerge.)

So, the situation for the N body problem is not very encouraging....

How much is "many" in the "many body problem"?

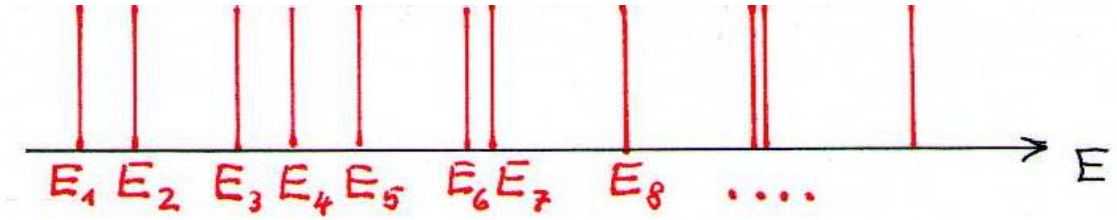
One — two — many!

Quantum mechanics

In the microscopic world (nano structures, molecules, atoms, nuclei, etc.) the laws of quantum mechanics prevail:

- no particles on orbits $\vec{\mathbf{r}}(t)$, but waves with probabilities for locations and momenta
- measurements don't always give exact results (uncertainty relations)
- expectation values $\langle \hat{O} \rangle$ of (hermitian) operators $\hat{O}$ instead of (phase-space) functions for observables $O(\mathbf{p}, \mathbf{r})$
- properties such as energy, angular momentum etc. can be quantised
- new properties (e.g. spin)

Here we speak of bound (valence) electrons with quantised energies $E = E_n, \quad (n = 1, 2, 3, \ldots)$



We call this an "energy spectrum" $\{E_n\}$

The quantum mechanical many body problem

Instead of equations of motion for N vectors $\vec{\mathbf{r}}_i(t)$ we must solve:
- the Schrödinger equation (SE) for a "wave funcion" $\Psi(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, ..., \vec{\mathbf{r}}_N, t)$
- $|\Psi|^2$ is the probability for the particles 1, 2, ..., N to be at $\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2, ..., \vec{\mathbf{r}}_N$, respectively, at the time t.

But the SE for $N \geq 3$ cannot be solved exactly!

A successful approach: the **"mean field" approximation**:
Replace the sum of all pair forces by a mean force field $\vec{\mathbf{K}}(\vec{\mathbf{r}})$ or, respectively, by a "mean potential" $V(\vec{\mathbf{r}})$ in which the N particles move independently of each other!

$V(\vec{\mathbf{r}})$ depends on $\Psi(...)$ and must be calculated "selfconsistently" (iteratively). This is still a huge task for large N, but with the help of fast computers it has today become standard (HF, DFT, CI, etc.).

But: results are purely numerical and can often not be interpreted intuitively!
$\Rightarrow$ need of simpler approaches (e.g. "semiclassics", see below) for a better understanding of the results!

Spin and Pauli principle

An important quantum-mechanical property: spin

- measured in units of $\hbar =$ Planck's action quantum (like angular momentum!)
- resembles a rotation, but different from angular momentum!
- exists also for point particles (electrons, neutrinos)
- exists also for particles with zero rest mass: e.g. photon
- has values $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$ (in units of $\hbar$)
- for $s = \frac{1}{2}$ only two states: $(\uparrow)$ and $(\downarrow)$

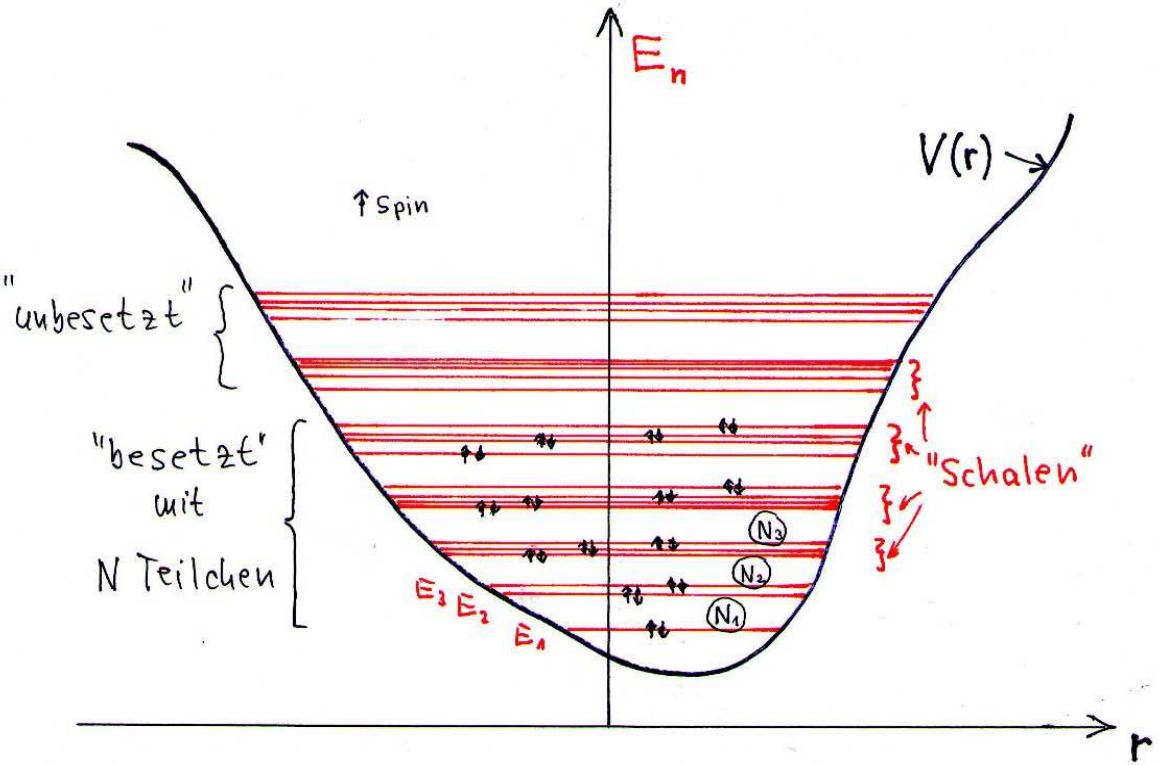
The value of the spin s determines the **social behaviour** of the particles:

- s integer: Bosons (e.g., photon: $s = 1$), like each other! ($\Rightarrow$ Bose-Einstein condensates!)
- s half-integer: Fermions (electrons: $s = \frac{1}{2}$), avoid each other! ($\Rightarrow$ Pauli principle!)

The Pauli (exclusion) principle (Pauli 1925) states:
Identical fermions may **not** agree in all properties (quantum numbers).
(As a consequence, their total wavefunction must be antisymmetric!)

N Fermions in a mean potential $V(r)$

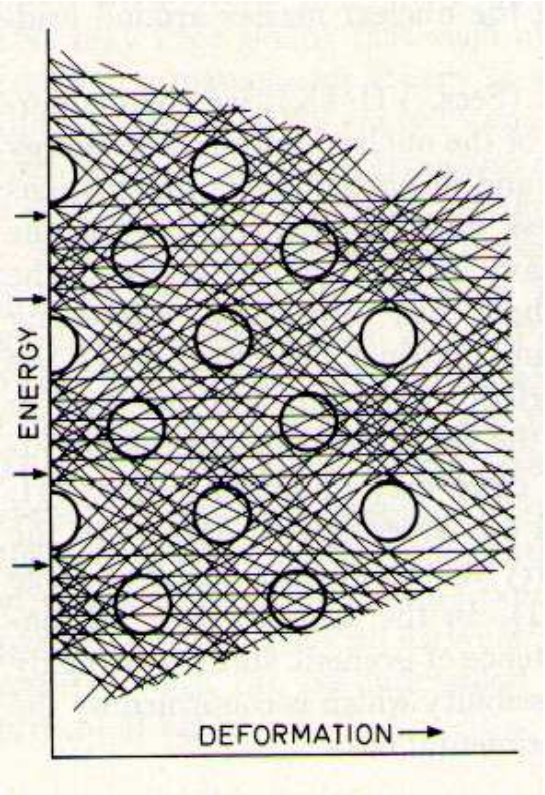
Following the Pauli principle, we fill the N particles in the lowest N energy levels E_n:



"Shell structure": Levels E_n often come in bunches.
Systems with filled "shells" have "magic numbers" N_m and are particularly stable. (In atoms: $\Rightarrow$ noble gases!)

Shell structure in a deformed system

Energy level spectrum E_n as a function of a deformation (schematic):



$\Rightarrow$ In a deformed system there are new magic numbers N_m!

Important interplay: deformation $\Longleftrightarrow$ shell structure
(e.g. in nuclei: $\rightarrow$ fission barriers)!

Hard stuff 1: the N body Schrödinger equation

We start from the approximation "cluster = ion + (valence) electron" and write the stationary Schrödinger equation*)

$$\hat{H}\,\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\,\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\,,$$

where the Hamiltonian is given by

$$\hat{H} = \sum_{i=1}^{N} \left\{ \frac{\hat{\mathbf{p}}_i^2}{2m} + V_{\mathrm{I}}(\mathbf{r}_i) \right\} + \frac{1}{2} \sum_{i,j(\neq i)=1}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}\,.$$

The first term is the sum of kinetic energies of the electrons, $V_{\mathrm{I}}(\mathbf{r})$ is the sum of (pseudo-)potentials of all ions felt by the valence electrons, and the last term is the sum of mutual electron-electron repulsion energies. (For simplicity, we neglect here the spin degrees of freedom.)

The above Schrödinger equation is extremely difficult to solve – even numerically on computers: the N body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ of the electrons depends on $3N$ variables!

*) We henceforth omit the arrows $\vec{}$ on vectors like $\mathbf{r}_i$ etc.

Hard stuff 2: Density functional theory (DFT)

From the N body wavefunction Ψ we define the local (one body) density $\rho(\mathbf{r})$ of the electrons by

$$\rho(\mathbf{r}) = \int_{d\mathbf{r}_2} \int_{d\mathbf{r}_3} \cdots \int_{d\mathbf{r}_N} |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2.$$

Note that one of the coordinates, $\mathbf{r}$, is not integrated over!
(Which one does not matter since the total wavefunction Ψ must be totally antisymmetric due to the Pauli principle.)

$\rho(\mathbf{r})$ is the probability that one of the electrons is located at $\mathbf{r}$.

A **Theorem of Hohenberg and Kohn (HK)** (1964) states:

The total energy E of the interacting system is a functional of the local density $\rho(\mathbf{r})$, given by the simple integral

$$E = \langle \Psi | \hat{H} | \Psi \rangle = E[\rho] = \int d\mathbf{r}\, \mathcal{E}[\rho(\mathbf{r})]\,.$$

Unfortunately, the functional $\mathcal{E}[\rho(\mathbf{r})]$ is known only approximately!

Hard stuff 3: The Kohn-Sham equations

Exploiting the HK theorem yields the Kohn-Sham (KS) equations:

$$\left\{\hat{T} + V_{KS}(\mathbf{r})\right\} \psi_i(\mathbf{r}) = E_i \, \psi_i(\mathbf{r}) \,. \quad (i = 1, 2, ...N)$$

These are N one-body Schrödinger equations, like for N non-interacting particles in a potential $V_{KS}(\mathbf{r})$ with an energy spectrum $\{E_i\}$.
$\hat{T}$ is the kinetic energy operator, and the KS potential is defined by

$$V_{KS}(\mathbf{r}) = V_{KS}[\rho(\mathbf{r})] = V_{\mathrm{I}}(\mathbf{r}) + V_H[\rho(\mathbf{r})] + V_{xc}[\rho(\mathbf{r})] \,.$$

$V_H(\mathbf{r})$ is the (classical) Hartree potential of the electrons:

$$V_H(\mathbf{r}) = \int d\mathbf{r}' \, \rho(\mathbf{r}') \, \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \,,$$

and $V_{xc}[\rho(\mathbf{r})]$ the so-called "exchange-correlation" potential which, again, is not exactly known. It is frequently approximated in the so-called LDA (local density approximation).

The Jellium model

The N positive ions at their positions $\mathbf{R}_i$ $(i = 1, 2, ..., N)$ are replaced by a (3-dimensional, deformable) constant charge

$$\rho_J(\mathbf{r}) = \rho_{I0}\,\Theta(|\mathbf{R}_S - \mathbf{r}|)\,,$$

where $\mathbf{R}_S$ describes the (sharp) **surface** of the cluster. [For spherical clusters: $\rho_J(r) = \rho_{I0}\,\Theta(R - r)$].

The ionic (pseudo-) potential $V_I = \sum_{i=1}^{N} V_{ps}(\mathbf{r} - \mathbf{R}_i)$ is then replaced by

$$V_J(\mathbf{r}) = \int d\mathbf{r}'\,\rho_J(\mathbf{r}')\,\frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

which for spherical clusters can be calculated analytically.

The relation of the density ρ_{I0} to the Wigner-Seitz radius r_s is $\rho_{I0} = [(4\pi/3)r_s^3]^{-1}$. r_s is the only parameter of the model!
r_s describes the kind of metal. (Na: $r_s \simeq 3.9$, K: $r_s \simeq 4.8$, etc.)

The Fermi wave length of the electrons is $\lambda = 2\pi/k_F = (32\pi^2/9)^{1/3} r_s$, $\lambda = 3.27\,r_s \gg r_s$, so they see only an averaged ionic distribution!

Hard stuff 4: The self-consistency problem

In terms of the KS single-particle wave functions $\psi_i(\mathbf{r})$, the one-body density can be written as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \,.$$

Since the potential $V_{KS}(\mathbf{r})$ depends on the density $\rho(\mathbf{r})$, which in turn depends on the $\psi_i(\mathbf{r})$, we have a **self-consistency problem:** $\psi_i(\mathbf{r})$ must be known before we can solve the KS equations which have them as their solutions!

Solution by an iterative process:

1. start with a guess for the potential $V_{KS}(\mathbf{r})$,
2. solve the KS equations to get the (new) $\psi_i(\mathbf{r})$,
3. calculate the (new) density $\rho(\mathbf{r})$ from the $\psi_i(\mathbf{r})$,
4. calculate the new $V_{KS}(\mathbf{r})$ from $\rho(\mathbf{r})$,
5. repeat this procedure, until the solutions have converged.

Contents of lectures:

1. Metal clusters: Phenomenology, electronic properties
2. The many body problem: An elementary introduction
3. Semiclassics: Quantum mechanics with classical orbits

We finally come to **3. Semiclassics**

Semiclassical quantization

The **Bohr-Sommerfeld quantization** postulates the quantization of the action integral along a classical periodic orbit:

$$S(E) = \oint p(x) \cdot dx = 2\pi\,\hbar\,(n + \alpha) \qquad n = 0, 1, 2, \ldots$$

(where α is a quantum correction derived by the WKB method for $D = 1$ dimension). This leads to quantized eneriges E_n which become exact in the limit $n \gg 1$ (Bohr's correspondence principle):

$$\boxed{S \gg \hbar} \qquad \text{"(semi-)classical limit"}$$

Surprisingly, it works often well already for $n = 0, 1, 2, \ldots$!

In $D > 1$ dimensions: **torus (EBK) quantization,** but this works only for **integrable systems!** (Einstein 1917).

Gutzwiller's trace formula (see below), derived (1968-71) from the Feynman path-integral formulation of quantum mechanics in the limit $S \gg \hbar$, works also for **non-integrable and chaotic systems!**

Triumph and fall of the Bohr-Sommerfeld quantization

The Bohr-Sommerfeld quantization yielded the correct **Rydberg spectrum** of the electron in the **hydrogen atom:**

$$E = E_n = -E_R \frac{1}{n^2} \qquad n = 1, 2, \ldots$$

where $E_R = \frac{me^4}{2\hbar^2} = 13.6\, eV$ is the "Rydberg energy".

[A historical remark: Bohr, in his first derivation, had quantized the 3rd component of the angular momentum: $L_z = n\hbar$ with $n = 1, 2, \ldots$. This yielded the same spectrum – but he could not explain why integers $n \leq 0$ had to be omitted (in particular, $n = 0$!). So, this derivation was faulty and the result fortuitous! But the essential idea of semiclassical quantization was correct.]

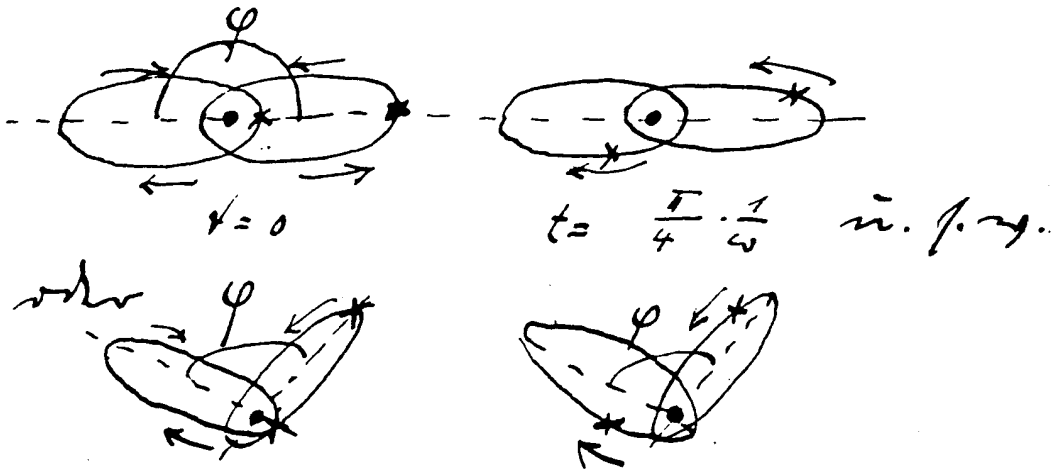
The "old quantum theory" failed when Bohr, Sommerfeld and Heisenberg attempted to derive the electron spectrum in the **He atom**!

Quantizing the helium atom?

The **helium atom** consists of a nucleus (α particle) and two electrons, i.e., it is a three-body system. The two electrons mutually disturb each others' orbits!

Werner Heisenberg, together with his teacher Sommerfeld and with Bohr, tried to generalize the quantization condition for the helium atom.

Sketches in a letter of Heisenberg to Sommerfeld (1922):



Note the angle φ between the planes of motion of the two electrons, which Heisenberg quantized by a quantum number n_φ!

Failure of the "old quantum theory"

Heisenberg obtained a good result for the ionization energy of helium (24.6 eV instead of 24.5 eV), but he needed a non-integer quantum number: $n_\varphi = \frac{1}{2}$. According to Bohr, this was **not allowed!**

Helium could not been understood. Bohr and Sommerfeld's quantum theory appeared to fail and was abandoned.

Hardly noticed by anybody, **Albert Einstein** had shown in 1917 that the Bohr-Sommerfeld quantization can only work for **integrable systems**!

Note: The hydrogen atom is integrable, but the helium atom is not!

The "old" (semiclassical) quantum theory was forgotten and replaced by the new wave mechanics (Schrödinger equation).

Only about 50 years later, new progress with semiclassical quantization was achieved through Gutzwillers trace formula (1969-1972)!

The Gutzwiller trace formula

The quantum-mechanical **density of states** (or: level density) is given by

$$g(E) = \sum_n \delta(E - E_n) = \widetilde{g}(E) + \delta g(E).$$

The smooth part $\widetilde{g}(E)$ can be obtained from the extended Thomas-Fermi (ETF) model (or a Weyl expansion).

For the oscillating part $\delta g(E)$, Gutzwiller derived a semiclassical trace formula (asymptotic, to leading order in $\hbar$):

$$\boxed{\delta g(E) \simeq \sum_{po} A_{po}(E) \cos\left[\tfrac{1}{\hbar} S_{po}(E) - \tfrac{\pi}{2}\,\sigma_{po}\right]}$$

The sum is over all periodic orbits (po) of the classical system.

$S_{po} = \oint_{po} \mathbf{p} \cdot d\mathbf{q}$ = action integral along po
A_{po} = amplitude (related to stability and degeneracy of orbits)
σ_{po} = Maslov index (= topological winding number)

Periodic orbits and chaos

Periodic orbits repeat themselves in phase space after a finite period T in time:

$$\mathbf{r}(\mathrm{t}+\mathrm{T}) \;=\; \mathbf{r}(\mathrm{t})\,, \qquad \mathbf{p}(\mathrm{t}+\mathrm{T}) \;=\; \mathbf{p}(\mathrm{t})$$

(e.g.: librations, circles, ellipses, figure-8 loops ...)

In **integrable** systems, all orbits are periodic (or quasi-periodic).
When there are continuous (e.g. rotational) symmetries, they come in degenerate families with identical properties.

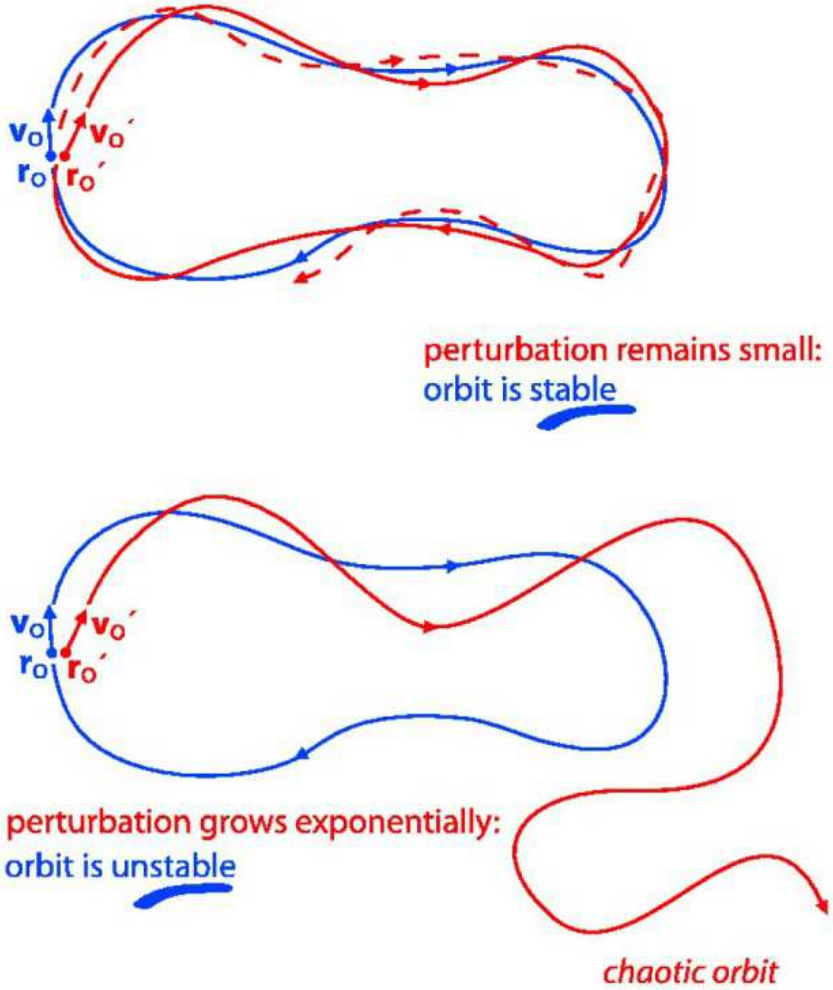
Non-integrable systems contain both periodic and irregular **chaotic** orbits which never repeat themselves.

An important aspect is the **stability** of orbits.
(See illustration below.)

Chaos: In a chaotic system, **all orbits are unstable.** Small perturbations (e.g., of the initial conditions) grow exponentially.
$\Rightarrow$ practically: no predictability in spite of determinism!

Stability of periodic orbits

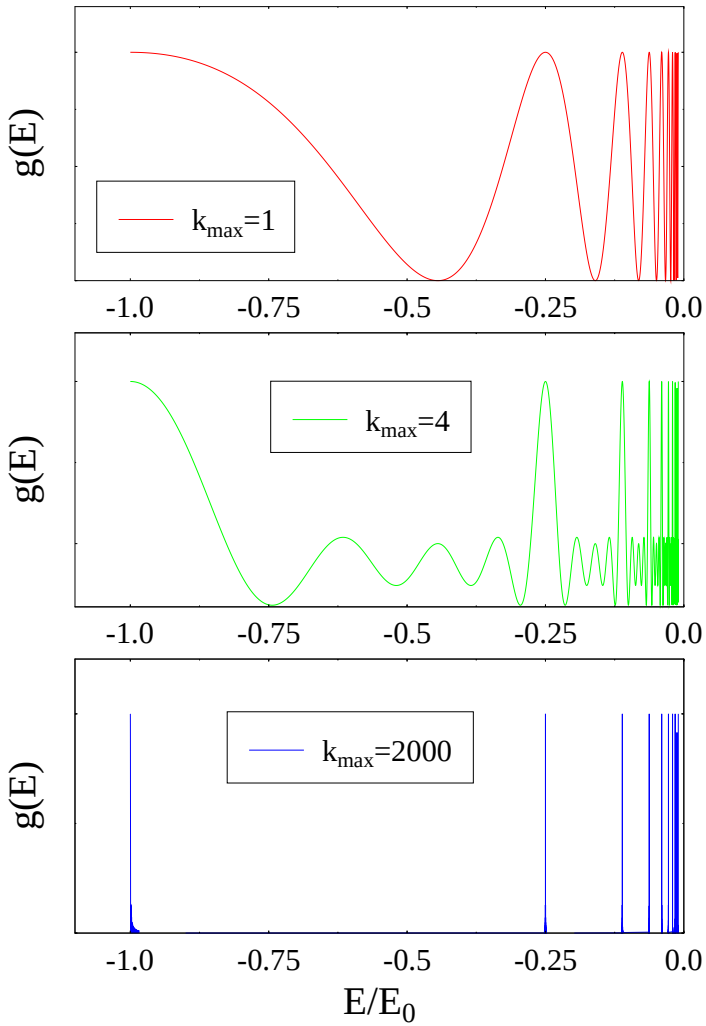
$(\mathbf{r}_0, \mathbf{v}_0) \longrightarrow (\mathbf{r}_0', \mathbf{v}_0')$ small change of initial conditions



Exact trace formula for the hydrogen spectrum

The exact level density (including the smooth part) is found to be:

$$g(E) = \frac{1}{2}\frac{E_R^{3/2}}{(-E)^{5/2}}\left\{1 + 2\sum_{k=1}^{\infty(k_{max})}\cos\left(2\pi k\sqrt{-E_R/E}\right)\right\}$$



The lowest Fourier component ($k = 1$), i.e., the shortest periodic orbit family, already yields maxima at the positions of the quantum energies.
$\Rightarrow$ "gross-shell structure"!

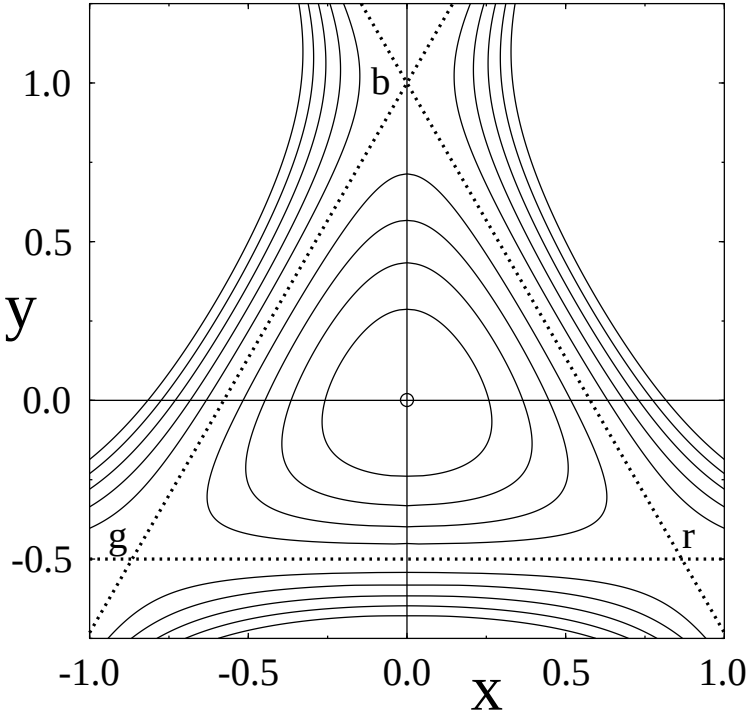
$k_{max} = 2000$ gives practically the exact quantum spectrum:
$E_n = -E_R/n^2$

A non-integrable system with chaos at high energy

A particle in the **Hénon-Heiles potential**[1]:

$$V(x,y) \;=\; 3\,(x^2+y^2) + 6\,x^2 y - 2\,y^3$$

Contour lines of constant energy:

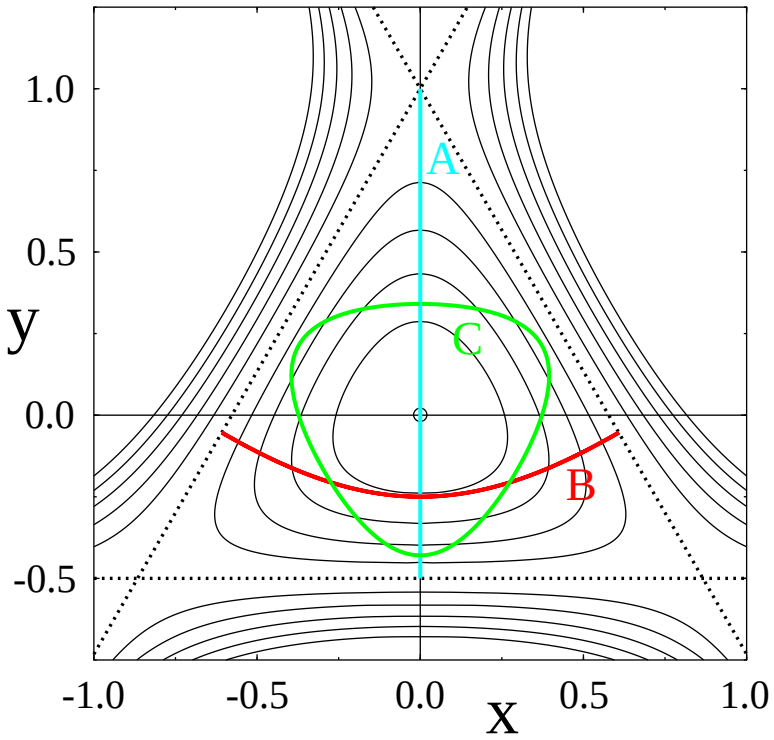


minimum: (x,y) = (0,0), energy E = 0; three saddle points at E = 1

[1] originally in astrophysics (1964): model for a star in a galaxy!

The shortest orbits in the Hénon-Heiles potential

The three shortest ("primitive") periodic orbits (shown at E = 1):



orbit A: stable up to E = 0.96, then oscillating between stable and unstable up to E = 1, giving rise to **bifurcations** of new orbits (⇒ **way to chaos!**)

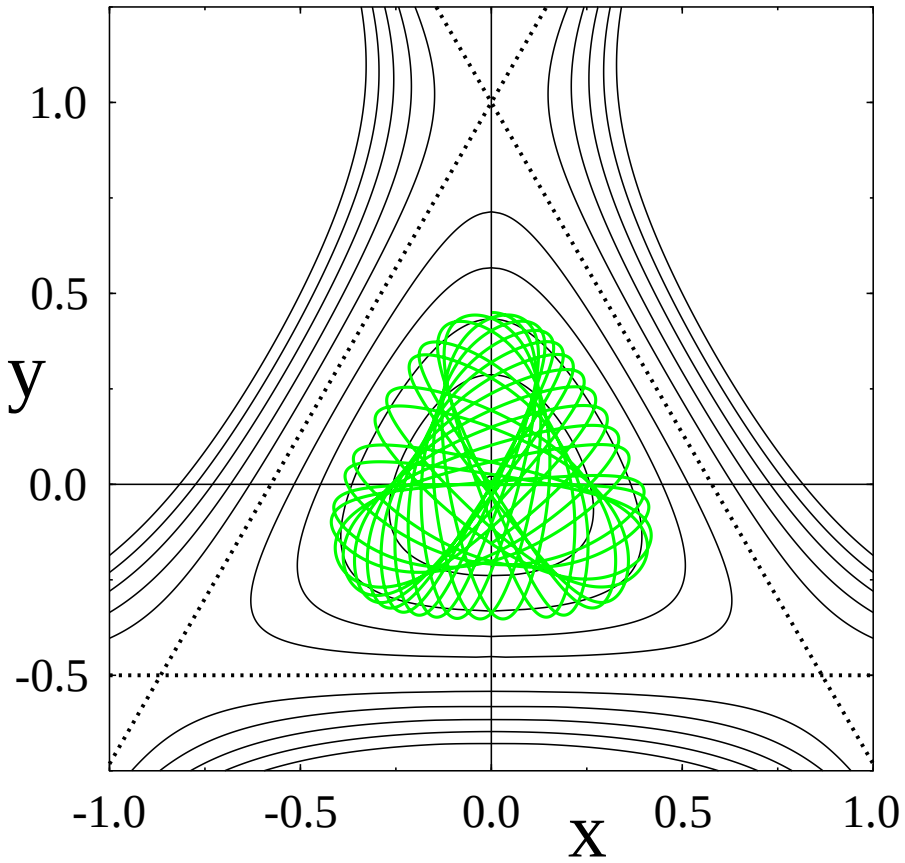
orbit B: unstable at all energies

orbit C: stable up to E = 0.89, then unstable

NB: The Hénon-Heiles potential may be used to model the **vibrational motion of a triatomic molecule**!
(The periodic solutions A, B and C near $E \sim 0$ then correspond to the elementary vibrational modes of the molecule.)

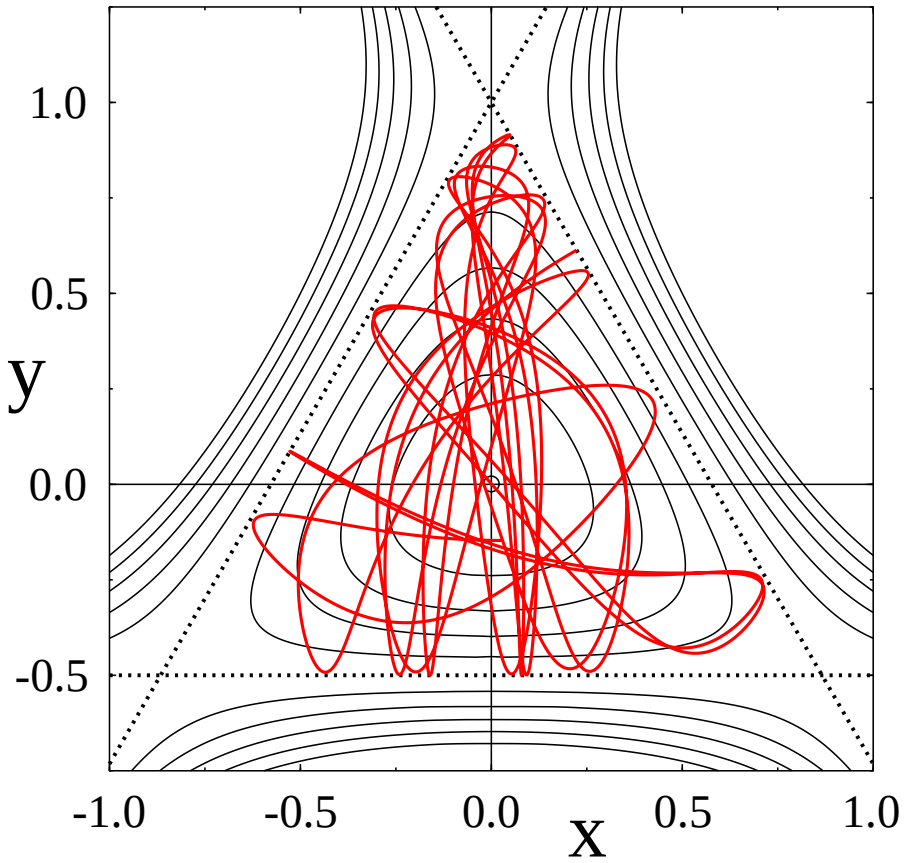
A quasi-periodic orbit in the Hénon-Heiles potential

A quasi-periodic orbit at E = 0.5: (stable)



A chaotic orbit in the Hénon-Heiles potential

A chaotic orbit at E = 1: (unstable)



Convergence problem of periodic orbit sum

In non-integrable systems, the sum over periodic orbits in general does not converge (due to bifurcations and exponential growth of the number of *pos*)! Furthermore, at bifurcations the amplitudes A_{po} diverge. (Remedy: so-called uniform approximations[1].)

Coarse-graining of the level density:
Convolution of the energy spectrum over a Gaussian with width γ:

$$g_\gamma(E) = \frac{1}{\sqrt{\pi}\gamma} \sum_n e^{-\left(\frac{E-E_n}{\gamma}\right)^2}$$

This yields an exponential damping factor in the trace formula:

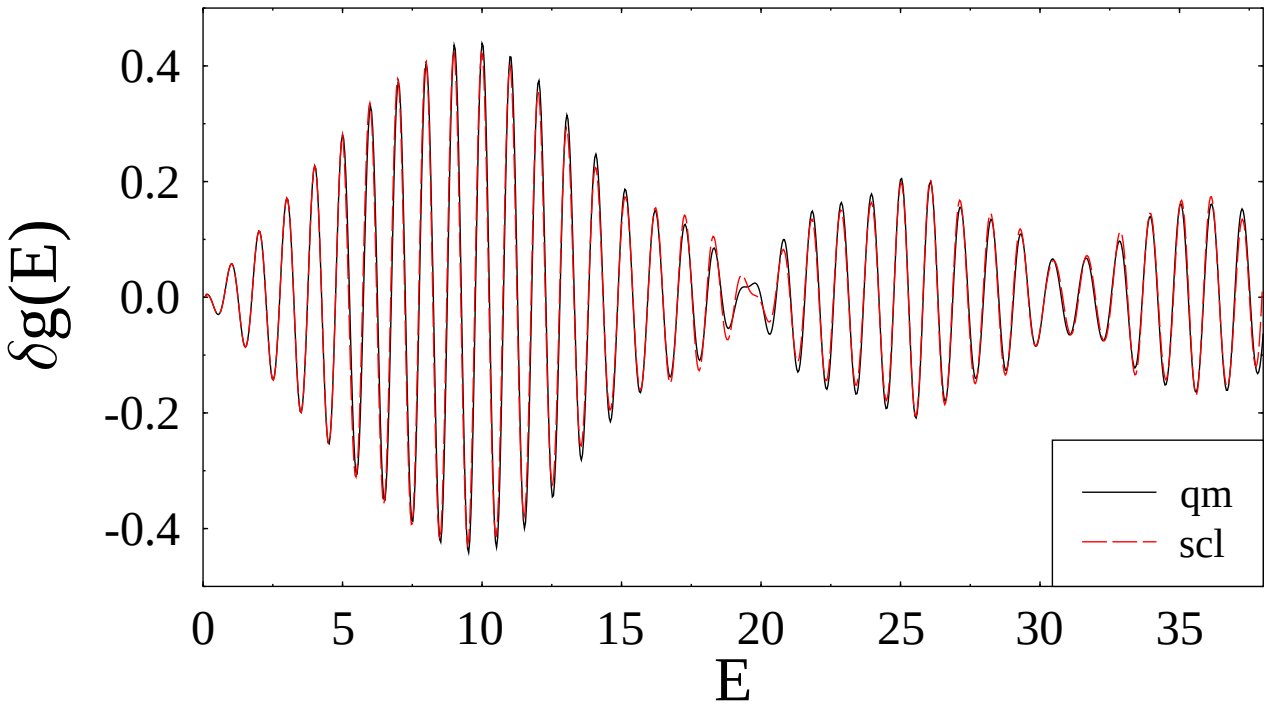
$$\delta g_\gamma(E) \sim \sum_{po} A_{po}(E)\, e^{-(\gamma T_{po}/2\hbar)^2} \cos\left[\frac{1}{\hbar} S_{po}(E) - \frac{\pi}{2}\sigma_{po}\right]$$

which suppresses the longer orbits and hence emphasizes the **gross-shell structure** of the spectrum! ($T_{po} = dS_{po}(E)/dE =$ period.)

[1] see Chap. 6.3 of book: "Semiclassical Physics", M. Brack and R. K. Bhaduri (Westview Press, USA, 2003)

Averaged level density of the Hénon-Heiles potential

Oscillating part of the coarse-grained level density:



Black curve: calculated from quantum mechanics
Red curve: from trace formula with periodic orbits A, B, and C

Note: The **beating** gross-shell structure comes about through the **interference** of the three shortest classical orbits!

Trace formulae for finite fermion systems

For N interacting fermions in a (self-consistent) mean field approximation (HF or DFT):

$$\left\{\hat{T} + V[\{\phi_i\}]\right\}\phi_n = E_n\phi_n$$

Total energy (Strutinsky theorem): $E = \widetilde{E} + \delta E$ (with $N = \widetilde{N} + \delta N$), $\widetilde{E}(\widetilde{N})$ from selfconsistent ETF model, $\delta E =$ 'shell-correction energy'

Trace formulae using the *pos* in the classical $H(\mathbf{r},\mathbf{p}) = \mathbf{p}^2/2m + V(\mathbf{r})$; practically, $V(\mathbf{r})$ is a model potential for $V[\{\phi_i\}]$

$$\delta g(E) \simeq \sum_{po} A_{po}(E)\cos\left[\frac{1}{\hbar}S_{po}(E) - \frac{\pi}{2}\sigma_{po}\right]$$

$$\delta E \simeq \sum_{po}\left(\frac{\hbar}{T_{po}}\right)^2 A_{po}(E_F)\cos\left[\frac{1}{\hbar}S_{po}(E_F) - \frac{\pi}{2}\sigma_{po}\right]$$

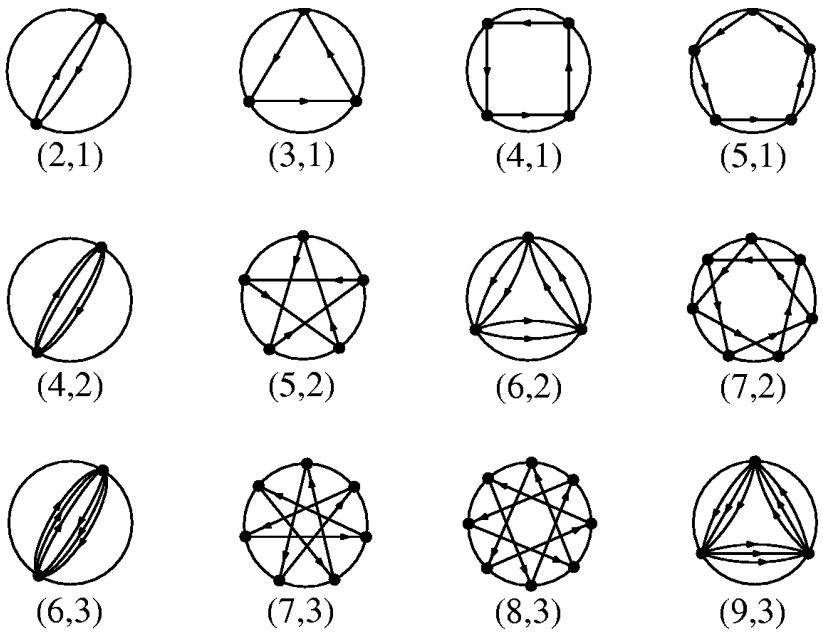
$$\delta N \simeq -\sum_{po}\left(\frac{\hbar}{T_{po}}\right) A_{po}(E_F)\sin\left[\frac{1}{\hbar}S_{po}(E_F) - \frac{\pi}{2}\sigma_{po}\right]$$

$E_F(N) =$ Fermi energy

A simple model for large metal clusters

As a model for $V[\{\phi_i\}]$ for large metal clusters, we choose a **spherical cavity** of radius R with ideally reflecting walls (with Dirichlet boundary conditions for the wave functions).

Its periodic orbits can be easily classified (Balian and Bloch, 1972):

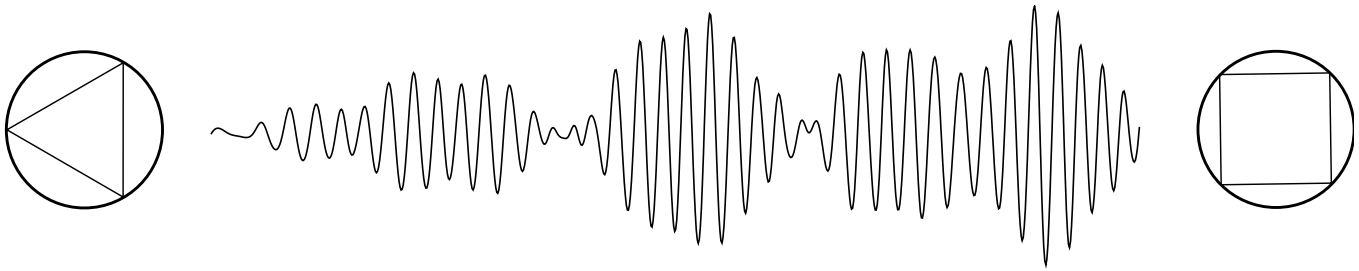


(v,w): v = # of reflexions, w = winding number
(includes repetitions of "primitive orbits"!)

Leading orbits in the spherical cavity

The orbits form families with a 3-fold continuous degeneracy (rotations about 3 Euler angles),
except for the diameter orbits which are 2-fold degenerate (no rotation about themselves!) and therefore have smaller amplitudes A_{po}.

The shortest orbits with the largest amplitudes A_{po} are the triangles (3,1) and squares (4,1).
Their interference in the trace formula[1] leads to a **beating** gross-shell structure:

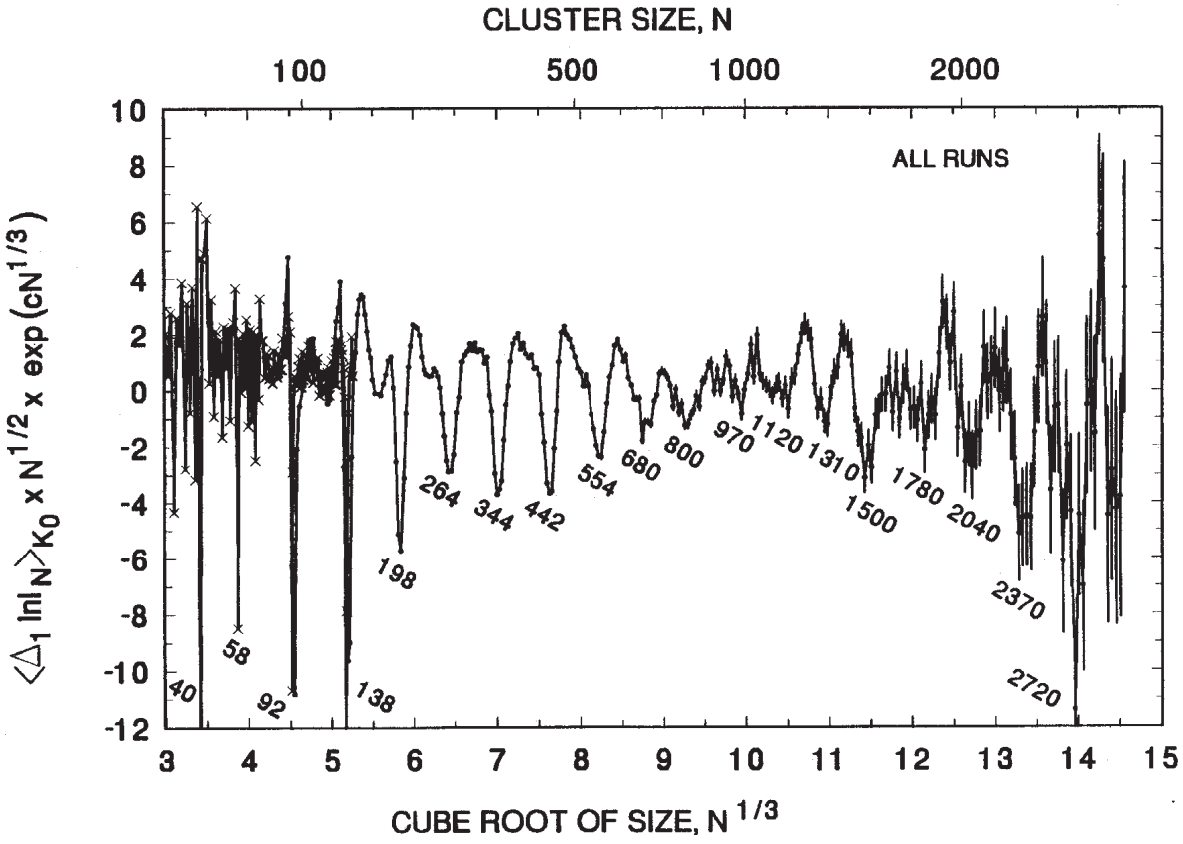


This is what we see as **"supershell" structure** in the yields of hot metal clusters!

[1]N.B.: Balian and Bloch [Ann. Phys. (N.Y.) **69**, 76 (1972)] have derived trace formulae for cavities!

Remember the supershells

Experimental abundances of hot Na clusters: (only oscillating part)

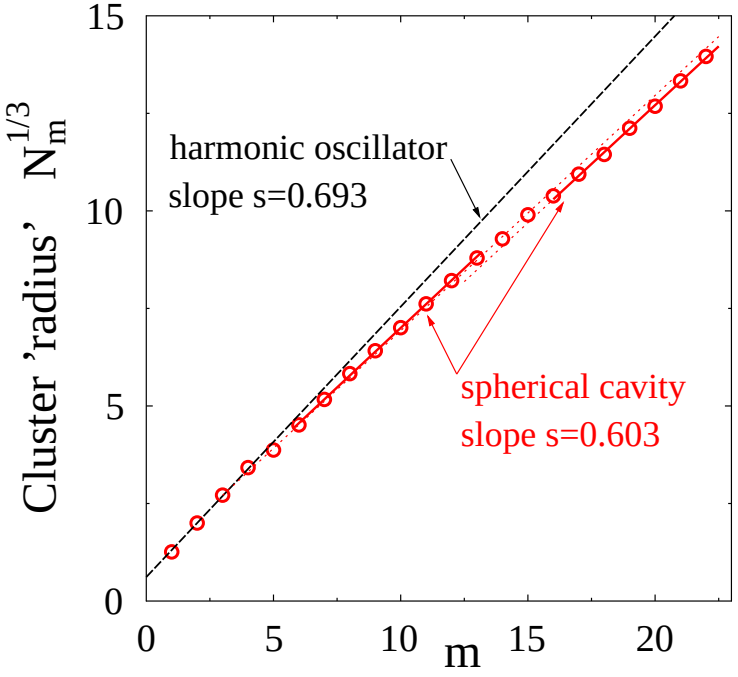


Minima: stable clusters with $N_m = 40, 58, 92, 138, 198, 264, 344, \ldots$

$N_m^{1/3}$ **are equidistant!**

Slope of magic cluster radii versus shell number

Remember the plot of $N_m^{1/3}$ against shell number m: $N_m^{1/3} = s\,m$



Experimental $N_m^{1/3}$: red circles
Slope for $m \geq 5$: $s_{exp} = 0.61 \pm 0.01$
(holds for Na and other metals: Li, Ga)

Harmonic oscillator gives $s = 0.693$, is good up to $m = 4$ (N_4=40)

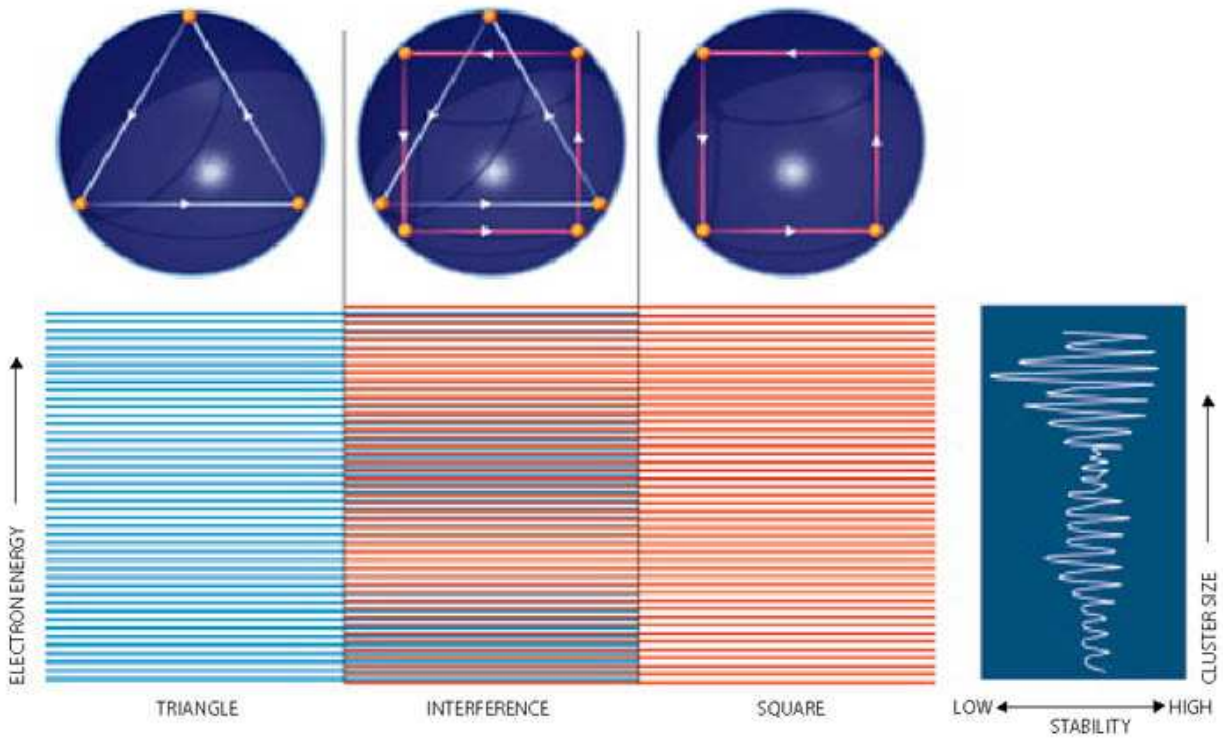
Red lines: $s = 0.603$, semiclassical from average length of △ and □ orbits in spherical cavity, independent of the Wigner-Seitz radius r_s (i.e. kind of metal!) (see exercises for details)

Dislocation near $m \simeq$ 14-15: from the difference between the lengths of △ and □ orbits; corresponds to the first minimum of the supershell beat!

Note: The quantum-mechanical slope (Jellium + DFT-LDA-Kohn-Sham) is $s = 0.61$ (like experiment)!

Supershells made semiclassically simple

Simplest model for the mean potential of the valence electrons:
3-dimensional cavity with reflecting walls



Superposition of two leading orbits ($\triangle$ and $\square$) yields:
- shell structure in the electron spectrum with correct slope $s \simeq 0.61$
- correct location of supershell beat minimum in the stabilities

THANKS!