

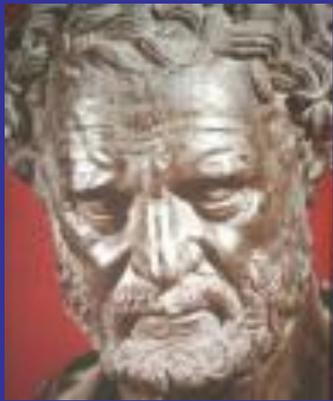
INTERNAL GEODYNAMICS
(ENDOGENOUS PROCESSES OF THE EARTH)

İÇ JEODİNAMİK
(*DÜNYANIN ENDOJEN OLAYLARI*)

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To the memory of Democritus of Abdera

Lesson 3:

The Composition of the Earth

*Part I: The atomic structure of
matter*

So far we have talked about the physical properties of rocks and minerals, such as density and velocities of seismic waves through them. But what are rocks? Let us go back to the formal definitions we gave in lesson two of a rock and of a mineral:

A rock is any naturally formed, firm and coherent aggregate or mass of mineral matter that constitutes a part of the universe.

A mineral is a naturally occurring inorganic crystalline solid of a definite (variable within fixed limits) chemical composition.

A naturally-occurring amorphous (i.e. without a long-range ordered structure) solid is called a mineraloid.

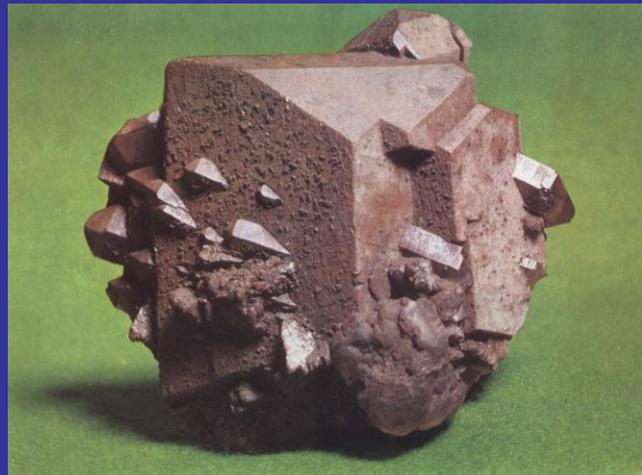
Since rocks consist of minerals and mineraloids, we had better begin with familiarising ourselves with minerals and the concepts that we see in their definition such as crystalline, solid and chemical composition.

So, what is a crystal?

A crystal is a homogeneous solid with long-range, three-dimensional order.



Beryl crystals (milky-green)



Orthoclase crystals



A topaz crystal

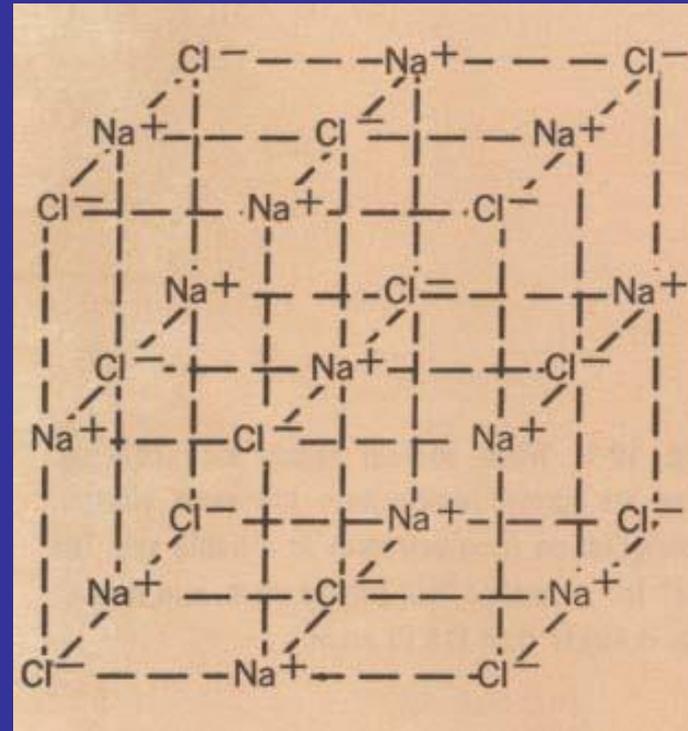


An halite crystal

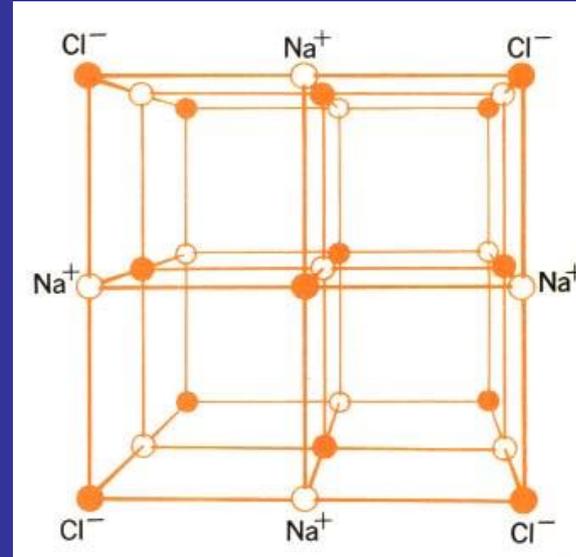
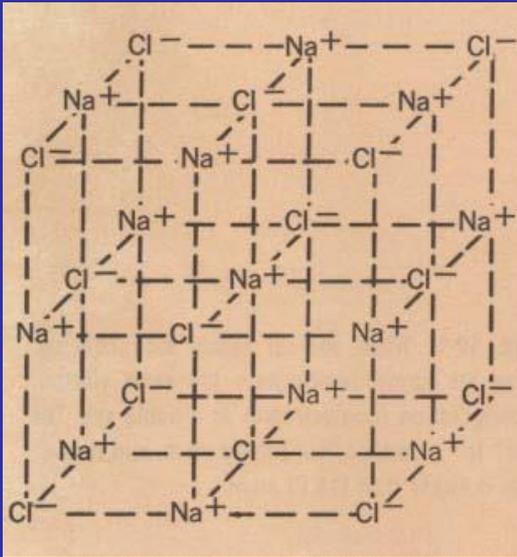


A
diopside
crystal

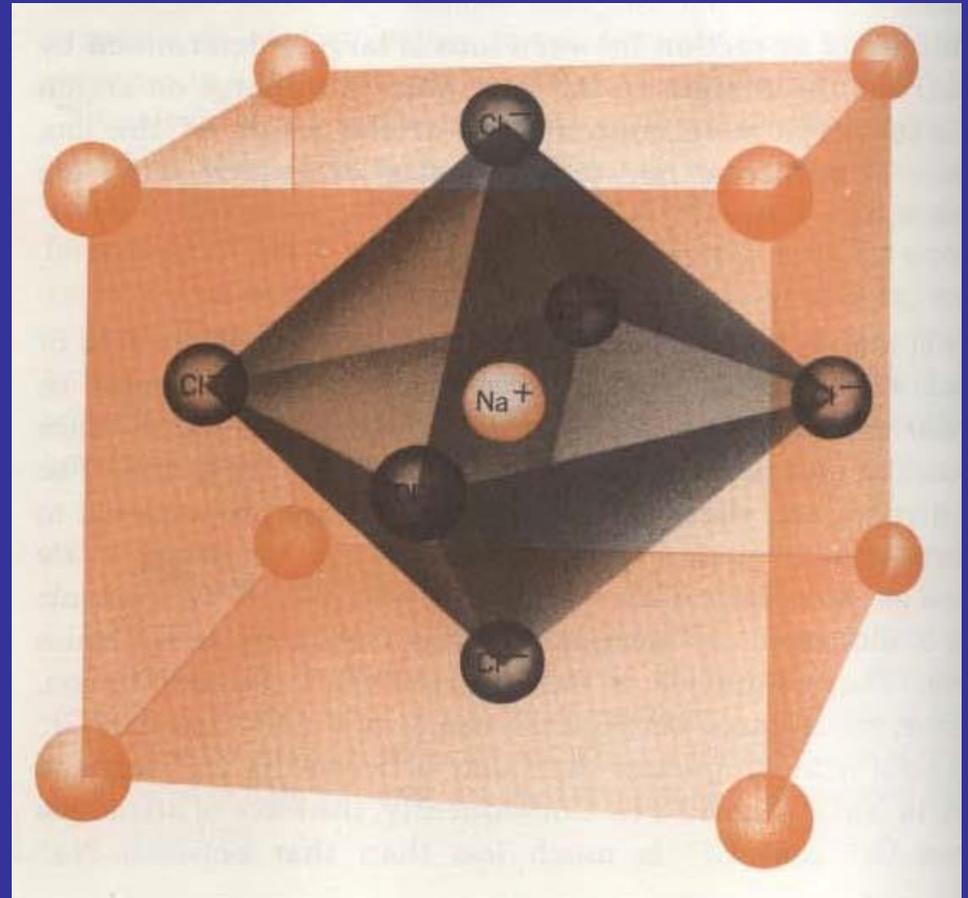
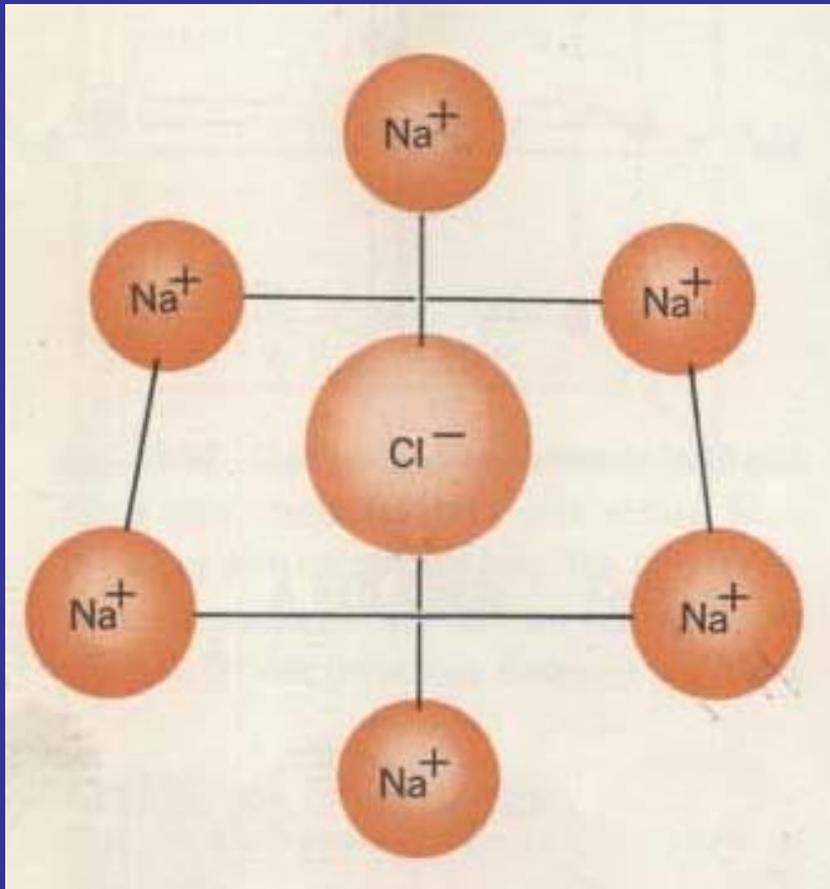
What do we mean by “long-range order”? Let us look at the structure of a halite crystal, NaCl, the common table salt.



Notice the cubic arrangement of the individual Na⁺ and Cl⁻ ions in a lattice framework. Let us now take a look at them a bit more closely.



NaCl crystal structure. Here what determines the structure is the size of the ions and their electrical charges. The distance between the nucleus of an Na^+ ion and a Cl^- ion in a halite crystal lattice is 2.814 \AA . The ions approach each other until the repulsive forces of their electron clouds stop them. This repulsive force increases the potential energy of the crystal. The interionic distance is established in a crystal when the potential energy is at a minimum.



In a halite crystal every Na^+ or Cl^- ion is surrounded by six ions of the other kind. These ions are said to have six-fold **coordination number**.

Since we began dealing with elements, atoms, ions etc., it is time we define what they are:

Elements are the most fundamental substances into which matter can be separated by *chemical* means

An atom is the smallest individual particle that retains all the properties of an element

An atom that is not electrically neutral is called an ion.

If an ion is positively charged it is called a **cation**; if it is negatively charged it is called an **anion**.

- The idea of “element” as fundamental substance was first used by the Greek philosopher **Empedocles** (fl. *ca.* 450 BC) as **rixwma** (*rixoma*), meaning “stem, root, element.” He thought there were only four elements, namely air, water, earth, fire (the “*anasir-i erbaa*” of the later Islamic philosophers and natural scientists). Later, **Plato** used the word **stoiceion** (*stoikheion*) for Empedocles’ **rixwma**. The Latin word **elementum** is considered its translation. In a modern chemical sense, one of the earliest definitions I have seen is by the great British chemist **Sir Humphrey Davy** (1778-1829), who simply said in 1813 that an element was a “body ... not capable of being decomposed.” This is exactly the definition that the great American chemist **Linus Pauling** (1901-1994) gives in his *College Chemistry* (3rd edition, 1964, p. 11), *with the reservation pertaining to radioactivity*.
- The word “atom” is directly of classical Greek origin and means “uncut” also “indivisible”. First attested usage as **atomos** (*atomos*) in a sentence is in the fragments of the Greek philosopher **Democritus** (fl. *ca.* 420 BC), the “atomist”, although it is known that **Leucippus** from Miletus (fl. *ca.* 430 BC) before him had used the same concept (the plural form **atomoi** {atomoi} has been attested in his lost writings). It comes from the root **tem-n-ein** (*temnein*) meaning **to cut**. The word atom entered the modern European languages in 1600 with the French **atome**, from which the English and German **atom** was derived.
- The word “ion” was introduced by the Great English polymath **William Whewell** (1794-1866) in 1834 during Faraday’s electrolysis experiments for particles that go to one of the “poles” or “electrodes”. It is derived from the classical Greek **ion**, the neutral present participle of the verb **ienai**, meaning “to go.” A “cation” is an ion that goes “down” to the anode (from classical Greek **kat-einai**). An “anion” is one that goes up to the cathode (**an-einai**).

The idea that substances consist of atoms was first proposed to explain a concrete scientific observation in 1805 by the English chemist (also empirical meteorologist and discoverer of colour blindness) John Dalton of Manchester to be able to account for relations among the weights of substances taking part in chemical reactions with one another.



John Dalton (1766-1844)

Dalton proposed his hypothesis to account for two observations:

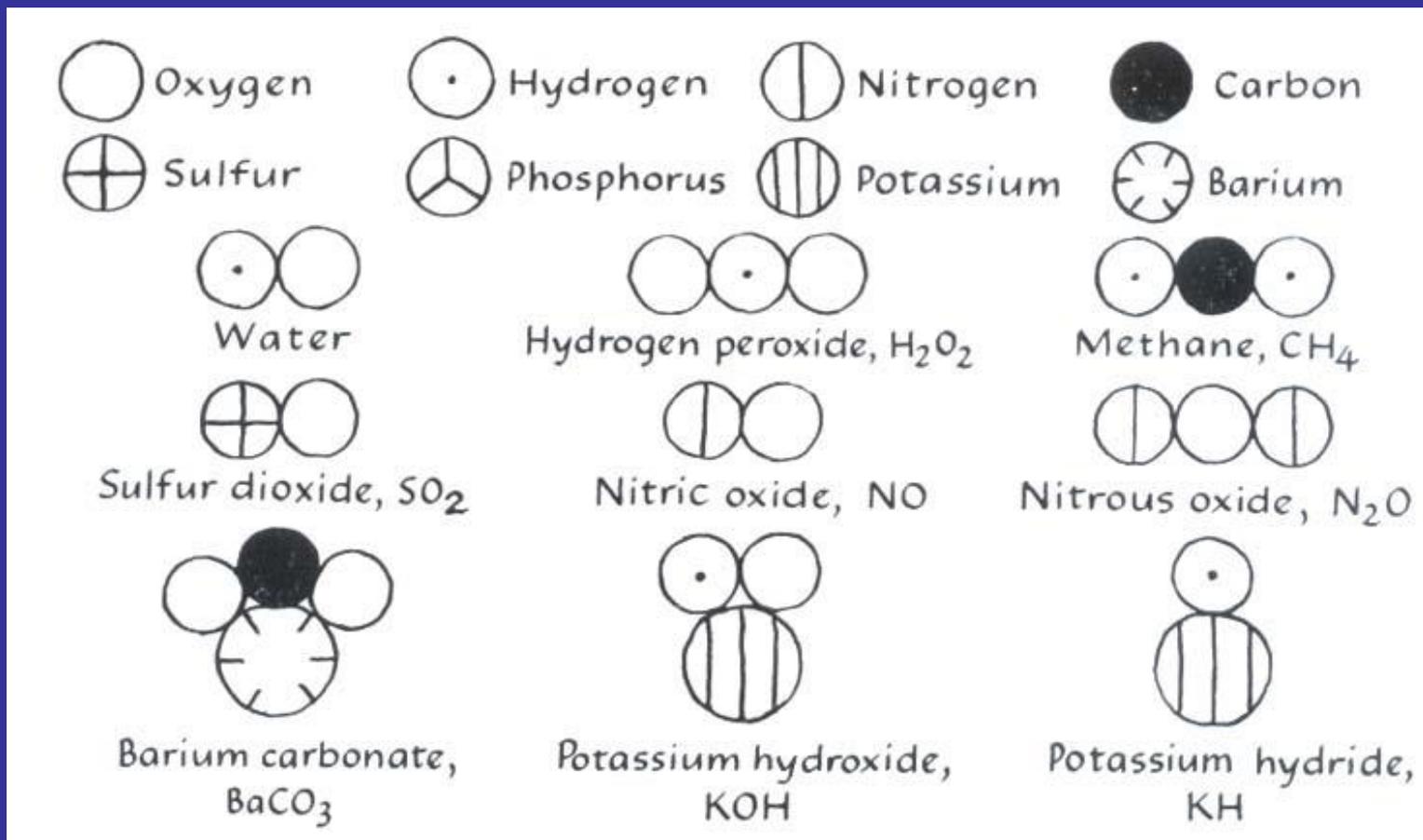
- 1) By the great French geologist and chemist Antoine Laurent Lavoisier (1743-1794), that there is no change of mass during a chemical reaction; in other words, the mass of the products equals the mass of the reacting substances (**law of conservation of mass**)
- 2) By the French chemist Joseph Louis Proust (1754-1826), that different samples of a substance contains its elementary constituents, i.e. elements, in the same proportions (**law of constant proportions**)



Lavoisier



Proust



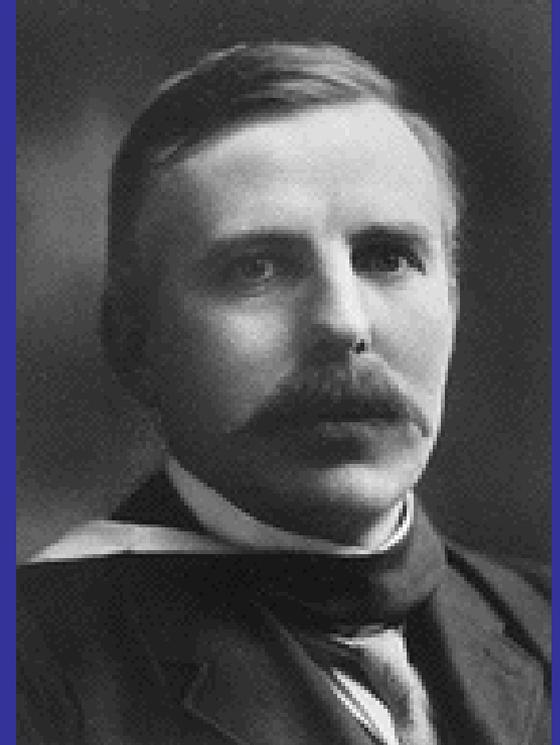
Dalton thought of the atoms as little indivisible balls. Here are some of the symbols he used to depict them and the molecules he believed formed from them.

(From Linus Pauling, *College Chemistry*, 3rd edition, 1964, fig. 2-1)

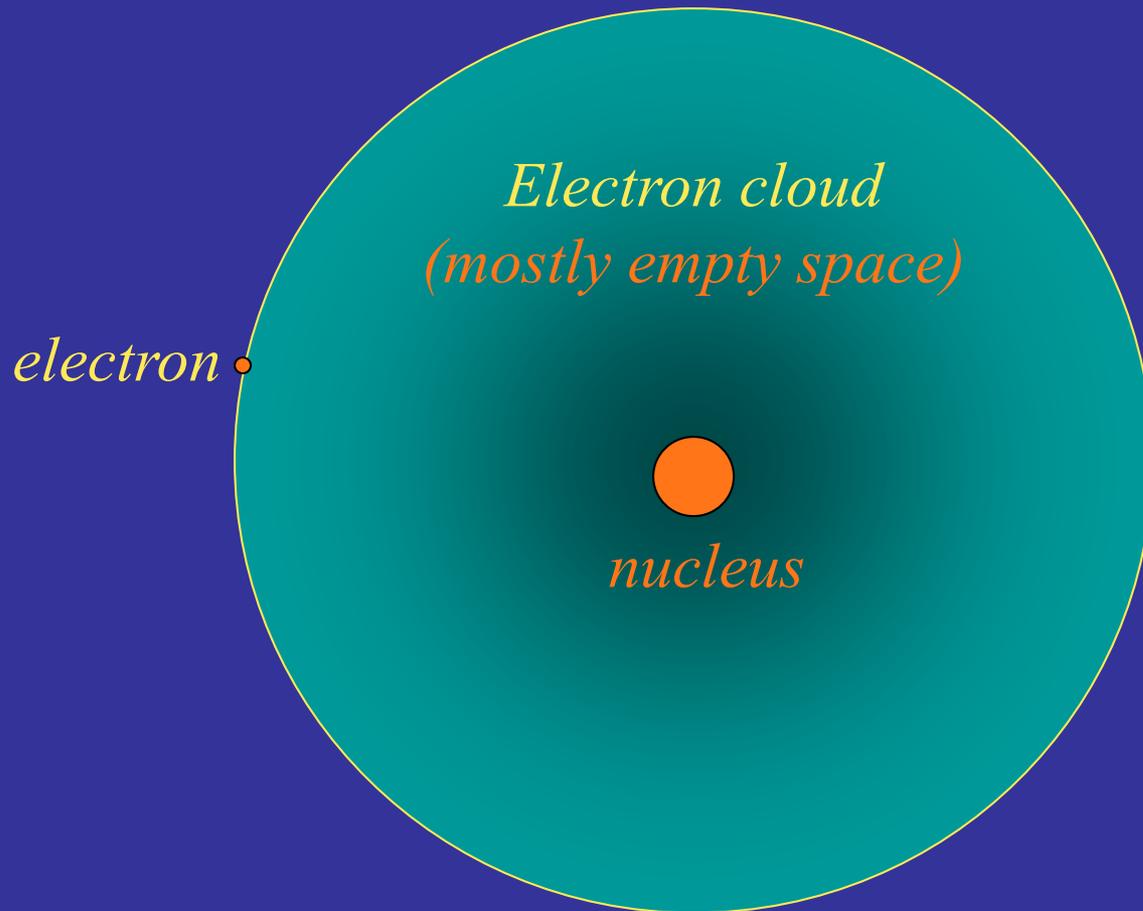
On the example of an halite crystal we saw that the Na^+ and Cl^- are bound together in a crystal lattice structure. The question is why would an Na atom wish to give up a part of its electrical charge or why would a Cl atom wish to accept an extra charge?

The answer to this question has to do with the *stability of the atomic structure*, which in turn has to do with the internal structure of atoms.

The simplest model of an atom is that proposed by the New Zealand physicist, **Ernst Lord Rutherford** (1871-1937), in 1911 which consisted of a nucleus and electrons whizzing around it. As a result of his famous gold foil experiment, **Rutherford found atoms to consist mostly of empty space!**



Rutherford



63350 cm

The diameter of the nucleus is 1/10,000 of the diameter of the atom

THE RUTHERFORD ATOM 1911

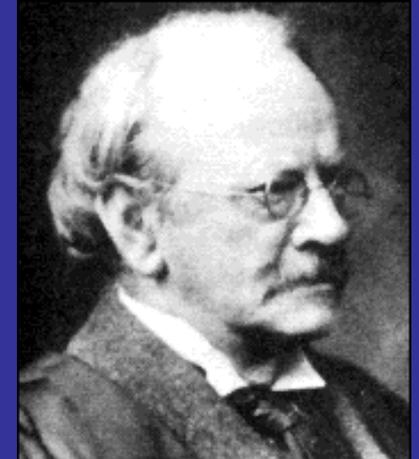
Tennis ball: 6,5 cm



In the **neutron stars**, the mass is so much (their masses are beyond the *Chandrasekhar's limit*) that the electron cloud completely collapses onto the nucleus and the electron enters the proton turning into a neutron. **Thus all atoms in neutron stars consist only of neutrons and no empty space.** You can imagine why they must be so immensely dense! These dwarf stars have densities of several tons per cubic centimetre!

The first component of the modern atomic structure to be discovered was the electron. In 1874, the Irish physicist and chemist George Johnstone Stoney (1826-1911) proposed that electricity exists in discrete units, because of Faraday's observation that during electrolysis a definite amount of electricity is needed to free a certain amount of an element from one of its compounds. He thought that this discrete amount of electricity had to be associated with atoms. In 1891, he suggested the name "electron" for this hypothetical electrical "thing" or unit.

The first test of Stoney's idea came from the great Cambridge physicist Sir John Joseph ('JJ') Thomson (1856-1940), for which he got the Nobel Prize for 1906



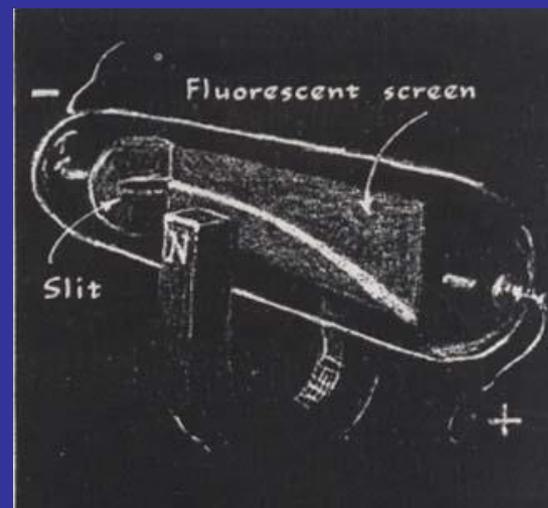
'JJ' Thomson

In 1897, J.J. Thompson experimented with Crookes tubes. Experiments were designed so that high voltage electrical current was passed between the two electrodes. Ray like emanations proceeded from the cathode electrode to the anode electrode. Since these emanations originated from the cathode electrode (−) they would be called "Cathode Rays". A Maltese Cross, placed just past the exit path of the cathode rays as they went from the cathode (−) to the anode (+). A shadow of the cross was cast upon the front of the tube. The only way that the "rays" could cast a shadow impression on the back of the tube was if they went past the exit path and struck the cross. This would strongly indicate that the rays possessed momentum, but in order for anything to have momentum that would mean that the rays would have to possess mass since

$\text{momentum} = \text{mass} \times \text{velocity}$.

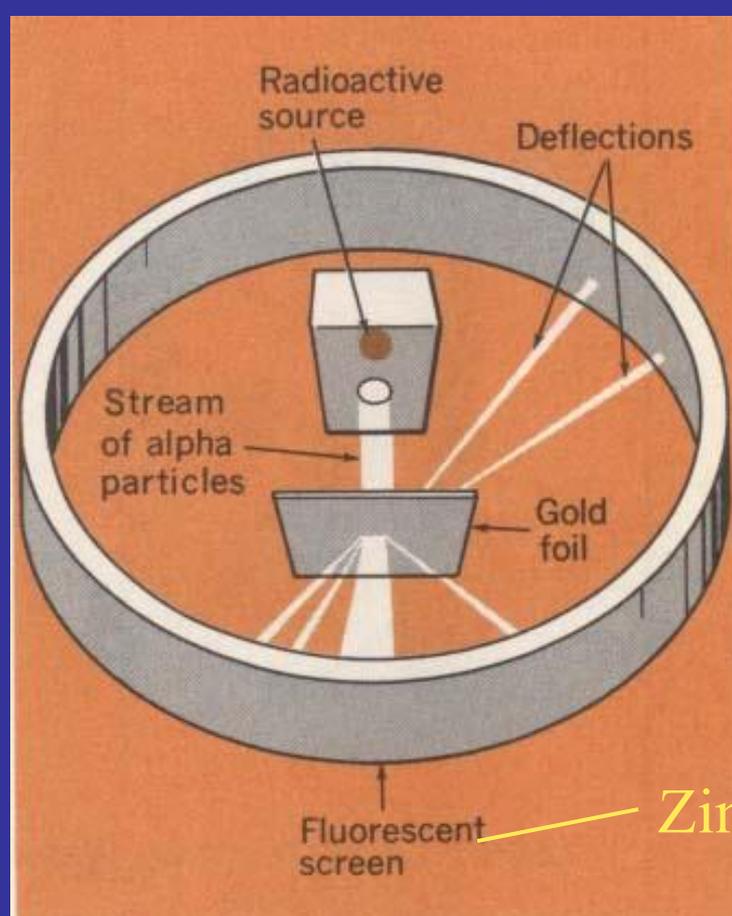
But if the "rays" possessed mass that would mean that they were *not* rays (pure radiation) at all but particles with a finite mass! Later J.J. Thompson designed some special tubes to investigate the properties of these particles. He designed a tube that allowed a beam of these Cathode Rays to impact against the surface of a zinc sulfide coated screen. As the rays impacted on the surface, it emitted a spark of light so that the invisible ray's path could be observed. He then proceeded to bring an electrical field consisting of a positive plate and a negative plate near the vicinity of the Rays. When the electrical current of the electrical field was turned on, the path of the particles was deflected away from the negative plate and toward the positive plate. This was a clear indication that the particles possessed a negative charge.

(modified from
<http://members.aol.com/profchm/jjthomp.html>)



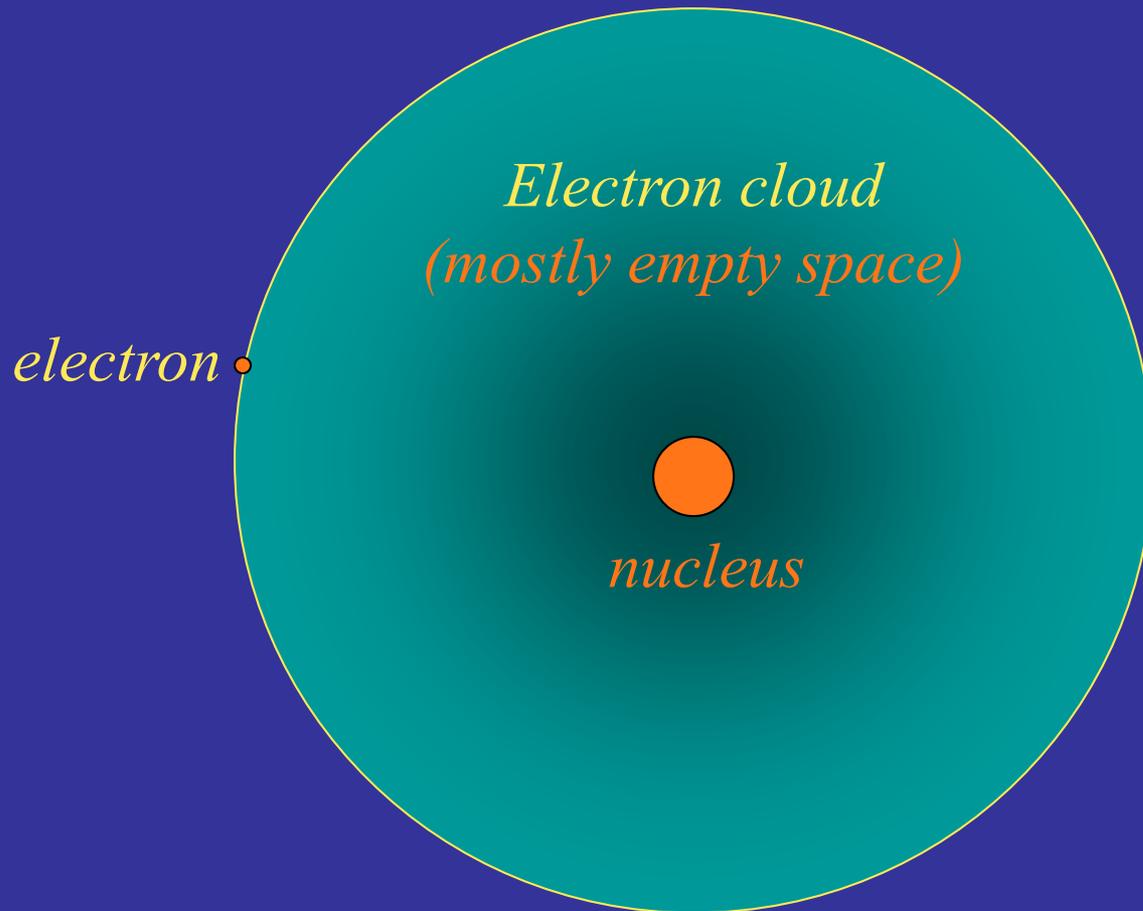
**Pictures
from
Pauling's
College
Chemistry**

What led Rutherford to undertake the gold foil experiment was his work on radioactivity, discovered in 1896 by the French physicist Henri Becquerel (1852-1908) quite by accident. Rutherford found in 1899 that radioactive radiation consisted at least of two types, which he named **alpha** and **beta radiation**. In 1900, the French physicist P. Villard found a third type of radiation called the **gamma rays**. Rutherford noted that the alpha rays carried positive electric charges and after they are slowed down by being shot through a thin gold foil, they produced helium atoms! He then concluded that the alpha particles were rapidly moving, positively charged parts of helium atoms!



Rutherford's
experiment 1911
(from Toon et al.,
1968, fig. 7-8)

But this experiment showed more: When a gold foil about 4000 \AA -thick (so that it had 1000 layers of atoms) was bombarded by alpha particles only one particle in 100,000 bounced back! So, only about one in 100,000,000 would be bounced back by a single layer of atoms. Therefore, Rutherford concluded, that the nucleus occupied about $1/10,000$ of the diameter of an atom!!!



63,350 cm

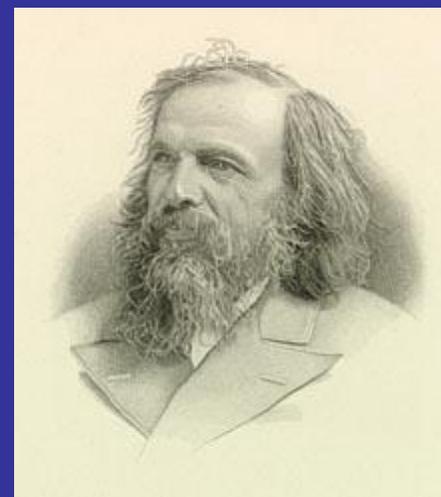
The diameter of the nucleus is 1/10,000 of the diameter of the atom

THE RUTHERFORD ATOM 1911

Tennis ball: 6,5 cm



Once Rutherford established that there were electrons and a nucleus in an atom, the next question was to find out what the electrical charges were of the atoms of individual elements in the periodic table of **Dmitri Ivanovich Mendeleev** (1834-1907). Mendeleev and his predecessors who attempted to find a sort of periodic relationship between successive elements, used **atomic weights**. The concept of atomic weight had been introduced by John Dalton by arbitrarily taking 1 for the “weight of hydrogen.” He then calculated the atomic weights of other elements relative to hydrogen. The Belgian chemist **Jean Servais Stas** (1813-1891) began using an oxygen base in 1850 taken to be 16, thinking that it was equivalent to the 1 of hydrogen. By 1895 the American chemist **E. W. Morley** (1828-1923) found that the H/O differed from 1/16 by nearly 1%. So now the atomic weight of O is taken to be 15.999. The way the other atomic weights is calculated is as follows:



Mendeleev

In one of his experiments Morley found that 1.8467 g of H combines with 14.656 g of O to form water, H₂O. What is the atomic weight of H calculated from the results of his experiment?

If the weight of O is multiplied by the fraction 15.999/14.656, it becomes 15.999, which is the atomic weight of O. Accordingly if the weight of H in the experiment is multiplied by the same fraction it ought to give the twice the weight of the hydrogen atom:

$$1.8467 \times (15.999/14.656) = 2.01594$$

This then is the weight of two atoms of H relative to O = 15.999. Hence the weight of one atom of H on this scale must be $2.01594/2 = 1.0080$.

(From Pauling, L., 1964, *College Chemistry*, 3rd edition, p. 113)

Just one month after Rutherford's 1911 gold foil experiments, the Dutch amateur physicist Antonius van den Broek (1870-1926; he was a real estate agent by profession) published a note in *Nature*:
The Number of Possible Elements and Mendeléeff's "Cubic" Periodic System

A. van den Broek

Nature, vol. 87

20 July 1911, p. 78

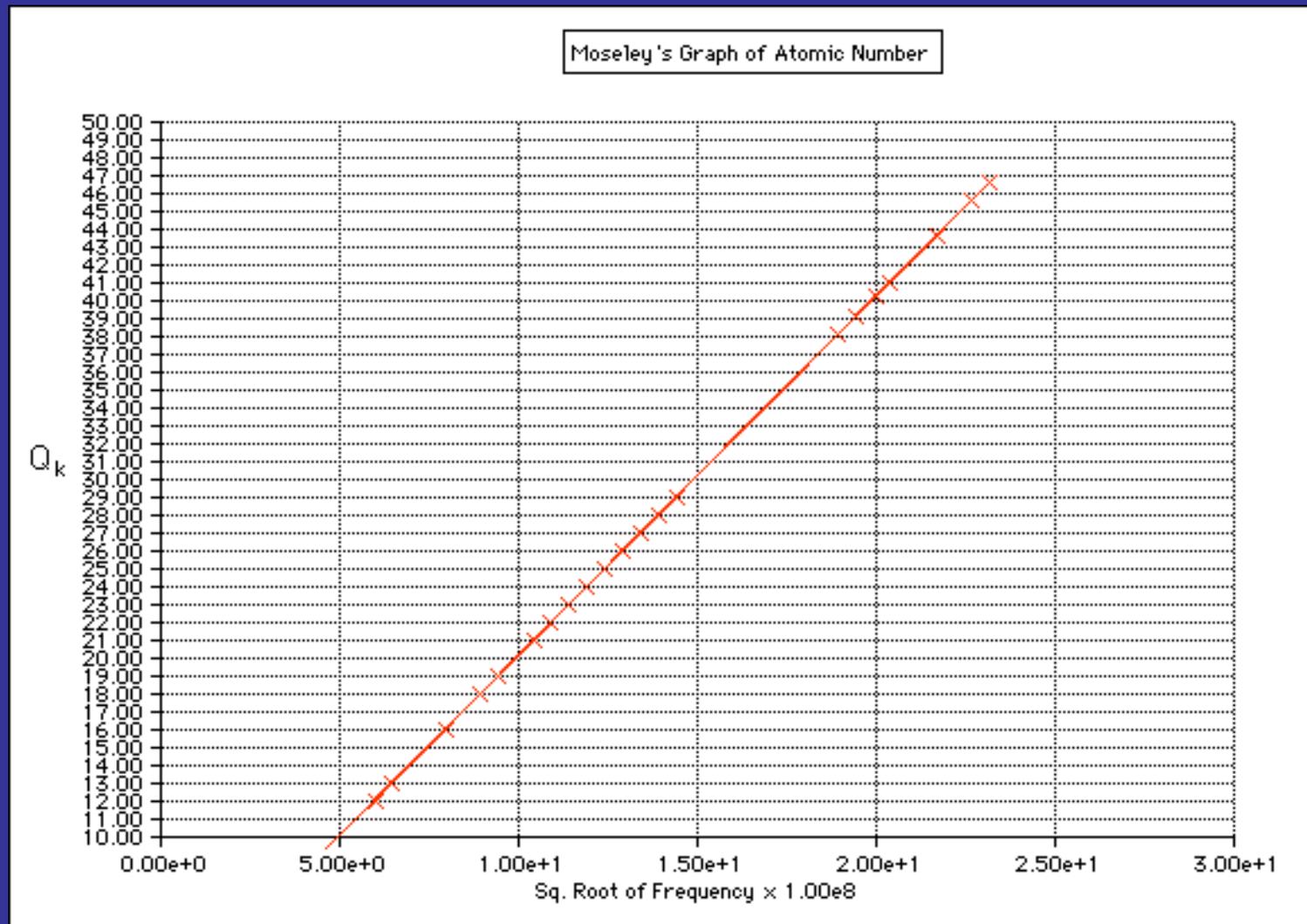
According to Rutherford's theory of "single scattering" ("On the Scattering of α and β Particles by Matter and the Structure of the Atom," *Phil. Mag.*, May, 1911), and to Barkla's "Note on the Energy of Scattered X-Radiation" (*ibid.*), the numbers of electrons per atom is half the atomic weight; thus, for U, about 120. Now, a reconstruction of Mendeléeff's "cubic" periodic system, as suggested in his famous paper "Die Beziehungen zwischen den Eigenschaften der Elemente und ihren Atomgewichten" (*Ostw. Klass.*, No. 68, pp. 32, 36, 37, and 74), gives a constant mean difference between consecutive atomic weights =2, and thus, from H to U, 120 as the number of possible elements (van den Broek "Das Mendelejeff'sche 'Kubische' Periodische System der Elemente und die Einordnung der Radioelemente in dieses System," *Physik. Zeitschr.*, 12, p. 490). Hence, if this cubic periodic system should prove to be correct, then the number of possible elements is equal to the number of possible permanent charges of each sign per atom, or to each possible permanent charge (of both signs) per atom belongs a possible element.

The problem for Moseley, one of Lord Rutherford's brilliant research students, was therefore to find a linear relationship between some nuclear property and the linearly increasing steps of the atomic weights in the periodic table of Mendeleev. He noticed, on the basis of the British physicist Charles Barkla's (1877-1944) work, that each element sent out a characteristic X-ray wavelength when bombarded by electrons. The inverse square root of the wavelengths plot linearly against the elements as they appear in Mendeleev's periodic table. From this, Moseley generated the following graph:



Henry Gwynn Jeffreys Moseley (1887-1915), who fell on 10th August 1915 at the Sarı Bayır

Battle in Gallipoli and joined those young men about whom Mustafa Kemal Atatürk said in 1935 "they are now also our children." When Moseley's death became known, even a German (i.e. an enemy) newspaper described it as "Ein schwerer Verlust" (=a heavy loss). I am not aware whether a similar notice appeared in any Turkish newspaper at the time.



From
<http://dbhs.wvusd.k12.ca.us/webdocs/AtomicStructure/AtNum-Moseley.html>

The concept of “atomic number” turned out to be a better guide to the position of any element in the periodic table because of the (then just discovered by Frederick Soddy, 1877-1956) isotopes (that have different atomic weights but the same atomic number). The atomic number increased perfectly linearly from one element to the next.



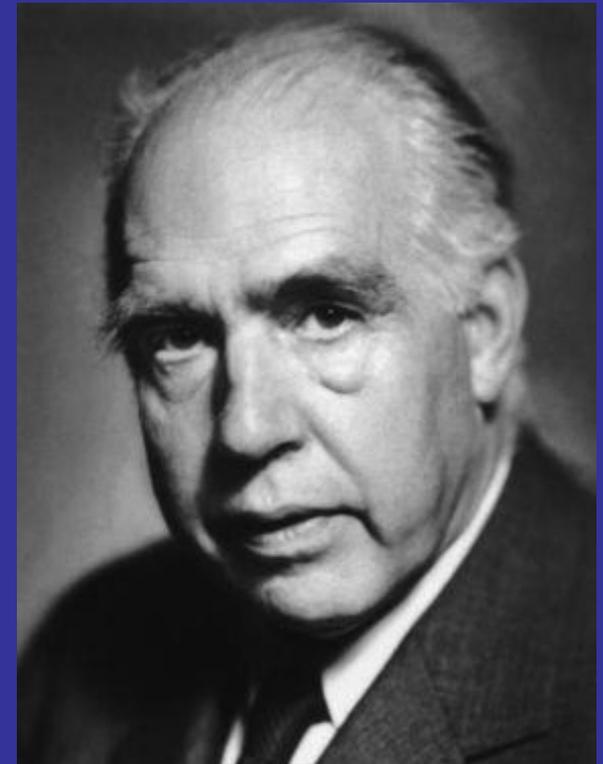
Sir James
Chadwick
(1891-1974)

In 1932, Sir James Chadwick, another student and close collaborator of Lord Rutherford, noticed that the radiation from beryllium, reported to be extremely penetrating by Curie’s daughter and her husband earlier in 1932, consisted of neutral particles with the mass of a proton. Already in 1920, Lord Rutherford had suspected the existence of **neutrons** consisting of one proton and one electron. This was their first experimental confirmation. Sir James Chadwick won the Nobel Prize for physics in 1935.

The next important step in our understanding of atomic structure came from **Niels Bohr**, a great Danish physicist, who used Einstein's concept of "light quanta" to explain the Swiss mathematician **Johann Jakob Balmer's** (1825-1898) formula of the atomic spectral lines of the hydrogen atom. This formula, published in 1885, is:

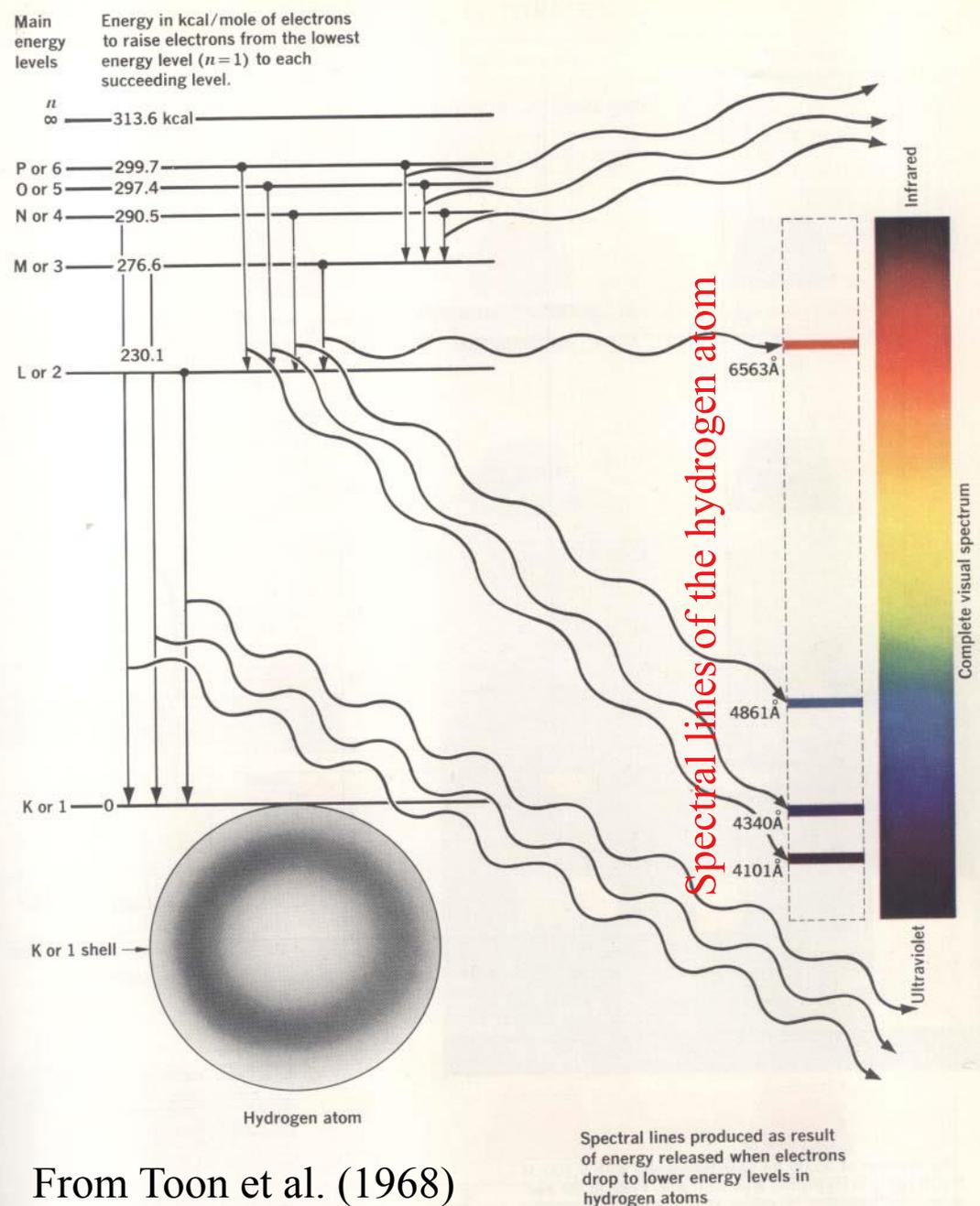
$$\frac{1}{\lambda} = R \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

Where λ is the wavelength of the emitted radiation, n is any integer larger than 2, and R is the so-called Rydberg constant, which is $1.097 \times 10^7 \text{ m}^{-1}$, if λ is measured in metres.



Niels Henrik David Bohr
(1885-1962)

The study of the spectral lines had begun seriously by 1880. They are parts of the light spectrum given off by individual atoms when they are losing an excited state, to which they had been brought by being energised (by light, or by an arc of electricity, or by a similar energy source). Nobody could quite understand how these lines formed until Niels Bohr's explanation.



From Toon et al. (1968)

To explain the spectral lines and the mathematical regularity they obey as expressed by Balmer's formula, Bohr made the following assumptions:

1. Electrons can travel only in certain specific energy levels called **orbits** or **shells**.
2. Energy is radiated only when an electron falls from one energy level to the next one down.
3. The angular momentum (mvr^*) of any electron is quantised.

Now where do the “energy levels” come from? They come from Bohr's *arbitrary* postulate that the angular momentum is quantised as follows: $mvr = nh/2\pi$, where **n** is any integer and **h** is Planck's constant ($=6.6 \times 10^{-27}$ erg sec).

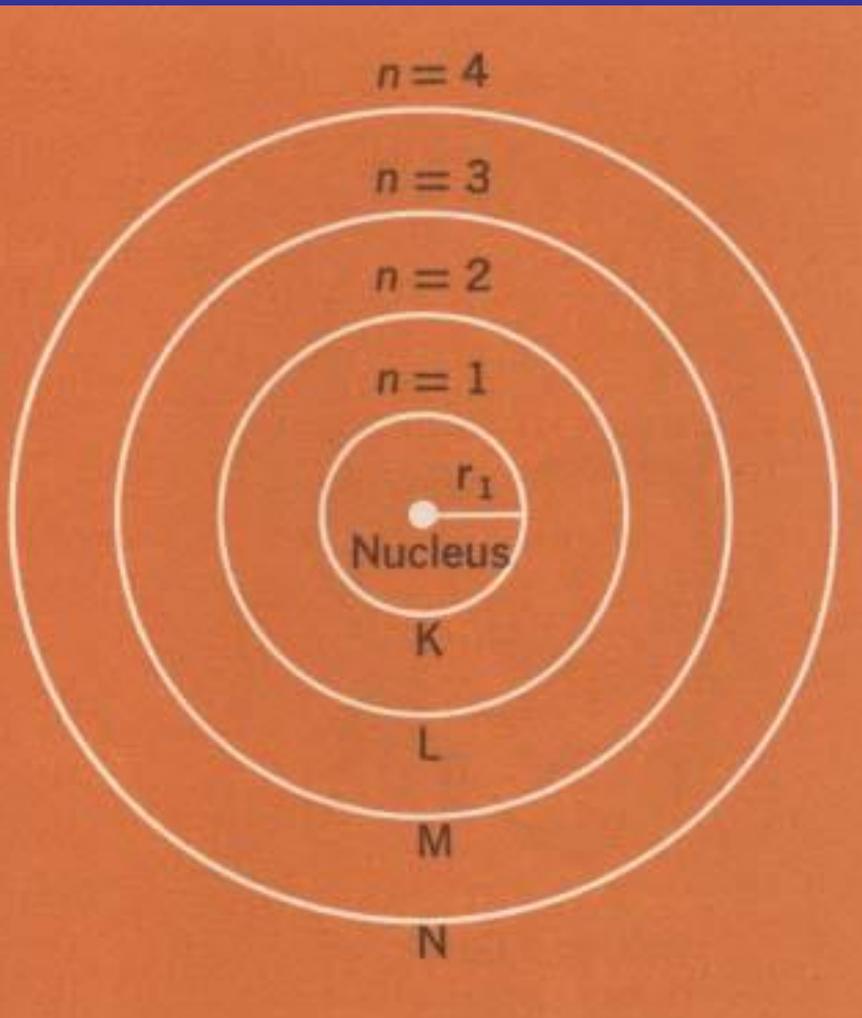
* m =mass of the electron, v = its velocity, r = its distance to the nucleus

Bohr assumed, following Lord Rutherford's model, that electrons orbited the nucleus as in a planetary system. To ensure the stability of the orbit he equated the centripetal force resulting from the circular movement of the electron, mv^2/r , with the electrostatic force attracting the electron to the nucleus, which is Ze^2/r^2 , where Z is the nuclear charge and e is the charge of the electron. Now, Bohr introduced his quantised amount of angular momentum into this equation and, after substitutions, he obtained

$$r = n^2/h^2(4\pi^2mZe^2)$$

where m is again the mass of the electron and h is Planck's constant. Using this equation Bohr calculated the radii which electrons are allowed (because of his quantisation of the angular momentum) to occupy in an hydrogen atom.

The resulting picture is the now-familiar Bohr "solar system" model of the hydrogen atom.



The “solar system” or “planetary” model of the atomic structure according to Niels Bohr (from Toon et al, 1968)

Now since the total energy of an electron must be the sum of its potential and kinetic energies, which can be expressed as

$$E = -Ze^2/2r$$

If we here substitute the expression for r obtained by Bohr, we get

$$E = (-2\pi^2Z^2e^4m)/(n^2h^2)$$

When an atom goes from an excited E_2 state of energy to an E_1 state, it emits energy (in the form of radiation). We can calculate the frequency of the waves of this radiation using Planck’s equation, $E=h\nu$, where ν is the frequency and h is Planck’s constant.

So $\nu = (E_2 - E_1)/h$ (*the Bohr frequency rule*)

and the wavelength λ is $\lambda = c/\nu$

This thus resolves the mystery of the Balmer formula.

The minimum energy state of the hydrogen atom is when the single electron occupies the $n = 1$ or K orbit or shell. This state is called the **ground state** or the **normal state** of the hydrogen atom. When the atom is excited the electron jumps to higher states. When the electron occupies any one orbit, the atom is said to be in its **stationary state**. The ground state is the lowest energy stationary state of an hydrogen atom.

Although Bohr was given the Nobel Prize for physics in 1922 for this work, his model left many problems outstanding. First, the quantisation of the angular momentum was an arbitrary choice just to “save the phenomenon.” Secondly, Bohr assumed that the position and the velocity of an electron were simultaneously knowable. This was shown to be impossible by the then 26-year-old Werner Heisenberg of the University of Göttingen in 1927 (***The Heisenberg Uncertainty Principle***). Moreover Bohr’s model could not be used for atoms with an atomic number higher than 1 (i.e. it was applicable only to the hydrogen atom).

The first important development upon the Bohr model came from the French physicist **Prince Louis-Victor de Broglie** when he showed that the quantisation of the position of the electron to certain “orbits” simply resulted from its wave nature. In his remarkable doctoral thesis in 1924, he showed that any matter must have both particle and wave nature, just as light does, because,



Prince Louis-Victor
de Broglie (1892-
1987)

if $E = mc^2$ and also $E = h\nu$, one can simply write

$mc^2 = h\nu$; since $\nu = c/\lambda$, we get

$\lambda = h/mv$ (*de Broglie equation*)

where v is simply velocity and h is Planck's constant ($v = c$ in case of light)

This was a shocking result for many at the time. But it had far reaching conclusions:

Prince de Broglie showed that that the wavelength of an electron calculated with the de Broglie equation had just the right value to reinforce the electron waves in the Bohr orbits!

Consider the following example given by Linus Pauling (*College Chemistry*, 3rd ed., 1964, pp. 79f.):

What is the wavelength of an electron with 13.6 eV of kinetic energy?

One volt is 1/300 statvolt and the electric charge of an electron is — 4.80×10^{-10} statcoulombs. The energy of a 13.6 eV electron then must be

$$E = 13.6 \times 4.80 \times 10^{-10} / 300 = 0.218 \times 10^{-10} \text{ erg}$$

This is equal to $(1/2)mv^2$, the kinetic energy of an electron moving with velocity v ; so:

$$mv^2 = 0.436 \times 10^{-10} \text{ erg}$$

Let us multiply both sides of the previous equation with m :

$$m^2v^2 = 0.436 \times 10^{-10} \times m = 0.436 \times 10^{-10} \times 9.107 \times 10^{-28} = 396 \times 10^{-38}$$

Now if we take the square root of each side:

$$mv = 1.99 \times 10^{-19} \text{ g cm sec}^{-1}$$

By use of the de Broglie equation we can then obtain the wavelength:

$$\lambda = h/mv = \frac{6.624 \times 10^{-27} \text{ g cm}^2 \text{ sec}^{-1}}{1.99 \times 10^{-19} \text{ g cm sec}^{-1}} = 3.33 \times 10^{-8} \text{ cm} = 3.33 \text{ \AA}$$

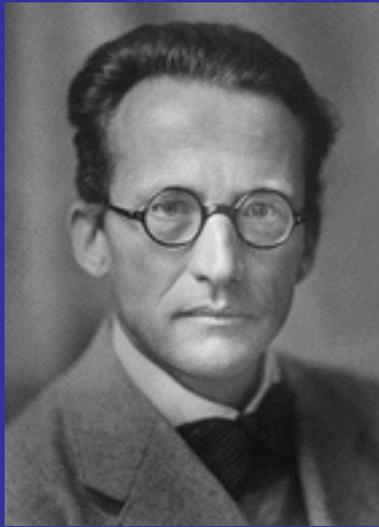
Now the kinetic energy of an electron in the first Bohr orbit (K , i.e. $n=1$), i.e. in the *ground state*, is 13.6 eV. We found the wavelength corresponding to this electron to be 3.33 Å. The radius of the first Bohr orbit is 0.53 Å. If we multiply this by 2π to obtain the orbital length, we get 3.33 Å! Thus, according to de Broglie there is just one wavelength of an electron in the first Bohr orbit.

According to Bohr's theory, the velocity of an electron in the n^{th} orbit is just $1/n$ of the velocity in the first Bohr orbit and the wavelength is thus $n \times 3.33 \text{ \AA}$.

But if $r = n^2 \times 0.53 \text{ \AA}$, then the circumference, $2\pi r$ must be $n^2 \times 3.33 \text{ \AA}$

The amazing result is that we thus see that there can only be n electron wavelengths in the circumference of the n^{th} orbit. Does this mean that only n electrons may occupy the n^{th} orbit? No, because when the Bohr model was developed certain attributes of the electron were not known. Now we know, for example, that into the Bohr orbit $n=1$ we can fit two electrons (in reality we are not fitting them into the Bohr orbit, but into the $1s$ orbital, but that will come later). The critical thing at this stage is that the Bohr model was found unsatisfactory, because it did not "explain" the quantisation of the angular momentum of the electron and hence its energy level. Bohr just assumed it to "save the phenomenon" of the Balmer series. But Prince de Broglie had opened a way to do the explaining.

If the electron behaves not only like a particle, but also like a wave, we can use not only Newtonian-like particle mechanics, but wave equations to describe its behaviour. This is exactly what the great Austrian physicist Erwin Schrödinger did. In 1926, he adopted Sir



Erwin
Schrödinger
(1887-1961)

William Rowan Hamilton's (1805-1865) equation for standing waves in a completely water-covered earth (Sir William had derived the equation to study the tides) and applied it to the electron using de Broglie's relation. This was the great breakthrough! Schrödinger showed that the quantised values of the electron positions are just the result of the wave-like behaviour of the electron. From this it was seen that the electrons occupied strange-shaped spaces around the nucleus. These spaces are probability amplitudes of where an electron might be found around the nucleus.

The Schrödinger equation is the following:

$$\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0$$

m = mass of the electron

h = 6.6×10^{-27} erg sec (Planck's constant)

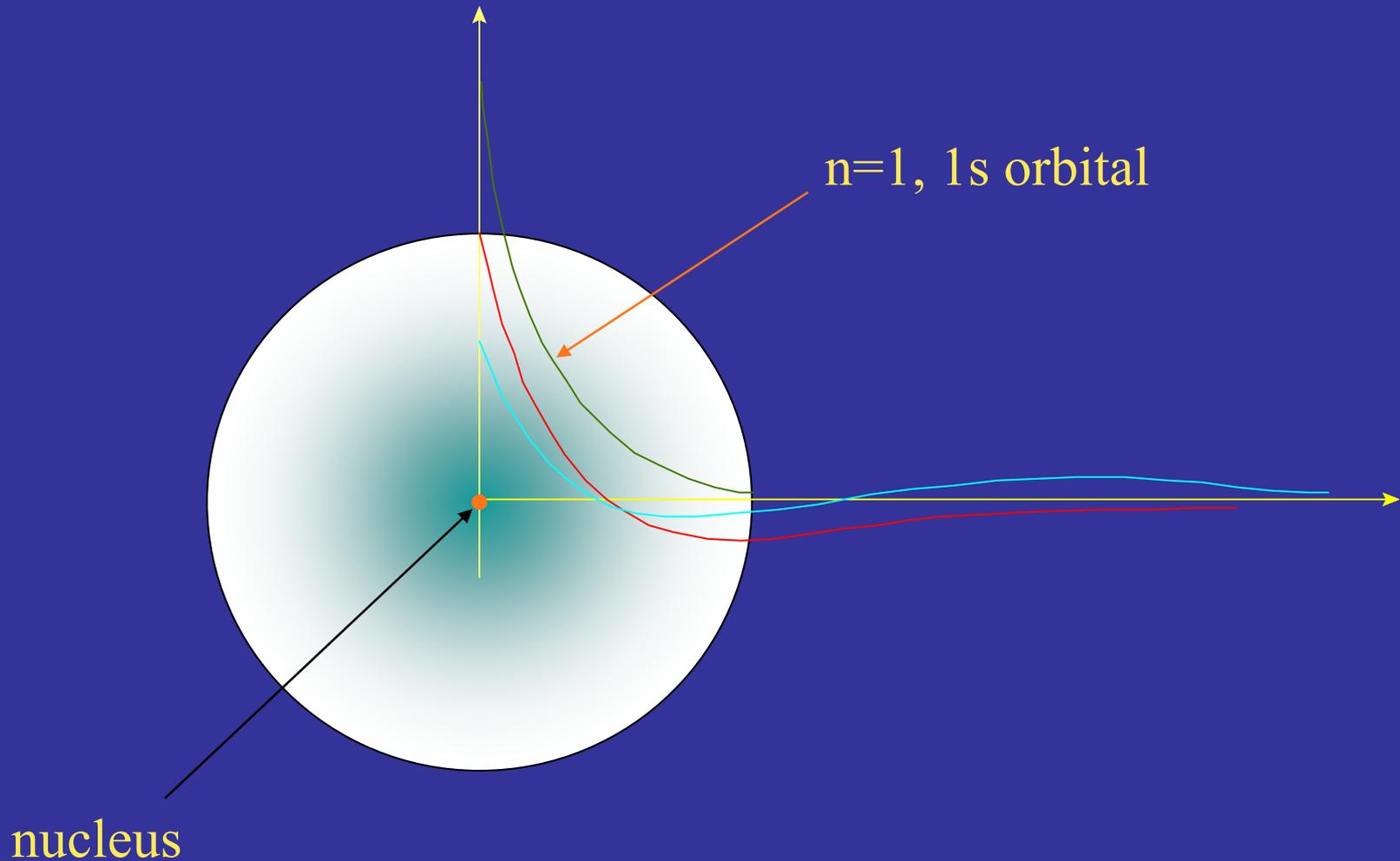
E = Total energy of the proton-electron system

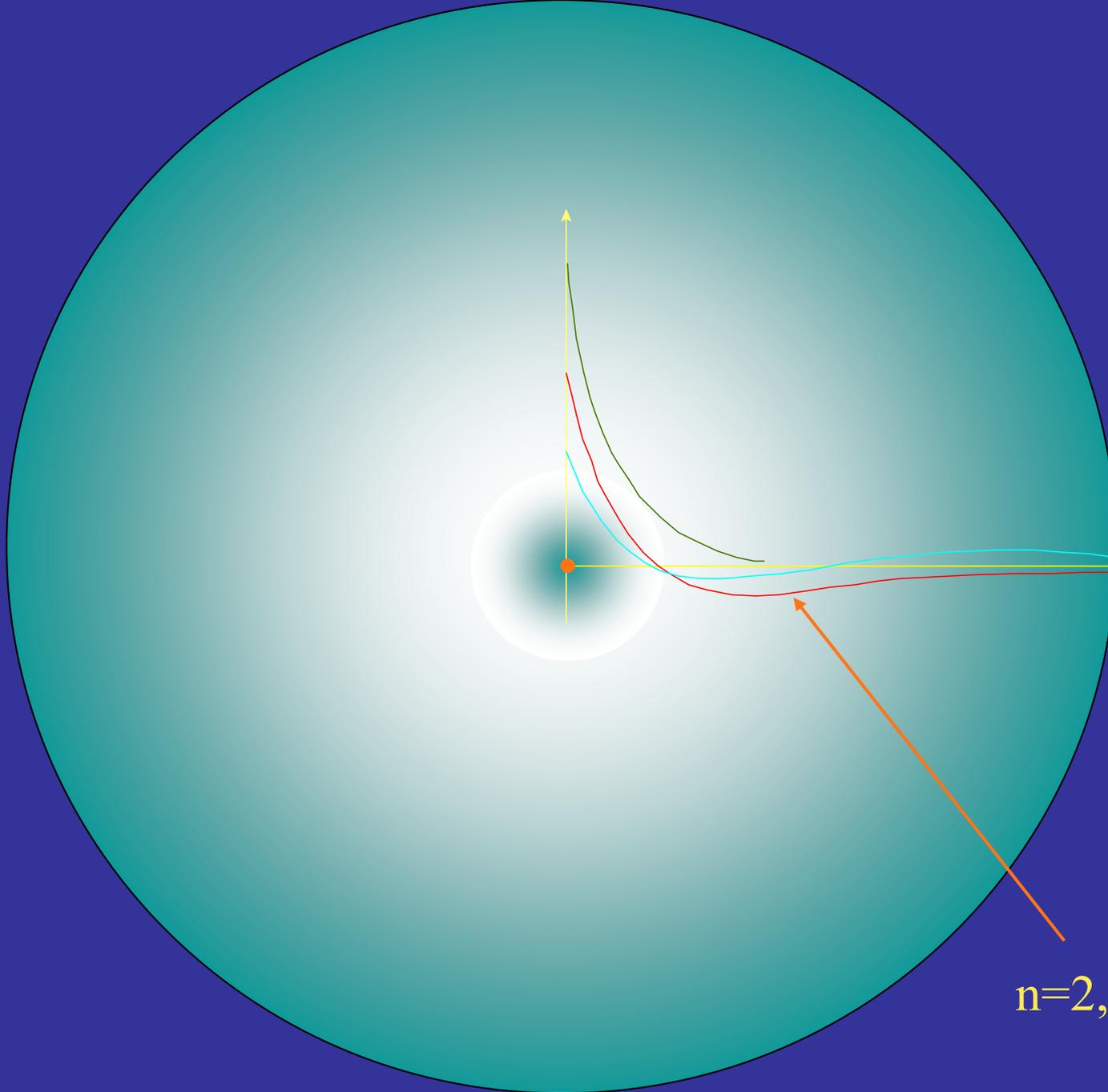
V = Potential energy

ψ = The wave function (its square, ψ^2 , is a **probability** function)

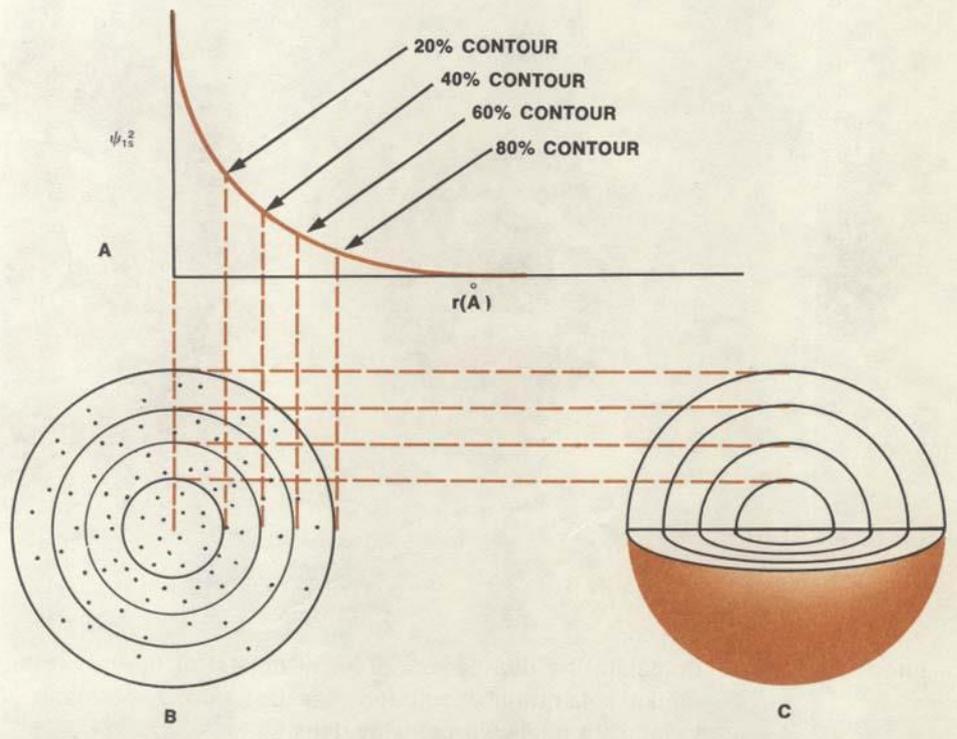
When this equation is solved, the square of every wave function, which is really a probability function, is seen to be associated with a series of integers, called the **principal quantum numbers**, designated **n**, **l**, **m_l** and **m_s**.

When, for instance, the ψ functions for the first three n numbers are solved they give the following probability plot about a nucleus:



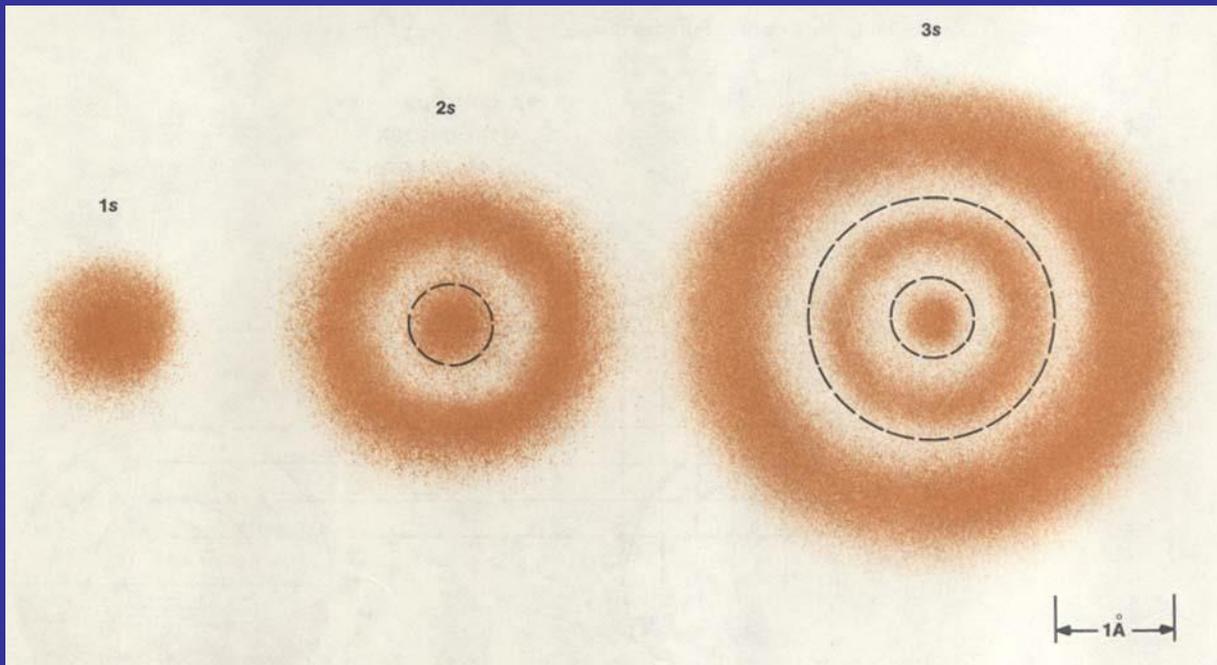


$n=2$, 2s orbital

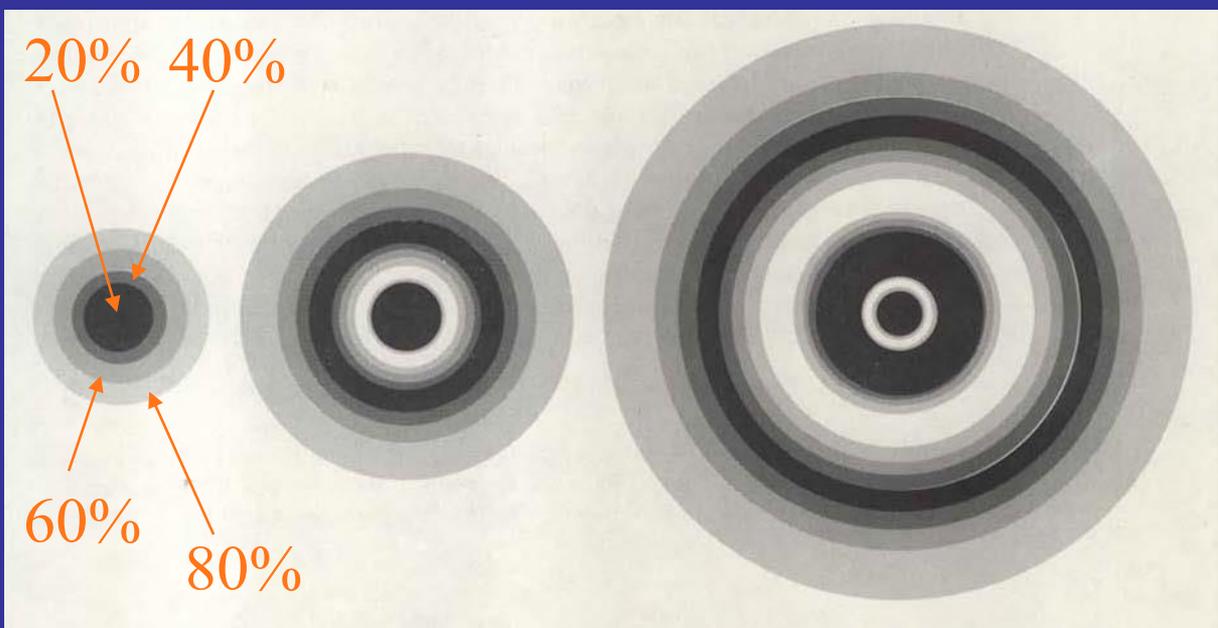


◀ This is the principle of the electron probability wave function we just saw

This is what the shapes of the first three s orbitals look like (in cross-section)



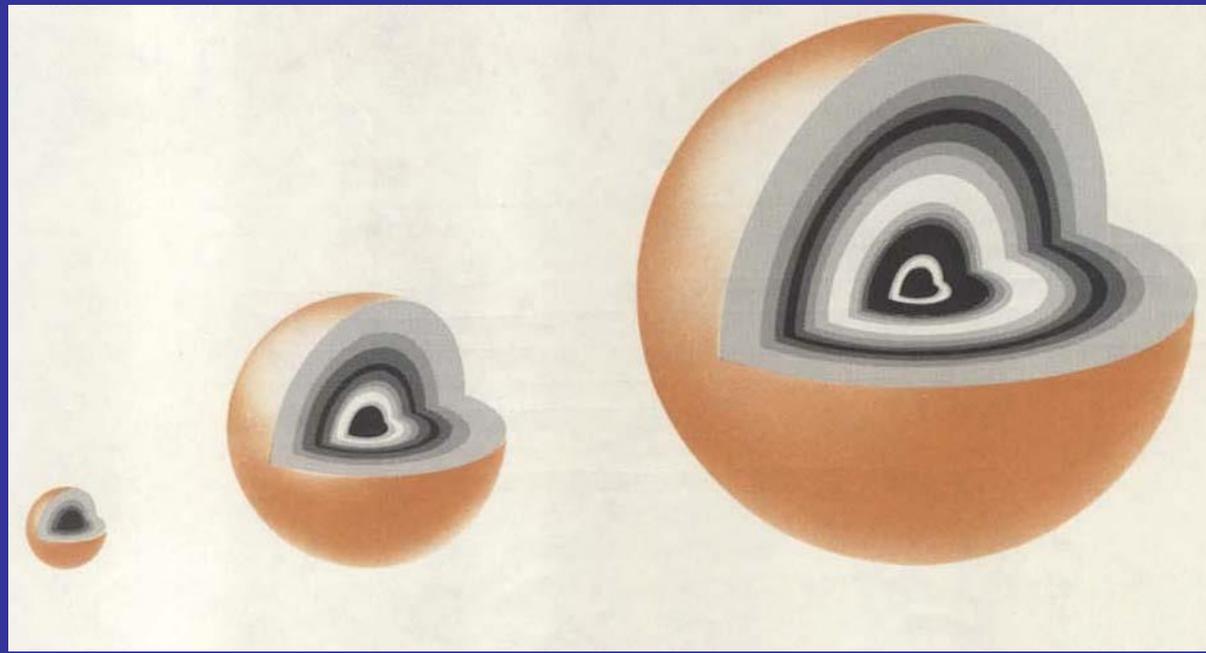
(From Becker and Wentworth, 1973)



1s

2s

3s

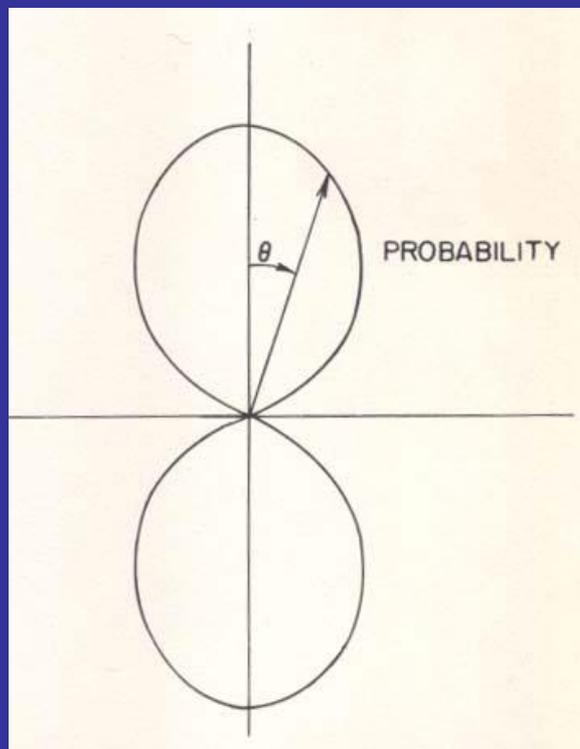


s-orbitals corresponding to the first three n numbers. The percentages show the probability of finding the electrons in any given space around the nucleus.

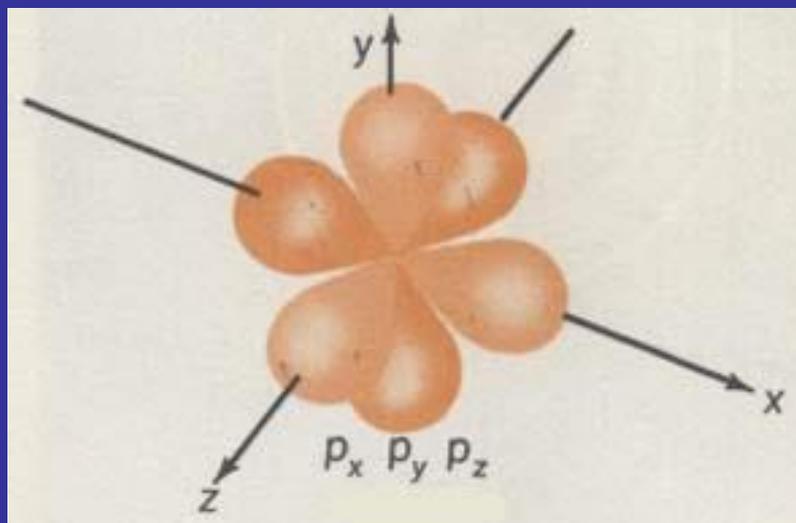
From Becker and Wentworth 1973

As we have just seen, the s-orbitals have spherical symmetry. Because their angle functions in polar coordinates in the Schrödinger wave equation are all zero. This corresponds with a state of zero orbital angular momentum. This is what we call the $l=0$ state.

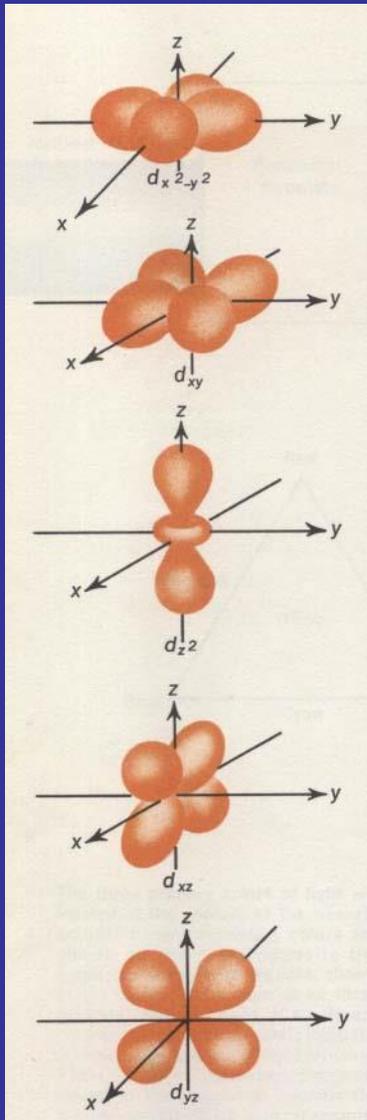
If $l=1$, i.e. if the orbital angular momentum is 1, then we have three possible wave probability functions defining the position of an electron about a nucleus. These are called the p-orbitals and are orientated along the three x, y and z axes at the origin of which is the nucleus.



◀ A p-orbital probability diagram (wave amplitude) from Feynman (1965, v. III)



All three p-orbitals
(from Toon et al 1968)



All five of the d-orbitals around a nucleus at the origin of the x, y, z coordinate system.

There are also 7 f orbitals in the N shell (the 4f orbitals) that are too complex to be rendered here.

The names of the **s**, **p**, **d** and **f** orbitals are left-overs from spectroscoper's terminology. They correspond with the adjectives *sharp*, *principal*, *diffuse* and *fundamental*. They do not describe the orbitals or the shells!

From Toon et al (1968)

What determines the number and orientation of orbitals in each of the s, p, d and f sublevels is the magnetic fields the electrons themselves create (because they are electric charges on the move). The *magnetic quantum number*, or the m_l number, is dependent on the subshell number, i.e., on l . So for $l=0$, $m_l = 0$ and therefore there a single, spherically symmetric orbital, s. For $l=1$, m_l can have three values, -1, 0, +1 corresponding to the three p orbitals. For $l=2$, we can have $m_l = -2, -1, 0, +1, +2$, so five orbitals in the d level. Finally for $l=3$, we can have $m_l = -3, -2, -1, 0, +1, +2, +3$, i.e. seven f orbitals.

Spectroscopic observation also observed very fine differences in energy between electrons in the same orbital. In 1925, two Dutch physicists, **Georg Uhlenbeck** (1900-1988) and **Samuel Goudsmit** (1902-1978) associated that difference with the interactions of the electrons with external magnetic fields and the orbital fields and pointed out that *the electron's own magnetic field could be interpreted as a spin that could be positive ($+\mu_B$) or negative ($-\mu_B$)*. The μ_B is a *Bohr magneton* = 0.927×10^{-20} erg/gauss. This gives us the final quantum number, m_s , that can take on a value either +1 or -1.

Now we are in a position to describe completely the electronic structure of an atom. Let us once more remember the relationships between the quantum numbers n , l , and m_l and the energy levels:

Shell	Principal quantum number n	Orbital quantum number l	Energy sublevel	Number of energy sublevels per principal energy level	Magnetic quantum number m_l	Number of orbitals per sublevel	
K	1	0	s	1	0	1	
L	2	0	s	2	0	1	
		1	p		+1, 0, -1		3
M	3	0	s	3	0	1	
		1	p		+1, 0, -1		3
		2	d		+2, +1, 0, -1, -2		
N	4	0	s	4	0	1	
		1	p		+1, 0, -1		3
		2	d		+2, +1, 0, -1, -2		
		3	f		+3, +2, +1, 0, -1, -2, -3		7

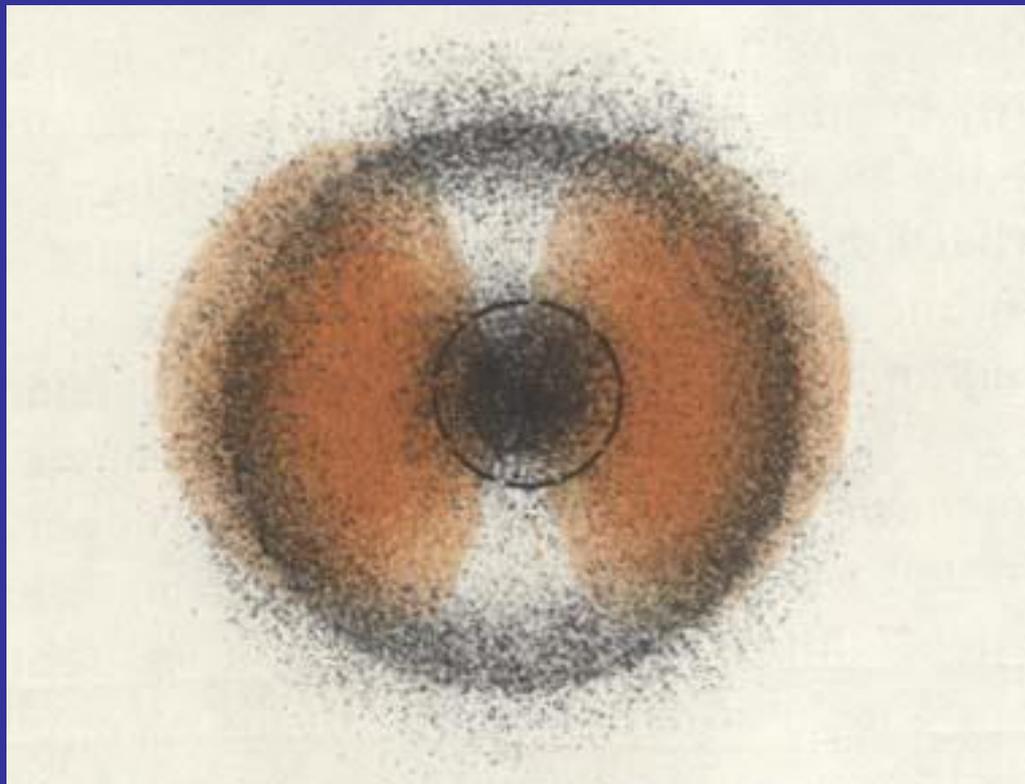
The table in the previous slide shows how we can fill up the sublevels with orbitals. In 1924, the Austrian physicist Wolfgang Pauli published his famous “**exclusion principle**” which stated that *no two electrons can have the same set of quantum numbers*. This



Wolfgang Pauli
(1900-1958)

automatically indicated that every orbital can have only two electrons, with different sets of four quantum numbers. This allowed the 1s orbital of the wave interpretation corresponding to the Bohr K orbit to have two electrons, each with a different spin. Using the four quantum numbers we can now build up any atom of any element to its ground state. This is called the “**Aufbau**” process which simply means “building up” process in German, showing that almost the entire set of ideas that led to the final quantum picture of the atom were published in German-language scientific media (mostly by scientists whose mother tongues were German).

Before we begin the *Aufbau*, let us look at an atom with more than one orbital. In the following picture the 1s (by dashed line), 2s (black stippling) and 2p (coloured stippling) orbitals are shown. **NOTICE THE INTERPENETRATION OF THE ORBITALS!** Remember that all orbitals are disposed in some form of symmetry with respect to the nucleus *and they all interpenetrate*.



(From Becker and
Wentworth 1973, p. 126)

The *Aufbau* is nothing more than just filling the orbitals with electrons. How this is done is dependent on the energy levels of the different orbitals. To do the *Aufbau* of an atom at its ground state, naturally the lowest energy orbitals must be filled first. To do this we must follow three simple rules:

1. Electrons enter the lowest energy orbital of the lowest energy shell first.
2. No electron pairing takes place in the p, d, and f orbitals until each of the orbitals (e.g. p_x , p_y and p_z) of a given group contains one electron with the same spin. This is known as the ***Hund's rule*** (after the German physicist **Friedrich Hund**, 1896-1997, who discovered it)
3. No orbital can contain more than 2 electrons (the ***Pauli exclusion principle***)

Let us once more specify what the four quantum numbers teach us:

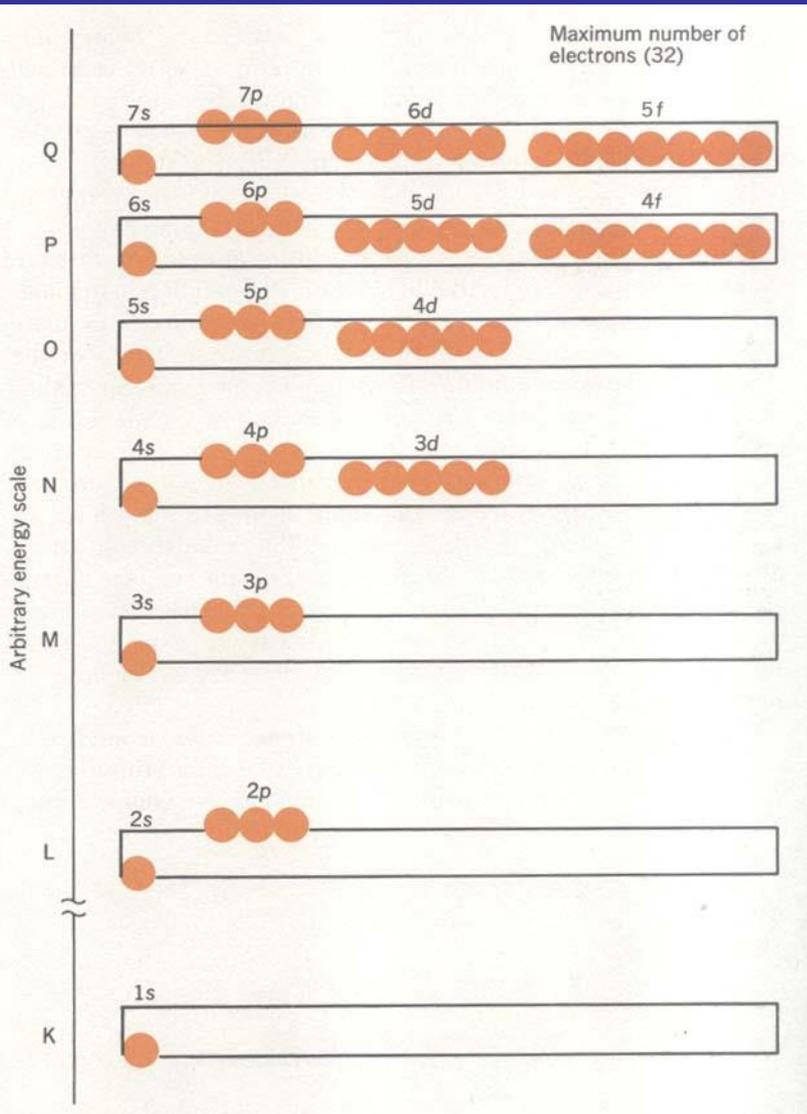
n gives the **shell** (corresponding with the *orbits* in the Bohr atom)

l gives the subshell. In other words it gives us an idea of the **shape** of various volumes that different groups of electrons might occupy about an atomic nucleus

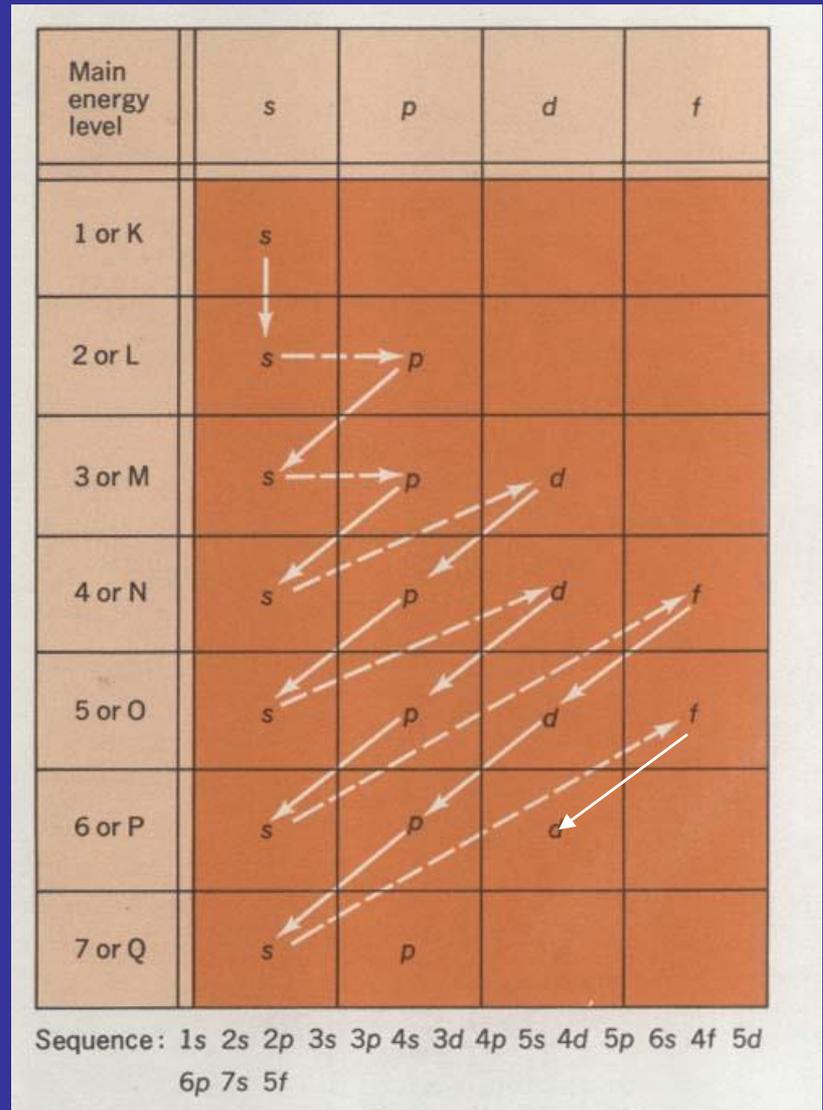
m_l gives the spatial **orientation** and thereby specifies individual orbitals in a subshell.

m_s identifies the **spin** of individual electrons in each orbital.

(From Toon et al., 1968)



Energy-level diagram of a multi-electron atom



Aide-mémoire for the *Aufbau* process of a multi-electron atom (slightly modified from Toon et al)

Note: After Sr (Z=38), the *Aufbau* gets complicated because of the high nuclear charges.

Element	Atomic Number	Orbitals								
		1s	2s	2p	3s	3p	4s	3d		
H	1	↑	—	—	—	—	—	—	—	—
He	2	↑↓	—	—	—	—	—	—	—	—
Li	3	↑↓	↑	—	—	—	—	—	—	—
Be	4	↑↓	↑↓	—	—	—	—	—	—	—
B	5	↑↓	↑↓	↑	—	—	—	—	—	—
C	6	↑↓	↑↓	↑	↑	—	—	—	—	—
N	7	↑↓	↑↓	↑	↑	↑	—	—	—	—
O	8	↑↓	↑↓	↑↓	↑	↑	—	—	—	—
F	9	↑↓	↑↓	↑↓	↑↓	↑	—	—	—	—
Ne	10	↑↓	↑↓	↑↓	↑↓	↑↓	—	—	—	—
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	—	—	—
Mg	12	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	—	—	—
Al	13	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	—	—
Si	14	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	—
P	15	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
S	16	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
Cl	17	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
Ar	18	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
K	19	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Ca	20	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Sc	21	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Ti	22	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
V	23	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Cr	24	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Mn	25	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Fe	26	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Co	27	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Ni	28	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Cu	29	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	30	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Any specific n level can have $2n^2$ number of electrons.

“Built-up” atoms to atomic number 30 (zinc) From Toon et al 1968

Some examples of how to do the *Aufbau*:



But there are exceptions! For instance, let us look at Cu:



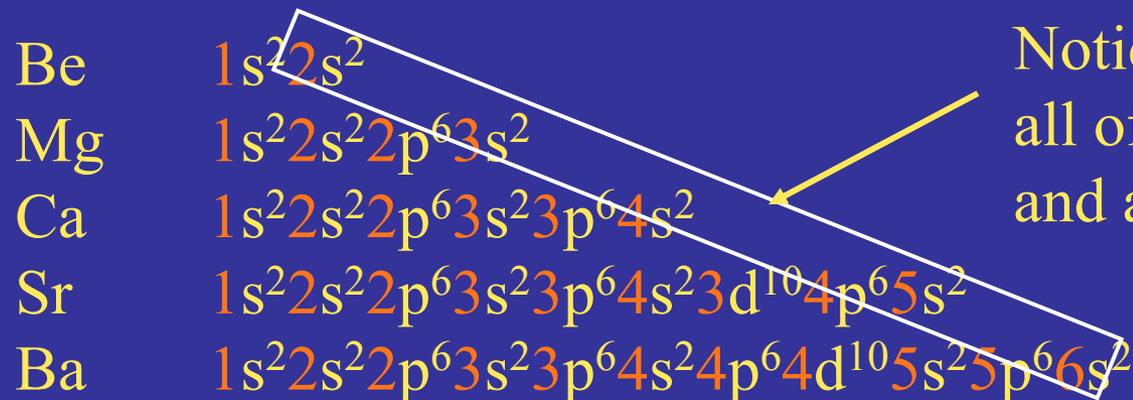
The underlined part is an anomaly, because normally it should have been $4s^2 3d^9$. There are 9 such exceptions to the filling order.

However, the order might also change once the electrons are all filled. This because as the atomic number increases the electrical environment of the atom changes. For instance, the Eu atom's (with 63 electrons) 2s and 2p orbitals are in a much different charge environment than the 2s and 2p orbitals of the Li atom (with only 3 electrons). Such changes are important for the ionisation of the elements.

Now we are in a position to consider how the atomic structure affects the structure of matter, including the minerals. To study this, we need to take a look at the periodic table and discuss certain characteristics of the elements in it with respect to the materials they may form.

First of all let us remember that the periodic table is called periodic, because there is a periodicity in the physical and chemical properties of the elements in the universe. But fundamentally *the periodic table is based on the periodic recurrence of an outer shell electronic configuration.*

For example let us take the group IIA (the rare earth metals):



Notice the last orbitals, all of which are s orbitals and all have 2 electrons

Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

GROUP IA

H	0.32 2.08(-)	2.1 0.108 0.014
Li	1.41 1.13(+)	0.004 0.77 3.45

IIA

Be	1.23 1.55 0.60(+)	1.0 1.12 0.31(+)	0.90 2.99 2.8
Mg	1.31 1.24	0.17 0.79	3.0 2.15

Na	1.54 1.90 0.93(+)	0.9 2.12 0.65(+)	1.36 2.517 2.14
K	2.17 1.90	0.32 0.295	1.40 0.38 0.25

Sub-Atomic Particles

Symbol	Electron	Positron	Proton	Neutron	Photon	Neutrino	Meson				Hyperon					
Mass*	1	1	1836.12	1838.65	0	0	206.84	273.23	264.4	966.6	974.4	2181.4	2327.7	2343.2	2584	1686
Charge**	-1	+1	+1	0	0	0	±1	±1	0	+1	0	0	+1	-1	-1	-1
Spin	1/2	1/2	1/2	1/2	1	1/2	1/2	0	0	0	0	1/2	1/2 integral	1/2 integral	1/2 integral	1/2 integral
Magnetic Moment	1.00 B.m.	1.00 B.m.	2.793 n.m.	-1.913 n.m.	0	0	0	0	0	0	0	0	0	0	0	0
Mean Life (sec.)	stable	stable	stable	1.11 × 10 ⁹	stable	stable	2.22 × 10 ⁻¹⁰	2.54 × 10 ⁻¹⁰	-10 ⁻¹³	-10 ⁻¹⁴	-10 ⁻¹⁰					
Decay Modes			-p + e + ν				-e + p + ν	-p + n + ν	ν + γ	ν + π [±]	ν + π [±]	ν + π [±]	ν + π [±]	ν + π [±]	ν + π [±]	ν + π [±]

B.m. = Bohr magneton n.m. = Nuclear magneton *In units of 9.1083 × 10⁻³¹ kg **In units of 4.80286 × 10⁻¹⁰ esu. †Exists as an antiparticle not listed.

VIIIA

He	0.93 0.020 0.005	0.003 0.0003 0.001
Ne	31.8 367	0.0003 0.001

IIIB IVB VB VIB VIIB VIII IB IIB

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2.03 2.35 1.33(+)	0.8 1.74 1.48(+)	1.0 1.42 0.99(+)	1.3 1.64 0.81(+)	1.5 1.47 0.90(+)	1.6 1.67 0.90(+)	1.6 1.72 0.90(+)	1.8 1.76 0.94(+)	1.8 1.76 0.94(+)	1.8 1.76 0.94(+)	1.8 1.76 0.94(+)	1.8 1.76 0.94(+)	1.6 1.22 0.58(+)	1.8 1.37 0.58(+)	2.0 1.39 0.58(+)	2.0 1.40 0.58(+)	2.8 1.14 0.39(+)	2.8 1.14 0.39(+)
45.3 100	0.23 0.177	29.9 141	0.3 0.15														
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
2.16 2.48 1.48(+)	0.8 1.61 1.48(+)	1.0 1.35 0.90	1.0 1.25 0.80	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.3 1.78 1.13(+)	1.4 1.66 0.81(+)	1.4 1.66 0.81(+)	1.4 1.66 0.81(+)	1.4 1.66 0.81(+)	1.4 1.66 0.81(+)	1.4 1.66 0.81(+)
55.9 86	0.080 0.080	33.7 131	0.043 0.043	0.019 0.019													
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
2.25 2.67 1.69(+)	0.7 1.98 1.50	0.9 2.22 1.35(+)	1.1 1.67 1.13(+)	1.3 1.44 0.81(+)	1.4 1.48 0.81(+)	1.4 1.48 0.81(+)	1.4 1.48 0.81(+)	1.4 1.48 0.81(+)	1.4 1.48 0.81(+)	1.4 1.48 0.81(+)							
70 90	0.053 0.052	0.016 0.068	0.031 0.045	0.031 0.035													
Fr	Ra	Ac															

Fr	Ra	Ac
0.7 1.76(+)	0.9 1.40(+)	1.1 1.88(+)
—	—	—
—	—	—

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1.65 1.81 1.01(+)	1.1 1.82 1.01(+)												
21.0 159	0.026 133	0.028 145	0.031 145										
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
1.65 1.90 1.14(+)	1.3 1.61 1.12(+)	1.5 1.38 0.98(+)	1.7 1.38 0.97(+)	1.7 1.38 0.97(+)	1.3 1.31 0.92(+)								
19.9 —	0.055 —												

NOTES:

- (1) For representative oxides (higher valence) of group. Oxide is acidic if color is red, basic if color is blue and amphoteric if both colors are shown. Intensity of color indicates relative strength.
- (2) Cubic, face centered; cubic, body centered; diamond; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.
- (3) At room temperature. (4) At boiling point. (5) From 0° to 20°C.
- (6) Ionic (crystal) radii for coordination number 6.
- (7) Metallic radii for coordination number of 12.

CRYSTAL STRUCTURE (2)

SYMBOL

ACID-BASE PROPERTIES (1)

KEY

COVALENT RADIUS, Å

ATOMIC RADIUS, Å (7)

IONIC RADIUS, Å (6)

ATOMIC VOLUME, W/D

FIRST IONIZATION ENERGY (kcal/g-mole)

SPECIFIC HEAT (cal/g/°C)

THERMAL CONDUCTANCE (cal/cm²/cm²/°C/sec) (3)

ELECTRONEGATIVITY (Pauling's)

HEAT OF VAPORIZATION (k-cal/g-atom) (4)

HEAT OF FUSION (k-cal/g-atom)

ELECTRICAL CONDUCTANCE (5) (microhms)⁻¹

Zn	1.25 1.38 0.74(+)	1.6 2.7 0.167
Al	0.92 0.27	0.0915

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The Periodic Table

1. The groups IA-VIIA are called the *representative elements*. These have an outer orbital configuration of **ns** or and **ns** and **np** combination. The outer shell is called the *valence shell*, in other words, *the shell that does the chemical bonding*.
2. The *rare* or the *noble gases* form the group VIIIA. All of them have a completely filled outer orbital, such as He ($1s^2$) or Ne ($1s^2 2s^2 2p^6$). *A filled valence shell represents a stable configuration for an atom, a condition that is not conducive to bonding*.
3. The groups IB to VIIIB are the *transition elements*. In these the d subshell is partially filled, as, for example, in iron:



here the d subshell is missing 4 electrons.

4. The *lanthanides* and *actinides* contain partially-filled f orbitals.

NOTE THAT APART FROM THE NOBLE GASES ALL OTHER ELEMENTS HAVE PARTIALLY FILLED VALENCE SHELLS

Elements	Ions	Spin Directions and Number of 3d Electrons for the Ions					Magnetic Moment	
Sc	Ti ³⁺ , V ⁴⁺	↑	—	—	—	—	1	1μ _B
Ti	Ti ²⁺ , V ³⁺	↑	↑	—	—	—	2	2μ _B
V	V ²⁺ , Cr ³⁺ , Mn ⁴⁺	↑	↑	↑	—	—	3	3μ _B
Cr	Cr ²⁺ , Mn ³⁺	↑	↑	↑	↑	—	4	4μ _B
Mn	Mn ²⁺ , Fe ³⁺	↑	↑	↑	↑	↑	5	5μ _B
Fe	Fe ²⁺ , Co ³⁺	↑↓	↑	↑	↑	↑	6	4μ _B
Co	Co ²⁺	↑↓	↑↓	↑	↑	↑	7	3μ _B
Ni	Ni ²⁺	↑↓	↑↓	↑↓	↑	↑	8	2μ _B
Cu	Cu ²⁺	↑↓	↑↓	↑↓	↑↓	↑	9	1μ _B
Zn	Zn ²⁺ , Cu ⁺	↑↓	↑↓	↑↓	↑↓	↑↓	10	0

Transition elements (Z=21 through Z=30), their common ions, number of 3d electrons, electron spin directions and their magnetic moment (expressed in terms of Bohr magnetons, μ_B.)

One **Bohr magneton**, μ_B, is 9.27 x 10⁻²⁴ Am². It is defined as the product of the area about which the electron spins in metre square (in m²) and the electron charge in amperes (A). (From Klein, 2002)