

# MOLECULES, ATOMS, AND NUCLEI

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## Summary

The constituents of matter are described in the language of quantum physics. Common properties are outlined, and their relative order of magnitudes discussed.

## 1. Introduction

The division of a sample of a substance into progressively smaller parts produces no change in either its composition or its chemical properties until parts consisting of single molecules are reached. Further subdivision of the substance leads to still smaller parts that usually differ from the original substance in composition and always differ from it in chemical properties. In this latter stage of fragmentation the chemical bonds that hold the atoms together in the molecule are broken.

Atoms consist of a single nucleus with a positive charge surrounded by a cloud of negatively charged electrons. They have the same amount of electrically positive charge in the nucleus as of negative charge in the electrons. Given that protons and electrons have exactly the same electric charge  $e$  (in magnitude), atoms have the same *atomic* number  $Z$  of protons and electrons. Their electromagnetic interaction is responsible for holding together the atom: the attraction exerted by the positive nuclei over the electrons is larger than the repulsion between the electrons. Protons are closely packed inside the atomic nucleus, having a large electric repulsion between them. It is the strong nuclear force, acting between both protons and neutrons, which holds the nucleons together inside the nucleus.

When atoms approach one another closely, the electron clouds interact with one another and with the nuclei. If this interaction is such that the total energy of the system is lowered, then the atoms bond together to form a molecule. Thus, from a structural point of view, a molecule may consist of a single atom, as in a molecule of a noble gas such as helium (He), or it may consist of an aggregation of atoms held together by valence forces.

Molecules, atoms and nuclei are composed systems, whose total mass is smaller than the sum of the mass of their constituents, the difference being the binding energy. These systems can absorb some amount of energy without breaking apart: they are pushed to an *excited state*, from which they can spontaneously decay to another excited state with a smaller energy or to the ground state, emitting electromagnetic radiation (photons). The sequence of photons emitted during a sequential decay form the spectral lines, which are the fingerprints of each complex system. If the energy absorbed is large enough, they can lose one of its components (one electron, one proton), or break in different pieces.

Molecules, atoms and nuclei have characteristic sizes, photon energies and wave lengths, which differ in order of magnitudes. Typical values are listed in Table 1.

System	size	Radiation	energy comments	wave length
nuclei	1-10fm	$\gamma$ -rays	0.1-5MeV	100-1000 fm
atoms	1-5 Å	X-Rays	1-100 keV inner shells electrons	0.1-10 Å
		ultraviolet	10 eV – 1 keV inner shells and	1-800nm
molecules	1 Å-1 μ m	visible light	1.6-3.2 eV valence electrons	0.39-0.78 μ m
		infrared	0.01- 1 eV molecular vibrations and rotations	1mm - 1 μ m
		microwave	10 <sup>-5</sup> - 10 <sup>-3</sup> eV electronic – nuclear spin	10cm – 1mm

Table1: Sizes of the systems, energies, wave lengths and types of radiation emitted

## 2. Atoms

### 2.1. The Quantum Formalism

The simplest atom in Nature is the hydrogen atom, formed by a nucleus consisting of a single positively charged proton and one electron orbiting around it, bounded by the attractive electric force. Its detailed description is performed using quantum mechanics, and exhibits both the power and sophistication of this theory. The study is performed using the reduced mass  $\mu = \left(\frac{m_p}{m_p + m_e}\right) m_e$ , and the Coulomb potential

$$V(r) = \frac{-e^2}{r}, \quad (1)$$

where  $r$  is the distance between the proton and the electron. The energies  $E$  accessible for the system, and the spatial distribution of the electron around the nucleus are obtained solving the stationary Schrödinger equation

$$\frac{-\hbar}{2\mu} \nabla^2 \psi_{nlm}(r, \theta, \phi) + V(r) \psi_{nlm}(r, \theta, \phi) = E \psi_{nlm}(r, \theta, \phi). \quad (2)$$

The square of the wave function  $\psi(r, \theta, \phi)$  describes the probability of finding the electron in close vicinity around the position  $\vec{r}$ , with

$$\begin{aligned} & \psi_{nlm}(r, \theta, \phi) \\ &= \left[ \left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!} \right]^{1/2} \exp \left\{ \frac{-r}{na_0} \right\} \left( \frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2r}{na_0} \right) Y_l^m(\theta, \phi), \end{aligned}$$

being  $L_{n-l-1}^{2l+1} \left( \frac{2r}{na_0} \right)$  the associated Laguerre polynomials,  $Y_l^m(\theta, \phi)$  the spherical harmonics and

$a_0 = \frac{\hbar^2}{\mu e^2}$  the Bohr radius. The quantum numbers  $n, l$  are positive integers, satisfying  $n-1 \geq l \geq 0$ . The spherical harmonics are normalized simultaneous eigenfunctions of the  $z$ -component of the angular momentum operator  $L_z$  and its square  $L^2$  such that

$$L_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi), \quad L^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi), \quad (2)$$

with  $m = l, l-1, l-2, \dots, -l$ .

The energies  $E_n$  depend only on the principal quantum number  $n$  as

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2} = -\frac{13.6\text{eV}}{n^2}, \quad (3)$$

which is known as the Balmer formula for the energy levels of the hydrogen atom. The ground state has quantum numbers  $n = 1, l = 0, m = 0$ . Its binding energy is 13.6eV.

The ground state wave function is  $\psi_{100} = \exp\{-r/a_0\} / \sqrt{\pi a_0^3}$ , which has an average radius  $\langle r \rangle = 1.5a_0$ .

The electron densities for quantum states  $n, l, m = 1,0,0, 2,0,0, 2,0,0, 2,1,0, 3,1,0, 2,1,1, 3,1,1, 3,2,0, 3,2,1, \text{ and } 3,2,2$  are shown in Figure 1. The  $x$  and  $z$  axis are measured in units of Bohr radius  $a_0$ . The plots show the probability  $P(x, z) = 2\pi |\psi(r, \theta, \phi = 0)|^2$  of finding the electron in a differential circular ring with radius  $x = r \sin \theta$  around the  $z$ -axis, with  $z = r \cos \theta$ . The “ring” structure is due to fact that  $|Y_l^m(\theta, \phi)|^2$  has no dependence on the azimuthal angle  $\phi$ . For  $l = 0$  the wave functions have spherical symmetry, with  $n - 1$  nodes where there is no chance to find the electron. In the other cases the probability of finding the electron is concentrated around the equatorial or polar regions.

## 2.2. The Spin

Many particles, including electrons, protons and neutrons, cannot be described as point particles whose wave function depends only on their position. It is necessary to explicitly include their *intrinsic angular momentum* or *spin*, and its associated magnetic moment. To determine its magnetic moment  $\vec{\mu}$  the particle, which can be an entire atom or molecule, is sent through a nonuniform magnetic field. The particle deflection is proportional to the component  $\mu_B$  of the magnetic moment in the direction of the magnetic field. The results of this experiment, first performed by Stern and Gerlach, show distinct traces, varying in equal steps from  $-\mu$  to  $\mu$ . The maximum projection  $\mu$  is regarded as the magnetic moment of the particle. The projection of the magnetic moment is proportional to the  $z$ -component of the angular momentum  $m\hbar$ :  $\mu_B = -\beta_0 m$ , where  $\beta_0 = e\hbar / (2m_e c) = 5.788 \times 10^{-5} \text{eV/T}$  is the Bohr magneton.

An electron, whether free or bound in an atom, does have a magnetic moment  $\mu_e = \beta_0$ . Therefore it has an intrinsic angular momentum  $\mathbf{s}$ , with magnitude  $s = \frac{1}{2}\hbar$ . This experimental fact can be deduced from the relativistic Dirac quantum theory. Formally, it implies that the electron wave function has two components, called *spinors*, one

associated to each spin projection. The spin  $\mathbf{s}$  and orbital angular momentum  $\mathbf{l}$  can be coupled to form the total angular momentum  $\mathbf{j} = \mathbf{l} + \mathbf{s}$ . This quantity, when referred to protons and neutrons, is particularly important in the description of the atomic nuclei. The interaction between the electron intrinsic magnetic moment and the magnetic field associated to its spatial displacement around the atomic nucleus is called the *spin-orbit* interaction. It produces the *fine structure* of the excited states of one-electron atoms, the splitting of the energy levels as a function of the total angular momentum  $j$ . This corrections modify the energy levels in one part in  $10^4$ .

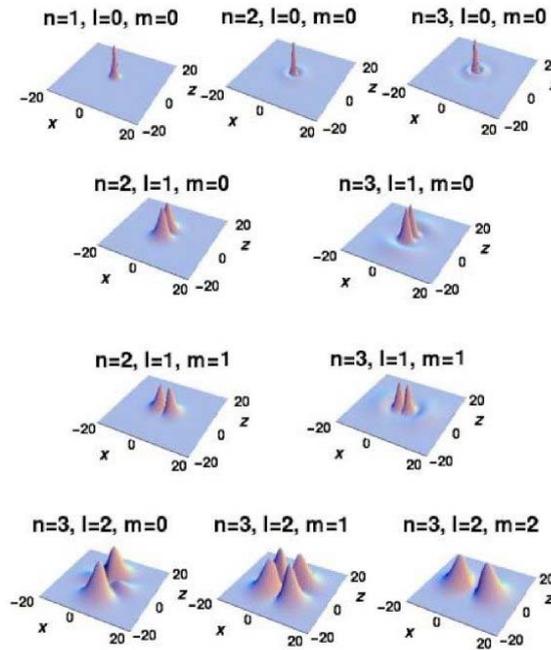


Figure 1: Electronic orbitals of the hydrogen atom.

### 2.3. Multielectron Atoms

At the microscopic level it is impossible to distinguish between the many electrons possessed by an atom distinct from H. It implies that any observable quantity must be independent of the labels assigned to the electrons. The same statement holds for protons or neutrons inside the nuclei, and for identical atoms in polyatomic molecules. The total wave-function, built from the products of the wave functions of the constituents, must be either *symmetric* or *antisymmetric* under the interchange of any two identical particles. The symmetric condition is valid for particles whose total spin is an integer multiple of  $\hbar$ , called *bosons*, as for example helium and oxygen atoms. Particles with half-integer spin, like electrons, protons and neutrons, are *fermions* and have antisymmetric total wave functions.

Any antisymmetric wave function is identically zero if two particles are in the same space and spin quantum state. It follows that fermions must obey the *Pauli exclusion principle* which, for multielectron atoms, states that there can never be more than one electron in a given quantum state.

The helium atom has two electrons. Their total wave function is antisymmetric. It can be written as the product of functions of the spatial coordinates and spin. Two electrons can be coupled to a total spin  $S = 0$  or  $S = 1$ . In the first case the spin wave function is antisymmetric, then the spatial one is symmetric, and the electrons can be close in space. For  $S = 1$  the spins are aligned, and the spatial wave function is antisymmetric, forcing the electrons to be spatially separated and having a larger energy. Both cases are schematically depicted in Figure 2.

In all multi-electron atoms, internal electrons have radius smaller than hydrogen by a factor  $Z$ , and their binding energy is larger by a factor close to  $Z^2$ . For the external shell, due to the charge shielding the situation is completely different. The radius of the heaviest elements is only three times as large as it is for hydrogen, and the energy of the most external electrons is comparable to that of an electron in the ground state of hydrogen.

The Coulomb repulsion between the electrons is included self consistently, building the helium wave function as a sum of products, and finding the configuration, which minimize the total energy of the system. The same approach is employed to describe atoms with many electrons. An electron in an internal orbit is strongly bounded, because it strongly feels the attraction of the nucleus, and at the same time the repulsions from the other electrons cancel in the average. When the electron is in an external orbit, the net effects of the repulsion add coherently, effectively *screening* the nuclear charge. The net potential seen by the electrons can be described as

$$V(r) = \frac{-Z(r)e^2}{r} \quad \text{with } Z(r) \rightarrow \begin{cases} Z & \text{when } r \rightarrow 0, \\ 1 & \text{when } r \rightarrow \infty \end{cases} \quad (4)$$

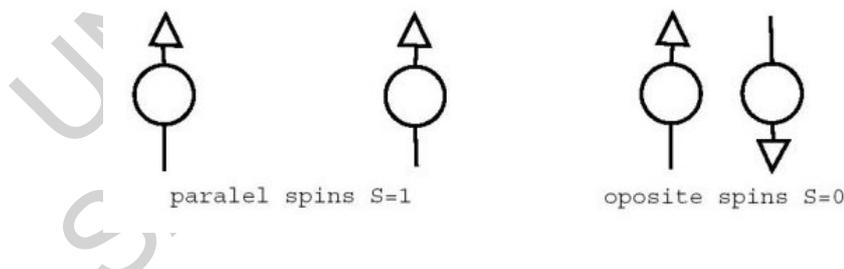


Figure 2: Symmetric and antisymmetric spin states for two electrons

## 2.4. The Periodic Table

Mendeleev was the first to recognize that most of the properties of the chemical elements are periodic functions of the atomic number  $Z$ . The *periodic table of the elements* presents this fact in a systematic fashion. Each element is represented by its chemical symbol and its atomic number. Elements with similar chemical and physical properties are in the same column. The first column list the alkalies, with valence +1, in the last column are the noble gases with valence 0. The periodic table is a fundamental

tool in chemistry. Element names are alphabetically listed, with their symbols and atomic numbers, in Table 2. The names of elements 110-118, not listed, are the Latin equivalents of those numbers.

The interpretation of the periodic table is based on the information about the ordering according to energy of the outer filled subshells of multielectron atoms. Subshells are classified according to the quantum numbers  $n, l$ . The *spectroscopic* notation assigns a letter to each orbital angular momentum  $l$ , following the rule: 0:  $s$ , 1:  $p$ , 2:  $d$ , 3:  $f$ , 4:  $g$ , 5:  $g$ , 6:  $i, \dots$ . Each subshell can accommodate  $2(2l + 1)$  electrons. The factor 2 is associated to the two possible projections of the electronic spin, and there are  $2l + 1$  projections of the angular momentum  $l$ . For a given  $n$ , subshells with the smaller  $l$  have the lower energy. Similarly, for a given  $l$  the states with the smaller  $n$  have lower energies. The full ordering depends on the actual number of electrons.

Symbol	Element	Z	Symbol	Element	Z	Symbol	Element	Z
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Ac	Actinium	89	Al	Aluminum	13	Am	American	95
Sb	Antimony	51	Ar	Argon	18	As	Arsenic	33
At	Astatine	85	Ba	Barium	56	Bk	Berkelium	97
Be	Beryllium	4	Bi	Bismuth	83	B	Boron	5
Br	Bromine	35	Cd	Cadmium	48	Ca	Calcium	20
Cf	Californium	98	C	Carbon	6	Ce	Cerium	58
Cs	Cesium	55	Cl	Chlorine	17	Cr	Chromium	24
Co	Cobalt	27	Cu	Copper	29	Cm	Curium	96
Dy	Dysprosium	66	Es	Einsteinium	99	Er	Erbium	68
Eu	Europium	63	Fm	Fermium	100	F	Fluorine	9
Fr	Francium	87	Gd	Gadolinium	64	Ga	Gallium	31
Ge	Germanium	32	Au	Gold	79	Hf	Hafnium	72
Ha	Hahnium	105	Hs	Hassium	108	He	Helium	2
Ho	Holmium	67	H	Hydrogen	1	In	Indium	49
I	Iodine	53	Ir	Iridium	77	Fe	Iron	26
Kr	Krypton	36	La	Lanthanum	57	Lr	Lawrencium	103
Pb	Lead	82	Li	Lithium	3	Lu	Lutetium	71
Mg	Magnesium	12	Mn	Manganese	25	Mt	Meitnerium	109
Md	Mendelevium	101	Hg	Mercury	80	Mo	Molybdenum	42
Ns	Neilsborium	107	Nd	Neodymium	60	Ne	Neon	10
Np	Neptunium	93	Ni	Nickel	28	Nb	Niobium	41
N	Nitrogen	7	No	Nobelium	102	Os	Osmian	76
O	Oxygen	8	Pd	Palladium	46	P	Phosphorus	15
Pt	Platinum	78	Pu	Plutonium	94	Po	Polonium	84
K	Potassium	19	Pr	Praseodymium	59	Pm	Promethium	61
Pa	Protactinium	91	Ra	Radium	88	Rn	Radon	86
Re	Rhenium	75	Rh	Rhodium	45	Rb	Rubidium	37
Ru	Ruthenium	44	Rf	Rutherfordium	104	Sm	Samarium	62
Sc	Scandium	21	Sg	Seaborgium	106	Se	Selenium	34
Si	Silicon	14	Ag	Silver	47	Na	Sodium	11
Sr	Strontium	38	S	Sulfur	16	Ta	Tantalum	73
Tc	Technetium	43	Te	Tellurium	52	Tb	Terbium	65
Tl	Thalium	81	Th	Thorium	90	Tm	Thulium	69
Sn	Tin	50	Ti	Titanium	22	W	Tungsten	74
U	Uranium	92	V	Vanadium	23	Xi	Xenon	54
Yb	Ytterbium	70	Yb	Yttrium	39	Zn	Zinc	30
Zr	Zirconium	40						

Table 2: Elements with their Symbol and Atomic Number

The energy difference between the  $p$  and the following  $s$  subshells is particularly large, because once the  $p$  subshell is filled, the next electron must start occupying the next shell, which has a larger average radius and a higher energy. In the case of noble gases, exciting an electron is particularly difficult. Together with the absence of magnetic dipole moments in these atoms, it explains the fact they hardly interact with other atoms to form chemical bonds, and have very low boiling and freezing points. For the same reason they exhibit the largest ionization energies. By contrast, the alkali elements contain a single weakly bound electron in an  $s$  subshell and are very active chemically. The halogens have an electron less than the number required to fill the  $p$  subshell, being very prone to capture an electron.

When an element in gaseous form is exposed to electric discharges, some electrons absorb energy and are promoted to excited orbits. They re-emit electromagnetic radiation when decaying. As shown in Table 1, excitation of valence electrons generates visible light, as the kind observed in the white street lamps, which use mercury vapor. The yellow fog lamps use sodium vapor. If internal electrons are excited, they decay emitting more energetic photons: ultraviolet and X rays. For each element the electromagnetic spectra of the emitted light is characteristic and unique. It has allowed the identification of many elements in the spectra of the Sun and in distant stars.

Element configuration	He $1s^2$	Ne [He] $2s^2 2p^6$	Ar [Ne] $3s^2 3p^6$	Kr [Ar] $4s^2 3d^{10} 4p^6$	Xe [Kr] $5s^2 4d^{10} 5p^6$	Ra [Xe] $6s^2 4f^{14} 5d^{10} 6p^6$
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Table 3: Electronic configurations of noble gases

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### Biographical Sketch

**Jorge Gustavo Hirsch**, was born in La plata, Argentina in 1955. He obtained the B.S. in physics at the Universidad Nacional Autonoma de Mexico (UNAM) in 1985, and the ph.D. in physics at the Universidad Nacional de La platta, Argentina, in 1990. At present he is full professor at the Instituto de Ciencias Nucleares, UNAM, Mexico. His area of expertise includes theoretical nuclear physics, nuclear structure, and many body quantum mechanics. He has published 76 articles in refereed scientific journals, 22 contributions in proceedings, and has edited 11 books. Besides teaching graduate and undergraduate courses, he has advised 1 B.S., 2 M.S. and 3 ph. D. theses. Dr. Hirsch's most relevant contributions involve the description of the double beta decay, a rare radioactive decay of great relevance in the determination of neutrino masses. It started with the description of the double beta decay with and without neutrino emissions in spherical nuclei using the quasiparticle random phase approximation (QRPA), and the associated (p,n) reactions. Extensions of the QRPA technique, and a critical analysis of its limitations, were studied in detailed in a series of articles. He used the pseudo SU (3) description of heavy deformed nuclei to estimate the double beta half-life in these nuclei, developing new techniques to include the occupation mixing in normal and unique parity orbitals. With his collaborators, he has performed extensive studies of the energy spectra and electromagnetic transition strengths in even-even and odd-mass heavy deformed nuclei.