

Orbitals, and the Periodic Table

Ram Seshadri MRL 2031, x6129, seshadri@mrl.ucsb.edu

These notes closely follow P. W. Atkins, Physical Chemistry

The Hydrogen atom: To understand the quantum mechanics of the hydrogen atom, we recognize that we need to set up the Hamiltonian \mathbf{H} that describes the kinetic energy of the electron and recognizes the potential energy (Coulombic) arising from the negatively charged electron being in the vicinity of a positively charged nucleus:

$$\mathbf{H} = \text{K.E.}(\text{electron}) + \text{K.E.}(\text{nucleus}) + \text{P.E.}(\text{electron-nucleus})$$

and the Schrödinger equation (S.E.) $\mathbf{H}\psi = E\psi$ can be written and solved. The best way to do this is to use polar coordinates and the equation as well as the solution is written $\psi(r, \theta, \phi)$ rather than $\psi(x, y, z)$.

Quantum numbers: From solving the S.E. for hydrogen-like atoms, one finds that electrons in many-electron atoms are completely described by a set of four quantum numbers:

1. The principal quantum number n , that can take on values 1, 2, 3 ...
2. The angular momentum quantum number l that takes on values 0, 1, 2 ... $n - 1$
3. The magnetic quantum number corresponding to the z component of the angular momentum m_l , which takes on the values 0, ± 1 , ± 2 , ... $\pm l$
4. The spin quantum number m_s which takes on the values $\pm \frac{1}{2}$

The energy of an electron in an orbital with quantum number n for an atom with atomic number Z is given by:

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

Where e is the charge on the electron, ϵ_0 is the vacuum permittivity, and μ is the reduced mass of the system.

Shells, subshells ...: The different quantum numbers define the shell, subshells ...

$$n = \begin{array}{cccccc} 1 & 2 & 3 & 4 & \dots \\ & \text{K} & \text{L} & \text{M} & \text{N} & \dots \end{array}$$

and

$$l = \begin{array}{cccccc} 0 & 1 & 2 & 3 & 4 & \dots \\ & \text{s} & \text{p} & \text{d} & \text{f} & \text{g} & \dots \end{array}$$

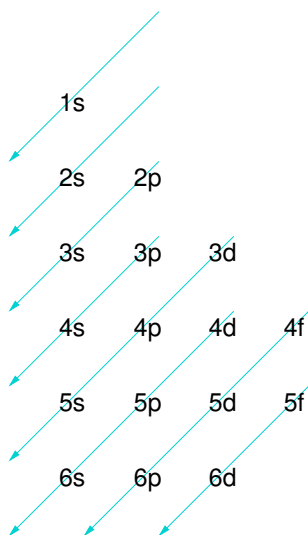
The s, p, d, f and g are called atomic orbitals. Filling up these orbitals with electrons builds atoms, and the way in which atoms are build up gives rise to the periodic table. There is only one s orbital ($m_l = 0$), but there are three p orbitals ($m_l = -1, 0, 1$), five d orbitals ($m_l = -2, -1, 0, 1, 2$), and seven f orbitals ($m_l = -3, -2, -1, 0, 1, 2, 3$).

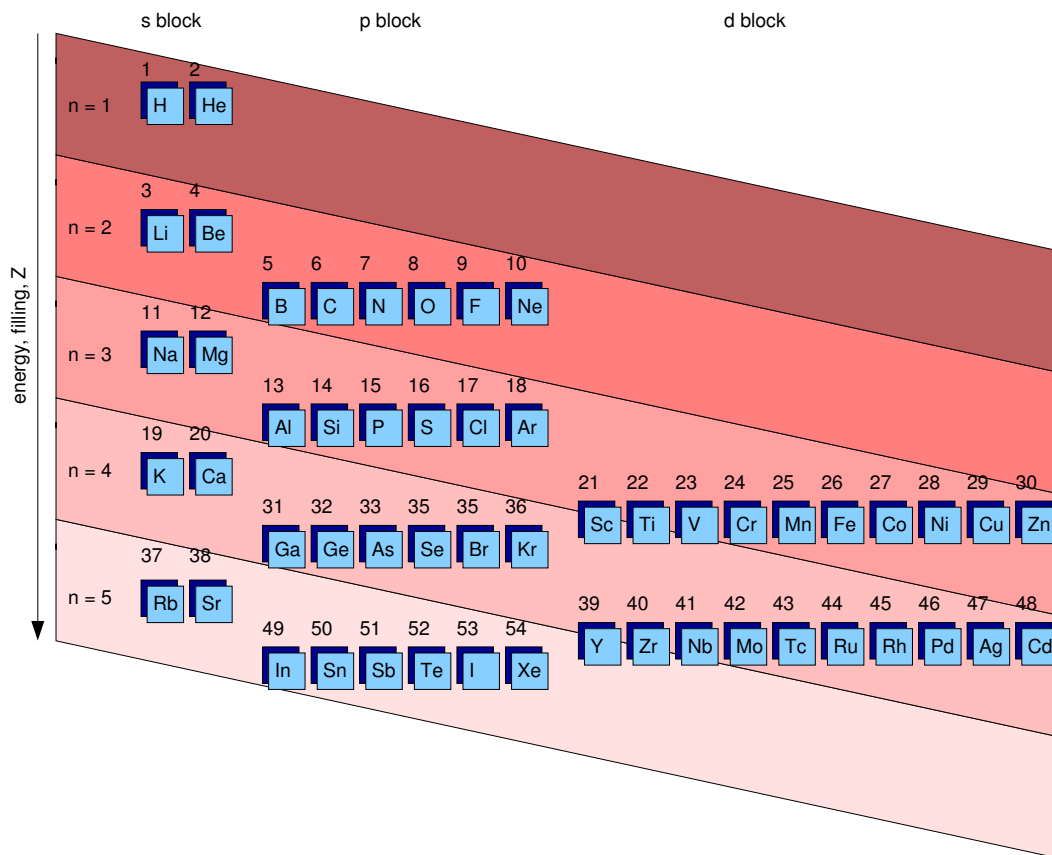
n	Shell	Subshells	States	Electrons
1	K	s	1	2
2	L	s	1	2
		p	3	6
3	M	s	1	2
		p	3	6
		d	5	10
4	N	s	1	2
		p	3	6
		d	5	10
		f	7	14

Rules for filling in the electrons: Atoms have in the nucleus, protons and neutrons and outside the nucleus, electrons. The number of electrons = number of protons = Z , the atomic number.

1. The Pauli principle: No more than two electrons can occupy a given orbital. If there are two electrons in an orbital, their spins must be paired (one must have $m_s = \frac{1}{2}$ and the other, $m_s = -\frac{1}{2}$).
2. The aufbau (building-up) principle: When electrons are filled in to orbitals in an atom, the orbitals with lower energy are filled first. The order of filling is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s ...
3. The Hund rule: Electrons will occupy different orbitals in a given subshell, before two electrons will occupy a single orbital.

There is a simple way of remembering how electrons fill up orbitals, shown in the accompanying diagrams:





From such diagrams, we are able to extract the electronic configurations of elements.

More about the atom: The atomic mass (which is numerically, a value close to the mass number) is the weighted average mass of a number of *isotopes* of the element, expressed in a system of units where the common isotope of carbon ^{12}C has an atomic mass of precisely 12.00000. The unit of atomic mass in g is equal to $1.00000/(\text{Avogadro Number}) = 1.00000/6.0221367 \times 10^{23} = 1.66054 \times 10^{-24}$ g. This is sometimes called the Lochschmidt number. One atom of ^{12}C weighs 12 times this, 1.99265×10^{23} g. If instead of counting atom by atom, we count in bunches corresponding to the Avogadro number, we have *moles* of something, and 1 mole of ^{12}C weighs *precisely* 12.00000 g. One mole of a normal carbon sample (which is a mixture of isotopes with different mass numbers) actually weighs 12.011 g.

The Periodic Table: The rules for filling up electrons in an atom result in the periodic table. Note that elements in the periodic table are separated into various categories. You must learn to understand these different categories: Alkali metals, alkaline earth metals, transition metals, main group elements (consisting of metalloids and non-metals) and the noble gases. Also, there are the lanthanide and actinide elements.

PERIODIC TABLE OF THE ELEMENTS

<http://www.kkf-split.hr/periodni/en/>

PERIOD	GROUP	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
		IA	IIA	IIIB	IVB	VB	VIB	VIB	VIB	VIB	VIB	VIB	VIB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1	H 1.0079 HYDROGEN																		He 4.0026 HELIUM
2	2	Li 6.941 LITHIUM	Be 9.0122 BERYLLIUM												B 10.811 BORON	C 12.011 CARBON	N 14.007 NITROGEN	O 15.999 OXYGEN	F 18.998 FLUORINE	Ne 20.180 NEON
3	3	Na 22.990 SODIUM	Mg 24.305 MAGNESIUM												Al 26.982 ALUMINIUM	Si 28.086 SILICON	P 30.974 PHOSPHORUS	S 32.065 SULPHUR	Cl 35.453 CHLORINE	Ar 39.948 ARGON
4	4	K 39.098 POTASSIUM	Ca 40.078 CALCIUM	Sc 39.889 SCANDIUM	Ti 47.867 TITANIUM	V 50.942 VANADIUM	Cr 51.996 CHROMIUM	Mn 54.938 MANGANESE	Fe 55.845 IRON	Co 58.933 COBALT	Ni 58.693 NICKEL	Cu 63.546 COPPER	Zn 65.39 ZINC	Ga 69.723 GALLIUM	Ge 72.64 GERMANIUM	As 74.922 ARSENIC	Se 78.96 SELENIUM	Br 79.904 BROMINE	Kr 83.80 KRYPTON	
5	5	Rb 85.468 RUBIDIUM	Sr 87.62 STRONTIUM	Y 88.906 YTTORIUM	Zr 91.224 ZIRCONIUM	Nb 92.906 NIOBIUM	Mo 95.94 MOLYBDENUM	Tc 98 TECHNETIUM	Ru 101.07 RUTHENIUM	Rh 102.91 RHODIUM	Pd 106.42 PALLADIUM	Ag 107.87 SILVER	Cd 112.41 CADMIUM	In 114.82 INDIUM	Sn 118.71 TIN	Sb 121.76 ANTIMONY	Te 127.60 TELLURIUM	I 126.90 IODINE	Xe 131.29 XENON	
6	6	Cs 132.91 CAESIUM	Ba 137.33 BARIUM	Lanthanide 57-71	Hf 178.49 HAFNIUM	Ta 180.95 TANTALUM	W 183.84 TUNGSTEN	Re 186.21 RHENIUM	Os 190.23 OSMIUM	Ir 192.22 IRIDIUM	Pt 195.08 PLATINIUM	Au 196.97 GOLD	Hg 200.59 MERCURY	Tl 204.38 THALLIUM	Pb 207.2 LEAD	Bi 208.98 BISMUTH	Po 209 POLONIUM	At 210 ASTATINE	Rn 222 RADON	
7	7	Fr 223 FRANCIUM	Ra 226 RADIUM	Actinide 89-103	Rf 261 RUFERFORDIUM	Db 262 DUBNIUM	Sg 266 SEABORGIUM	Bh 277 BOHRMIUM	Hs 277 HASSIUM	Mt 281 MEITNERIUM	Uun 281 UNUNUNIUM	Uuu 285 UNUNUNIUM	Uub 285 UNUNBIUM	Uuq 289 UNUNQUADIUM						

RELATIVE ATOMIC MASS (1)

GROUP IUPAC

GROUP CAS

ATOMIC NUMBER

SYMBOL

ELEMENT NAME

Legend:

- Metal
- Semimetal
- Nonmetal
- Alkali metal
- Alkaline earth metal
- Transition metals
- Lanthanide
- Actinide
- Chalcogens element
- Halogens element
- Noble gas

STANDARD STATE (100 °C; 101 kPa)

- Ne - gas
- Ga - liquid
- Tc - synthetic

LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La LANTHANUM	Ce CERIUM	Pr PRASEODYMIUM	Nd NEODYMIUM	Pm PROMETHIUM	Sm SAMARIUM	Eu EUROPIUM	Gd GADOLINIUM	Tb TERBIUM	Dy DYSPROSIUM	Ho HOLMIUM	Er ERBIUM	Tm THULIUM	Yb YTTERBIUM	Lu LUTETIUM

ACTINIDE

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac ACTINIUM	Th THORIUM	Pa PROTACTINIUM	U URANIUM	Np NEPTUNIUM	Pu PLUTONIUM	Am AMERICIUM	Cm CURIUM	Bk BERKELIUM	Cf CALIFORNIUM	Es EINSTEINIUM	Fm FERMIUM	Md MENDELEVIUM	No NOBELIUM	Lr LAWRENCIUM

Copyright © 1998-2002 EniG. (eni@kf-split.hr)

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements with no stable isotopes, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Count the electrons in the noble gases. Note that they correspond to filled K shells (He), filled L shells (Ne), filled M shells (Ar) These are stable configurations and the noble gases are rather unreactive. It is always useful to know how far an element is from the nearest noble gas. For instance, Br is just one electron away from Kr, and as a result, will grab an electron whenever it gets the chance. K has just one electron more than Ar and is always trying to get rid of it (the one electron). Another way of stating this is that Br has 7 valence electrons (and tries to get one more to reach 8) while K has 1 valence electron and tries to get rid of it to reach zero.

In general, atoms that can adopt the configuration of the nearest noble gas by gaining electrons, have a tendency to grab electrons from other atoms. This tendency is called electronegativity, and Pauling introduced a scale to describe this tendency. The scale runs to 4 (corresponding to F) which is an atom that always tries very hard to grab electrons. Atoms that have can gain a noble gas configuration by giving up electrons are electropositive, and their electronegativity values are small (usually below 1.5).

Bonding:

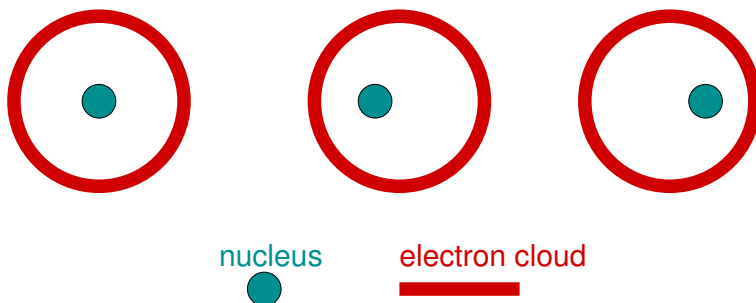
- There are four forces in nature. The *strong* and the *weak* interactions act between electrons, protons, neutrons and other elementary particles and do not concern us. We do not know of any normal material whose properties (melting point, for example) depend on the magnitude of these forces. The two other forces are *gravitational* and *electromagnetic*.
- Gravitational forces account for large scale phenomena such as tides, and seasons, and together with intermolecular forces, decide the length of a giraffe's neck. We shall not discuss gravitation.
- All interactions that are important for solids, should in principle, come out as solutions of the Schrödinger equation (SE). Unfortunately, solutions of the SE are hard to come by for many real systems, and even if they were available, their utility would not be assured. We therefore continue to propagate the useful fiction that cohesive interactions in materials can be classified as belonging to one of four categories – van der Waals, ionic, covalent or metallic.¹ We keep in mind that these are not very easily distinguished from one-another in many solids.

For a delightfully readable text on the nature of cohesion between molecules, and between molecules and surfaces, look at J. N. Israelachvili, *Intermolecular and Surface Forces*.

van der Waals:

- The simplest solids are perhaps those obtained on cooling down a noble gas – He, Ne, Ar, Kr or Xe. He does not form a solid at ambient pressure. All the other noble gases do.
- The interactions between noble gas atoms (which have closed shells of electrons) is of the van der Waals type (note: van der Waals, not van der Waal's !) which means that the interaction is between instantaneous dipoles formed because the atoms “breathe” and this breathing causes the centers of positive and negative charges to, from time to time, not coincide. The forces are therefore also referred to as induced dipole-induced dipole interactions, or London dispersion forces (after F. W. London).

¹Hydrogen bonds are somewhere between being ionic and covalent and we do not see a good reason to place them in a class by themselves.



- If we were to believe the above scheme, it should come as no surprise that the largest noble gas atom should be the most *polarisable* and therefore the most cohesive. The boiling points (often better indicators of cohesion than melting points) testify to this:

Atom	T_M (K)	T_B (K)
Ne	24	27
Ar	84	87
Kr	116	120
Xe	161	165

- Other columns of elements in the periodic table don't follow this simple trend. For example:

Atom	T_M (K)	T_B (K)
Cu	1353	2833
Ag	1235	2433
Au	1333	3133

Ionic

- As a good thumb rule, atoms at the two ends of the electronegativity scale either give up their valence electrons very easily to form stable cations (ions with small values of electronegativity) or take up electrons very easily to form anions (ions with large electronegativities).

H		...					
2.2		...					
Li	Be	...	B	C	N	O	F
1.0	1.6	...	2.0	2.6	3.0	3.4	4.0
Na	Mg	...	Al	Si	P	S	Cl
0.9	1.3	...	1.6	1.9	2.2	2.6	3.2
K	Ca	...	Ga	Ge	As	Se	Br
0.8	1.0	...	1.8	2.0	2.2	2.6	3.0
Rb	Sr	...	In	Sn	Sb	Te	I
0.8	0.9	...	1.8	1.9	2.1	2.1	2.7
Cs	Ba	...	Tl	Pb	Bi	Po	At
0.8	0.9	...	1.8	2.1	2.0	2.0	2.2

- The process of giving up electrons (in the case of cations) and of taking electrons (anions) permits the ion to achieve a stable electronic configuration such as that of
 - a noble gas: For example, Na^+ and F^- have the Ne configuration
 - the d^{10} configuration: Ga^{3+} takes this up

– the s^2 configuration: Pb^{2+} and Bi^{3+} take this up

- Once they have done this, they can pair up suitably to form *ionic* solids that are held together by Coulombic interactions
- For any ionic crystal, the attractive Coulombic part (per mole) is:

$$\Delta U_{\text{Att.}} = - \left(\frac{LA|z_+||z_-|e^2}{4\pi\epsilon_0 r} \right)$$

L is the Avogadro number.

- The repulsive part arises because atoms and ions behave nearly like hard spheres. This is a consequence of the *Pauli exclusion principle* which says that no two electrons in a system can have all four quantum numbers the same.
- The repulsion can be approximated by the expression:

$$\Delta U_{\text{Rep.}} = \frac{LB}{r^n}$$

where B is called the repulsion coefficient and n is the Born exponent. n is normally around 8 or 9.

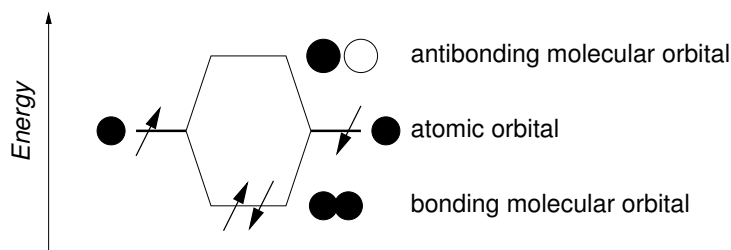
The two terms add:

$$\Delta U(0 \text{ K}) = - \frac{LA|z_+||z_-|e^2}{4\pi\epsilon_0 r} + \frac{LB}{r^n}$$

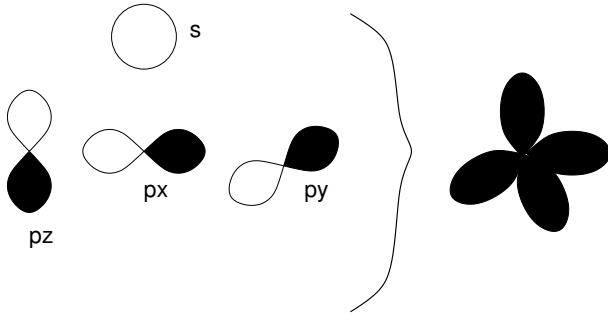
Covalent bonding

- Covalent bonds are formed between non-metallic (usually) atoms of similar electronegativity. s or p orbitals are used.

For example, the $1s$ orbitals on two hydrogen atoms combine to form the molecular orbitals $\sigma(1s)$ which is bonding and $\sigma^*(1s)$, which is antibonding. The two electrons occupy the bonding level and leave the antibonding level empty. In the following depiction, the circles are the $1s$ orbitals:



- Why is covalent bonding *strongly directional* ? The example of sp^3 hybrids in diamond and Si:



Hybrid orbitals are obtained from linear combinations of atomic orbitals on the *same* atom. These hybrid orbitals can then overlap with similar hybrid orbitals on neighboring atoms, just as the 1s orbitals do in the hydrogen chain.

Metallic bonding

This is a special case of covalent bonding where all the states are not filled up, and the electrons float around fixed nuclei in the solid.