AGH

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Modern physics

7. Many particles - complex atoms and molecules

AGH

Outline

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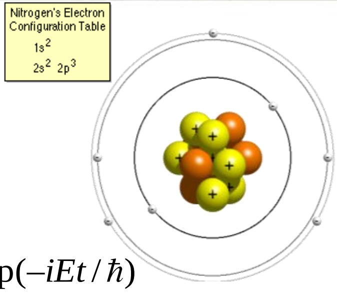
7.1. Many particles



Up till now, we have studied the wave equation for a single particle in hydrogen atom (one electron only). More complex atoms contain many electrons so we have to formulate and solve the multiparticle Schrödinger equation

Simple generalization of a one-particle wave function to a many-particle wave function:

$$\psi(x_1, x_2, \dots, x_N; t) = u(x_1, x_2, \dots, x_N)\exp(-iEt/\hbar)$$

N-number of particles, x_i is the position variable of particle *i* in 1D

and the generalized multiparticle Schrödinger equation takes a form

$$i\hbar\frac{\partial\psi(x_1, x_2, \dots, x_N; t)}{\partial t} = H\psi(x_1, x_2, \dots, x_N; t$$

H is the energy operator, Hamiltonian

7.1.1. Many independent particles

Hamiltonian in the most general case is:

$$H = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2} - \dots - \frac{\hbar^2}{2m_N}\frac{\partial^2}{\partial x_N^2} + V(x_1, x_2, \dots, x_N)$$

The simplest case when we treat the particles as independent we can write:

$$V(x_1, x_2, \dots, x_N) = V_1(x_1) + V_2(x_2) + \dots + V_N(x_N)$$

Independent particles do not interact with each other but each of them may experience a different external potential V_i

Total energy E is the sum of the single particle energies:

$$E = E_1 + E_2 + \dots + E_N$$

7.1.2. Identical particles

One of the most striking features of the microscopic world is indistinguishability of particles. On our human scale, no two planets are the same, no two sets of fingerprints match, and no two snowflakes are identical. This is due to complexity of systems. At the atomic scale it is impossible to distinguish among constituents of a specific kind.

Spectroscopic evidence tells us that there is only one kind of hydrogen atom (we neglect the isotopes), and one kind of helium atom. Even though there is an infinite number of excited states for hydrogen atom, all hydrogen atoms have the same set of excited states and the same spectrum.

All electrons are the same. They have exactly the same mass, electric charge, magnetic dipole moment, etc. The same applies to protons, neutrons and other particles.

7.1.2. Identical particles

Identical particles are subject to the same external potential (otherwise one could distinguish between them):

$$V(x_1, x_2, \ldots, x_N) = V(x_1) + V(x_2) + \ldots + V(x_N)$$

For the same reason, there are two classes of time-independent wave functions: symmetric u_S and antisymmetric u_A

For a two-particle system:

$$u_S(x_1, x_2) = \frac{1}{\sqrt{N_S}} \left[u_m(x_1) u_n(x_2) + u_m(x_2) u_n(x_1) \right]$$

$$u_A(x_1, x_2) = \frac{1}{\sqrt{N_S}} \left[u_m(x_1) u_n(x_2) - u_m(x_2) u_n(x_1) \right]$$

7.1.2. Identical particles

Symmetric wave function is invariant under the exchange of particles and applies to bosons:

$$u_S(x_2, x_1) = +u_S(x_1, x_2)$$

Antisymmetric wave function changes sign under the exchange of particles and applies to fermions:

$$u_S(x_2, x_1) = -u_S(x_1, x_2)$$

All particles fall into two classes: fermions and bosons.

Fermions consist of electrons, protons, neutron, and, in general, system whose total angular momentum, including spin, is 1/2, 3/2, 5/2

Bosons consist of photons, helium nuclei, hydrogen atoms, and, in general, system whose total angular momentum, including spin, is 0, 1, 2

7.2. Pauli exclusion principle

No more than one electron can have a given set of quantum numbers (including spin)

Wolfgang Pauli (1900-1958), an Austrian-born theoretical physicist, formulated this principle in 1924. At that time Schrödinger equation did not exist. Even, the existence of the electron spin was also proposed a few years later by the Dutch physicists Samuel Goudsmit and George Uhlenbeck.

After formulation of the Schrödinger equation, the generalized Pauli principle, called the **exchange symmetry principle**, appeared:

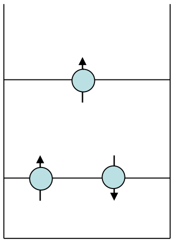
The wave function of a many-particle system is antisymmetric under the exchange of two identical fermions and symmetric under the exchange of two identical bosons.

⇩

No two identical fermions can be in the same quantum mechanical state.

7.2.1. The consequences of Pauli exclusion principle

Electrons in an infinite well



The energy level n=1 corresponds to the lowest energy and therefore represents the ground state for a single electron.

With spin present, *two* electrons can be accommodated for each state labeled n (n=1), one electron with spin up, the other with spin down. Third electron must go to n=2 by the exclusion principle.

Exchange forces

These are not forces in the usual Newtonian sense. They come as a consequence of exchange symmetry principle. Even if the identical fermions in the potential well do not interact, there is something like *repulsion* between them. For the identical bosons there is *attraction*

7.2.1. The consequences of Pauli exclusion principle

The principle plays a critical role in the structure of atoms, molecules, and nuclei, as well as in the technology of semiconductor and laser devices. Metals contain many „free" electrons. When many identical particles appear together we have ***degenerate matter**.*

Examples of degenerate matter

On Earth, we see degenerate matter in the form of electrons in metals. The valence electrons in a metal behave as a degenerate fermionic system at low temperatures. This behavior explains many experimental features of metals: their heat capacity, their electric conduction properties, the dependence of electron emission on temperature.

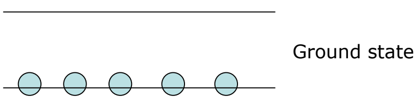
The resistance to compression originating in the exclusion principle plays an important role in stellar evolution. This explains the formation of **white dwarfs, neutron stars** and **black holes.**

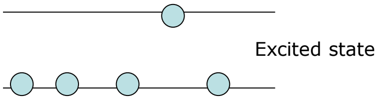
7.2.2. Fermi energy

Fermi energy applies to fermions and is also a consequence of Pauli exclusion principle.

The case of 1D infinite well

We start with the case of N bosons – no exclusion principle.





The ground state will be that in which all N bosons occupy the n=1 level

The total ground-state energy:

$$E_g = NE_1$$

The average energy per particle:

$$\frac{E_g}{N} = E_1$$

The first excited state will be that in which N-1 bosons occupy the n=1 level and one boson is in the single n=2 state.

The energy of the N-particle excited state:

$$E^* = (N-1)E_1 + E_2$$

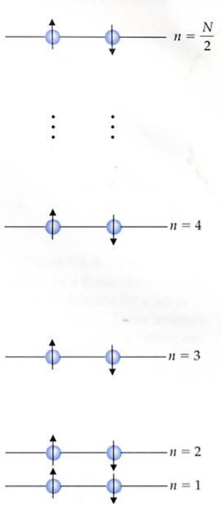
7.2.2. Fermi energy

Fermi energy E_F is an important parameter of the electronic structure of semiconductors and metals. <u>It is defined as the energy of the highest level to be filled with electrons in the ground state.</u>

The case of 1D infinite well

We cannot put all N-fermions (electrons) in one state (exclusion principle). With N electrons *all* the levels up to n=N/2 are occupied in the ground state. Using the fact that the single particle energies are $E_n=n^2E_1$, the N-particle ground state energy is:

$$E_g = E_1\left[2(1)^2 + 2(2)^2 + \ldots + 2\left(\frac{N}{2}\right)^2\right] = 2E_1\sum_{j=1}^{N/2} j^2$$



7.2.2. Fermi energy

The sum can be calculated exactly: $\sum_{j=1}^{n} j^2 = \frac{1}{6}n(n+1)(2n+1)$

which, for large *n* can be approximated by $n^3/3$

Since *n* is large and equals N/2: $E_g \approx \frac{N^3}{24}$

The average energy per particle n the ground state is: $\frac{E_g}{N} \approx \frac{N^2}{12}E_1$

The average energy is quite different from that in the boson case, because, in contrast to this case, in which the average energy is constant, for the fermion case, the average energy grows with the number of fermions as N^2

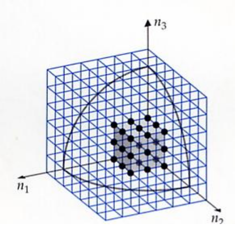
In the construction of the N-fermion ground state, the highest energy level to be filled, the Fermi energy, E_F corresponds to n=N/2 and (in 1D case) equals to

$$E_F = \frac{\pi^2\hbar^2N^2}{8mL^2}$$

7.2.2. Fermi energy

3D case

In the real world we deal with three-dimensional case. The calculation of Fermi energy is more complicated technically but the reasoning is the same as in 1D case.



We start by enumerating the possible single-particle energies in the 3D infinite well formed by a cube whose sides have length L.

The single-particle levels are the sum of three allowed 1D energy levels:

$$E(n_1,n_2,n_3) = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2+n_2^2+n_3^2) = E_1(n_1^2+n_2^2+n_3^2)$$

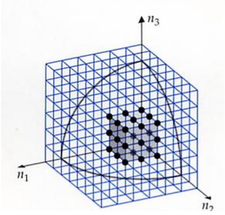
There is an allowed energy state corresponding to any triplet of integers (n_1,n_2,n_3)

The possibility of degeneracy in the energy is the major difference between 1D and 3D cases.

7.2.2. Fermi energy

3D case

We have N fermions (N is large), and fill up the energy levels in the box, two fermions per level, starting at the bottom. The energy of the last fermion to be accommodated is the Fermi energy E_F



How many states are there with energy less than or equal to some value of E?

Once we know that, we set the number of states equal N/2 and that will correspond to $E=E_F$

This question is equivalent to:

How many triplets of integers are there such that $n_1^2+n_2^2+n_3^2 \le \frac{E}{E_1}$

For the estimation (assuming N, hence E_F large), we plot the set of three integers as a cubic lattice. Each point on the lattice corresponds to some triplet of integers (n_1,n_2,n_3)

In order to answer the question we need to find the number of lattice points that satisfy $n_1^2+n_2^2+n_3^2 \le R^2$ $\qquad R^2=\frac{E}{E_1}$

7.2.2. Fermi energy

3D case

Since the integer triplets make lattice points with a spacing of one unit in each Cartesian direction, the lattice is formed of cubes of unit volume. Thus, we can calculate the number of lattice points in question by calculating the volume of a sphere with radius R.

$$\frac{N}{2}=\frac{1}{8}\frac{4\pi R^3}{3}=\frac{\pi}{6}\left(\frac{E_F}{E_1}\right)^{3/2}$$

Finally we get:

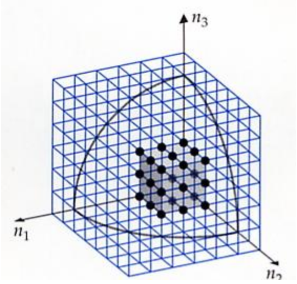
$$E_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{L^3}\right)^{2/3}$$

Or, if we define the fermion density as

$$n_f=N/L^3$$

we get rid of the size of the box, L

$$E_F=\frac{\hbar^2}{2m}\left(3\pi^2 n_f\right)^{2/3}$$



In order to avoid the overcounting, we restrict ourselves to positive n by taking 1/8 of the volume

7.2.2. Fermi energy

3D case

There is a simple way to think about the Fermi energy. The magnitude of the electron momentum (Fermi momentum) at that energy is

$$p_F = \sqrt{2mE_F} = \hbar\left(3\pi^2 n_f\right)^{1/3}$$

The de Broglie wavelength corresponding to the Fermi momentum is

$$\lambda_F = \frac{h}{p_F} = 2\left(\frac{\pi}{3}\right)^{1/3}\underbrace{n_f^{-1/3}}$$

the average interfermion spacing *a*

The closest that two electrons can get to each other is roughly the half a de Broglie wavelength corresponding to the Fermi energy

$$a \cong \frac{\lambda_F}{2}$$

7.3. Complex atoms

Hydrogen atom with its atomic number Z=1 is a simple atom. It contains only one electron and one proton, thus its potential describes only the Coulomb interaction between these two particles. Therefore, the Schrödinger equation for H atom has been solved directly.

In contrast, the next element in the periodic table: helium atom (Z=2) is quite a complex atom. The fact that it contains two electrons and two protons contributes to three (instead of one) terms in the potential energy:

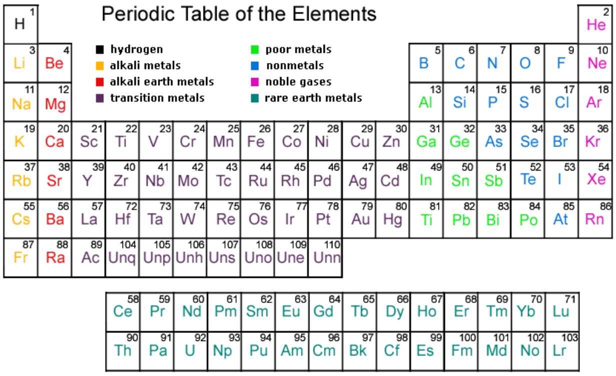
- two terms represent the interaction of the two electrons with the nucleus of charge Z=2, one for each electron
- the third terms represents the electron-electron repulsion

The wave functions for a multielectron atom are not the same as the wave functions for the corresponding states of hydrogen atom

Solutions of the Schrödinger equation have to be carried out numerically.

7.3. Complex atoms

Periodic repetition of the properties of atoms as a function of their position in the periodic table suggests some ordering of elements.



Periodic Table of the Elements

- ■ hydrogen
- ■ alkali metals
- ■ alkali earth metals
- ■ transition metals
- ■ poor metals
- ■ nonmetals
- ■ noble gases
- ■ rare earth metals

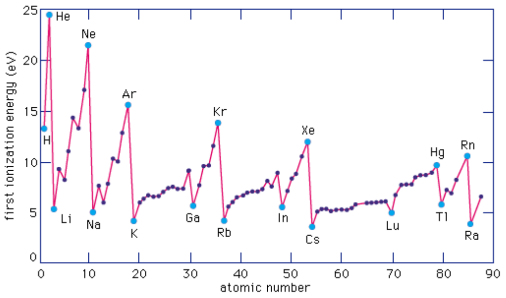
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

An atom of atomic number Z and mass number A has, at its core, a nucleus of Z protons and A-Z neutrons. Nucleus is treated as fixed in space because it is more heavy (x2000 than electron).

7.3. Complex atoms

The example of periodic properties is the ionization energy as a function of the atomic number Z.



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Ionization energy is the energy required to remove the most loosely bound electron from a neutral atom.

The remarkable similarities in the chemical and physical properties of elements in each vertical column of the periodic table are evidence that the atoms are constructed according to systematical rules.

7.3.1. How to build up the periodic table

Rules:

1. Electrons go into lowest energy orbitals first.
2. No more than two electrons in any one orbital. Filled orbitals have spins paired – Pauli exclusion principle.
3. When there are orbitals of equal energy in a subshell to fill, the electrons first go into different orbitals with parallel spins one at a time.

7.3.1. How to build up the periodic table

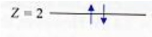
Spectroscopic notation – historical labeling of states („sharp", „diffuse" spectral lines)

ℓ-value	0	1	2	3	4
letter label	s	p	d	f	g

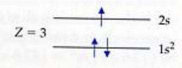
According to the Pauli principle the number of electrons that can be accommodated in a state with angular momentum ℓ is 2x($2\ell+1$), where the factor ($2\ell+1$) counts the number of angular-momentum projections and the exterior factor 2 counts the number of spin projections – spin „up" or spin „down"- for the electron.

hydrogen, 1s

helium, $1s^2$



lithium, $1s^22s$



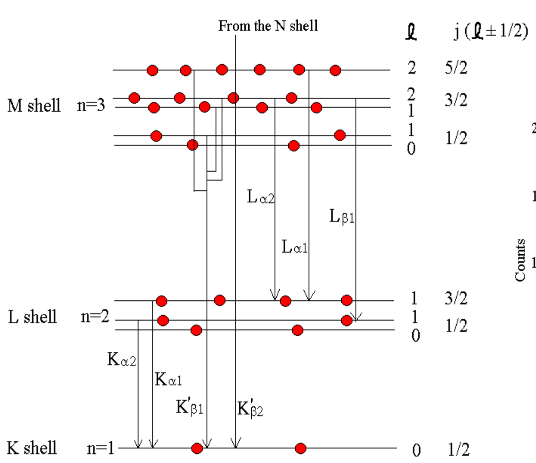
The chemical activity depends on the configuration. Lithium with one electron beyond the closed subshell is very active (alkaline metal). Helium has a closed shell and is an inert gas.

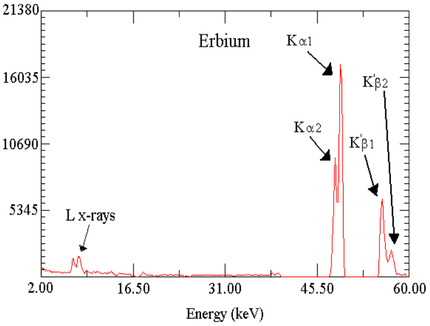
7.3.1. How to build up the periodic table

Atom	Configuration	Comment
^{11}Na	[Ne]2s	Paramagnetic
^{12}Mg	[Ne] $2s^2$	Closed shell (diamagnetic)
^{13}Al	[Ne] $2s^22p^1$	Paramagnetic
^{14}Si	[Ne] $2s^22p^2$	Paramagnetic
^{15}P	[Ne] $2s^22p^3$	Paramagnetic
^{16}S	[Ne] $2s^22p^4$	Paramagnetic
^{17}Cl	[Ne] $2s^22p^5$	Paramagnetic
^{18}Ar	[Ne] $2s^22p^6$	Closed shell (diamagnetic)

7.3.2. X-rays and ordering of the elements

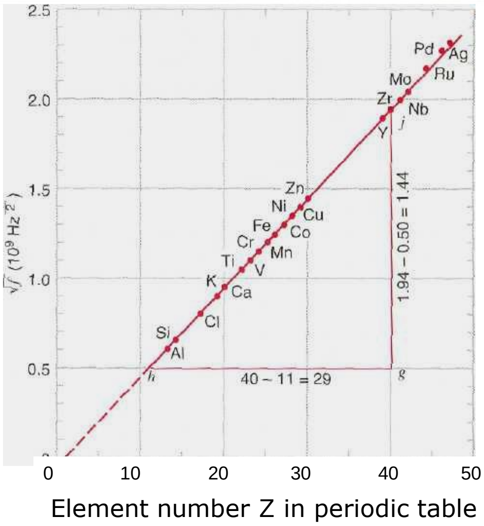
Generic Energy Level Diagram





7.3.2 X-rays and ordering of the elements

Moseley showed that the characteristic X-rays followed a straight line when the atomic number *Z* versus the square root of frequency was plotted.



7.4 Molecules and chemical bonding

A **molecule** (HCl, O_2, N_2, CO_2 and NH_3) is a stable arrangement of electrons and more than one nucleus. Even for diatomic molecules the system is more complicated than two separate atoms.

Quite simple molecule H_2 consists of two protons and two electrons. Once the center of mass is fixed, the electrons can move relative to the center of mass and to each other, and so can two nuclei. In the first approximation, we use the fact that electrons are at least 2,000 times less massive than nuclei. Thus, the nuclear motion is much slower than that of the electrons, and we can use the following procedure:

1. First we assume that the nuclei are fixed in space. This allows us to treat the motion of electrons in the electric field of the fixed nuclear charges.

2. The moving electrons create a smeared-out charge distribution. In the next approximation, the nuclei are allowed to move in this charge distribution

7.4 Molecules and chemical bonding

The **H_2^+** is the simplest molecule. It is singly ionized H_2 and consists of two protons and one electron.

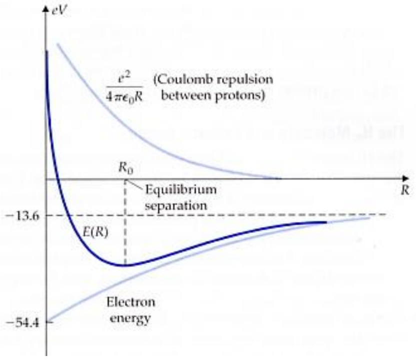
If the protons are very close (R → 0) – the molecule looks exactly like a singly ionized helium atom (Z=2). The **electronic energy** is:

$$E_{elec}(0) = -13.6\ Z^2 = -54.4eV$$

If the two protons are far apart(R→ ∞) – the electron will be bound to one proton or the other as in ordinary hydrogen, so that:

$$E_{elec}(\infty) = -13.6\ eV$$

The full electronic expression $E_{elec}(R)$ will interpolate between these two values, approaching -13.6 eV at a distance of at most a few hydrogen atom radii a_0



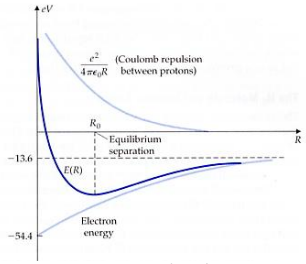
Energy E(R) of H_2^+ molecule as a function of the distance R between the protons

7.4 Molecules and chemical bonding

Apart from the electronic energy, there is also a contribution to the energy that comes from the **proton-proton repulsion:**

$$E_{nucl}(R) = \frac{e^2}{4\pi\varepsilon_0 R}$$

The total energy E(R) of the molecule is the sum of electronic and nuclear contributions



There is a minimum at $R=R_0$; this is a stable equilibrium point, and it characterizes the size of the molecule.

$$R_0 = 0.106\ nm$$
$$E(R_0) = -10.8eV$$

If the electrons were localized in some outer region surrounding the two protons, the repulsion between the protons would raise the energy. But for the electron lying between two protons, the energy would be lowered, because both protons are attracted to the electron (protons are **screened** from one another by the electron). Thus the situation in which the electron lies between the protons is favored, and the electron is tied not to one proton or the other, but to both of them

7.4 Molecules and chemical bonding

Chemical bonding is when two or more atoms combine by sharing electrons so that a new substance is produced that has different physical and chemical properties than its component elements

Chemical bonding occurs when atoms share **valence electrons**. Atoms 'want' to share electrons so that their valence shells are full and they are chemically stable.

Binding energy is the energy necessary to dissociate the solid into separated atoms, molecules or ions. The binding energy is taken at room temperature, except for molecular crystals where it is taken at the melting point.

Classification of crystals is based on binding energy.

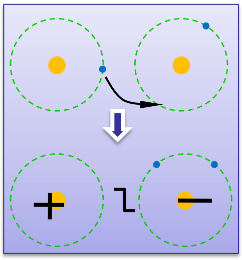
We have strong bonding: ionic and covalent and very weak bonding: molecular

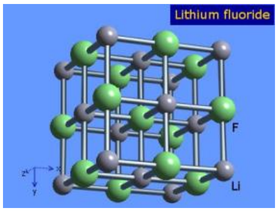
Crystal type	Examples	Binding energy (kcal/mole)	Characteristics of type
Ionic	NaCl LiF	180 240	strong infrared absorption, low electrical conductivity at low temperatures, good ionic conductivity at high temperatures
Covalent	Diamont SiC	≈170 283	great hardness, low conductivity at low temperatures when pure
Metallic	Na Fe	26 94	high electrical conductivity
Molecular	Ar CH_4	1.8 2.4	low melting and boiling points, very compressible
Hydrogen-bonded	H_2O (ice) HF	12 7	tendency to polymerize (i.e. to form groups of many molecules), increased binding energy of molecules in comparison with similar molecules without hydrogen bonds

7.4 Molecules and chemical bonding

Ionic crystals

In ionic crystals electrons are transferred from atoms of one type to atoms of second type, so that the crystal is made up of positive and negative ions.





The ions arrange themselves so the Coulomb attraction between ions of opposite sign is stronger than the Coulomb repulsion between ions of the same sign. The ionic bond is thus essentially the bond resulting from the electrostatic interaction of oppositely charged ions.

7.4 Molecules and chemical bonding

Ionic bonding concerns binding of atoms one of which has a single electron outside a shell (as in **alkaline** metals) and the other of which has a single hole in a closed shell (as in **halogens**)

Example: LiF

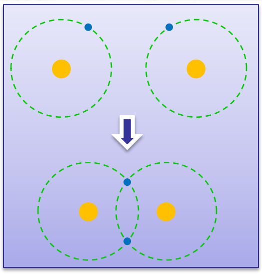
neutral atoms Li: $1s^2 2s$ F: $1s^2 2s^2 2p^5$

singly charged ions: $\left.\begin{array}{l} Li^+: 1s^2 \\ F^-: 1s^2 2s^2 2p^6 \end{array}\right\}$ closed shells as for helium and neon, respectively

The inert gas atoms have closed shells, and the charge distributions are spherically symmetric. We may expect accordingly that the charge distributions on each ion in an ionic crystal may have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms.

7.4 Molecules and chemical bonding

Covalent crystals

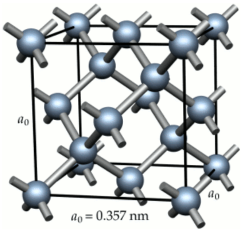


When a covalent bond is formed we imagine that an electron from each atom is transferred to the region between the two atoms joined by the bond. The charge density between the two atoms is high and the valence electrons are to an appreciable extent shared between two atoms.

Covalent bond is particularly encountered in **organic chemistry**.

The carbon bond is a good example of the **directional** properties of the covalent bond.

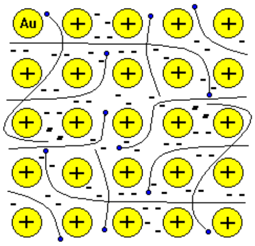
Carbon atoms often prefer to join onto each other or to other atoms by four bonds making tetrahedra angles with each other. Diamond and methane are typical examples of the tetrahedral covalent bond.



7.4 Molecules and chemical bonding

Metal crystals

A metallic bond occurs in metals. A metal consists of positive ions surrounded by a „sea" of mobile electrons.



Metals are characterized by high electrical conductivity and so a portion of electrons in a metal must be free to move about. The electrons available to participate in the conductivity are called **conduction** electrons.

In alkali metals the interaction between the conduction electrons and ion cores is relatively weak. The interatomic distances are large because of the kinetic energy of electrons. In transition metals there may be also binding effects from covalent-type bonds among the inner electron d-shells (incomplete). High binding energies characterize the transition metals (W – 210 kcal/mole)

7.4 Molecules and chemical bonding

Molecular crystals

Inert gas atoms and saturated molecules are bound together in the solid phase by weak electrostatic forces known as **van der Waals forces**.

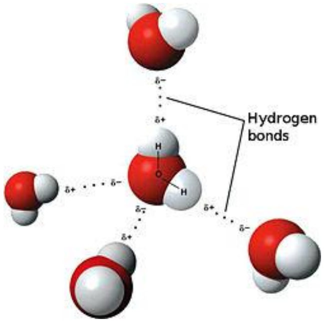
Even in an atom or molecule which has on the average an electric dipole moment of zero, there will be a fluctuating dipole moment associated with the instantaneous position of the electrons in atom. The instantaneous electric field associated with the moment will induce a dipole moment in neighboring atoms. The average interaction of the original moment and the induced moment gives rise to an attractive force between the atoms.

The inert gas crystals crystallize with cubic close packing.

7.4 Molecules and chemical bonding

Hydrogen-bonded crystals

Neutral hydrogen has only one electron, and it should form a covalent bond only with one other atom. It is known, however, that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming a **hydrogen bond**, with a bond energy of about 5 kcal/mole.



Hydrogen bond is formed by protons and connects only two atoms (as in H_2O molecule).

Hydrogen bond is responsible for the striking properties of water and ice.

7.4 Molecules and chemical bonding

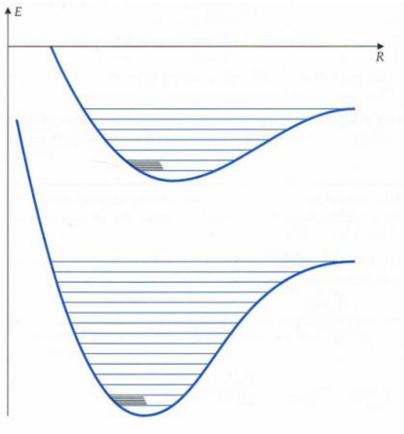
Nuclear motion and its consequences

The complex shapes of molecules allow energy levels other than the electronic levels characteristic of atoms.

The two new types of energy levels are **vibrational levels** (blue lines) and **rotational levels** (black, closely spaced lines).

Vibrational levels are associated with restoring forces around the minimum in the energy of nuclei.

Rotational levels are associated with the rotation as a whole of the nuclei in the molecule.



The electronic, vibrational, and rotational energy-level spacing is in the ratio 1:10^2:10^4

Conclusions

1. Quantum mechanics provides an intellectual structure for describing all of the properties of atoms and molecules.
2. For atoms, quantum mechanics the concept of orbitals (wave functions) provides a description of the energies, the sizes of atoms and the basis for bonding of atoms and the construction of the periodic table.
3. The orbitals for the H atom, which are known precisely, are used as starting approximation for building up the electron configuration of multielectron atoms.
4. In complex atoms, electrons are placed in successive states, with two electrons per state according to the Pauli exclusion principle.
5. Chemistry is associated with unpaired electrons and with shells that are incomplete. The most chemically inactive elements are those with shells that are filled
6. Molecules are formed when there is more than one fixed center of force (the nuclei of atoms that form the molecule) with electrons in the eigenstates of the resulting potential. Molecules can form when there is a minimum in the potential energy of electrons.