

# Lecture 5 Bonding

*Simon: Chapter 6 (p49-60); Kittel: Chapter 3 (p49-70)*

Bonding holds matter together. Bonding requires a stable equilibrium between both attractive and repulsive forces. Without repulsion an attractive force alone would just cause all matter to collapse to a singularity.

Where do the *repulsion* and the *attraction* come from? In this lecture we will look at these two different types of physical force which exists between atoms and molecules.

## Repulsion

This occurs when we bring atoms very close together  $r < 0.3 \text{ nm}$ . Where does this come from?

Consider simple Bohr model of the atom with nucleus at the centre and electron cloud on the outside. As electron clouds come very close together the electron clouds begin to repel each other.

The repulsion is quantum in nature and is related to the Pauli Exclusion Principle (Young and Freedman Chapter 41).

*No two electrons in an atom can be in the same quantum state*

In quantum mechanics a quantum state is labelled by quantum numbers examples of these are position, energy, spin, angular momentum etc.

In other words, the Pauli exclusion principle tells us that no two electrons can have the same energy, position etc.

Applying this to atoms: 1) when atoms are far apart with no overlap we can observe two electrons on separate atoms. 2) when atoms are closer together - electron clouds overlap, electrons begin to occupy the same region (and thus quantum number) 3) the exclusion principle causes electrons to go into higher energy states increasing energy of the system this all leads to a repulsive force.

The repulsive force is quantum in nature and increases sharply with reducing separation of the atoms. The exact form requires quantum mechanics to describe the dependence on  $r$ . This is generally modelled using empirical functions – we will look at these later in the lecture.

Note that bringing together two electrons from a large distance will also see them subject to the repulsive force associated with their respective electric fields. This is different from the quantum repulsion discussed above. Applying a sufficiently large external force can overcome the electric forces but not the quantum force.

## Attraction

The attractive force arises from electromagnetism as gravity is too weak. To describe accurately, we need quantum mechanics but we can use a simpler approach to describe the main features in a qualitative approach.

We will consider a number of different attractive forces which form bonds in a range of substances.

The electrostatic interaction between the negatively charge electrons and the positively charged nuclei are solely responsible for the cohesion and physical properties of solids. Magnetic forces have only a weak role and gravity is negligible. Furthermore, it turns out that it is a consequence of the electrons in the outermost shells which have the biggest impact on the physical properties of solids.

The **cohesive energy** of a crystal (or other solid) is defined as the energy required to separate its constituent parts into neutral free atoms at rest with an infinite separation.

The term **lattice energy** applies to ionic crystals (e.g. salts) and is defined as the energy required to create free ions (at infinite separation) from the crystal.

Table 1 Cohesive energies																	
Li 158. 1.63 37.7	Be 320. 3.32 76.5	Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer.															
Na 107. 1.113 25.67	Mg 145. 1.51 34.7	B 561. 5.81 134	C 711. 7.37 170	N 474. 4.92 113.4	O 251. 2.60 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46										
Rb 82.2 0.852 19.64	Sr 166. 1.72 39.7	Al 446. 4.63 106.7	Si 331. 3.43 79.16	P 275. 2.85 65.75	S 135. 1.40 32.2	Cl 7.74 0.080 1.85	Ar 11.2 0.116 2.68										
K 90.1 0.934 21.54	Ca 178. 1.84 42.5	Sc 376. 3.90 89.9	Ti 468. 4.85 111.8	V 512. 5.31 122.4	Cr 395. 4.10 94.5	Mn 282. 2.92 67.4	Fe 413. 4.28 98.7	Co 424. 4.39 101.3	Ni 428. 4.44 102.4	Cu 336. 3.49 80.4	Zn 130. 1.35 31.04	Ga 271. 2.81 64.8	Ge 372. 3.85 88.8	As 285.3 2.96 68.2	Se 237. 2.46 56.7	Br 118. 1.22 28.18	Kr 11.2 0.116 2.68
Cs 77.6 0.804 18.54	Ba 183. 1.90 43.7	Y 422. 4.37 100.8	Zr 603. 6.25 144.2	Nb 730. 7.57 174.5	Mo 658. 6.82 157.2	Tc 661. 6.85 158.	Ru 650. 6.74 155.4	Rh 554. 5.75 132.5	Pd 376. 3.89 89.8	Ag 284. 2.95 68.0	Cd 112. 1.16 26.73	In 243. 2.52 58.1	Sn 303. 265. 72.4	Sb 211. 2.75 63.4	Te 107. 2.19 50.34	I 15.9 1.11 25.62	Xe 11.2 0.116 3.80
Fr 160. 1.66 38.2	Ra 410. 4.25 98.	La 431. 4.47 103.1	Hf 621. 6.44 148.4	Ta 782. 8.10 186.9	W 859. 8.90 205.2	Re 775. 8.03 185.2	Os 788. 8.17 188.4	Ir 670. 6.94 160.1	Pt 564. 5.84 134.7	Au 368. 3.81 87.96	Hg 65. 0.67 15.5	Tl 182. 1.88 43.4	Pb 196. 2.03 46.78	Bi 210. 2.18 50.2	Po 144. 2.03 34.5	At 19.5 0.202 4.66	Rn 19.5 0.202 4.66
Ac 160. 1.66 38.2		Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm 206. 2.14 49.3	Sm 206. 2.14 42.8	Eu 179. 1.86 95.5	Gd 400. 4.14 93.4	Tb 391. 4.05 70.2	Dy 294. 3.04 72.3	Ho 302. 3.14 75.8	Er 317. 3.29 55.8	Tm 233. 2.42 37.1	Yb 154. 1.60 102.2	Lu 428. 1.60 102.2		
Ac 160. 1.66 38.2		Th 598. 6.20 142.9	Pa 536. 5.55 128.	U 347. 4.73 109.	Np 347. 3.60 83.0	Pu 264. 2.73 63.	Am 385. 3.99 92.1	Cm 264. 2.73 92.1	Bk 385. 3.99 92.1	Cf 429.8. 3.99 92.1	Es 505.1. 5.00 92.1	Fm 505.1. 5.00 92.1	Md 505.1. 5.00 92.1	No 55.8. 1.60 37.1	Lr 55.8. 1.60 37.1		

The table of cohesive energies shows these vary from 1.92 kJ per mole to 859 kJ per mole (a factor of 450).

Melting points range from 4 K to 3770 K (He → diamond C).

Table 2 Melting points, in K. (After R. H. Lamoreaux)																	
Li 453.7	Be 1562	B 2365	C 63.15	N 54.36	O 53.48	F 24.56	Ne 24.56										
Na 371.0	Mg 922	Al 933.5	Si 1687	P w 317 r 863	S 388.4	Cl 172.2	Ar 83.81										
K 336.3	Ca 1113	Sc 1814	Ti 1946	V 2202	Cr 2133	Mn 1520	Fe 1811	Co 1770	Ni 1728	Cu 1358	Zn 692.9	Ga 302.9	Ge 1211	As 1089	Se 494	Br 265.9	Kr 115.8
Rb 312.6	Sr 1042	Y 1801	Zr 2128	Nb 2750	Mo 2895	Tc 2477	Ru 2527	Rh 2236	Pd 1827	Ag 1235	Cd 594.3	In 429.8	Sn 505.1	Sb 903.9	Te 722.7	I 386.7	Xe 161.4
Cs 301.6	Ba 1002	La 1194	Hf 2504	Ta 3293	W 3695	Re 3459	Os 3306	Ir 2720	Pt 2045	Au 1338	Hg 234.3	Tl 577	Pb 600.7	Bi 544.6	Po 527	At 102	Rn 102
Fr 973	Ra 973	Ac 1324	Ce 1072	Pr 1205	Nd 1290	Pm 1346	Sm 1346	Eu 1091	Gd 1587	Tb 1632	Dy 1684	Ho 1745	Er 1797	Tm 1820	Yb 1098	Lu 1938	
Ac 973		Th 2031	Pa 1848	U 1406	Np 910	Pu 913	Am 1449	Cm 1613	Bk 1562	Cf 1613	Es 1613	Fm 1613	Md 1613	No 1613	Lw 1613		

The tables illustrate considerable variation with period. Noble gases are weakly bound, alkali metals intermediate and transition metals very strongly bound. The melting temperatures of the elements vary roughly in line with the cohesive energy. The simplest crystals are formed by the noble or inert gases.

The crystals are weakly bound with low melting temperatures. These properties arise because the outer shell is completely filled with electrons and the free atoms have a spherical distribution of charge (no preferred orientation for bonding). In the crystalline form the inert atoms pack together as closely as possible in the cubic close packing (fcc) structure.

We need to consider what forces hold together a crystal composed of inert gas atoms. The energy that is required to hold the crystal together (the cohesion energy) is about 1% of the energy required to remove an electron from an atom and create an ion (the ionisation energy).

The force that gives cohesion to these systems is the Van der Waals force.

### Van der Waals Interaction

This is named after a Dutch scientist, Johannes Diderik van der Waals (Nobel prize 1910). The force is responsible for holding together systems where there is no covalent or ionic bonding. It is substantially weaker than these forces. The Van der Waals interaction occurs in different types of systems:

1. Two permanent dipoles
2. One permanent dipole and one induced dipole
3. Two induced dipoles.

The latter is sometimes called the London force.

Van der Waals forces always occur between atoms irrespective of which other forces are present. They are often much weaker and have little impact. At sufficiently low temperatures these forces will cause all substances (except He) to condense into a liquid then a solid. Van der Waals forces are also important in crystals formed from organic molecules.

We now develop an expression for this force.

Consider two identical inert (gas) atoms at a separation  $r$  from each other where  $r$  is large compared to the radii. What interactions exist between these two atoms?

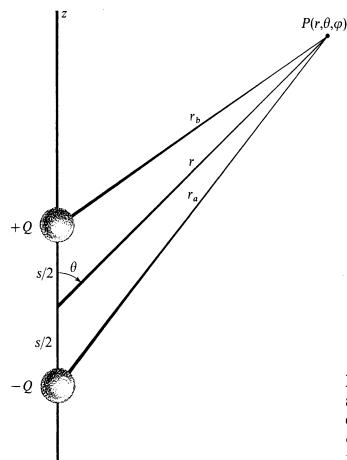
The outer shells consist of electrons in well-defined energy states (described by a range of “good” quantum numbers). The electrons in the shells are best considered as an electron cloud with an electron density. (This is related to the electron wavefunction  $\Psi$  obtained from solving the Schrodinger equation).

Bringing the atoms together results in an induced effect which changes the electron distribution the other atom. We describe this as an induced electric dipole. This causes an attractive interaction between the atoms.

Kittel derives an expression through a consideration of coupled harmonic oscillators. A consideration of the electric dipole achieves the same result and will be used here.

If we consider a spherically symmetric atom with an amount of charge  $q$  moving a distance  $L$  the dipole moment is then  $p = q L$

An electric dipole is considered as a positive charge  $+q$  separated from a negative charge  $-q$  separated by the distance  $L$ .



**Figure 2-8.** The two charges  $+Q$  and  $-Q$  form a dipole. The electric potential at  $P$  is the sum of the potentials due to the individual charges.

At an arbitrary point  $P$  the electric potential is given by:

$$V = \frac{Q}{4\pi\epsilon_0} \left( \frac{1}{r_b} - \frac{1}{r_a} \right)$$

(Missing step expand equation relating  $r$ ,  $r_a$ ,  $s$  and  $\cos\theta$  as a series to get  $1/r^2$  behaviour)

It can be shown that the electric potential is then:

$$V(r) = \frac{\mathbf{p} \cdot \mathbf{r}_1}{4\pi\epsilon_0 r^2}$$

where  $\mathbf{p}$  is the electric dipole vector and  $\mathbf{r}_1$  is the unit vector along  $r$ .

The derivation then follows (not necessary to know details) to give the potential energy as

$$U(r) = \frac{A}{r^6}$$

The force between the atoms is given by

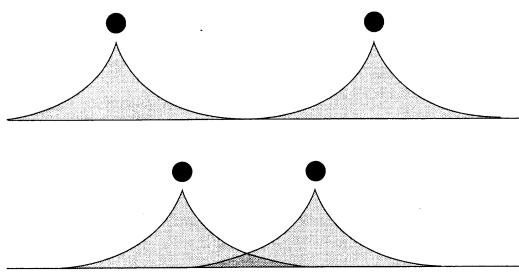
$$F(r) = \frac{-dU}{dr} = \frac{A}{r^7}$$

which is much weaker than other forces.

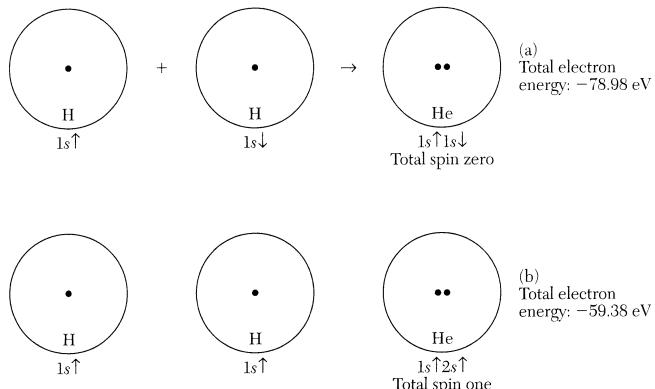
### Repulsive Interaction

As discussed above a stable bond requires an equilibrium between an *attractive* and a *repulsive* force. The repulsive force is quantum in nature and arises because of the *Pauli Exclusion Principle*.

The effect of the Pauli Exclusion Principle is illustrated in the figure below:



**Figure 4** Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.



**Figure 5** The effect of Pauli principle on the repulsive energy: in an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. In (a) the electrons have antiparallel spins and the Pauli principle has no effect: the electrons are bound by  $-78.98$  eV. In (b) the spins are parallel: the Pauli principle forces the promotion of an electron from a  $1s\uparrow$  orbital of H to a  $2s\uparrow$  orbital of He. The electrons now are bound by  $-59.38$  eV, less than (a) by  $19.60$  eV. This is the amount by which the Pauli principle has increased the repulsion. We have omitted the repulsive coulomb energy of the two protons, which is the same in both (a) and (b).

The Pauli Exclusion Principle prevents multiple electrons occupying quantum states. It manifests itself in practice by increasing the energy of a system as individual atoms are brought together.

The exact functional form of the repulsion is difficult to determine. Experimental data on inert gas solids shows that an *empirical function* of the form  $\frac{B}{r^{12}}$  works well.

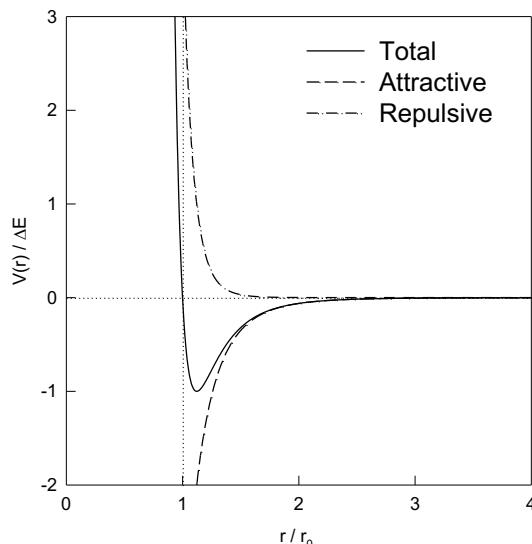
Considering an inert gas solid with both attractive and repulsive elements gives the expression:

$$U(r) = 4\epsilon \left[ -\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12} \right]$$

This is often called the Lenard-Jones 6-12 potential where constants  $A$  and  $B$  are used:  $4\epsilon\sigma^6 = A$  and  $4\epsilon\sigma^{12} = B$

The potential can be used to model the interatomic behaviour and predict a range of phenomena.

### Lennard - Jones (6-12) Potential



Kittel compares the Lennard –Jones potential with a range of physical properties of inert gas solids and shows that this empirical function works well for these systems.

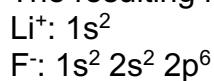
### Ionic Crystals

Ionic crystals are made up of positive and negative ions. The ionic bond originates from the electrostatic interaction between oppositely charged ions. Salts are common examples of ionic solids. The electronic configuration of *ions* in an ionic crystal corresponds to closed shells. These are achieved through the transfer of electrons to form negative ions (cations) leaving behind positive ions (anions).

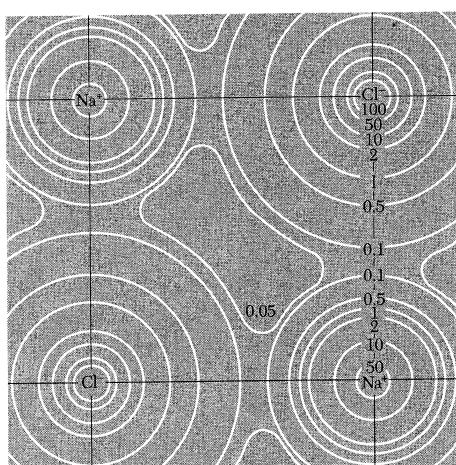
Example LiF (lithium fluoride):



The resulting ions have the configuration:



This corresponds to the closed shell stable structures of He and Ne. The charge distribution in the ions is approximately spherical – this is confirmed by x-ray measurement of electron distributions.



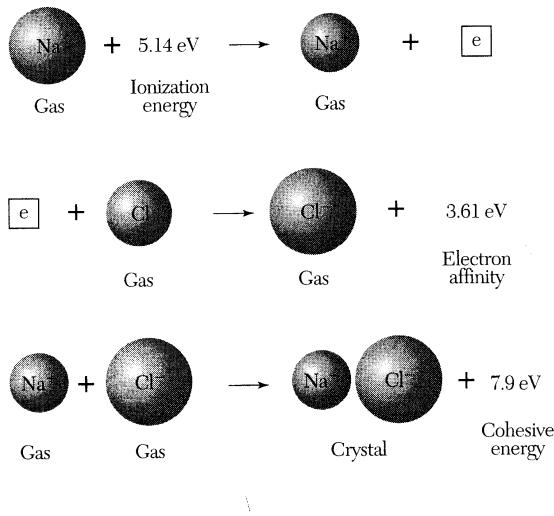
**Figure 7** Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

In NaCl it is known that the distance between a positive and negative ion is 0.28 nm. The energy of Coulomb attraction of this system is 5.1eV. This compares with the experimental value of 7.9 eV per molecule for NaCl.

In considering the overall energy of an ionic bond there are two energies that must be considered:

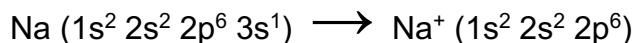
1. The ionisation energy
2. The electron affinity.

This process is illustrated in the figure

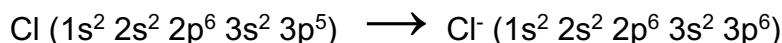


**Figure 8** The energy per molecule unit of a crystal of sodium chloride is  $(7.9 - 5.1 + 3.6) = 6.4$  eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 5, and values of the electron affinity are given in Table 6.

Ionisation of sodium:



This process has an ionisation energy of 5.14 eV (energy must be supplied)



Electron affinity = -3.61 eV (energy released)

The formation of one ion pair of  $\text{Na}^+\text{Cl}^-$  requires an energy of  $5.14 \text{ eV} - 3.62 \text{ eV} = 1.52 \text{ eV}$ .

This energy is provided by the electrostatic attraction between the ions:

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r} .$$

We know the experimental value of the cohesive energy for a  $\text{Na}^+\text{Cl}^-$  molecule is 7.9 eV

The total energy per ion pair is then  $7.9 - 5.1 + 3.6 = 6.4 \text{ eV}$

To calculate the energy more closely we introduce the **Madelung Constant**

The full derivation of an expression for this constant is given in Kittel Chapter 3 (page 62 8<sup>th</sup> edition) and a more general method given in Appendix B of Kittel.

The coefficient of  $I/R$  is called the **Madelung Constant**. It is generally denoted by the symbol  $\alpha$  and its value depends on the lattice structure.

It is in reality a correction factor which tells of the impact of only considering the influence of nearest neighbours in a lattice rather than considering all the atoms in a lattice.

In 3D its evaluation is complicated by difficulties with finding a functional representation which will converge with increasing  $j$ . Sometimes as you increase  $j$  the number of atoms increases faster than the reduction in the strength of the interaction.

For a face centre cubic lattice  $\alpha = 1.7475$ .

## Covalent Crystals

This is a very different form of bonding which occurs when very similar or identical atoms bond together. Atoms share electrons to fill an outer shell and achieve a stable noble gas configuration. Examples of this type of bonding are  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO_2$  etc. It is extremely common in organic systems. The C-C covalent bond in diamond is roughly the same strength as ionic bonds.

Covalent bonds are bonds where electrons are shared between atoms. It involves two electrons one from each atom. The electrons are localised in the region between the two atoms. As expected from the Pauli Exclusion Principle the spins of the electrons are different. The covalent bond is also highly directional.

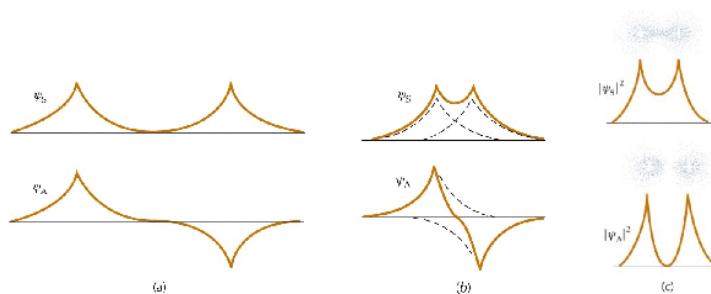
In the diamond structure each atom is bonded to 4 others in a tetrahedral arrangement (fcc lattice with 2 atom basis). This gives a space filling of 0.34 compared with 0.74 for close packing.

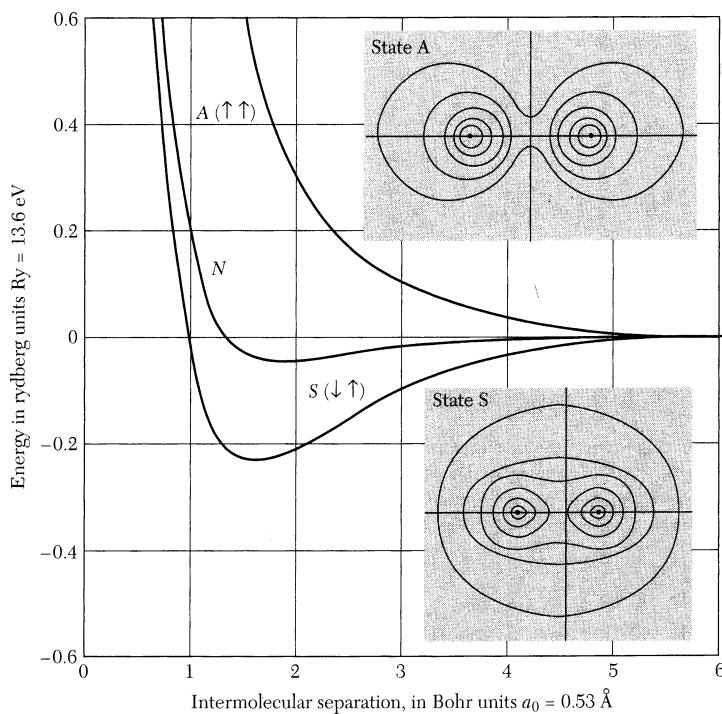
Molecular hydrogen is often used as an example of a covalent bond.

As two hydrogen atoms approach each other this sharing produces a decrease in energy. We can understand this using simple quantum mechanics.

The bonding depends upon the symmetry of the wavefunction. This is best illustrated using the example of a hydrogen atom  $H_2$ .

The binding depends on the relative spin orientation. The Pauli Exclusion Principle modifies the distribution of charge according to the spin orientation. The spin dependent Coulomb energy is called the **exchange interaction**.





**Figure 12** Energy of molecular hydrogen ( $H_2$ ) referred to separated neutral atoms. A negative energy corresponds to binding. The curve  $N$  refers to a classical calculation with free atom charge densities;  $A$  is the result for parallel electron spins, taking the Pauli exclusion principle into account, and  $S$  (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states  $A$  and  $S$ .

The electron configuration of 2 hydrogen atoms  $2(1s^1) H_2$  and both atoms have the  $(1s^2)$  helium electronic structure. The diagram shows symmetric and anti-symmetric wavefunctions for 2 H atoms (a) far apart and close together (b). {Note there is no classical analogue to the symmetry of the wavefunction}

We know from quantum mechanics that there is a difference between symmetric and antisymmetric wavefunctions when describing identical particles (Young and Freedman Chapter 40).

{Reminder: Electrons belong to a class of particles called fermions which are subject to the Pauli Exclusion Principle: “No two fermions in an atom can have the same quantum number”}.

We can show that for a wavefunction describing two identical particles that the antisymmetric wavefunctions are identical for all values of position  $x$ , whereas the symmetric wavefunctions are not (Young and Freedman Chapter 41).

Because of the Pauli Exclusion Principle the total wavefunction must be antisymmetric when electrons are exchanged.

The total wavefunction consists of two parts, a spatial part and a spin part (using position and spin quantum numbers).

- For an electron spin can either be spin up  $+1/2$  or spin down  $-1/2$ .
- When the electron spins are opposite, total  $S = 0$ , the spin wavefunction is antisymmetric.
- When the electron spins are parallel  $S = 1$ , the spin wavefunction is symmetric.
- When  $S = 1$  (symmetric spin) the position wavefunction must be antisymmetric.

- When  $S = 0$  (antisymmetric spin, the position wavefunction must be symmetric).

**The symmetric position wavefunction has a large electron density between the protons - this negative charge density forms the covalent bond.**

For the antisymmetric position wavefunction there is a low electron charge density between the atoms - no covalent bond is formed.

The total wavefunction is  $\Psi_{\text{Total}} = \psi_{\text{pos}} \varphi_{\text{spin}}$

The covalent bond is  $\Psi_{\text{Anti}} = \psi_{\text{sym}} \varphi_{\text{anti}}$  where  $\varphi_{\text{anti}} = \uparrow_1 \downarrow_2$  which has  $S = 0$ .

## Metals

Metals have a high electrical conductivity and a high thermal conductivity. This is a consequence of the very high electron density which exists in metals (typically 1 or 2 electrons per atom). The free electrons which move about are called the conduction electrons. When atoms are brought together to form a metallic crystal the valence electrons of the atom become the conduction electrons of the crystal.

In metallic binding the total energy of the system is lower in the bound state as compared with the free atoms.

The metallic bond is weaker than the ionic bond. This gives metals their physical properties including a highly malleable state.

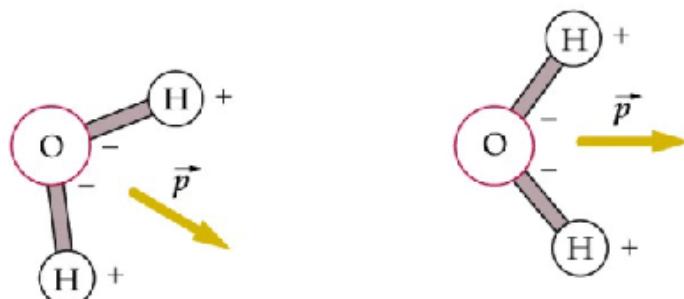
Metals occupy close packed configurations hcp, fcc and bcc structures.

Metals are treated as a “gas” of free electrons. More on this later in the course.

## Hydrogen Bonds

Because hydrogen has only one electron it should only form covalent bonds with one other system. However, it is observed that hydrogen often forms a bond with two other atoms. Typical bond strengths are 0.1 eV.

The hydrogen bond is formed by the sharing of a proton (hydrogen nucleus) between two atoms. The bond is mainly ionic in character and forms with most electronegative atoms (F, O, N) An example of this is DNA where the hydrogen bond helps maintain the stable double helix structure.



The diagram shows the hydrogen bond in water where it is responsible for some of the unusual physical properties of water and ice.