

Chapter 3

Before going into a more detailed description of crystalline order and associated language and concepts, let us look into the different types bonding between atoms in a solid. The nature of the bonding determines the structure.

Bonding in solids and the impact on structure

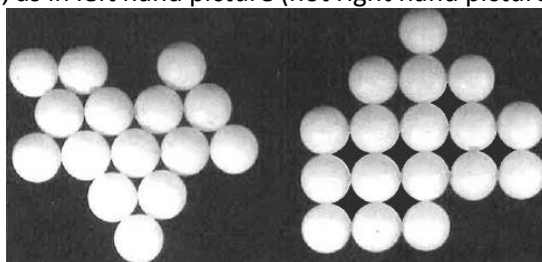
What are the forces that bond atoms together in solids? There are different types of bonding which dominate in different materials. The atoms will arrange themselves in order to minimise the total energy [and hence maximise the cohesive energy]. How this is done depends on the nature of the bonds.

This bonding is an extension of the concept of valence in chemistry (building molecules from atoms). In all cases the forces/bonding is electrostatic in origin. How is that the case, given that atoms are electrically neutral? Answer roughly speaking: Because the outermost atomic electrons are donated to or shared between atoms in different ways. This occurs because it results in a reduction of total energy. There is one exception and that is van der Waals bonding, which we consider first.

Van der Waals bonding

These forces, and the associated interatomic potential, were studied in PH1610. This is the relevant bonding mechanism in inert gas solids [He, Ne, Ar, Kr, Xe]. These atoms all have complete outer shells of electrons, and thus high ionisation energy, and are chemically inert. They do not want to donate/receive/share electrons. So they are always uncharged. But if the negative electron cloud is slightly displaced with respect to the positive nucleus there is an electric dipole moment. Quantum fluctuations give rise to such randomly fluctuating electric dipole moments. Opposite dipoles attract. So you end up with weak attractive forces (Xe has the highest melting temperature of 161 K). The resultant forces between atoms have no directionality and the interatomic potential varies with separation as $-r^{-6}$. [That minus sign is important. The potential energy $V(r) = -A/r^6$ decreases with decreasing separation. The force $F(r) = -dV/dr$ is attractive. At short separations the potential shoots up to large and positive, due to a term B/r^{12} ; this “short range hard-core repulsion” arises from overlap of electron clouds of neighbouring atoms at separations approaching atomic diameter. Inert gas atoms are therefore like weakly attracting hard spheres.

The potential energy is lowered by packing these spheres as closely together as possible. First pack spheres together in a plane, as in left hand picture (not right hand picture, which is not close packed):



Now stack a sheet on top, to maximise packing density. Then add a third sheet. Here there are two possible inequivalent choices. These correspond to the hexagonal close packed (hcp) [ABABA...stacking, see (a)] and face centred cubic (fcc) [sometimes called cubic close packed], [ABCABC.....stacking, see (b)]. Spheres close packed in hcp or fcc arrangement fill 74% of the available space.

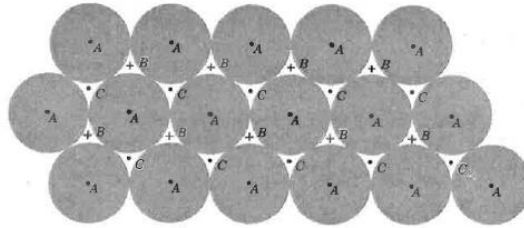
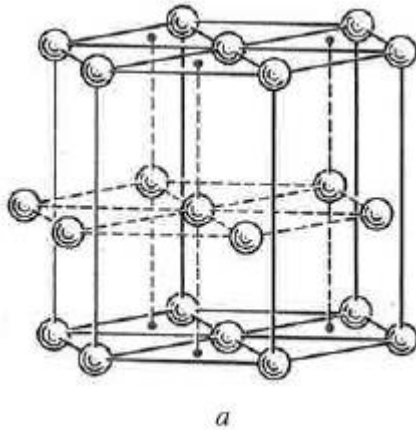
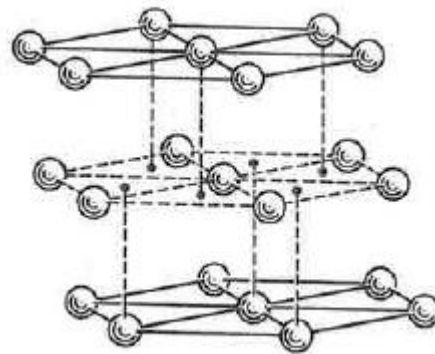


Figure 27a A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed over this, with centers over the points marked *B* (or, equivalently, over the points marked *C*). If the second layer goes in over *B*, there are two nonequivalent choices for a third layer. It can go in over *A* or over *C*. If it goes in over *A* the sequence is *ABABAB*... and the structure is hexagonal close-packed. If the third layer goes in over *C* the sequence is *ABCACABC*... and the structure is face-centered cubic; the plane is a (111) plane, as in Fig. 27b.



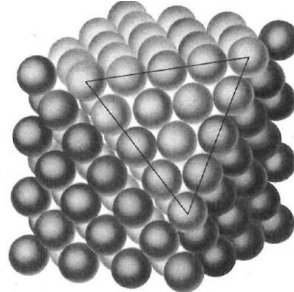
a



b

A He-4 crystal is hcp, solid Ne, Ar, Kr, and Xe are fcc.

The orientation of the close packed planes in the face centred cubic structure, is shown below. [Also see later discussion of crystal structure and planes].



Ionic bonding

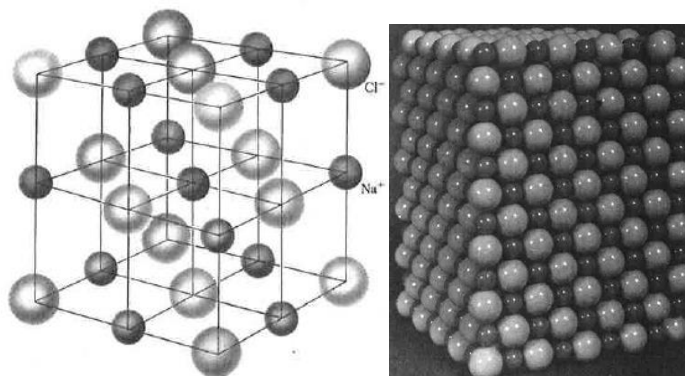
Consider common salt NaCl. Sodium, Na, is an alkali metal in group 1 of the periodic table. Its outer shell has a single electron [$1s^2 2s^2 2p^6 3s^1$], (that's like Ne plus one 3s electron). The halogen chlorine, Cl is in group 7. Its outer shell has just 7 electrons in its $n=3$ shell [$1s^2 2s^2 2p^6 3s^2 3p^5$]. That electronic structure is like Ar minus one 3p electron. So the Na atom donates its outer electron to Cl, becoming a positively charged ion Na^+ ; the chlorine becomes a negatively charged ion Cl^- . They attract by the Coulomb attraction of + and - charges. That describes a NaCl molecule.

In more detail the energetics of this are as follow. The energy required to remove the outer 3s electron from Na [called the ionization energy] is 5.14eV. The energy gained by Cl capturing an additional electron to complete its $n=3$ shell [called the electron affinity] is 3.61eV. So the total energy cost of making an ion pair is 1.53eV. However when you bring the two ions together to separation d , you

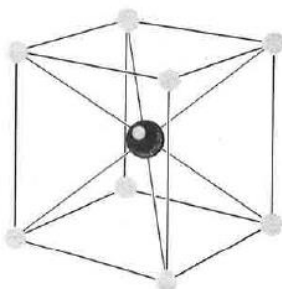
reduce the potential energy by $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{d}$, and this more than compensates to give an overall energy

reduction. The effective radius of a Na^+ ion is 0.95 angstrom, and Cl^- ion 1.81 angstrom. At a separation of 2.76 angstrom the potential energy is -5.2eV.

This process, the creation of Na^+ and Cl^- ions also occurs in the NaCl crystal. How do these ions arrange themselves? The crystal forms the following structure. Note that the sodium ions are smaller than the chlorine ions, as stated above [you can understand this from electronic structure]. Ions of the opposite charge want to be close together, ions of the same charge want to be as far apart as possible. This crystal structure achieves that. Each ion of one sign has six of the opposite sign as nearest neighbours. [Note that this absolutely does not look like an assembly of NaCl molecules, as the chemists would believe would happen pre-1912].



On the other hand, in CsCl the ions are of comparable size (0.169 and 0.181 nm respectively). So you get a different structure in which ion is surrounded by eight nearest neighbours of opposite sign, thus:



Quantitative discussion of ionic bonding and the Magdelung constant

The Coulomb potential energy of two ions, one positive the other negative, each of charge $\pm e$, separated by d is $-\frac{1}{4\pi\epsilon_0} \frac{e^2}{d}$, representing the Coulomb attraction. The full potential energy also has a positive part, representing repulsive forces, that kicks in at small separations. So we have

$U = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{d} + \frac{B}{d^n}$. Potential energies add! Typically the exponent n is around 9.

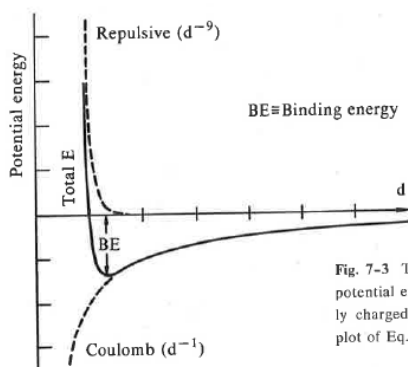
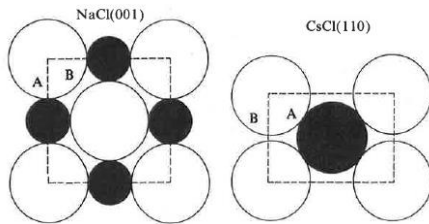


Fig. 7-3 The radial dependence of the potential energy for a pair of oppositely charged ions. This is a schematic plot of Eq. 7-1 for $n = 9$.

This potential energy curve reminds us of the van der Waals 6-12 potential. You can see there will be an equilibrium spacing (potential energy minimum, force zero) around the “hard core” diameter. In other words ions are like hard spherical (billiard) balls, and they will tend to pack as tightly as possible together at a separation around the sum of the hard core radii of the positive and negative

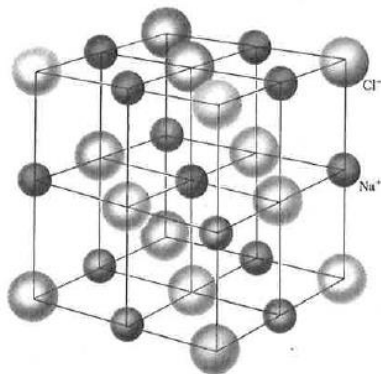
ions. Indeed the length of the NaCl cubic unit cell is 0.563 nm: compare that to the sum of the ionic diameters $2 \times (0.095 + 0.181) = 0.552$ nm.



Let us evaluate the contribution to the cohesive energy, holding the crystal together, by summing the Coulomb potential energy over all ion pairs in the crystal. An ion pair with the same charge will

contribute $+\frac{1}{4\pi\epsilon_0} \frac{e^2}{d}$.

We do this for the NaCl structure. Here it is again;



Look at the sodium ion at the centre of this unit cell. Let us call the nearest neighbour separation R . There are six nearest neighbours, with opposite charge, at separation $d = R$.

12 next nearest neighbours with the same charge at $d = \sqrt{2}R$.

8 second nearest neighbours, with opposite charge, at $d = \sqrt{3}R$.

So the potential energy can be written: $U = -\frac{e^2}{4\pi\epsilon_0 R} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \dots \right)$, where the

continuation indicates the additional terms from third nearest neighbours etc. This lattice sum is not converging very rapidly and we need a better way to work out the total potential energy.

Nevertheless it is clear that it must take the form: $U = -\frac{e^2\alpha}{4\pi\epsilon_0 R}$, where α is a number. For the NaCl structure $\alpha=1.75$.

We can introduce another constant β , and write the contribution of the repulsive part of the p.e. to

the total energy as $U = -\frac{e^2\beta}{4\pi\epsilon_0 R^n}$. In this way the total p.e. is written as the sum:

$$U = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{\alpha}{R} - \frac{\beta}{R^n} \right).$$

The separation R will adjust to minimize this energy. So we find this minimum in the usual way:

$$\frac{dU}{dR} = \left(\frac{-e^2}{4\pi\epsilon_0} \right) \left[-\frac{\alpha}{R^2} + n \frac{\beta}{R^{n+1}} \right], \text{ put } \frac{dU}{dR} = 0 \text{ at } R = R_0 \text{ (the equilibrium separation) to find}$$

$$\beta = \frac{R_0^{n-1}\alpha}{n}. \text{ So we can get rid of } \beta \text{ and write } U \text{ in terms of equilibrium separation:}$$

$$U = -\frac{e^2}{4\pi\epsilon_0} \frac{\alpha}{R} \left(1 - \frac{1}{n} \frac{R_0^{n-1}}{R^{n-1}} \right). \text{ So at the equilibrium separation: } U_0 = U(R_0) = -\frac{e^2}{4\pi\epsilon_0} \frac{\alpha}{R_0} \left(1 - \frac{1}{n} \right)$$

To get the total Coulomb energy of the crystal, multiply by N, the number of ion pairs.

With a little more work it is possible to determine the compressibility from $U(R)$. A comparison with measurement determines $n=9.4$ [Not that R_0 is determined experimentally by x-ray diffraction and α is calculated]. With this value of n we see that the influence of the repulsive part on the cohesive energy is only about 10%.

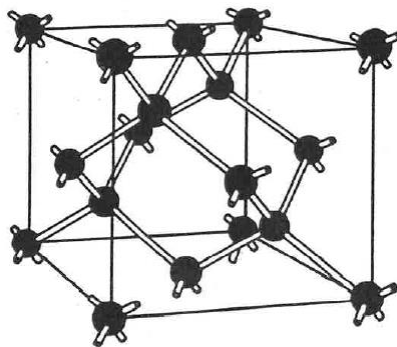
Covalent bonding

We have just seen that both ionic and van der Waals bonding is about packing billiard balls together to minimise the potential energy, arising from attractive interactions.

Covalent bonding is totally different. It is a very important type of bonding which occurs in crystals of group IV elements: carbon, silicon and germanium. It gives rise to tetrahedral bonding and determines the structure of the diamond (carbon) crystal. Both diamond and silicon have huge technological importance. You need to look at the diamond structure and see these tetrahedra.

The bonding occurs by a rearrangement of the electronic structure of the outermost electrons from the free atom ground state to a bonding state. This occurs in such a way as to maximise overlap of the electronic wavefunctions of neighbouring atoms. This sharing of two electrons across each covalent bond delocalises the electrons, and the reduction of quantum zero point energy that results contributes towards binding energy. [Recall that confinement of a particle costs kinetic energy, via Heisenberg uncertainty relation].

These bonds are rather like the covalent bonds that occur in molecules, but occur in a distinctive way in a solid. The highly directional tetrahedral bonds determine the structure.



These atoms have electronic structures as follows: C [$1s^2 2s^2 2p^2$]; Si [$\{\text{Ne}\} 3s^2 3p^2$]; Ge [$\{\text{Ar}\} 4s^2 4p^2$]. Thus they have four electrons in their outermost shell. They form covalent bonds in which they share these electrons with another four atoms to essentially complete the shell. Thus a C atom bonds strongly with four other C atoms, and that's it. Thus covalent bonding is referred to as saturated. The four nearest neighbours are at the corners of a tetrahedron. This is because the quantum states of four outer electrons hybridize to form four equivalent orbitals. These are the sp^3 orbitals because they are each a linear combination of the s orbital and all three of the three possible p -wave orbitals [$l=1$ and thus three-fold degenerate].

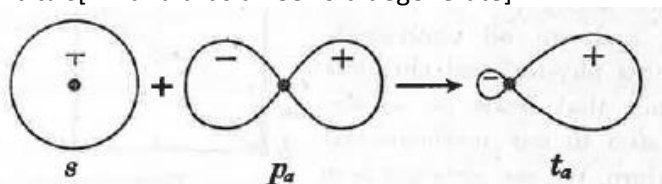
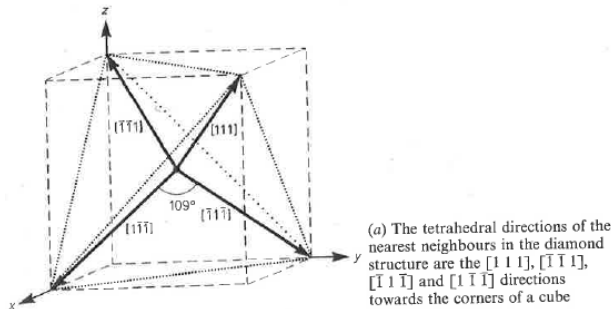


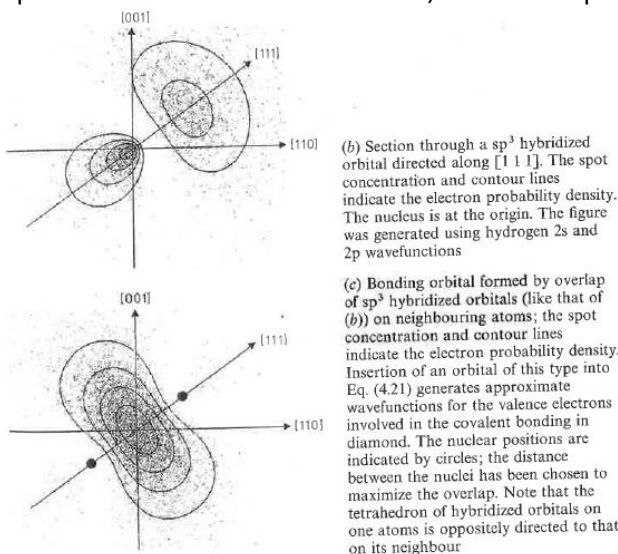
FIG. 8.2. Boundary surfaces in the formation of an sp^3 -hybrid atomic orbital.

Tetrahedral bonds are naturally directly towards the corner of a cube, as shown.



[Later on we will see that the diamond structure is two interpenetrating face centre cubic lattices displaced on the body diagonal; an fcc lattice with a two atom basis].

The diamond structure is dominated by these strong/local/oriented/saturated bonds. If you pack spheres into the diamond structure, the volume packing fraction is only 34%.

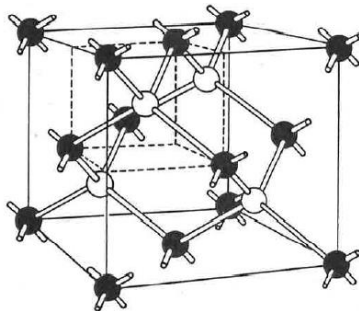


More detail on the quantum mechanics of the covalent bond is provided in a later section.

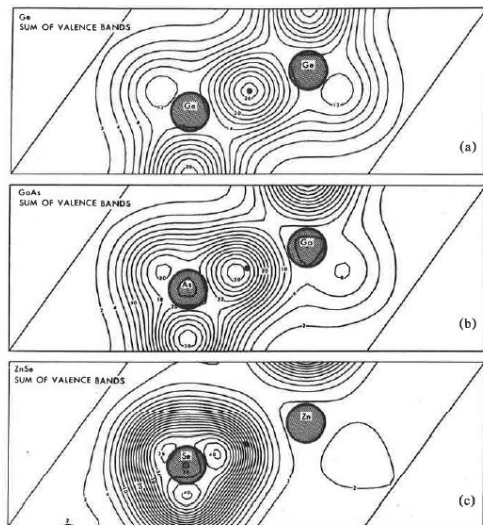
Mixed ionic-covalent bonding

This occurs in III-V compounds such as GaAs, InSb, InAs, BN. These also form crystals with the diamond structure, and thus tetrahedral bonds. GaAs is a technologically important semiconductor, and with devices (so-called heterostructures) made from this material the Quantum Hall Effect and Fractional Quantum Hall effect are observed [subject of two Nobel Prizes].

Consider GaAs (gallium arsenide). Ga is group III with structure $[Ar]3d^{10}4s^23p^1$. As is group V with $[Ar]3d^{10}4s^23p^3$. So, roughly speaking, the Ga receives an electron from the surrounding As and now the ions have four electrons in their outer shells which they can share. The bonds have thus a mixed ionic/covalent character, are highly directional. Tetrahedral bonds form as in diamond and Si.



Going further: what about II-VI compounds? Here the degree of ionicity is obviously larger. Things can go either way. MgO forms a crystal with the ionic NaCl structure. On the other hand ZnS forms the same structure as GaAs.



Metallic bonding

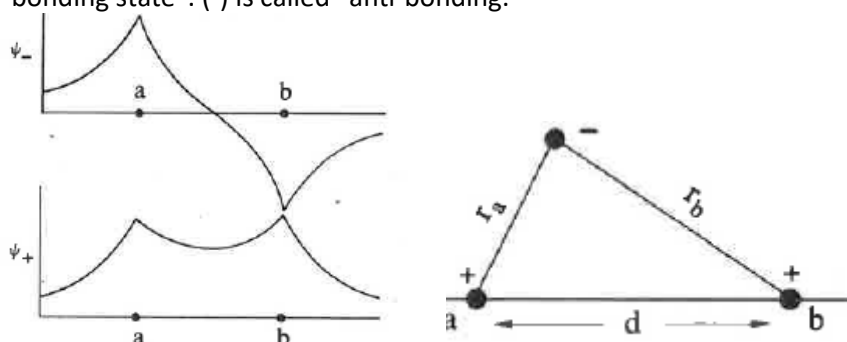
In metals the valence electrons are detached from atoms (leaving behind a localised positive ion core) to form a delocalised sea. The metallic structure can be thought of as arising from the packing of positive ions with the mobile electrons acting like glue. The delocalisation of electrons lowers their zero point energy and this contributes to the total solid binding energy. Of course the electrostatic potential energy is also important.

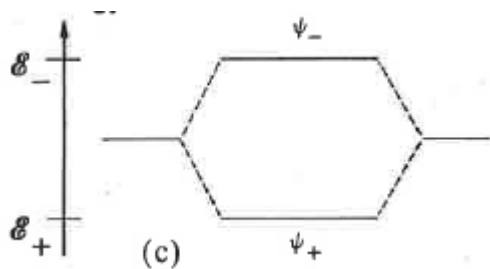
Metals form structures with high coordination numbers, such as the close packed fcc and hcp lattices with 12 nearest neighbours. Some form the bcc structure with only 8 nearest neighbours. But even here, there are 6 more next nearest neighbours only 15% further away. The close packed structures are consistent with bonds with no directionality. In some metals there is some element of covalent-bond-like directionality, indicated by those with bcc structure.

Understanding covalent bonding in more detail

We need a simple way to understand how it is that the sharing of electrons between atoms leads to a lowering of energy and bonding.

We first consider the H_2^+ ion (an ionised hydrogen molecule). This system has the virtue of simplicity. It turns out that on removing one electron from the hydrogen molecule the remaining one electron is shared between two protons. If the electron were in 1s orbit around atom a it would have wavefunction $|a\rangle$; If the electron were in 1s orbit around atom b it would have wavefunction $|b\rangle$. The actual wavefunction has to be a linear superposition: $|\psi\rangle = c_a |a\rangle + c_b |b\rangle$. And since by symmetry we must have $c_a^2 = c_b^2$, and therefore $c_a = \pm c_b$. So there are two possible wavefunctions: $|\psi_{\pm}\rangle = c [|a\rangle \pm |b\rangle]$. The symmetric state (+), which clearly is a state in which the electron is more "shared" between the two atoms, has a lower energy. As demonstrated below. This is called the "bonding state". (-) is called "anti-bonding".





Normalisation of the wavefunctions requires $\langle \psi | \psi \rangle = 1$. Thus $c^2 [\langle a | \pm b \rangle \langle a | \pm b \rangle] = 1$ and $c^2 [2 \pm 2 \langle a | b \rangle] = 1$. Here $\langle a | b \rangle = S$ is the overlap integral of the two 1s orbitals.

To calculate the energy of the two states, we determine the expectation value of the Hamiltonian H , which consists of the k.e + Coulomb energy terms. If $\langle a | H | a \rangle = \langle b | H | b \rangle = E_0$ and

$\langle a | H | b \rangle = \langle b | H | a \rangle = E_{ab}$ then the two states $|\psi_+\rangle$ and $|\psi_-\rangle$ have energies $E_{\pm} = \frac{E_0 \pm E_{ab}}{1 \pm S}$ and

since E_0 and E_{ab} are both negative, the bonding state (+) state is of lower energy.

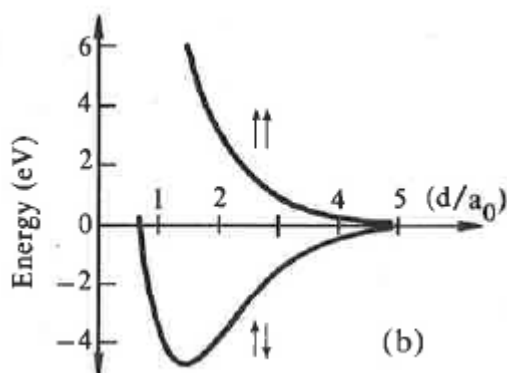
Now we consider the hydrogen molecule in the Heitler-London (valence bond) approach. We have two electrons and two protons. The possibility that both electrons are on proton a or b [the ionic configuration] is ignored. Instead the electronic wavefunction is a linear combination electron 1 on a, electron 2 on b and electron 1 on b, electron two on a. Again there are two possible linear superpositions: Since we have two electrons, which are fermions, it is required that the wavefunction is antisymmetric (changes sign when we swop the particles = odd parity). Since the wavefunction is the product of a space part and a spin part, the possibilities are:

$\psi = [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)] |\uparrow\downarrow - \downarrow\uparrow\rangle$ where a, b label protons and 1,2 label electrons, or the triplet state

$\psi = [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] |\uparrow\uparrow\rangle$, $\psi = [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] |\downarrow\downarrow\rangle$,

$\psi = [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] |\uparrow\downarrow + \downarrow\uparrow\rangle$

The first of these, with a symmetric space part (correlated with the total spin $S=0$, s, spin state singlet spin state, maximises the overlap of the electronic wavefunctions. Our discussion of the hydrogen ion motivates the result that this is the lowest energy state.



Covalent bonding of carbon: quantum mechanics of hybridized bonds

Now we give the outline of the quantum mechanical discussion of the tetrahedral covalent bonding of carbon in the diamond structure.

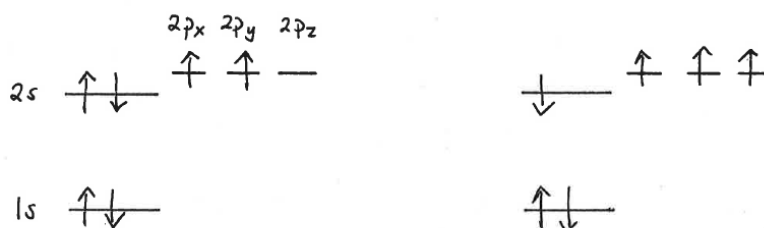
First, for comparison, consider the divalency of oxygen, sulphur and trivalency of nitrogen.

Oxygen atom is $1s^2 2s^2 2p_z^2 2p_x^1 2p_y^1$. So there are 6 electrons in the outer $n=2$ shell. Two are unpaired in p_x , and p_y orbitals oriented at right angles. So you might expect O to be divalent ($6+2=8$) and to bond to two hydrogen atoms to form tasty H_2O , with a bond angle of 90° ; actually the bond angle is

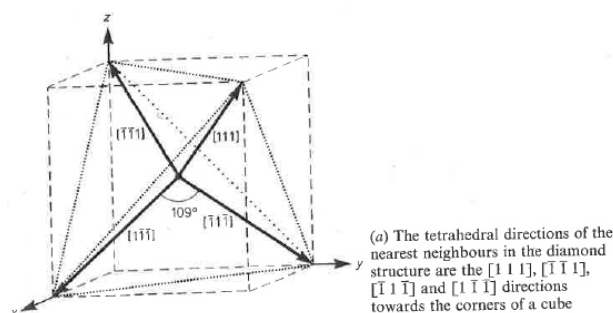
105° since it is modified by the H-H interaction. Sulphur S [$\{\text{Ne}\}3s^23p^4$] is also divalent in the same way: here stinky H_2S forms with a bond angle of 92°.

By contrast nitrogen is trivalent. Its electronic structure is $1s^22s^22p_z^12p_y^12p_x^1$. So there are 5 electrons in the $n=2$ shell, of which three are unpaired electrons in the outer 2p orbital shell. Naively you expect 3 bonds at 90°. NH_3 comes close.

Now finally (!), what about carbon? Carbon is $1s^22s^22p_y^12p_x^1$. There are 4 electrons in the outer $n=2$ shell, and carbon has valence 4. But this happens in a distinctive way. In a compound one of the s electrons is promoted to the $2p_z$ orbital:



The 2s and 2p levels hybridize into 4 sp^3 states. Each of these is a linear superposition of the s and three possible p states. These 4 quantum states are tetrahedrally oriented, pointing to the corners of a cube thus:



The p orbitals can be written like this, where the $f(r)$ is such that each is normalised:

$$p_x = xf(r) \quad p_y = yf(r) \quad p_z = zf(r)$$

The linear superposition of s and p states is:

$$\psi = Af_s(r) + B(\alpha x + \beta y + \gamma z)f(r)$$

$$\alpha^2 + \beta^2 + \gamma^2 = 1$$

The three linear combinations $x+y+z$, $-x+y-z$, $x-y-z$, $-x-y+z$ give bonds along the directions shown. The angle between bonds (take scalar products) is 109.47°.