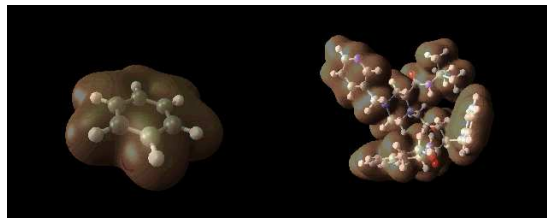


[PDF file of this section](#)

STICKY ATOMS

Atoms are electrically neutral; the negative charge of the electrons balances the positive charge of the nucleus. But almost all atoms bind both to other atoms of the same type and to different atoms. (The exceptions to this rule are of particular interest as discussed below.) The science of chemistry is largely concerned with atomic aggregates (which when they involve a small number of atoms are, as we learned earlier, called molecules). It is at first sight very difficult to understand why these electrically neutral entities should stick to each other so strongly and so comprehensively. Indeed, the nature of the bonding between atoms is the most fundamental problem in chemistry. It is, however, a problem that has been solved, and one to which modern computational methods have made an essential contribution.

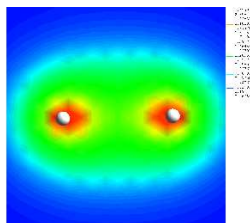


Benzene (left) and aspartyl protease inhibitors (right) showing an iso-contour through their respective electron densities

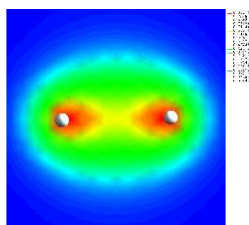
The key to understanding chemical bonding is the ability to explore the complex *rearrangements* of the atomic electron clouds which occur when atoms interact. As we have seen, atoms are themselves very complicated; and we can only write down an exact mathematical solution of the Schrödinger equation for the simplest of cases, the hydrogen atom. For all other atoms we must use approximate solutions (which can, however, achieve a high level of accuracy) whose derivation requires intensive numerical work for which a computer is ideal. Molecules represent an even higher order of complexity; and computational methods are essential if we are to solve the Schrödinger equation at a sufficient level of accuracy. This can now be achieved, and, as discussed in detail in Section ** accurate wave functions are widely available for molecules containing an increasingly large number of atoms. The image above, for example, illustrates the calculated electron densities in the benzene molecule and a pharmaceutical molecule to which we return later.

The atomic electron clouds rearrange when atoms interact because, of course, the atoms perturb or influence each other. The rearrangement occurs almost entirely in the highest energy orbitals or outermost shell of electrons; electrons in the lower energy states are too strongly bound to their nuclei. It is indeed fair to say that chemistry is about what goes on at the margins of atoms.

There are three broad classes of rearrangement which we will denote as *CONCENTRATION*, *TRANSFER* and *DELOCALISATION* (or spreading out), which are responsible for the different types of chemical bonding. Concentration is the most universal form of electron redistribution. It involves electron density being drained away from the outermost orbitals of the interacting atoms and concentrated in the region between the nuclei. Here the negatively charged electrons are close to the positive nuclei of *both* atoms and therefore have a low energy (because, of course, positive attracts negative). Indeed, the enhanced electron density in the region can be thought of as a sort of glue which holds the atoms together. This type of bonding is illustrated below for the simplest of all assemblies, the hydrogen molecule, (H_2) - two hydrogen atoms stuck together. We show a contour plot of the calculated electron density; The second shows a more subtly revealing difference contour plot which represents the difference in the electron density in the molecule compared with that for two non-interacting atoms. Enhancement of the density between the nuclei and depletion around the peripheries of the atom is clearly seen.

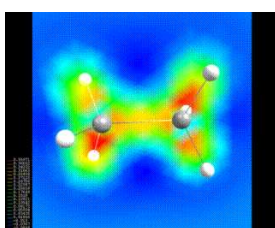


Colour coded contours showing the electron density about two hydrogen atoms (shown in white) in a hydrogen (H_2) molecule.

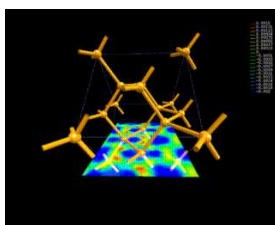


Colour coded contours showing the difference in electron density about two hydrogen atoms (shown in white) in a hydrogen (H_2) molecule and the electron density of a hydrogen atom; Increased electron density between the hydrogen atoms can be seen.

Chemists have traditionally assigned the term *COVALENCE* to this type of bonding which is very widespread. The bonds between carbon atoms in the diverse ring and chain compounds formed by this element - compounds which are of immense industrial importance and which are found in our bodies and those of all living matter - are covalent in nature. Moreover, the silicon atoms in crystalline silicon - the material at the heart of the ongoing electronics revolution - are again held together by covalence as illustrated below. Indeed, covalent bonding - the possibility of draining off a small amount of electron density from the edges of atoms and concentrating it as a 'glue' between them - makes both life and the electronic age possible.

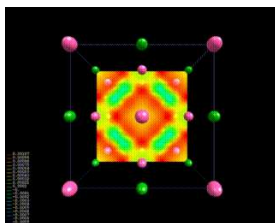


Electron density build up along the covalent bonds of ethane

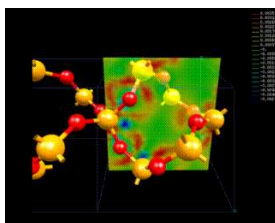


Covalent bonding in the structure of silicon.

Our next mode of density rearrangement - transfer between different atoms - is even easier to understand. Different atoms have different affinities for electrons. For example, atoms like oxygen, fluorine and chlorine tend to pull electrons into their outermost orbitals; while atoms such as sodium, potassium and magnesium only hold their electrons in these orbitals weakly. The greatest of all twentieth century chemists, Linus Pauling, coined the term *ELECTRONEGATIVITY* to quantify the electron attracting powers of atoms; a more detailed discussion is given in the Glossary. Thus low 'electronegativity' atoms like sodium will easily lose or transfer electron density from its outermost orbital to a high electronegativity chlorine atom. The sodium atom will then have a positive charge and the chlorine a negative charge. These oppositely charged atoms, which are given the name *IONS*, attract each other. This simple process of transfer of electron density with accompanying electrostatic binding between oppositely charged ions is known as *IONIC BONDING*. It is illustrated on the left for the case of sodium chloride ($NaCl$), the archetypal ionic compound. As is the case with most ionically bonded systems, $NaCl$ forms a crystal structure in which there is a regular arrangement of atoms in three dimensions. The figure on the left displays difference contour maps which clearly show the transfer of electron density from the sodium to the chlorine. A more subtle example is provided by quartz, an important, naturally occurring mineral and industrial material which has the chemical formula SiO_2 . The image shows how density is redistributed in this compound. Clearly there is transfer of density from silicon to oxygen; but there are some indications of concentration of density between the nuclei. Quartz shows bonding that is intermediate between ionicity and covalence. Both silicon and oxygen are widespread in the earth's crust and mantle; and together with atoms of metallic elements they form an enormously diverse range of silicate compounds. The partially ionic silicon-oxygen bond is therefore of equal importance to the mineralogist as is the carbon-carbon bond to organic and biochemists.

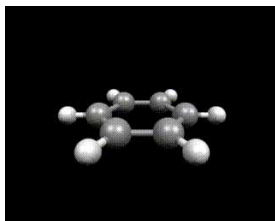


The electron density differences within sodium chloride, NaCl.

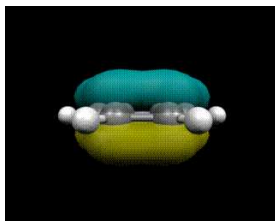


The electron density differences within quartz, SiO₂.

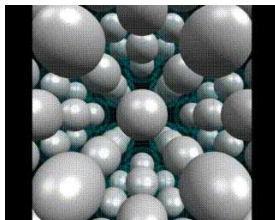
Our third type of electron density redistribution is *DELOCALISATION*; spreading out of electron density over several atoms results in a reduction in the electronic energy. The classic example is benzene, the hexagonal ring structure molecule illustrated on the left (and which was first isolated from whale oil by Michael Faraday in The Royal Institution in 1825). The molecule shows considerably greater stability - is far less reactive - than might be expected. Understanding this phenomenon was one of the major challenges in the development of theoretical organic chemistry. We now know that this stability is conferred by some of the electron density in the molecule spreading out over the whole ring as illustrated. Delocalisation is also the basis of the bonding between metal atoms. When, for example, sodium atoms come together to form a metallic crystal, the electrons from the outermost orbitals become delocalised over the entire crystal, as shown on the left. And it is the existence of the delocalised 'sea' of electrons which results in the characteristic high electrical conductivity of the metal. Interestingly, it is possible to produce one dimensional metals from chains of carbon atoms. These 'polyacetylenes' have very high metallic-like electrical conductivities, but with mechanical properties more like those of plastics.



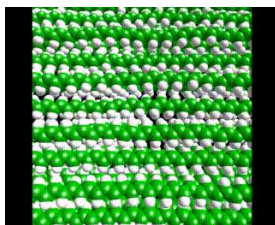
The structure of benzene, C₆H₆



Delocalized molecular orbitals in benzene.



Sodium atoms in metallic sodium.



A packed assembly of polyacetylene molecules.

All chemical bonding thus involves one or more of those three modes of redistribution of the loosely bound outermost electrons so as to lower the energy of the resulting atomic assembly. Moreover, this process is one which can be modeled in great detail and with high accuracy using computational methods. The problem of the chemical bond is solved!

[Molecular Shape](#)