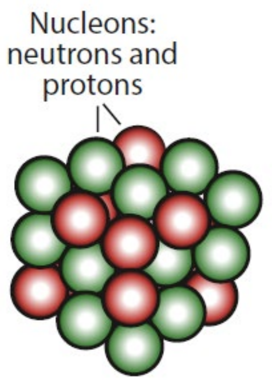
4.6 Atomic structure and interatomic bonding

The structure of the atom The core of an atom is its *nucleus* (Figure 4.14). The nucleus accounts for almost all the atomic mass and almost none of its volume. It is made up of protons (charge) and neutrons (no charge), known collectively as *nucleons*. The nucleus of a given element contains protons equal in number to its atomic number but can exist as isotopes with differing numbers of neutrons and thus atomic weights. Isotopes have identical chemical properties but differ in their nuclear properties, particularly in their nuclear stability.



The most stable nuclei are those with the greatest binding energy per nucleon — they cluster around iron, atomic number 26 (Figure 4.15). Nuclei above iron in atomic number can release energy by fission; those below iron can do so by fusion. Fission releases, at most, a few hundred keV per event; fusion can release much more.

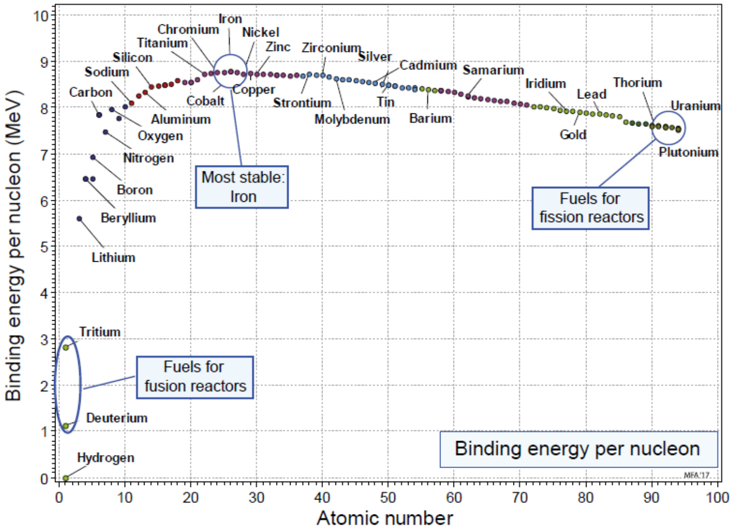


Figure 4.15 The binding energy per nucleon, a measure of nuclear stability.

One might expect that the most stable elements would also be the most abundant in the Earth's crust. Figure 4.16 shows that, broadly speaking, this is true. Silicon, aluminium, iron, calcium, sodium, magnesium and oxygen, between them, account for over 80% of content of the crust. The high-atomic number platinum group, by contrast, accounts for only $10^{-7}\%$ (1 part in 10^9) of it.

Electronic structure of atoms Electrons (– charge) orbit the nucleus in discrete, quantised energy levels (Figure 4.17). Their behaviour requires quantum mechanics for explanation. This involves accepting the idea that electrons behave both as particles and as waves, a more diffuse existence in which the probability of their presence in wave mode (shown in green on this and subsequent figures) has meaning, although their precise position in particle mode (shown as blue spheres) does not. The wavelengths of electrons round an atomic core, like the vibrational modes of a taut string, have discrete values characterised by a principal quantum number $n = 1, 2, 3, 4$ or 5. The principal shells split into sub-shells corresponding to a second quantum number, taking the values 0, 1, 2 or 3, designated by the letters ***s, p, d*** and ***f***.[8] Figure 4.17 suggests the first five energy levels (there are more) and the maximum number of electrons each can contain. The filling of a given orbit is described by the two quantum numbers with a superscript indicating the number of electrons in it – a number that can't exceed the values indicated on the figure. Thus, if the first, lowermost, orbit ($n = 1$, sub-shell s) contains two electrons – the maximum allowed – it is described as $1s^2$. If the level $n = 3$, sub-shell d has 6 electrons in it (it can hold 10), it becomes $3d^6$.

Filled principal shells impart maximum stability. The inert gases helium ($1s^2$), neon ($1s^2 - 2s^2\ 2p^6$) and argon ($1s^2 - 2s^2\ 2p^6 - 3s^2\ 3p^6 - 3d^{10}$) are so stable that almost nothing reacts with them. Atoms with unfilled shells like sodium, with one $3s$ electron, can revert to the electron count of neon by giving up an electron. Chlorine, with five $3p$ electrons, can acquire the electron count of argon by capturing one. Bringing one sodium atom and one chlorine atom together and transferring one electron from the sodium (making it a positive ion) to the chlorine (making it negative) allows both to acquire 'inert gas' electron shells (Figure 4.18).

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[8] ***s, p, d***, and ***f*** stand for 'sharp', 'principal', 'diffuse', and 'fundamental', describing the spectral lines of an atom.

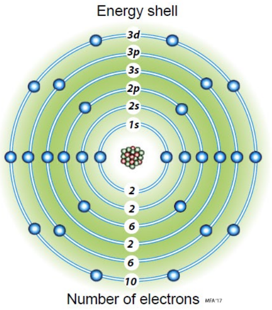


Figure 4.17 Electron orbitals and the number of electrons they can contain.

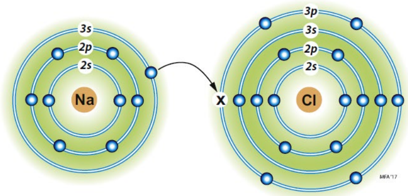
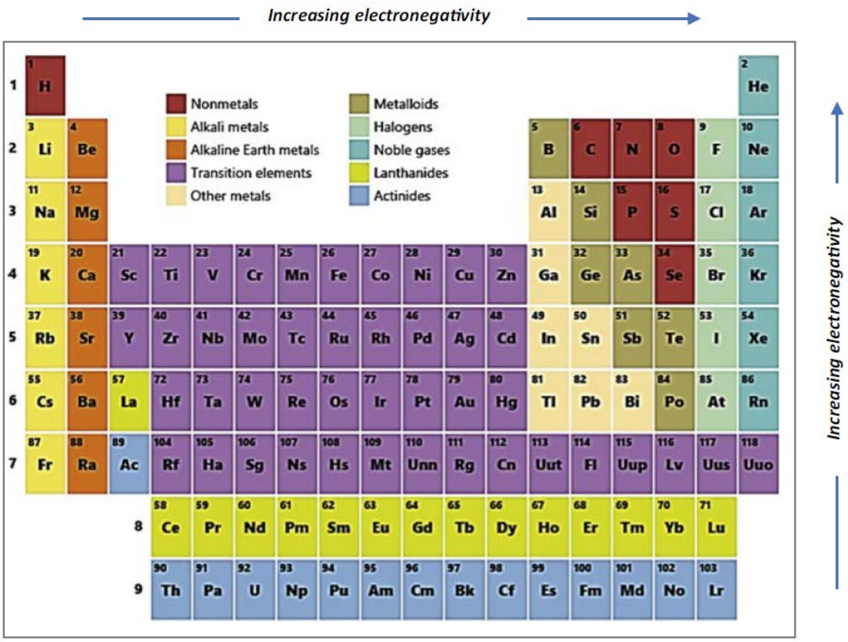


Figure 4.18 Electron transfer from Na to Cl, creating positive and negative ions with more stable electron configurations (*1s* shell not shown).

As the atomic number of an atom increases, the electrons fill the energy levels, starting with the lowest, the *1s*. The electrons in the outermost shell, known as valence electrons, largely determine the chemical character of an atom. This leads to a periodic pattern of properties as the shells fill, moving from inert gas behaviour when a set of shells is filled completely, to a reactive, electropositive (electron-donating) character as the first electrons enter the next level, up to an electronegative (electron-attracting) response when the shell is nearly full, reverting to inert-gas behaviour when the next level is completely full. The cycle is reflected in the periodic table of the elements, shown in Figure 4.19.



1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	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
5	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
6	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 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 Unn	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			8	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	
			9	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	

- Nonmetals
- Alkali metals
- Alkaline Earth metals
- Transition elements
- Other metals
- Metalloids
- Halogens
- Noble gases
- Lanthanides
- Actinides

Figure 4.19 The periodic table of the elements.

Material properties that depend on electronegativity change in a cyclic way across the rows of the periodic table. Figures 4.20 and 4.21 show examples. The first is a plot of atomic volume against atomic number, colour-coded row by row. The volume occupied per atom depends on the packing density of atoms in the crystal (and thus on the crystal structure), but the position in the row has a greater influence: the atomic volume is a minimum in the middle of a row, rising steeply at the ends. This is because the atom 'size' reflects the radius of the outermost valence shell of electrons. Explaining this needs the concept of screening, the degree to which the inner filled electron shells block the outer, valence, electrons from the positive charge of the nucleus. We define the effective nuclear charge, Z_{eff}, as

$$Z_{eff} = Z - S$$

Here S is the number of electrons in the inner filled shells, equal to the atomic number of the noble gas that ends the row above the element in the periodic table. As an example, the S-value for chlorine is 10, the atomic number of neon. The quantity Z is the total number of electrons, equal to the atomic number of the element itself, 17 for chlorine. The 10 inner electrons (S) of chlorine screen out the positive charge of 10 protons, leaving an effective nuclear charge Z_{eff} of $(17 - 10) = +7$ that pulls the outer electrons closer to the nucleus, reducing the atomic radius. The imperfect screening is a maximum in the middle of the row, leading to the minimum. The effective nuclear charge increases, and the atomic volume decreases from left to right across a row in the periodic table. Moving down a column of the periodic table, the number of filled electron shells increases. The effective nuclear charge remains the same, but now the orbitals are farther from the nucleus, which exerts less pull on the outer electrons, increasing the atomic radius.

Figure 4.20 shows atomic volume, not radius. Screening explains the plunging volume from the start of a row towards the middle (lithium to carbon in row 2, for instance), and the slower increase in volume in moving down a column of the periodic table (the sequence lithium – potassium – rubidium – caesium, for example). Superimposed on this is the effect of atom packing: elements at the start of a row are metallic and mostly close-packed. Elements towards the end of a row are non-metallic and have crystal structures with lower packing density.

Young's modulus (Figure 4.21) and many other properties show similar progressions. The modulus peaks at the centre of each row, falling sharply at the end of one row and the start of the next. This is partly explained by the cyclic atomic volume shown in the previous figure: the smaller the atomic volume, the greater the number of bonds per unit volume and the larger the modulus. Superimposed on this is a change in *cohesive energy* across a row, associated with the number of free electrons per ion (in a metal) and the number of shared electrons (in a covalently bonded solid). We come to that next.

Interatomic bonding Many aspects of interatomic bonding can be understood in terms of *electronegativity*, the propensity of an atom to attract one or more electrons to become a negative ion. Electronegativity is measured on an arbitrary, dimensionless scale proposed by Pauling[9] that ranges from 0.7 (francium, the least electronegative) to 4.0 (fluorine, the most), and it, too, varies in a cyclic way across the rows of the periodic table (Figure 4.22). We will use this plot in a moment as a tool for estimating bond type.

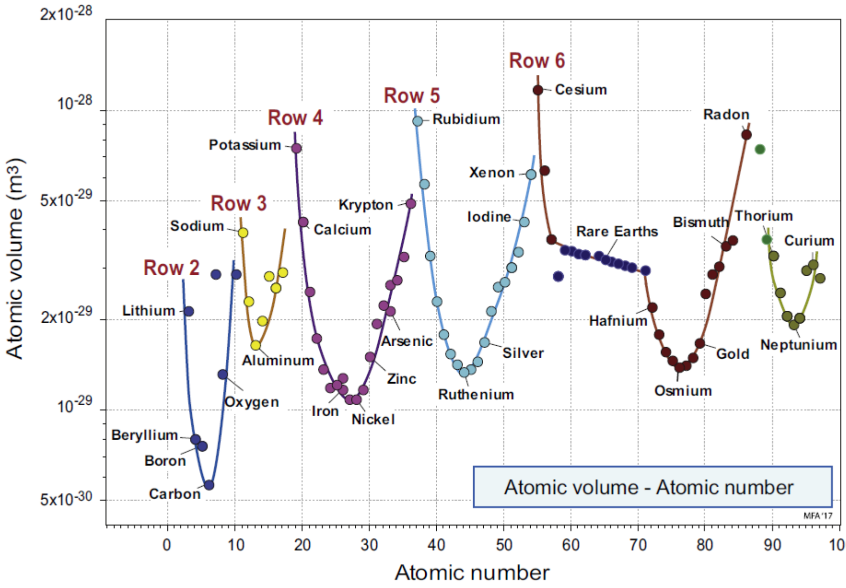
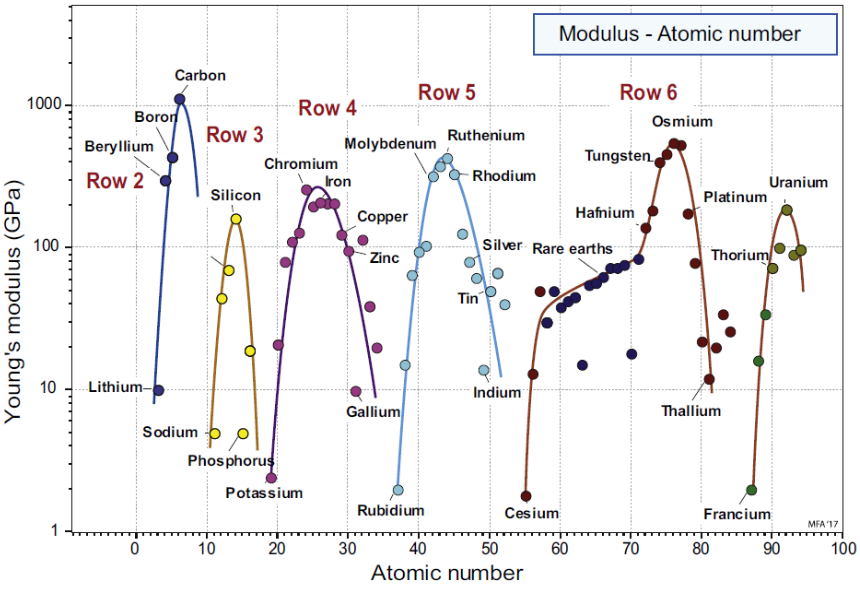


Figure 4.20 The cyclic change of atomic volume across the periodic table.



As neutral atoms are brought together from infinity, their electrons begin to interact, tending to form a bond. Some bonds are so weak that at room temperature, thermal energy is enough to disrupt them. Others are so strong that, once formed, they are stable to over 3000°C. As the bond forms and the atoms are drawn together, the energy at first falls; but when filled electron shells start to overlap, the energy rises again because, while unfilled shells can share electrons, the Pauling exclusion principle prohibits filled shells from doing the same. This generates a balancing repulsive force, causing the atoms to sit at an equilibrium spacing. The *cohesive energy*, H_c, is the energy per mol (a mol is 6.022×10^{23} atoms) required to separate the atoms of a solid completely, giving neutral atoms at infinity. The greater the cohesive energy, the stronger are the bonds between the atoms. We see later that this energy correlates closely with properties that are governed directly by atomic bonding. There is a number of characteristic types of bonding in solids that depend on how the valence electrons interact. They can do this in several ways, of which we'll examine four.

Metallic bonding About 80% of the elements of the periodic table are metals – the box lists some examples, showing the wide range of cohesive energy. Valence electrons in metallic solids detach themselves from their parent atoms (leaving them as positive ions) and form a negatively charged swarm of almost-freely moving charge carriers (Figure 4.23). The swarm screens the array of positive ions from their mutual repulsion, shutting each off, so to speak, from its repulsive neighbours. The coulombic attraction between the swarm and the array of positive ions creates the bond. It is not directional, so metallic solids are usually close-packed because this minimises the average distance between the positively charged ions and the negatively charged electron swarm. Electronegative atoms attract rather than donate electrons, so they are generally non-metallic. Those that are electropositive do the opposite, so that a boundary (blue line) can be sketched onto Figure 4.22, dividing the elements on it, very roughly, into those with metallic character and those with non-metallic.

Metallic bonded materials
H_c = 60–850 kJ/mol

- Copper
- Aluminium
- Lead
- Tungsten

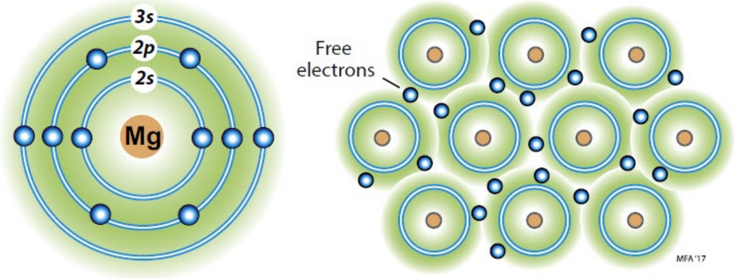


Figure 4.23 Metallic bonding in magnesium. The two ***3s*** valence electrons detach and move freely through the array of positively charged ions.

An electric field, applied to a metallic solid, exerts a force on the free, or nearly free, electrons, accelerating them in the direction of the field. If they are totally free, they move without resistance, and the material is superconducting. A few materials, when at very low temperatures, are superconducting. In most, the electrons are scattered as they move, giving what we know as 'resistivity'. More on this in Chapter 15.

Ionically bonded materials
$H_c = 600-1600$ kJ/mol

- Sodium chloride, NaCl
- Potassium chloride, KCl
- Calcium chloride, $CaCl_2$
- Magnesium oxide, MgO

Ionic bonding If a strongly electro-positive atom approaches one that is strongly electronegative, there is a tendency for electrons to leave the first and join the second, giving both filled outer shells in the way illustrated by Figure 4.18. The first atom acquires a positive charge, the second a charge that is negative, and the two are drawn together by coulombic attraction. The resulting ionic bond is non-directional, attracting equally in all directions. Ionically bonded compounds tend to form when the difference in electronegativity of the atoms (plotted in Figure 4.22) is greater than 1.7. Crystal structures held together by ionic crystals must meet two further conditions: that of overall charge neutrality and that of ensuring that every positive ion has only negative ions as its nearest neighbours and vice versa. The box lists some common ionically bonded materials. The cohesive energy is generally higher than for metallic bonding.

Covalently bonded materials
$H_c = 100-1200$ kJ/mol

- Diamond
- Silicon
- Polyethylene, along chain
- Quartz

Covalent or molecular bonding Covalent bonding is so called because it arises from the sharing of valence electrons between atoms in such a way that each acquires an inert-gas electron structure. It operates in a diverse range of elements and compounds, including carbon crystals and molecules, with cohesive energies spanning a wide range overlapping both metallic and ionic bonding (see box).

To understand covalent bonding, however, we start with the water molecule (Figure 4.24). Here the *1s* electrons of the two hydrogens are shared with the almost-full *2p* shell of the oxygen, giving it the electron structure of neon. It, in turn, shares an electron with each hydrogen, giving them the helium configuration.

Covalent bonds tend to form in molecules when the electronegativity difference between the two atoms is less than 1.7. For water, this difference is 1.4, large enough that the electrons tend to spend more time on the oxygen than on the two hydrogens, giving a *polar* bond (i.e. the bond is directional, with a permanent *dipole moment*). When the difference is less than about 0.4, the electrons are more equally shared, and the bond is non-polar.

Carbon, particularly, forms strong covalent bonds both with itself and with other atoms. To understand these, we need the idea of orbital mixing or **hybridisation**. Carbon, $1s^2\ 2s^2\ 2p^2$, can mix *2s* with *2p* electrons to create new orbitals that have directionality (Figure 4.25). Mixing one *2s* electron with the two *2p* electrons gives three sp^2 orbits lying in a plane and directed at 120 degrees to each other. Mixing all four *2s* with *2p* electrons gives four new sp^3 orbits directed at the four corners of a tetrahedron. Each hybrid orbit can hold two electrons but has only one until it shares it with another atom, creating a covalent bond.

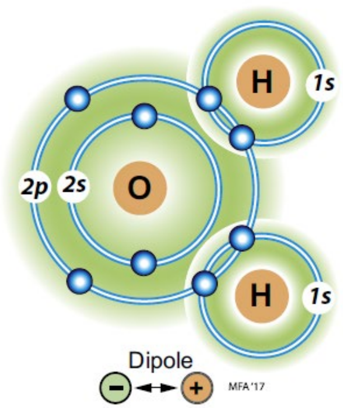


Figure 4.24 Covalently bonded water molecule.

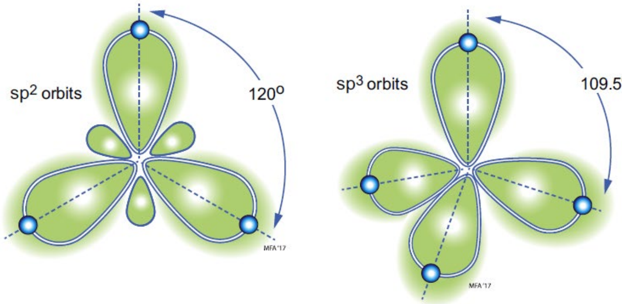


Figure 4.25 sp^2 and sp^3 orbitals of carbon atoms.

These new orbits have fundamental significance for the compounds of carbon. *Graphite* is a hexagonal net of sp^2-bonded carbon atoms, each of the three orbits sharing its one electron with another identical atom to form covalently bonded sheets. *Diamond* is a three-dimensional network of sp^3-bonded carbon atoms, similarly bonded to other identically hybridised C atoms. Many polymers and many organic molecules are based on sp^3-bonded carbon: two of the four orbits are used to make long chain molecules, with other atoms (such as hydrogen) or molecular groups being attached to the other two. The bonding within the polymer chain is covalent, but we also need to consider the bonding between them – that comes next.

Dipolar or van der Waals bonding Inert gases become liquid or solid at sufficiently low temperatures. They already have full electron shells, so what is binding the atoms together? The bond has its origins in dipole–dipole attraction, illustrated in Figure 4.26. The charge distribution on an atom fluctuates as the electrons move; at any instant, the charge is unevenly distributed, giving the atom a temporary dipole moment. The dipole of one atom induces a dipole in an adjacent atom and the pair of dipoles attract, creating a weak bond.

Dipolar-bonded materials
$H_c = 7–50$ kJ/mol

- Ice
- Dry ice (solid CO_2)
- Paraffin wax
- Polyethylene, between chains

Dipolar bonding can arise in another way. As explained above, polar covalent bonds like that of water (Figure 4.24) carry a permanent dipole moment. It is this that binds water molecules together to form ice. The same dipolar bonding glues one polymer chain to its neighbours, such as in polyethylene (PE) and polypropylene. The box shows that the cohesive energy associated with dipolar bonding is much lower than metallic, ionic or covalent.