5.3: Vertical Relationships

Table 5-2 lists the atomic radii and the ionization potentials of the elements found in the first column of the periodic table, the group I elements.

Table 5-2: Atomic Radii and Ionization Potentials of Group I Elements

Element	Li	Na	K	Rb	Cs
Radius (Å)	1.50	1.86	2.27	2.43	2.62
I_1 (ev)	5.4	5.1	4.3	4.2	3.9

The average value of the distance between the electron and the nucleus increases as the value of the principal quantum number is increased. The increase in the atomic diameters down a given group in the periodic table is thus understandable. Each of the group I elements represents the beginning of a new quantum shell. There will be a very sharp decrease in the effective nuclear charge on passing from the preceding closed shell element to a member of group I, as the number of the inner shell electrons is increased by eight. This large sudden reduction in the effective nuclear charge and the fact that the electron, because of the Pauli exclusion principle, must enter a new quantum shell, causes the group I elements to be larger in size and much more readily ionized than the preceding noble gas elements. The decrease in the effective nuclear charge and the increase in the principal quantum number down a given family bring about a steady decrease in the observed ionization potentials. Thus the outer 6s electron in cesium is on the average, further from the nucleus than is the outer 2s electron in lithium. It is also more readily removed.

So far we have considered the periodic variations in the energy required to remove an electron from an atom:

$\mathrm{M} \rightarrow \mathrm{M}^+ + e^-$	I_1 = a positive value
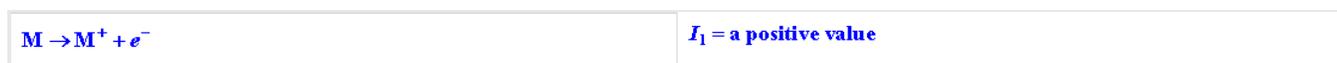
In some favourable cases it is possible to determine the energy released when an electron is added to an atom:

$\mathrm{M} + e^- \rightarrow \mathrm{M}^-$	ΔE = a negative value

The magnitude of the energy released when an atom captures an extra electron is a measure of the atom's *electron affinity*.

It might at first seem surprising that a neutral atom may attract an extra electron. Indeed many elements do not have a detectable electron affinity. However, consider the outer electronic configuration of the group VII elements, the halogens:

ns^2np^5
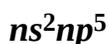
There is a single vacancy in the outer set of orbitals and the effective nuclear charge experienced by the valence electrons in a halogen atom is almost the maximum value possible for any given row. Because of the incomplete screening of the nuclear charge by the outer electrons, the remaining vacancy in the outer shell will, in effect, exert an attractive force on a free electron large enough to bind it to the atom.

The electron affinities for the rare gas atoms will be effectively zero even though the effective nuclear charge is a maximum for this group of elements there are no vacancies in the outer set of orbitals in a rare gas atom and as a result of the Pauli principle, an extra electron would have to enter an orbital in the next quantum shell. The electron in this orbital will experience only a very small effective nuclear charge as all of the electrons originally present in the atom will be in inner shells with respect to it. Elements to the left of the periodic table, the alkali metals for example, do have vacancies in their outer quantum shell but their effective nuclear charges are very small in magnitude. Thus these elements do not exhibit a measurable electron affinity. The electron affinity increases across a given row of the periodic table and reaches a maximum value with the group VII elements. This is a direct reflection of the variation in the effective nuclear charge.

The orbital vacancy in which the extra electron is placed is found at larger distances from the nucleus when the principal quantum number is increased. Thus the electron affinity should decrease down any given family of elements in the periodic table. For example, the electron affinities for the halogens should decrease in the order F > Cl > Br > I. (Click here for note.)

The variation in the ionization potentials across a given row is reflected in the values shown in the atomic orbital energy level diagram for the elements from hydrogen through to neon (Fig. 5-3).
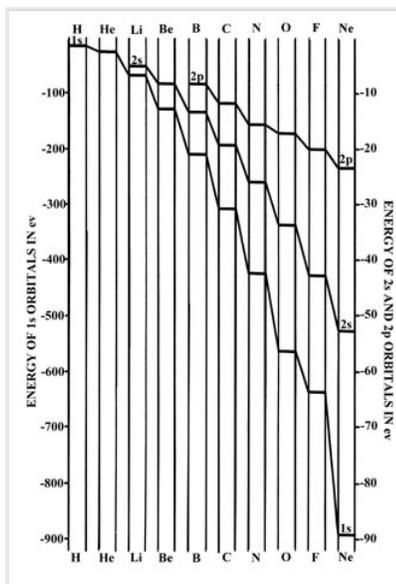
Fig. 5-3. An orbital energy level diagram for the elements H to Ne

(Note that the energy scale used for the 1*s* orbital differs by a factor of ten from that for the 2*s* and 1*p* orbitals.) The orbital energies show a uniform decrease when the nuclear charge is increased, reflecting an increase in the binding of the electrons. The total energy of a many-electron atom is ***not*** simply the sum of the orbital energies. Summing the orbital energies does not take proper account of the repulsions between the electrons. The orbital energies do, however, provide ***approximate*** estimates of the ionization potentials. The ionization potential is the energy required to remove one electron from an atom, and an orbital energy is a measure of the binding of a ***single electron*** in a given orbital. Thus the ionization potential should be approximately equal to ***minus*** the orbital energy. For example, the ionization potential of lithium is 5.39 ev and the 2*s* orbital energy is -5.34 ev. Similarly I_1, for neon is 21.56 ev and the 2*p* orbital energy is -23.14 ev.

Shell structure is also evident in the ionization potentials and orbital energies of atoms. By exposing the atom to light of very short wavelength (in the X-ray region of the spectrum), it is possible to ionize one of the inner shell electrons, rather than a valence electron. That is, the energy of an X-ray photon is comparable to the binding energy of an inner shell electron. The resulting ion is in a very unstable configuration and after a very brief period of time an electron from the outer shell "falls" into the vacancy in the inner shell. In falling from an outer to an inner shell the binding of the electron is greatly increased and a photon is emitted. The energy of this photon should be ***approximately*** equal to the difference in energies of the outer shell and inner shell orbitals. For example, the photon emitted when neon loses an inner shell electron has an energy of 849 ev. The difference in energy between the 2*p* and 1*s* orbitals of neon is 869 ev. Photons with energies in this range occur in the X-ray region of the spectrum. It is apparent from the variation in the 1*s* orbital energies shown in Fig. 5-3 that the energies and hence the frequencies of the X-ray photons will increase as the nuclear charge is increased. It was from a study of the X-ray photons emitted by the elements that Moseley was first able to determine the nuclear charges (the atomic numbers) of the elements.