7.19: Isotope effects

The existence of different isotopes of an element gives rise to what could be called hyperfine structure, except that we are restricting the use of the term hyperfine structure to the splitting caused by nuclear spin. There are two quite different isotope effects, which I refer to as the *mass effect* and the *volume effect.*

The effect of different isotopic masses is to displace the centre of mass between nucleus and electrons a small amount. In the hydrogen atom, for example, the term values (neglecting fine structure and referring to the Bohr model) are given by equation 7.4.9, in which the expression for the Rydberg constant includes the reduced mass $\mu = \frac{Mm}{M+m}$ of the electron. It becomes a simple matter to calculate the energy levels and Balmer wavelengths of D, He^+, Li^{++}, etc., merely by exchanging the reduced mass in H by the reduced mass in the other species. I commend this exercise to the reader. For example, by how much does the wavelength of Hα differ in the spectra of ordinary hydrogen and deuterium? For more complex atoms, the calculation of the isotope shift is more difficult, but the basic reason for the shift is the same.

It might well be thought that isotope shifts would be greatest for very light atoms, but would be negligible for heavier atoms, because the displacement of the position of the centres of mass in different isotopes of a heavy atoms such as, for example, iron, would be negligible. This is indeed the case for the mass isotope effect. It comes as something of a surprise, therefore, to learn that there are significant isotope shifts between isotopes of quite massive isotopes, such as lead, cadmium, gold, mercury, promethium and osmium, and that such shifts have even been observed in stellar spectra. The shift is a result of the relatively large *volumes* of these nuclei. There is no need to go into the detailed theory of the volume effect here, though it is at least useful to know of its existence and, to some extent, its cause. An allowed electric dipole line always involves a transition between two levels belonging to different configurations, and the volume effect is most marked for those transitions in which the two configurations have different numbers of s-electrons. These are electrons with zero orbital spin angular momentum, and, in the Bohr-Sommerfeld atomic model (mentioned briefly in section 7.4), these orbits would be ellipses that have degenerated into straight lines through the nucleus. In other words, we can understand that the volume effect is related to the penetration of the nuclei by s-electrons, and we can see why the effect is most marked in the largest nuclei.