Environmental Physics for Freshman Geography Students

Professor David Faiman. Lecture 8. v.6.1 (December 23, 2003)

1. Larger atoms than hydrogen

In the previous lecture we saw how a hydrogen atom can exist in various energy states, specified by a quantum number n which may take any positive integer value: 1, 2, 3, ... etc. For each of these allowed energy states we calculated that the total energy of the electron (i.e. kinetic plus potential) takes the value:

$$E = - m K^2 q^4 / (2 n^2 L_0^2) \qquad (8.1)$$

where m is the electron mass, = 9.11×10^{-31} kg, K is Coulomb's electrostatic constant, = 8.99×10^9 kg m^3 s^{-2} C^{-2}, q is the magnitude of the electric charge of the electron, = 1.60×10^{-19} C, L_0 is the fundamental unit of angular momentum, = 1.05×10^{-34} J s (better known as "Planck's constant divided by 2π"), and n is the integer which tells us which energy level we are talking about.

We also learned that the energy of a photon is simply related to the wavelength, λ, of the corresponding light wave, via the relationship:

$$E = 2\pi L_0 c / \lambda \qquad (8.2)$$

where c is the velocity of light in a vacuum, = 3.00×10^8 m s^{-1}, and λ is measured in meters.

This simple mathematical model provided a qualitative *and* quantitative explanation of the spectrum of light that was observed from evacuated electrical discharge tubes in which trace amounts of hydrogen were present. The explanation was that:

1. Energetic photons in the electric field within the tube (which had obtained their energy from the external electric power supply) collide with electrons in the ground states, n = 1, of the hydrogen atoms, and excite them to one of their higher energy states, $n = n_i$.

2. Hydrogen atoms in excited states are unstable and get rid of their unwanted energy by emitting photons.

3. The energy carried off by each photon is precisely the amount which enables an atom to de-excite to one of its less excited states, until, ultimately, it is in its ground state, n = 1.

4. It is the discrete wavelengths of these emitted photons that are observed by the spectroscopists.

5. For an atomic de-excitation from state $n = n_i$ to a state $n = n_f$, (where $n_i > n_f$), eq. (8.1) tells us that the hydrogen atom will lose an amount of energy equal to:

$$E_i - E_f = [m K^2 q^4 / (2L_0^2)] (1/n_f^2 - 1/n_i^2) \qquad (8.3)$$

And from eq. (8.2), the emitted light will have a wavelength:

$$\lambda = 2\pi L_0 c / (E_i - E_f) \qquad (8.4)$$

For other kinds of atom the story is similar but, not surprisingly, more complicated. The reasons for the additional complication are: (1) All other atoms, being more massive than hydrogen, contain more than a single electron, and those electrons interact with one another, in addition to interacting with the positively charged atomic nucleus; (2) It turns out that further quantum numbers (in addition to the number n which we encountered for hydrogen) restrict the allowed energies of the various electrons. Let me give two examples.

My first example is *helium*, the second lightest atom (denoted by the symbol He). The He nucleus contains 2 protons and is surrounded by 2 electrons. Incidentally, you may think that a helium atom has twice the mass as an atom of hydrogen, but, in fact, it has 4 times the mass. This is because its nucleus contains 2 other, electrically neutral, particles called *neutron*s. The neutron and proton have almost precisely the same mass as one another. Fortunately, the presence of neutrons in the nucleus does not complicate the "chemistry". I.e., they do not effect the motion or energies of the electrons.

Now, the allowed energy levels of helium are qualitatively quite similar to those of hydrogen, as you will discover when you solve homework problem 1 for the case of *singly-ionized* helium (where one electron has been removed, so as not to complicate the calculation). Here we have an electron of charge -q that is attracted to a nucleus of charge +2q. The result is that each helium energy level n has 4 times the magnitude of the corresponding hydrogen level. Other than this overall energy scale difference, the results are qualitatively similar for the two kinds of atom. However, helium has 2 electrons in its natural (i.e. un-ionized) state. Therefore, you might guess that in the ground state of helium, both electrons would sit in the n = 1 energy state (or the n = 1 *orbital*, as chemists call it). And you would be correct. The fact that there are two electrons does not disturb the energy levels very much. There would naturally be a tendency for the two negatively charged electrons to be as far apart from one another as possible within the n = 1 orbital. But otherwise there are no particular surprises for this atom.

My second example is *lithium*, the third lightest atom (denoted by the symbol Li). The lithium nucleus contains 3 protons and usually 4 neutrons. This atom therefore contains 3 electrons. Now, you might guess that when a lithium atom is in its ground state, all three of the electrons would be in the n = 1 orbital. But this is not the case. Only 2 of its electrons occupy the n = 1 orbital; the third electron resides in the n = 2 orbital. Why is this the case?

It turns out that because of further quantum properties of electrons, that I shall not discuss here, a maximum of 2 electrons are allowed in the n = 1 orbital. Any further electrons have to reside in the higher orbitals staring with n = 2. But the n = 2 orbital can only contain up to a maximum of 8 electrons. If the atom contains more than 10 electrons (i.e. 2 in the n = 1 orbital and 8 in the n = 2 orbital), then the remaining electrons have to reside in the n = 3 orbital, but again, only up to a certain allowed maximum, above which, any further electrons have to sit in the n = 4 orbital, etc.

2. Interactions among atoms: molecules

If this sounds complicated, I apologize, but that's the way it *is*. In fact, I have actually over-simplified (!) this description in order to make it seem as simple and plausible as possible.

Perhaps a diagram will help. **Fig. 1** shows a table of the atoms which have all of their electrons in the first 3 orbitals. The first row, H and He, are those atoms whose electrons occupy the n = 1 orbital. The second row, Li - Ne, are those atoms with full n = 1 orbitals and, successively, from 1 to 8 electrons in their n = 2 orbital. The third row, Na - Ar, are atoms which have full n = 1 and n = 2 orbitals, and which have electrons in their n = 3 orbital. Those of you having a familiarity with chemistry will recognize **Fig. 1** as being the first 3 rows of the famous *Periodic Table of the Elements*, discovered empirically by Mendeleev in the 18th century. Mendeleev created this table by studying the way in which chemical compounds react with one another. For example, the column of gases on the extreme right (He, Ne, Ar,...) have no chemical reactions with other elements. Chemists call them "The noble gases". On the other hand, those elements in the column immediately preceding these noble gases, (F, Cl, ...), known as "the halogens", react very strongly with the column of elements (H, Li, Na, ...), known as "the alkali metals", which immediately follows the noble gases.

1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar

Figure 1: The first 3 rows of the Periodic Table of the Elements

Mendeleev could not understand the atomic basis that causes chemical reactions to exhibit these regularities, but we can. It turns out that atoms with all orbitals full are stable, in the sense that they have minimum energies. These are the noble gases. Because they already exist in minimum energy states, they can not reduce their energies by entering into chemical reaction with other elements.

On the other hand, look at the situation of fluorine (F) in the halogen column. This element has 7 electrons in its n = 2 orbital. If it could "find" another electron it too would be energetically stable. But ... now look at the alkali metals column. Lithium has only 1 electron in its n = 2 orbital. If it could get rid of that electron it too would be energetically stable (having a complete n = 1 orbital). Thus, the situation is perfect for lithium and fluorine to "do a deal". Li donates an electron to F. In this way, they are both energetically more stable. However, in the process, Li becomes positively charged (having lost an electron) and Li becomes negatively charged (having gained an electron). They solve this problem by "sticking together" to form LiF, thereby preserving charge neutrality. In this way, a *molecule* of LiF has lower energy than a pair of free Li and F atoms. It is consequently more stable.

But chemical reactions can also occur between 2 atoms of the same kind. Take the case of hydrogen. As two free hydrogen atoms approach one another, each "thinks" that if it could capture the other's electron, it could complete its own n = 1 orbital. So they too "do a deal": Some of the time one atom has both electrons and some of the time the other atom does. Here too, the possession of both electrons renders the *acceptor* atom negatively charged and the *donor* atom positively charged. They therefore stick together, forming an electrically neutral

hydrogen molecule. Again, the energy of a hydrogen molecule is lower than that of two free hydrogen atoms.

3. Atomic number, ionization, atomic mass and isotopes

A number of terms that are commonly used by chemists are easy to understand using the simple picture of atoms we have described above. First, *atomic number* Z is simply the number of protons in the nucleus of an atom. It is also equal to the number of electrons if the atom has not lost any by *ionization.* Atomic numbers are, obviously, always integers: for H, Z = 1; for He, Z = 2; for Li, Z = 3, etc.

What is ionization? If an atom is hit by a sufficiently energetic photon, one of its electrons can be removed completely. The resulting atom is then said to be "ionized" An ionized atom is positively charged so it can not remain free for long before regaining the lost electron in some way or other (usually by combining with another atom that has an "extra" electron - or, rather, one that can be borrowed).

The *atomic mass* A is the number of particles, i.e. protons and neutrons, in the nucleus. Simple hydrogen has atomic mass A = 1 because its nucleus contains only one particle, a proton. However, hydrogen can also exist in two heavier forms: *deuterium*, which has a neutron added to its nucleus; and *tritium*, which has 2 neutrons in its nucleus. These three forms of hydrogen are called *isotopes* of hydrogen. They all have the same chemical reactions because they all have only one electron, i.e. Z = 1. However, deuterium has atomic mass A = 2 and tritium has atomic mass A = 3. Water that contains deuterium atoms is sometimes known as "heavy water".

Now, if you consult a "more serious" edition of the periodic table of the elements, than that shown in **Fig.1**, you will discover that atomic masses are generally not integers. For example, boron (B) has atomic mass A = 10.8. How can this be? All this means is that boron occurs naturally in nature in a number of isotopes. Some boron atoms will have 5 protons and 5 neutrons, and others will have 5 protons and 6 neutrons. There may also be small admixtures of other boron isotopes. The value 10.8 is simply the *average* atomic mass of boron.

4. The size of atoms and their constituents

From the previous lecture we might expect that the approximate shape and size of a hydrogen atom would be a sphere of radius:

$$r = n^2 \ L_0^{\ 2} / (K \ m \ q^2) \qquad n = 1, 2, 3, ... \qquad (8.5)$$

If you plug in numbers you will find that this turns out to be 5.29×10^{-11} m for the n = 1 (ground) state, four times as large if the electron is in the n=2 energy state, etc. In the more modern quantum theory of matter, the so-called "first Bohr radius" takes on a more complex interpretation than the simple "radius of a circle" as we have developed it in this course. However, its value represents the approximate size of all atoms, in so much as "size" is a useful concept.

In the case of atoms with higher mass values than hydrogen, it is easy to see that for an ionized atom containing Z protons in its nucleus and a single orbital electron, the first Bohr radius takes the value:

$$r = n^2 L_0^2 / (K m Z q^2) \quad n = 1, 2, 3, \ldots \qquad (8.6)$$

Therefore, for a given value of n, the "size" of the atom decreases as Z increases, provided that the number of electrons in the inner orbital shells remains constant.

But what about all of those protons and neutrons in the nucleus? The nucleus and its constituents are several orders of magnitude smaller than the atom. Protons and neutrons have sizes that are typically of order 10^{-15} m. Hence, even if you pack a few hundred of them into a small ball so that they touch one another, the resulting ball will not be much larger than about 10^{-14} m. Thus it is the orbital electrons that determine the size of an atom – not its nucleus.

Of course, the more protons you try to pack into such a small volume, the stronger will be their electrostatic repulsion against one another. Very heavy nuclei will consequently tend to lose some protons, spontaneously - they are said to be *radioactive*.

You are probably wondering how it is possible to place even 2 protons in an atomic nucleus (as in helium) and stop them from blowing each other apart. The answer is that, in addition to electrostatic interactions, protons also possess so-called *strong interactions.* Strong interactions, as their name suggests, are stronger than electrostatic interactions, and attractive. They have a different mathematical from than the Coulomb interaction, and one which is extremely short range. Two neutrons, which also possess strong interactions but no electrostatic interactions, would not begin to feel each other until they approached within a distance of about 10^{-14} m of one another. Electrons, on the other hand, possess electrostatic interactions but no strong interactions. Consequently they can not feel neutrons. Apart from holding the constituents of atomic nuclei together, strong interactions play no role in nature at large. We therefore don't need to know anything about how the protons and neutrons behave within the nucleus. All we *do* need to know, in order to understand nature in its large-scale manifestations (i.e. chemistry, solids, etc.) is how the electrons behave.

Problem set 8 (atoms and molecules)

1. Derive a formula for the energy levels for an atom of singly-ionized helium (in a similar manner to which we derived the Bohr formula for hydrogen atom energies). Calculate the numerical values of the first 3 energy levels (i.e. for n = 1, 2, 3) for this atom. [Note: You may picture an atom of singly-ionized helium as consisting of a single electron orbiting a nucleus which contains 2 protons and 2 neutrons].

2. Calculate the wavelengths of the light from photons that are emitted in the (n = 3 -> n = 1), and the (n =2 -> n=1) transitions in an atom of singly-ionized helium. Compare these results with the corresponding wavelengths for photons emitted by a hydrogen atom.

3. As you move from left to right along the 3rd row of the Periodic Table in **Fig.1**, would you expect the size of the atoms to increase or decrease? Explain your reasoning.

4. Look at the positions of hydrogen (H), carbon (C), and oxygen (O) in the table shown in **Fig.1** and explain *in words*, why the molecules CH_4 (methane), H_2O (water) and CO_2 (carbon dioxide) may be expected to be particularly stable.