2.6: Orbitals, Electron Clouds, Probabilities, and Energies

Our current working model of the atom is based on quantum mechanics that incorporate the ideas of quantized energy levels, the wave properties of electrons, and the uncertainties associated with electron location and momentum. If we know their energies, which we do, then the best we can do is to calculate a probability distribution that describes the likelihood of where a specific electron might be found, if we were to look for it. If we were to find it, we would know next to nothing about its energy, which implies we would not know where it would be in the next moment. We refer to these probability distributions by the anachronistic, misleading, and Bohrian term orbitals. Why misleading? Because to a normal person, the term orbital implies that the electron actually has a defined and observable orbit, something that is simply impossible to know (can you explain why?)

Another common and often useful way to describe where the electron is in an atom is to talk about the electron probability density or electron density for short. In this terminology, electron density represents the probability of an electron being within a particular volume of space; the higher the probability the more likely it is to be in a particular region at a particular moment. Of course you can't really tell if the electron is in that region at any particular moment because if you did you would have no idea of where the electron would be in the next moment.

Erwin Schrödinger (1887–1961) developed, and Max Born (1882–1970) extended, a mathematical description of the behavior of electrons in atoms. Schrödinger used the idea of electrons as waves and described each atom in an element by a mathematical wave function using the famous Schrödinger equation ($H\Psi = E\Psi$). We assume that you have absolutely no idea what either $H\Psi$ or $E\Psi$ are but don't worry—you don't really need to. The solutions to the Schrödinger equation are a set of equations (wave functions) that describe the energies and probabilities of finding electrons in a region of space. They can be described in terms of a set of quantum numbers; recall that Bohr's model also invoked the idea of quantum numbers. One way to think about this is that almost every aspect of an electron within an atom or a molecule is quantized, which means that only defined values are allowed for its energy, probability distribution, orientation, and spin. It is far beyond the scope of this book to present the mathematical and physical basis for these calculations, so we won't pretend to try. However, we can use the results of these calculations to provide a model for the arrangements of electrons in an atom using orbitals, which are mathematical descriptions of the probability of finding electrons in space and determining their energies. Another way of thinking about the electron energy levels is that they are the energies needed to remove that electron from the atom or to move an electron to a "higher" orbital. Conversely, this is the same amount of energy released when an electron moves from a higher energy to a lower energy orbital. Thinking back to spectroscopy, these energies are also related to the wavelengths of light that an atom will absorb or release. Let us take a look at some orbitals, their quantum numbers, energies, shapes, and how we can used them to explain atomic behavior.

Examining Atomic Structure Using Light: On the Road to Quantum Numbers

J.J. Thompson's studies (remember them?) suggested that all atoms contained electrons. We can use the same basic strategy in a more sophisticated way to begin to explore the organization of electrons in particular atoms. This approach involves measuring the amount of energy it takes to remove electrons from atoms. This is known as the element's ionization energy which in turn relates directly back to the photoelectric effect.

All atoms are by definition electrically neutral, which means they contain equal numbers of positively- and negatively-charged particles (protons and electrons). We cannot remove a proton from an atom without changing the identity of the element because the number of protons is how we define elements, but it is possible to add or remove an electron, leaving the atom's nucleus unchanged. When an electron is removed or added to an atom the result is that the atom has a net charge. Atoms (or molecules) with a net charge are known as ions, and this process (atom/molecule to ion) is called ionization. A positively charged ion (called a cation) results when we remove an electron; a negatively charged ion (called an anion) results when we add an electron. Remember that this added or removed electron becomes part of, or is removed from, the atom's electron system.

Now consider the amount of energy required to remove an electron. Clearly energy is required to move the electron away from the nucleus that attracts it. We are perturbing a stable system that exists at a potential energy minimum – that is the attractive and repulsive forces are equal at this point. We might naively predict that the energy required to move an electron away from an atom will be the same for each element. We can test this assumption experimentally by measuring what is called the ionization potential. In such an experiment, we would determine the amount of energy (in kilojoules per mole of molecules) required to remove an electron from an atom. Let us consider the situation for hydrogen (H). We can write the ionization reaction as:

$$\mathrm{H}\,(\mathrm{gas}) + \text{energy} \rightarrow \mathrm{H}^{+}(\mathrm{gas}) + \mathrm{e}^{-}. \tag{2.6.1}$$

[15]

What we discover is that it takes 1312 kJ to remove a mole of electrons from a mole of hydrogen atoms. As we move to the next element, helium (He) with two electrons, we find that the energy required to remove an electron from helium is 2373 kJ/mol, which is almost twice that required to remove an electron from hydrogen!

Let us return to our model of the atom. Each electron in an atom is attracted to all the protons, which are located in essentially the same place, the nucleus, and at the same time the electrons repel each other. The potential energy of the system is modeled by an equation where the potential energy is proportional to the product of the charges divided by the distance between them. Therefore the energy to remove an electron from an atom should depend on the net positive charge on the nucleus that is attracting the electron and the electron's average distance from the nucleus. Because it is more difficult to remove an electron from a helium atom than from a hydrogen atom, our tentative conclusion is that the electrons in helium must be attracted more strongly to the nucleus. In fact this makes sense: the helium nucleus contains two protons, and each electron is attracted by both protons, making them more difficult to remove. They are not attracted exactly twice as strongly because there are also some repulsive forces between the two electrons.

The size of an atom depends on the size of its electron cloud, which depends on the balance between the attractions between the protons and electrons, making it smaller, and the repulsions between electrons, which makes the electron cloud larger.[16] The system is most stable when the repulsions balance the attractions, giving the lowest potential energy. If the electrons in helium are attracted more strongly to the nucleus, we might predict that the size of the helium atom would be smaller than that of hydrogen. There are several different ways to measure the size of an atom and they do indeed indicate that helium is smaller than hydrogen. Here we have yet another counterintuitive idea: apparently, as atoms get heavier (more protons and neutrons), their volume gets smaller!

Given that

i. helium has a higher ionization energy than hydrogen and
ii. that helium atoms are smaller than hydrogen atoms, we infer that the electrons in helium are attracted more strongly to the nucleus than the single electron in hydrogen.

Let us see if this trend continues as we move to the next heaviest element, lithium (Li). Its ionization energy is 520 kJ/mol. Oh, no! This is much lower than either hydrogen (1312 kJ/mol) or helium (2373 kJ/mol). So what do we conclude? First, it is much easier (that is, requires less energy) to remove an electron from Li than from either H or He. This means that the most easily removed electron in Li is somehow different than are the most easily removed electrons of either H or He. Following our previous logic we deduce that the "most easily removable" electron in Li must be further away (most of the time) from the nucleus, which means we would predict that a Li atom has a larger radius than either H or He atoms. So what do we predict for the next element, beryllium (Be)? We might guess that it is smaller than lithium and has a larger ionization energy because the electrons are attracted more strongly by the four positive charges in the nucleus. Again, this is the case. The ionization energy of Be is 899 kJ/mol, larger than Li, but much smaller than that of either H or He. Following this trend the atomic radius of Be is smaller than Li but larger than H or He. We could continue this way, empirically measuring ionization energies for each element (see figure), but how do we make sense of the pattern observed, with its irregular repeating character that implies complications to a simple model of atomic structure?

Questions

Questions to Answer

- Why are helium atoms smaller than hydrogen atoms?
- What factors govern the size of an atom? List all that you can. Which factors are the most important?

Questions to Ponder

- What would a graph of the potential energy of a hydrogen atom look like as a function of distance of the electron from the proton?
- What would a graph of the kinetic energy of an electron in a hydrogen atom look like as a function of distance of the electron from the nucleus?
- What would a graph of the total energy of a hydrogen atom look like as a function of distance of the electron from the proton?