

## Many-particle Systems, 2

### Multi-electron atoms

The rich diversity of chemical structures and processes is directly related to the diversity of electronic states of multi-electron atoms that, in turn, is dictated by the Pauli Exclusion Principle. To see how the Pauli Exclusion Principle produces atomic diversity, it is useful to begin simply, in particular, by considering the most elementary multi-electron “atom”: the hydrogen anion,  $\text{H}^-$ .

$\text{H}^-$  is a system of one proton and two electrons. Suppose the two electrons interact only with the proton and not with each other. Each would then be described by a single particle wavefunction with quantum numbers  $n l m_l m_s$ . Being identical, noninteracting fermions, the two-electron wavefunction would be antisymmetric under state label switch or position switch. This forbids the two electrons from being in the same state. The ground state for this system would therefore be  $\{100 \uparrow; 100 \downarrow\}$ , where the arrows refer to “up” and “down” spin states. The energies of all bound

states of this system would be  $-13.6 \text{ eV}(\frac{1}{n_1^2} + \frac{1}{n_2^2})$ . Therefore, the energy of the ground state would

just be  $-13.6 \text{ eV} \times 2 = -27.2 \text{ eV}$ . Ionization from the ground state would require exciting just one of the single particle states into the “continuum,” an energy equal to 13.6 eV. Laboratory measurement of the ionization energy of  $\text{H}^-$  yields only 0.75 eV, however. The discrepancy is because the assumption that the electrons don’t interact is not very good. The repulsive electron-electron interaction raises the ground state energy from  $-27.2 \text{ eV}$  to  $-1.5 \text{ eV}$  (i.e.,  $-0.75 \text{ eV} \times 2$ ). That is, the repulsion adds about 25.7 eV to the total energy of the ground state. The question arises: Are the single particle quantum numbers  $n l m_l m_s$  still appropriate for multi-electron systems when the electrons interact? Not really, but it is customary to use them anyway. But, remember: the two-electron energy is *not*  $-13.6 \text{ eV}(\frac{1}{n_1^2} + \frac{1}{n_2^2})$ .

The second simplest multi-electron atom is neutral helium with 2 electrons and *two* protons. First, consider the helium cation,  $\text{He}^+$ , i.e., helium with only one electron. The length scale in hydrogen is set by the ratio  $a_0 = \hbar^2 / m k_e e^2$  and the energy scale by  $E_0 = \hbar^2 / 2 m a_0^2$ . One of the  $e$ s in the expression for  $a_0$  is due to the electron, the other due to the proton. If the nucleus has two protons, the length scale decreases by a factor of 2 and the energy scale, in turn, *increases* by a factor of 4. In other words, the electronic energy levels in  $\text{He}^+$  are  $-54.4 \text{ eV} \frac{1}{n^2}$ . Indeed, the *observed* ionization energy of  $\text{He}^+$  from the ground state is exactly 54.4 eV. In neutral helium with two *noninteracting* electrons, the ionization energy would also be 54.4 eV and the ground state energy would be  $-108.8 \text{ eV}$ . The measured ionization energy from the ground state is 24.6 eV, however, meaning that electron-electron repulsion has raised the ground state energy from  $-108.8 \text{ eV}$  to  $-49.2 \text{ eV}$  ( $-24.6 \text{ eV} \times 2$ ), an addition of 59.6 eV. Why is this repulsion so much larger than in  $\text{H}^-$ ? Because the length scale decreases by a factor of 2 in He, the electrons are closer, on average, to each other than in  $\text{H}^-$  and therefore repel more.

A similar situation prevails for  $\text{Li}^+$ , with 2 electrons, but now 3 protons. The ground state energy of  $\text{Li}^+$  without electron repulsion should be  $-13.6 \times 3^2 \times 2 \text{ eV} = -244.8 \text{ eV}$ . The ionization energy for  $\text{Li}^+$  in the ground state is measured to be 75.6 eV. Thus, electron repulsion raises the ground state energy by  $-151.2 \text{ eV} - (-244.8 \text{ eV}) = 93.6 \text{ eV}$ . This is greater than in He because,

again, the electrons are closer in  $\text{Li}^+$  than in He. Neutral lithium has three electrons. The  $n = 1$  states can only accommodate 2 electrons (with spin up and down), so the third electron must have a different  $n$  value. In hydrogen, the next lower energy corresponds to  $n = 2$ , but in hydrogen there are four orbital angular momentum states for  $n = 2$  that are degenerate in energy. Is that also true for Li?

No. The reason is that electrons with different  $n$  and  $l$  values have different average distances from the nucleus. **The higher the value of  $n$ , the greater the average distance from the nucleus.** Thus,  $n = 2$  electrons are not as close on average to the positive nuclear charge as are  $n = 1$  electrons. An  $n = 2$  electron is partially screened from the nucleus by the  $n = 1$  electrons. The  $n = 2$  electron doesn't "feel" all three protons. Moreover, **for the same  $n$ , electrons with low  $l$  values spend more time near the nucleus than those with high  $l$  values.** The low  $l$  value electrons "feel" more of the nuclear charge than high  $l$  electrons. Electrons with  $n = 2$  and  $l = 0$  "penetrate the  $n = 1$  core" more than electrons with  $n = 2$  and  $l = 1$ . The former are therefore more tightly bound than the latter. The net result for Li is the ground state is  $\{100 \uparrow; 100 \downarrow; 200 \uparrow \text{ or } \downarrow\}$ , where the spin direction of the  $n = 2$  electron is irrelevant (ignoring small magnetic effects). Electron-electron repulsion causes the  $l$  degeneracy observed in hydrogen to be partially removed in Li. In Li, the  $n = 2$  level is split into two  $n = 2$  levels, the lower one having  $l = 0$ , the higher  $l = 1$ . The latter still has three  $m_l$  values that are degenerate in energy (ignoring small magnetic effects). Incidentally, we can estimate how much of the positive nuclear charge the  $n = 2$  electron "feels" by setting the ionization energy of ground state Li (5.39 eV) equal to  $13.6 \text{ eV} \frac{Z_{\text{effective}}^2}{2^2}$ , where  $Z_{\text{effective}}$  is the effective number of protons the  $n = 2, l = 0$  electron "feels," and solving for  $Z_{\text{effective}}$ : that is, in general,

$$Z_{\text{effective}} = \sqrt{\frac{n^2 E_{\text{ionization}}}{13.6}} \quad (1)$$

which yields 1.26 for Li. The two  $n = 1$  electrons reduce the effective nuclear charge for the  $n = 2$  electron by 1.74 protons. The screening isn't perfect (i.e., where  $Z_{\text{effective}} = 3 - 2 = 1$ ) because the  $n = 2$  electron penetrates the  $n = 1$  core. These screening effects persist for atoms with even more electrons.

**Example:** The two least bound electrons in the ground state of U are in  $n = 7, l = 0$  states. The ionization energy is 6.3 eV. Using the same algorithm as above we find  $Z_{\text{effective}} = 4.76$ . U has 92 electrons and protons. Because of electron screening, the least bound electrons only "feel" a few of the nuclear protons.

The electron state-filling rules for all atoms are: (a) *generally* (exceptions are discussed below), electron energy increases with increasing  $n$ ; (2) for a given  $n$ , energy increases with increasing  $l$ ; (3) for a given  $l$ ,  $m_l$  states are degenerate and each can accommodate two electrons (with spin up and down). An **electronic configuration** of a multi-electron atom is a string of symbols of the form

$$(\text{number} = n)(\text{letter for } l)^{(\text{number of electrons with } nl)}(\text{number} = n)(\text{letter for } l)^{(\text{number of electrons with } nl)} \dots$$

The string starts with lowest  $n$  and extends to the right with successively higher energies.

Example: The ground state electronic configuration for H is  $1s^1$ ; the first excited state (ignoring small magnetic effects) is  $2s^1$ . The ground state for He is  $1s^2$ ; the first excited state is  $1s^1 2s^1$ . The ground state for Li is  $1s^2 2s^1$ ; the first excited state is  $1s^2 2p^1$ , not  $1s^1 2s^2$ . The reason for the latter is that electronic bound state energies get closer and closer as they approach zero (remember: hydrogen energies are  $-13.6/n^2$ ). Thus, to excite the  $2s$  state to  $2p$  requires less energy than to excite a  $1s$  state to  $2s$ .

The maximum number of electrons in an  $l$  state is  $(2l+1) \times 2$ , i.e., the number of  $m_l$  states  $\times$  the number of  $m_s$  states. Thus, the maximum number of s-electrons is 2, p-electrons is 6, d-electrons is 10, and so on.

Important exceptions to the filling rules occur at “4s after 3p” and “5s after 4p”: that is,  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  *not*  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  (at atomic number 19, K) and  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$  *not*  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^1$  (at atomic number 37, Rb). These exceptions occur because the splitting of the 3d and 4s levels and the 4d and 5s levels, due to electron repulsion, overlap. The chart below (<http://hyperphysics.phy-astr.gsu.edu/hbase/perstab/perfill.html>) is helpful for approximately constructing ground state electronic configurations for any atom. There are exceptions to the predictions of the chart (e.g., the ground state of chromium (atomic number 24) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$  not  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$  as the chart says) that only chemists remember.

