Building a Better Model of the Atom - Key

The electron impact method for finding ionization energies (described in an earlier worksheet) provides information about the energy needed to remove valence electrons, but doesn't provide information about the ionization energy for core electrons. One experimental technique that can provide this information is photoelectron spectroscopy (PES). This technique uses photons of electromagnetic radiation (ER) to provide the necessary energy. Here is how it works – we focus a high energy source of ER, usually an X-ray of know frequency, on the gas phase atoms. An atom absorb a single photon, which, if its energy is sufficient, ejects a single electron from the atom. Because the photon's energy (hν) is greater than the electron's ionization energy (IE), the electron escapes with some kinetic energy (KE). The relationship between all these energies is

$$E_{photon} = h\nu = IE + KE$$

Because E_{photon} is known and the electron's KE is measured, the electron's IE is easily determined.

Every electron in an atom, whether it is a core electron or a valence electron, is equally likely to absorb a photon. Although each atom ejects only a single electron, a large sample of atoms will eject electrons from all shells in an amount that is proportional to the number of electrons in each shell. A PES spectrum of the relative number of electrons emitted vs. IE, therefore, consists of peaks showing an atom's ionization energies and the relative number of electrons with each ionization energy.

Questions to Consider

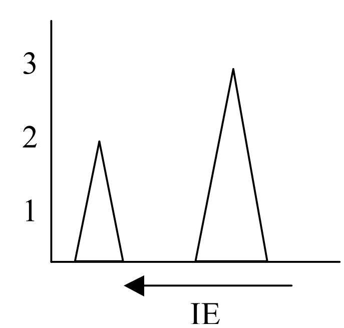
Suppose you have an atom that has two shells with 2 electrons in the shell closest to the nucleus and 3 electrons in the shell furthest from the nucleus. How many peaks do you expect in the PES spectrum for this atom? Explain.

There are two peaks in the PES spectrum since all electrons in the same shell should have the same ionization energy.

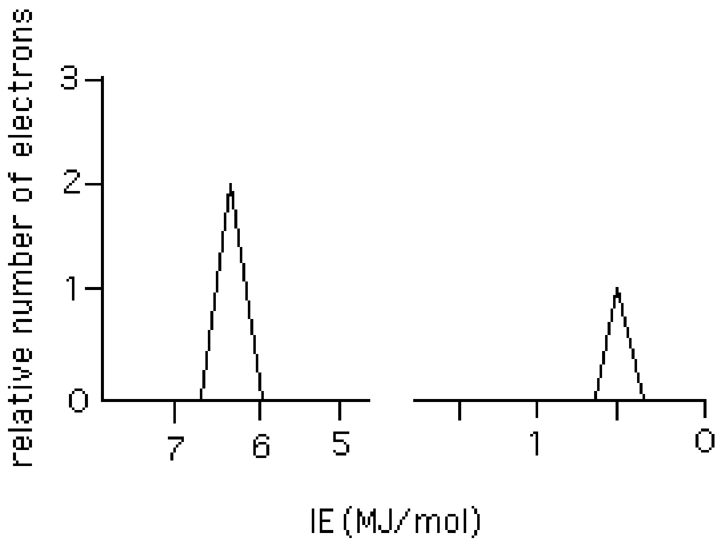
What is the relative height of these peaks. For example, you might decide that all peaks are of equal height or that peak X is 3 times larger than peak Y. Explain.

Given the relative number of electrons, the peak representing the shell closest to the nucleus will have a height that is two-thirds of that for the peak representing the shell furthest from the nucleus.

Sketch a picture of the PES spectrum placing the relative number of electrons on the *y*–axis and the IE on the *x*-axis. The convention in PES spectra is to show ionization energies increasing to the left-side of the *x*-axis.

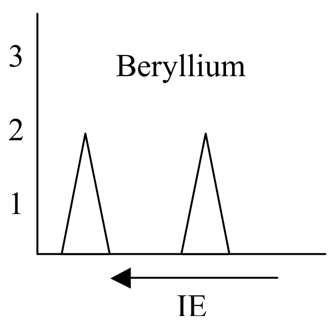


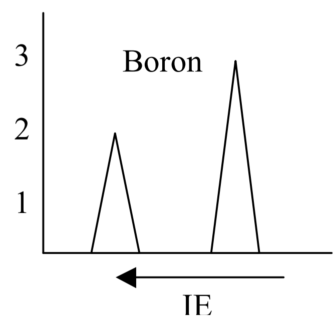
Shown here is a simulated sketch of the PES spectrum for a Li atom. Note that the *x*-axis has a break where there is change in scale. This is necessary because of the large difference in ionization energies between different shells. Is this PES spectrum consistent with our current shell model for the Li atom? Explain. As part of your answer, identify each shell that is shown in the PES spectrum by stating it's value of *n* and the number of electrons in the shell.



Yes – this is consistent with our current model that allows only two electrons in the first shell (n = 1) and up to eight electrons in the second shell (n = 2).

Draw sketches showing your best guesses for the PES spectra of Be and B. Don't worry about the scale on the *x*-axis; all that is important now is how many peaks you expect to find and their relative heights.





Now, examine Figure 3.15 on page 83 of your text and comment on the agreement or disagreement between your predictions and the actual PES spectra for these two atoms. Where there are disagreements, speculate on how we can modify the shell model so that it still explains the PES data.

The prediction for beryllium is consistent with the experimental results shown in Figure 3.14. The prediction for boron, however, does not agree with the experimental result, which shows three peaks. The second peak in our predicted PES spectrum for boron is split into two peaks, one accounting for two electrons and one accounting for one electron. The similarity in IE suggests that the n = 2 shell actually consists of two different types of electrons with slightly different ionization energies. We can modify our model to account for this by introducing the idea of subshells.