

Question: Do all electrons in the same level have the same energy?

From the Shells Activity, one important conclusion we reached based on the first ionization energy experimental data is that electrons in higher shells require less energy to remove. We have experimental data that relates energy required to remove an electron depending on the shell the electron occupies. (In which shell does an electron require more energy to remove? An electron in the second shell or the fourth shell?) An interesting question we could ask, that can not be answered from the experimental data of the first ionization energy is, do all electrons in the same shell require the same amount of energy to remove? We can answer this question if we look at photoelectron spectroscopy (PES) data for the atoms.

In a photoelectron spectroscopy experiment any electron can be ionized when the atom is excited. Like the first ionization only one electron is removed from the atom, however in the PES experiment it can be any electron, not just the electron that requires the least amount of energy.

Additional examples of photoelectron spectra data are available at <http://www.chem.arizona.edu/chemt/Flash/photoelectron.html>. Open this web page. To display the first spectrum, click on hydrogen in the periodic table.  
Bodner, Spencer and textbook. 5<sup>th</sup> Edition Wiley and Sons.

<http://www.cbc.arizona.edu/rss/pes/tutorials/tutorials.htm>

It is recommended that you have the Shells Activity for reference while working on this activity. The Shells Activity is available at [http://genchem1.chem.okstate.edu/CCLIEMD09/Shells\\_Activity.pdf](http://genchem1.chem.okstate.edu/CCLIEMD09/Shells_Activity.pdf)

Look at the PES spectrum for Hydrogen shown in Figure I.

1. The label on the  $y$ -axis is energy and the units are in megajoules( $\text{M J mol}^{-1}$ ). What does the  $x$ -axis depict?

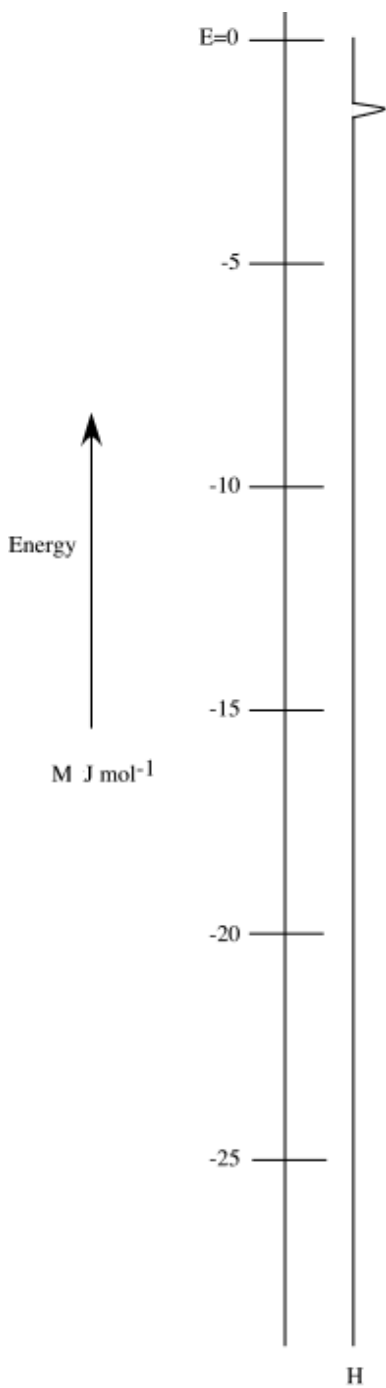


Figure I.

**The  $y$ -axis has units of megajoules per mol, the  $x$ -axis is number of electrons.**

2. What is interesting about the photoelectron spectrum for hydrogen atom and the first ionization energy for hydrogen?

**Since hydrogen has only one electron we would expect its photoelectron spectrum to consist of a single peak. The energy ( $y$ -axis) is  $1.312 \text{ MJ mol}^{-1}$ . Which is the same as the 1<sup>st</sup> ionization energy for hydrogen ( $1312 \text{ KJ mol}^{-1}$ ).**

3. Helium is next, but before looking at its photoelectron spectrum;
  - a. how many electrons does helium have in its first shell?

**Helium has two electrons. Remember the way the PES works...only one electron can be removed per atom. If we sample enough atoms we will obtain the energy of both electrons. So the issue is, does the spectrum consist of one peak that integrates for two electrons, or two peaks, of different energy each integrating for one electron.**

- b. Refer back to the Shells Activity, and obtain the first ionization energy for a helium atom.

**The first ionization energy for helium was  $2373 \text{ KJ mol}^{-1}$ .**

- c. Can you predict what the PES would look like if the same amount of energy is required to remove each of the electrons? If different amounts of energy are required to remove each electron? Go to Figure I and sketch each case.

**So the issue is, does the spectrum consist of one peak that integrates for two electrons, or two peaks, of different energy each integrating for one electron.**

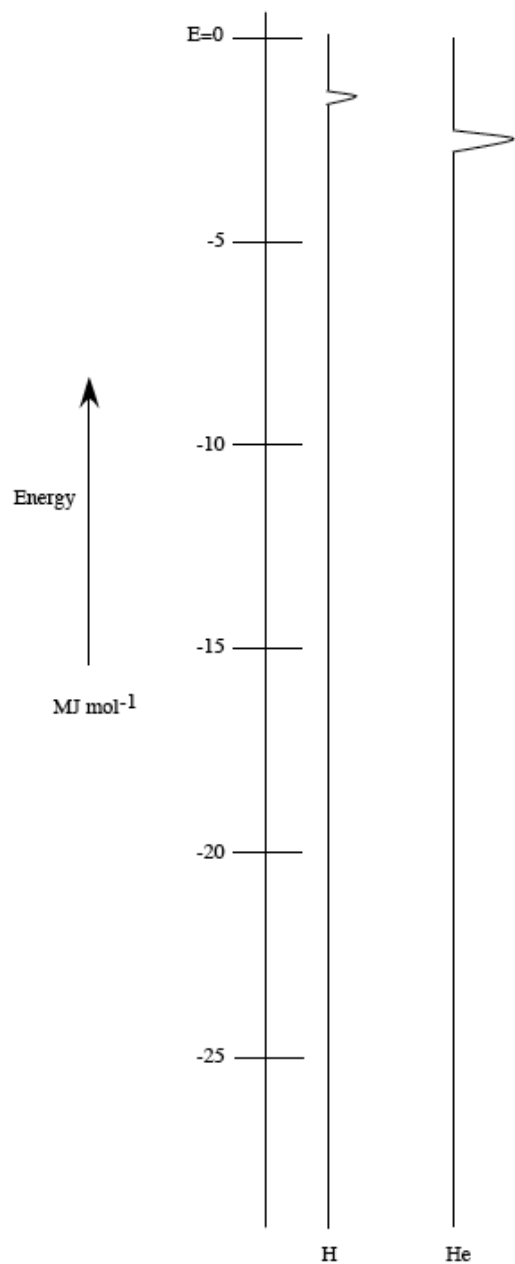


Figure II: PES for Hydrogen and Helium

4. Look at the PES in Figure II. and compare it to the prediction from the previous question. Describe what you see and the conclusion(s) you reached? (Note: be sure to comment about the relative energy of the peak(s) and the number of electrons for each peak in the PES for He and the PES for H.)

**Note: The PES spectra show the energy of every electron in an atom, while the ionization energy information only provides the energy of the electron in the atom that is the easiest to remove. The PES spectrum of hydrogen and helium**

**shows that the electrons in helium are at lower energy, therefore requiring more energy to remove each electron.**

5. The next element is lithium.
  - a. How many electrons does lithium have and what shells do those electrons occupy?

**Lithium has three electrons, two electrons in the first shell, which is at low energy, and one electron at higher energy.**

- b. Before looking at the PES for lithium predict what you believe the spectrum would look like? Note: you do not have to predict the exact energies of each electron but you can make reasonable estimates based on the first ionization energy for lithium and the PES for helium. Use the data for lithium from Shell Activity to help make your prediction.

**When the students predict there are two peaks, then ask what is the relative energy of each peak and how do the peaks integrate for numbers of electrons.**

**The peak at lowest energy (so it takes the most energy to remove) should integrate for two electrons, and the peak at higher energy should integrate for one electron. Which is exactly what you see.**

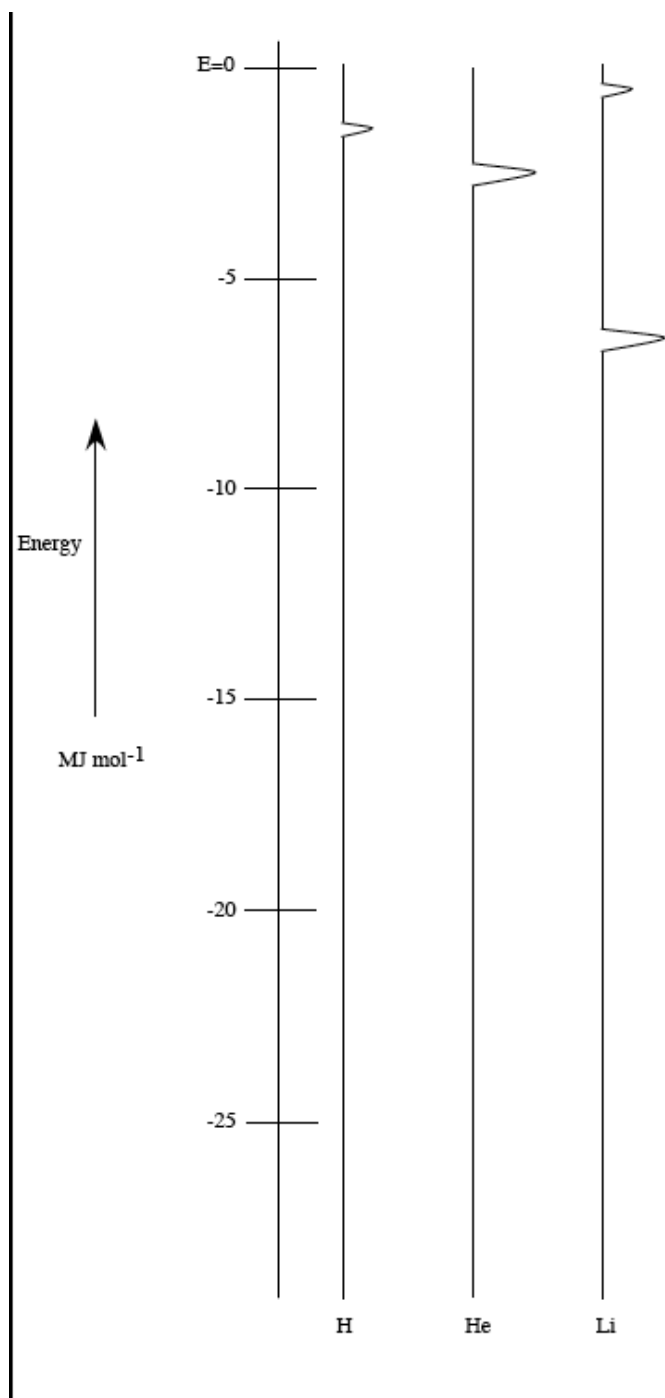


Figure III PES for H, He and Li

- Look at the PES in Figure III. and compare it to the prediction from the previous question. For each peak in the PES identify the shell the electrons represented by that peak occupy. Describe what you see and the conclusion(s) you reached? (Note: be sure to comment about the relative energy of the peak(s) and the number of electrons for each peak in the PES for Li.)

**The peak at lowest energy (so it takes the most energy to remove) should integrate for two electrons, and the peak at higher energy should integrate for one electron. Which is exactly what you see.**

6. The next element is beryllium.
  - a. For the PES for beryllium predict how many peaks, the number of electron for each peak and the estimate the relative energies. How many electrons does beryllium have and what shells do those electrons occupy?

**There are four electrons in beryllium, two in the first shell, at low energy, and two in the second shell at high energy. For beryllium there should be two peaks, one at low energy and one at higher energy. Each should integrate for two electrons. This is exactly what the PES looks like.**

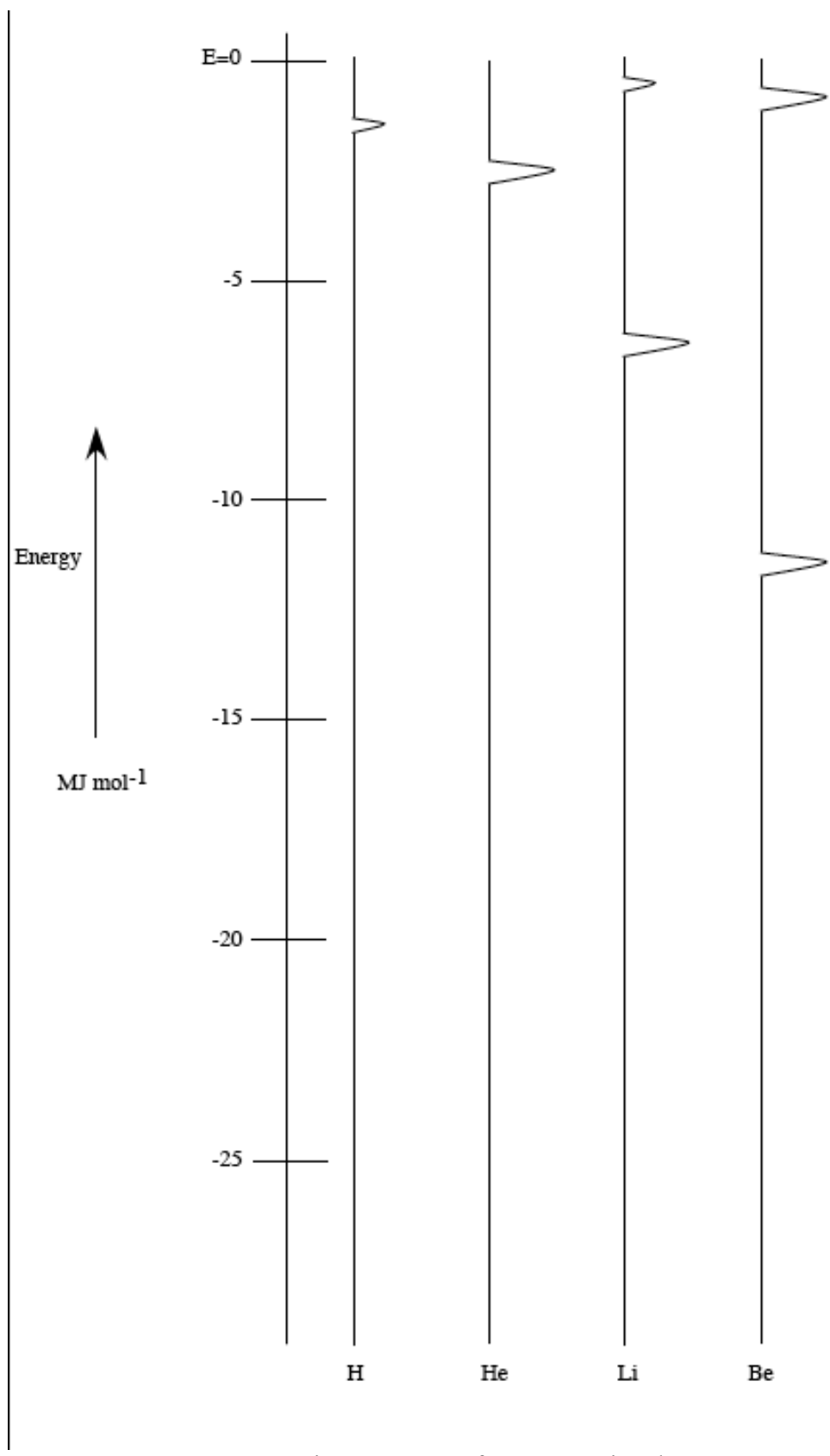


Figure IV. PES for H, He, Li and Be



7. The next element is boron.
  - a. How many electrons does boron have and what shells do those electrons occupy?

**Boron has five electrons, two in the first shell at low energy, and three in the second shell at higher energy. It is important to get the students to describe the energies of the electrons in this way, so they will then predicts only two peaks in the PES. The peak at lower energy integrates for two electrons and the peak at high energy integrates for three electrons.**

- b. For the PES for boron predict how many peaks, the number of electron(s) for each peak and estimate the relative energies.

**The peak at lower energy integrates for two electrons and the peak at high energy integrates for three electrons.**

- c. Describe the experimental PES for boron. Briefly describe how to interpret the PES for boron.

**NOTE: The PES for boron has three peaks! The peak at lowest energy has two electrons so we see the electrons for that peak are the electrons in the first shell. Boron has three electrons in the second shell, but according to the PES those three electrons have different energies, although relatively close together. One interpretation of this observation is that the three electrons in the second shell occupy two 'subshells' of different energy. So the idea of subshells within shells must be introduced to understand the different energies of the three electrons. If the PES had shown two peaks, one integrating for two electrons and one integrating for three electrons the concept of a subshell would not be required.**

8. Predict what changes in the PES you would expect to see going from carbon to neon? Look at the PES for these second period elements.

**We expect the elements from carbon to neon to all show three peaks with the two peaks at low energy moving to lower energy for each atom as we move across the periodic table. The peak at high energy continues the integrate for more electrons (two electrons for carbon, three electrons for nitrogen, ...to six electrons for neon).**

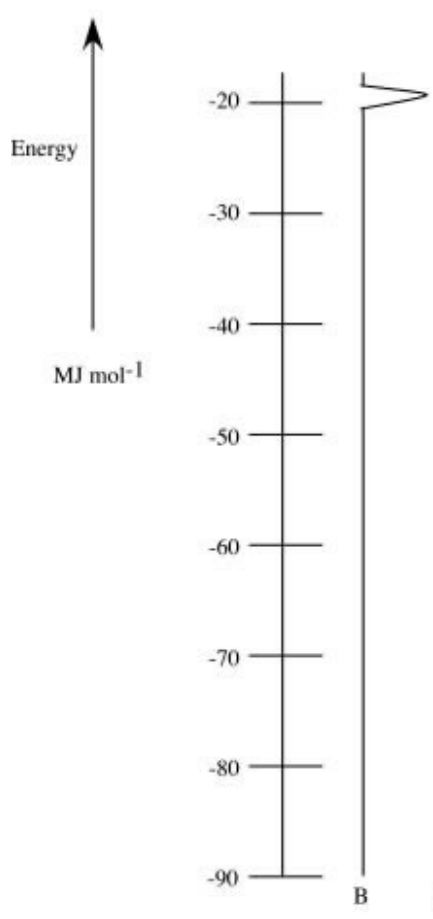
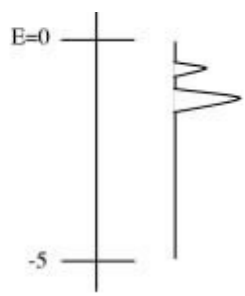


Figure IV. PES for Boron (B)

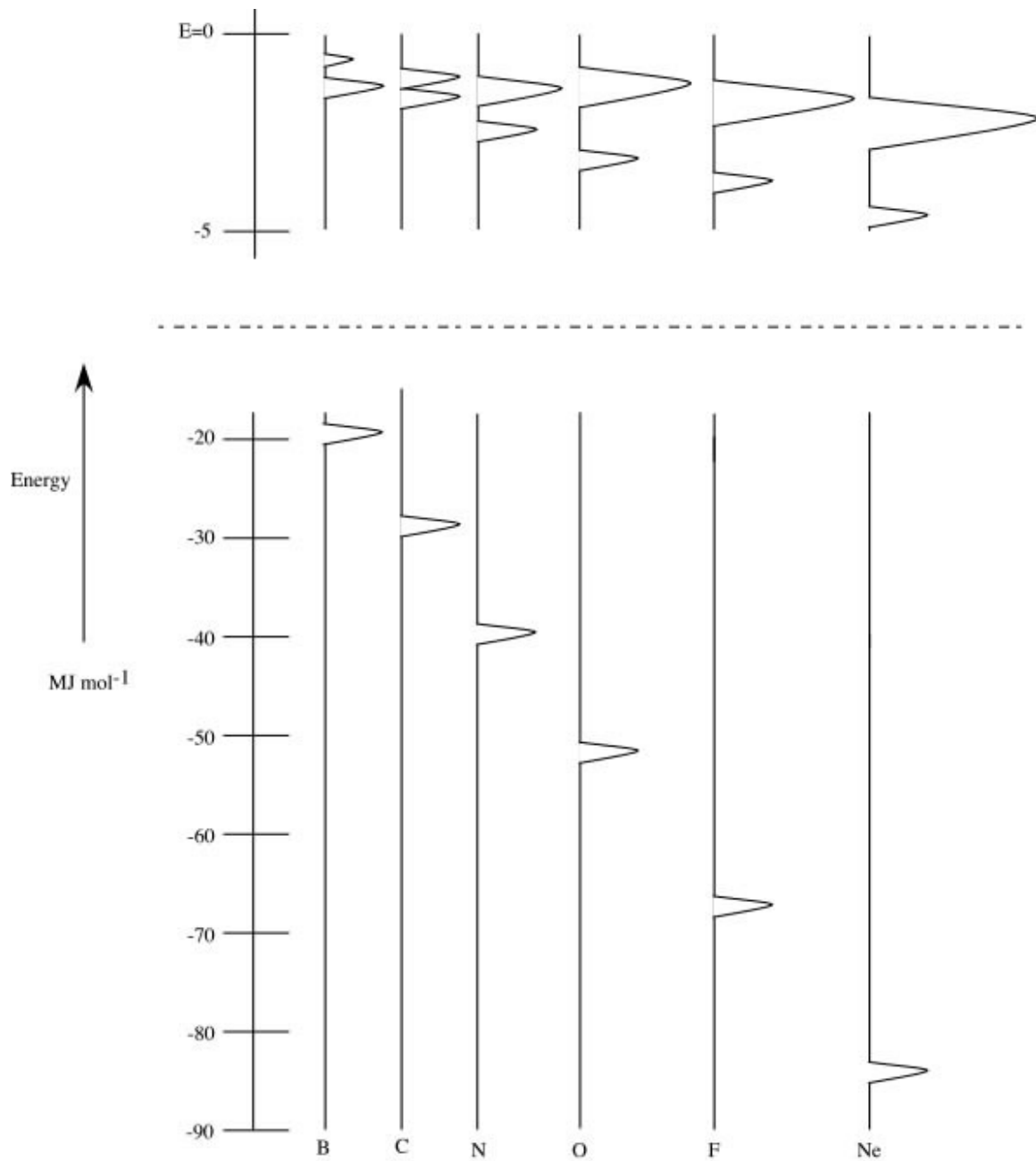


Figure V. PES for Boron (B) through Neon (Ne)

9. Answer the following questions after looking at the PES for hydrogen through neon.

- a. Would you agree or disagree with the following statement? Explain.  
'The electrons in the second shell all have the same energy.'

**Disagree, clear the PES show there are two different types of electrons, two have the same energy and six have a different, but identical energy.**

- b. How many 'subshells' are found in the second shell? How many 'subshells' are found in the first shell?

**So there are two subshells in the second shell. In the first shell there is only one subshell. This is a little complex for the student but we have to ask them to accept it. This is helped by pointing out in the second shell there are two electrons in one of the subshells and six in the other. In the first shell there are two electrons so we can claim that those two electrons must be in a subshell similar to one of the subshells in the second shell.**

- c. How many electrons are in each subshell in the second shell? In the first shell?

**Two electrons in the subshell of lower energy and six electrons in the subshell of higher energy.**

- d. Moving systematically from lithium to neon;  
i. How many electrons are in the first shell?

**Always two electrons in the first shell.**

- ii. what happens to the energy required to remove an electron in the first shell moving from left to right in the second period? Support your observation with a meaningful explanation.

**The energy of the electrons in the first shell becomes lower and lower from lithium to neon, because the number of protons increases from lithium to neon. Since these electrons are closest to the nucleus, they experience the full nuclear charge, so with each added electron it takes more energy to remove those electrons.**

- iii. What happens to the energy of the electrons in the outer most shell?

**The energy of the electrons in the outer most shell also decreases as we move from lithium to neon. These electrons are further from the nucleus, and are shielded by the two inner shell electrons. But the shielding of the inner shell electrons is constant going across the period, while the nuclear charge is increasing so the energy of the electrons decreases, but since the electrons experience a lower nuclear charge and are further away from the nucleus, the energy required to remove them is less compared to electrons in the first shell.**

10. Look at the PES for the elements in the third period (sodium – argon) and briefly describe your observations. Any surprises? Briefly explain your observations.

**We do not have these spectra in this activity, but the PES for the third period pattern that of the second period. So for Sodium the PES shows four peaks with the peak at highest energy integrating for one electron (3s). Magnesium also has four peaks, but the peak at highest energy integrates for two electrons. Remember the three peaks at lower energy continue towards even lower energy with each added proton. At aluminum a fifth peak appears at high energy and integrates for one electron. Moving across from aluminum to argon the peak at highest energy grows from one electron to six electrons (3p subshell).**

A notation has been agreed upon for writing an electron configuration to identify the location of the shell and subshell of each electron in an atom. Shells are labeled with a number; 1, 2, 3, etc. and subshell are labeled with letters; *s*, *p*, *d*, and *f*. Every shell contains an *s* subshell.

11. Write the complete electron configuration for the first ten elements in the periodic table?

H	$1s^1$
He	$1s^2$
Li	$1s^2 2s^1$
Be	$1s^2 2s^2$
B	$1s^2 2s^2 2p^1$
C	$1s^2 2s^2 2p^2$
N	$1s^2 2s^2 2p^3$
O	$1s^2 2s^2 2p^4$
F	$1s^2 2s^2 2p^5$
Ne	$1s^2 2s^2 2p^6$

12. Look at the PES for potassium, calcium and scandium. Something very interesting happens when we look at the PES for scandium that has not occurred in any element prior to scandium. Briefly explain.

**The interesting thing happens with scandium. At potassium and calcium the sixth peak integrates for one electron for potassium and then it integrates for two electrons in calcium. But with scandium the new peak (for the 3d subshell) actually appears at lower energy than the peak for the 4s subshell. This is different than for any other case to this point. Every time a new subshell was added the new peak is always at the highest energy, but not in the case for scandium.**

13. If one electron is removed from scandium, which electron (identify the shell and subshell) requires the least amount of energy to remove?

**The electron must come from the highest energy (the electron that requires the least amount of energy to remove) which comes from the 4s subshell. Remember the energy for the electron in the 3d subshell for scandium comes in at lower energy compared to the 4s.**

This activity along with the activity that invents shells provide experimental data for an electron configuration for elements in the periodic table.

We have not invented orbitals or electron spin.

Another experiment was performed by two researchers in 1920. Stern and Gerlach investigated the behavior of gas phase silver atom moving in a magnetic field. To interpret their experiment they had to conclude that the electron has another property besides mass and charge. What they called spin. Since the electron has charge and is 'spinning' it can produce a magnetic field. The Stern-Gerlach experiment demonstrated that electrons produce magnetic fields. The experiment suggested that there were two possible spin states for an electron. Silver has an odd number of electrons so must have an unpaired electron, and exhibits some magnetic properties. Elements with all the electrons paired are nonmagnetic.

Additional information regarding the behavior of the electron in terms of its spin has accumulated over the years.

- 1) electrons with the same spin do not like to be in the same region of space and therefore have a low probability of being close together. The region of space that electrons with opposite spin are excluded is called an orbital.
- 2) Electrons with opposite spin can occupy the same region of space.

The Pauli Exclusion Principle summarizes the behavior of electrons as it relates to spin an orbital occupancy. No more than two electrons can occupy an orbital, and the spins of these electrons must be opposite.

How can (2p subshell) six electrons distribute themselves? No more than two electrons can occupy the same region of space, and a 2p subshell can hold a maximum of six electrons than we can conclude that three unique regions of space each two electrons. So the question is how can these three regions of space (in 3-dimensional space) arrange themselves so they have the same energy and do not impinge on each other? We find that the only arrangement is the dumb-bell shape each aligned along the axis of a 3-dimensional Cartesian coordinate system.

NOTE: The PES spectrum that will be used in this activity will have energy on the y-axis and number of electrons on the x-axis. The energies on the y-axis are negative, so the lowest (most negative) energy is on the bottom of the graph and zero energy (the electron is separated from the nucleus) is at the top of the graph.

If we generate the energies of the electrons in the atoms using PES and place energy on the y-axis we can build the energy level diagram for a multi-electron atom. Doing it this way allows us only to show the energy level diagram with energies for only those subshells that exist in the atom.