What Is the Evidence for Energy Levels in Atoms?

Why are we doing this?

The number of valence electrons in the outermost shell of an atom is related to the position of the element on the periodic table. Therefore, the number of valence electrons is an important factor in determining the physical and chemical properties of the element. One such property is ionization energy. The ionization energy was previously defined in Activity 11 as the minimum energy needed to remove an electron from an atom. The most easily removed electron always resides in the valence shell, since that is the shell that is the farthest from the nucleus. For atoms with many electrons, we would expect that the energy needed to remove an electron from an inner shell would be greater than that needed to remove an electron from the valence shell, because an inner shell is closer to the nucleus and is not as fully shielded as the outer valence electrons. Thus, less energy is needed to remove an electron from an $n = 2$ shell than from an $n = 1$ shell, and even less is needed to remove an electron from an $n = 3$ shell. But do all electrons in a given shell require precisely the same energy to be removed? In order to answer this question, we must consider ionization energies in greater detail.

Your Learning Outcomes

You will be able to:

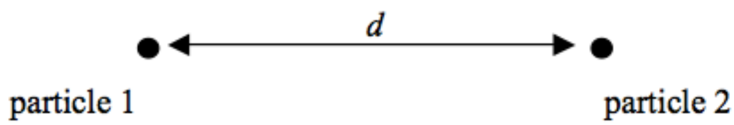
1. Describe the relationship between Coulombic Potential Energy, Ionization Energy, and the Kinetic Energy of ejected electrons.
2. Describe the technique and evidence provided by Photoelectron Spectroscopy.
3. Draw and interpret a photoelectron spectrum.

The Plan

1. Assign roles*.
   a. ***Manager*** – This person will keep the team on task and provide direction to the group. This person is responsible for uploading the group's work to Gradescope. Make sure you make a note of everyone in the group. You must add everyone's name when submitting your answers to Gradescope.
   b. ***Spokesperson*** – This person will represent the group be responsible for speaking for the group to the rest of the class.
   c. ***Recorder*** – This person will be responsible for recording the team's answers to the Critical Thinking Questions in an organized and coherent manner.
   d. ***Analyst*** – This person will be responsible for critical analysis of the team's work (i.e., the Devil's Advocate). This person should make sure everyone understands what is happening before the group moves forward.
2. Complete the Critical Thinking Questions as a group.
3. Submit your team's work via Gradescope. Groups may choose to work in a Word document or write out their answers on a separate sheet of paper. All work must be upload to Gradescope as a PDF file.

**Students may choose to complete this activity independently if they are unable to attend discussion due to illness or injury; in which case, the student must perform all roles and complete all aspect of the activity. To receive full credit, documentation as to the need for the absence from discussion must be included with the submission and your TA must be notified of the absence.*

Model 1: Coulombic Potential Energy



charge on particle 1 = q_1

charge on particle 2 = q_2

$$V = \frac{kq_1q_2}{d}$$

According to Coulomb, the **potential energy** (V) of two stationary charged particles is given by the equation above, where q_1 and q_2 are the charges on the particles (for example: –1 for an electron), d is the separation of the particles (in pm), and k is a positive-valued proportionality constant.

$$1 \text{ pm} = 10^{-12} \text{ m}$$

Critical Thinking Questions

1. Assuming that q_1 and q_2 remain constant, what happens to the magnitude of V if the separation, d, is increased?
   The magnitude of V decreases.

2. If the two particles are separated by an infinite distance (that is, $d = \infty$), what is the value of V?
   V=0

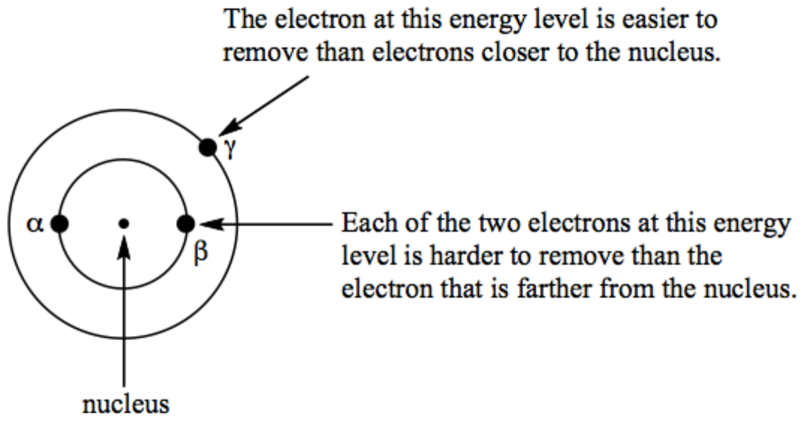
3. If d is finite, and the particles have the same charge (that is, $q_1 = q_2$), is $V > 0$ or is $V < 0$? Explain your answer.
   V must be positive (V>0).

4. If q for an electron is –1,
   a. what is q for a proton?
      +1
   b. what is q for a neutron?
      0
   c. what is q for the nucleus of a C atom?
      +6

5. Recall that a ^{1}H atom consists of a proton as the nucleus and an electron outside of the nucleus. Is the potential energy, V, of a hydrogen atom a positive or negative number? Explain your answer.
   V is a negative number because k(1)(–1)/d is negative. This indicates attraction between oppositely charged particles. A positive V would represent the repulsive energy generated between two like charged particles.

Model 2: Ionization Energies and Energy Levels.

We know that an electron in a given shell will require a certain energy to be separated from the atom. Thus, an electron can be said to occupy an **energy level** in an atom. Within our model, each electron must be in a shell at a particular distance from the nucleus, and the energy levels corresponding to these shells are **quantized**—that is, only certain discrete energy levels should be found.



Critical Thinking Question

6. Suppose that the values for the two energy levels for the atom in Model 2 are –0.52 MJ/mole and –6.26 MJ/mole.
   a. How much energy, in MJ, is required to remove electron "α" in Model 2 from one mole of neutral atoms?
      6.26 MJ
   b. What is the potential energy, *V*, of each of the three electrons in Model 2?
      α: -6.26 MJ/mole β: -6.26 MJ/mole γ: -0.52 MJ/mole
   c. Determine the ionization energies of each of the three electrons in Model 2.
      α: 6.26 MJ/mole β: 6.26 MJ/mole γ: 0.52 MJ/mole

Information

When comparing the energy level of two different electrons, the electron with the higher ionization energy is said to occupy the lower energy level.

Critical Thinking Question

7. Provide a statement, similar to the Information statement, that uses the potential energies of the electrons rather than the ionization energies.
   When comparing the energy level of two different electrons, the electron with the lower (more negative) potential energy is said to occupy the lower energy level.

Model 3: Photoelectron Spectroscopy (PES)

Ionization energies may be measured by the electron impact method, in which atoms in the gas phase are bombarded with fast-moving electrons. These experiments give a value for the ionization energy of the electron that is most easily removed from the atom—in other words, the ionization energy for an electron in the highest occupied energy level. An alternative, and generally more accurate, method that provides information on all the occupied energy levels of an atom (that is, the ionization energies of all electrons in the atom) is known as photoelectron spectroscopy or PES; this method uses a photon (a packet of light energy) to knock an electron out of an atom. Electrons obtained in this way are called photoelectrons.

Very high energy photons, such as very-short-wavelength ultraviolet radiation, or even x-rays, are used in this experiment. The gas phase atoms are irradiated with photons of a particular energy. If the energy of the photon is greater than the energy necessary to remove an electron from the atom, an electron is ejected with the excess energy
appearing as kinetic energy, $\frac{1}{2} mv^2$, where v is the velocity of the ejected electron. In other words, the speed of the ejected electron depends on how much excess energy it has received. So, if IE is the ionization energy of the electron and KE is the kinetic energy with which it leaves the atom, we have

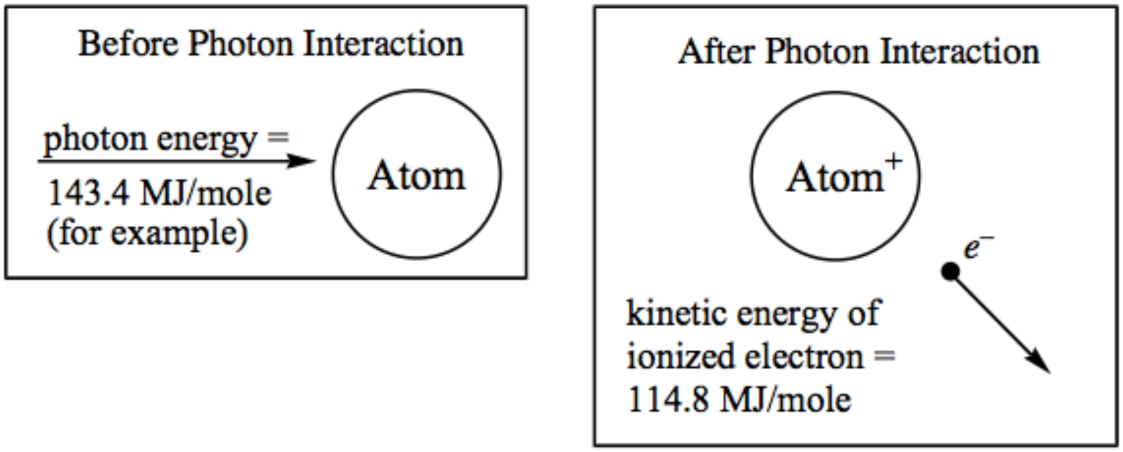
$$E_{photon} = IE + KE$$

or, upon rearranging the equation,

$$IE = E_{photon} - KE$$

Thus, we can find the ionization energy, IE, if we know the energy of the photon and we can measure the kinetic energy of the photoelectron. The kinetic energy of the electrons is measured in a photoelectron spectrometer.

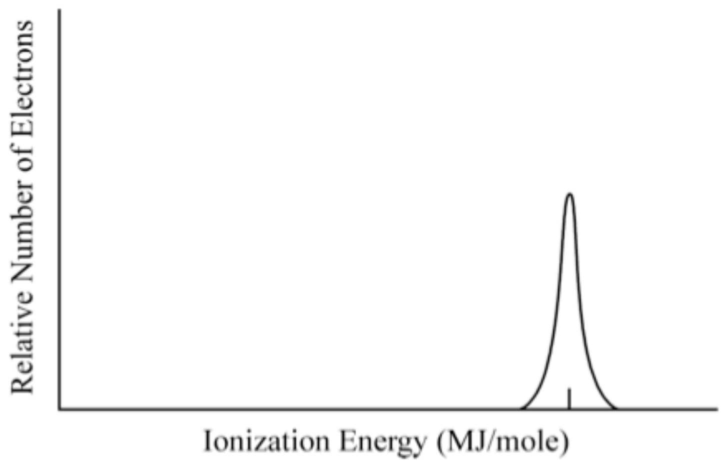
Figure 1: Photoelectron spectroscopy of a hypothetical atom.



If photons of sufficient energy are used, an electron may be ejected from any of the energy levels of an atom. Each atom will eject only one electron, but every electron in each atom has an (approximately) equal chance of being ejected. Thus, for a large group of identical atoms, the electrons ejected will come from all possible energy levels of the atom. Also, because the photons used all have the same energy, electrons ejected from a given energy level will all have the same energy. Only a few different energies of ejected electrons will be obtained, corresponding to the number of energy levels in the atom.

The results of a photoelectron spectroscopy experiment are conveniently presented in a **photoelectron spectrum**. This is essentially a plot of the number of ejected electrons (along the vertical axis) vs. the corresponding ionization energy for the ejected electrons (along the horizontal axis). It is actually the kinetic energy of the ejected electrons that is measured by the photoelectron spectrometer. However, as shown in the equation above, we can obtain the ionization energies of the electrons in the atom from the kinetic energies of the ejected electrons. Because these ionization energies are of most interest to us, a photoelectron spectrum uses the ionization energy as the horizontal axis.

Figure 2: A simulated photoelectron spectrum of the hypothetical atom in Figure 1.



Critical Thinking Questions

8. Use the data presented in Figure 1 to verify that the IE of the ejected electron is 28.6 MJ/mole.
   143.4 MJ/mole - 114.8 MJ/mole = 28.6 MJ/mole.

9. What determines the position of each peak (where along the horizontal axis the peak is positioned) in a photoelectron spectrum?
   The position of a peak is determined by the ionization energy of the electron ejected.

10. What is the numerical value at the position of the hatch mark in the photoelectron spectrum of Figure 2?
    28.6 MJ/mole

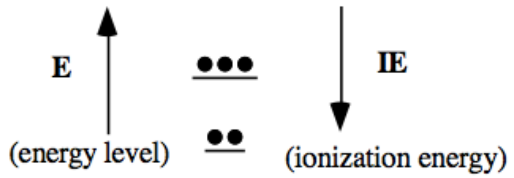
11. What energy is associated with the energy level of the electron in Figure 2?
    -28.6 MJ/mole.

12. What determines the height (or intensity) of each peak in a photoelectron spectrum?
The number of electrons at that energy level.

13. Explain why it is not possible to determine the number of electrons in an individual hypothetical atom from the photoelectron spectrum in Figure 2.
Regardless of the number of electrons at this ionization energy (28.6 MJ/mole), the spectrum would look the same.

Model 4: The Energy Level Diagram of Another Hypothetical Atom.

A hypothetical atom in a galaxy far, far away has 2 electrons at one energy level and 3 electrons at another energy level as shown in the energy level diagram below:

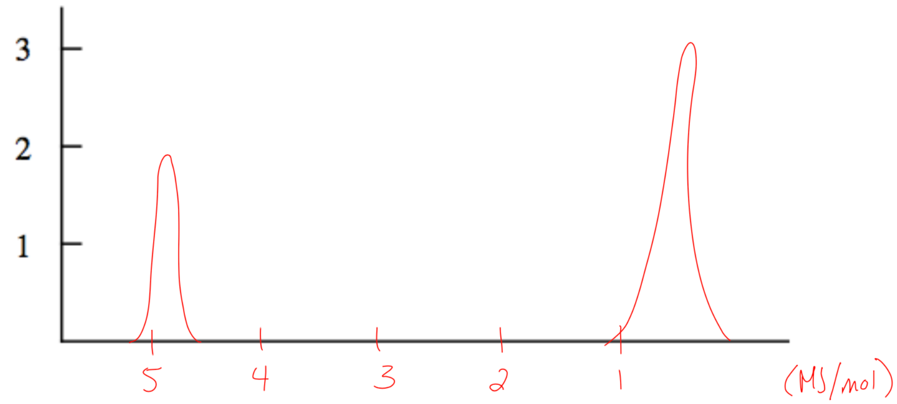


Critical Thinking Questions

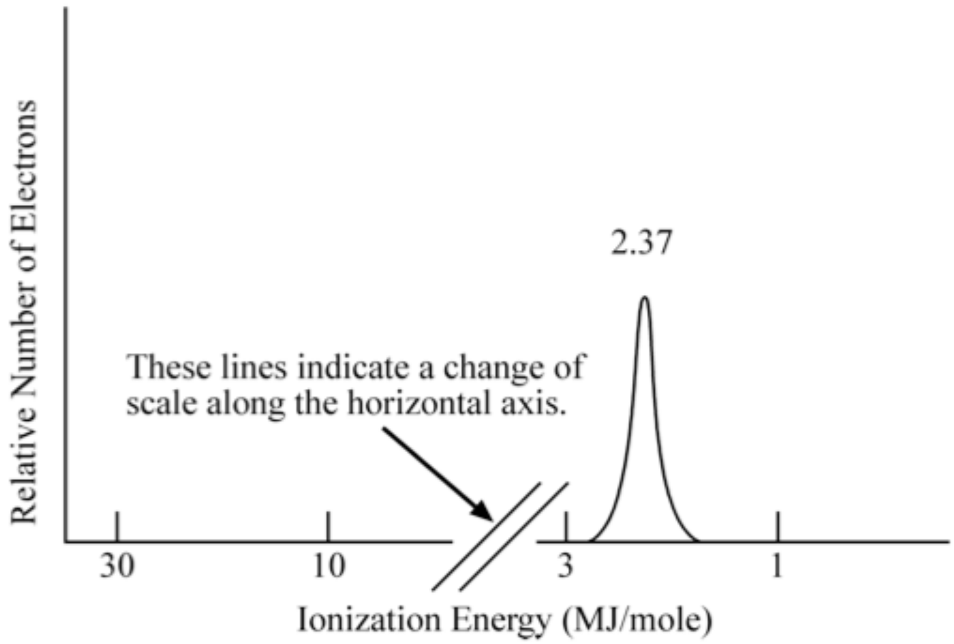
14. How many peaks (1, 2, 3, 4, 5) will appear in a photoelectron spectrum of a sample of this hypothetical atom? Why?
There should be two peaks because there are electrons at two different energy levels.

15. Describe the relative height of the peaks in the photoelectron spectrum of a sample of this hypothetical atom.
The relative heights of the peaks will be 3 to 2.

16. Suppose that the two energy levels are –0.85 MJ/mole and –4.25 MJ/mole. On the axes below, make a sketch of the photoelectron spectrum of a sample of this hypothetical atom. Make sure to label the axes appropriately.



Model 5: A Simulated Photoelectron Spectrum of an "Unknown" Atom.



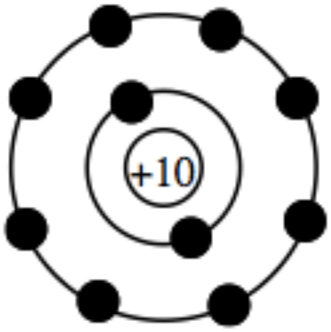
Critical Thinking Questions

17. Based on the number of peaks (one), the intensity of the peak, and your understanding of the shell model:
    a. Explain why it is not possible to determine if the "unknown" atom is H or He?
    The single peak indicates that all (one or more than one) electrons are at the same energy level.

    b. Explain why the "unknown" atom cannot be Li.
    Li has two different types of electrons (in two different shells) so there would be 2 peaks.

18. Based on the value of the IE given in Model 5 above and on the values given in Table 1 of Discussion Activity 10, identify the "unknown" atom.
    The unknown atom is He. The ionization energy matches that of He.

Model 5: The Neon Atom.



Let us now predict what the photoelectron spectrum of Ne will look like, based on our current model of the Ne atom. In this model, there are 2 electrons in the n =1 shell, and 8 electrons in the n = 2 shell of a Ne atom. Assuming that all of the electrons in each of the shells has the same energy, we would expect two peaks in the photoelectron spectrum. One peak, from the electrons in the n = 2 shell, should appear at an energy of 2.08 MJ/mole, because that is the first ionization energy of Ne as determined previously. The second peak should be at a significantly higher energy, because it corresponds to the ejection of electrons from the n = 1 shell, which is significantly closer to the nucleus. At this point we do not have any good way of estimating what that energy is, but we know that it will be a lot higher than 2.08 MJ/mole. Finally, we also can predict the relative sizes of the two peaks—that is, the relative areas under the two curves on the spectrum. Recall that in photoelectron spectroscopy, the bombarding photon ejects an electron at random from each of the atoms in the sample. Thus, of the 10 electrons in Ne, we would expect that 2/10 of the time the electron is ejected from the n = 1 shell, and 8/10 of the time it is ejected from the n = 2 shell. The size of the peak in the spectrum is determined by the relative number of electrons with a given IE. Thus, the peak at 2.08 MJ/mole should be 4 times as large as the peak at a much higher energy, which corresponds to the ejection of electrons from the n = 1 shell. *To summarize, our prediction is that the photoelectron spectrum of Ne should consist of two peaks, one at an energy of 2.08 MJ/mole and one at much higher energy, and the relative sizes of these two peaks should be 4:1.*

Critical Thinking Questions

19. The peak due to the n = 1 shell is predicted to be at a much higher ionization energy than the n = 2 peak because the n = 1 shell is "significantly closer to the nucleus." Why is the distance of the shell from the nucleus important in determining the corresponding peak position in the photoelectron spectrum?
    Electrons that are closer to the nucleus are harder to remove.

20. Why is it expected that 2/10 of the ejected electrons will come from the n = 1 shell, and 8/10 of the electrons from the n = 2 shell?
    Because there are 2 electrons in the first shell and 8 electrons in the second shell.

21. Make a sketch of the predicted photoelectron spectrum of Ne based on the description given above. Indicate the relative intensity (peak size) and positions of the two peaks.
    The spectrum should have two peaks with a ratio of intensities of 8 (low ionization energy) to 2 (high ionization energy).