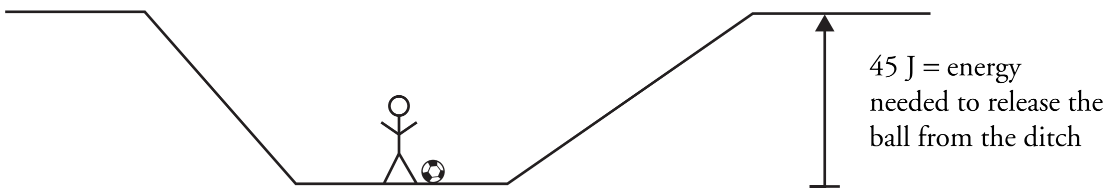
# Photoelectron Spectroscopy

What does a photoelectron spectrum tell us about the structure of an atom?

## Why?

When scientists first discovered X-rays, they realized they could do more than just make images of people's bones. X-rays could also allow them to "see" inside the atom. They could not do this directly, but in looking for patterns in ionization energy data they were able to determine the energy levels and sublevels of electrons and how many electrons were in each level.

## Model 1 – A Soccer Player in a Ditch




1. Consider Model 1. Imagine that a soccer player is trying to kick a ball out of a ditch.
   *a.* What force of attraction is keeping the soccer ball at the bottom of the ditch?

   *b.* Which type of energy must be overcome to get the ball out of the ditch—potential or kinetic?

   *c.* Which type of energy must the ball have to get out of the ditch—potential or kinetic?

2. How much energy must be given to the ball by kicking it to get it out of the ditch?

3. Describe what happens to the ball if the soccer player's kick provides:
   *a.* 30 J of energy to the soccer ball in the ditch.

   *b.* 45 J of energy to the soccer ball in the ditch.

   *c.* 60 J of energy to the soccer ball in the ditch.

4. For each of the scenarios in Question 3 where the ball successfully leaves the ditch, determine the kinetic energy the ball will have when it reaches the top of the ditch.

5. Construct an algebraic equation that shows the relationship among the energy of the player's kick ($KE_{kick}$), the potential energy of gravity on the ball (PE) and the kinetic energy the ball will have as it leaves the ditch ($KE_{roll}$).

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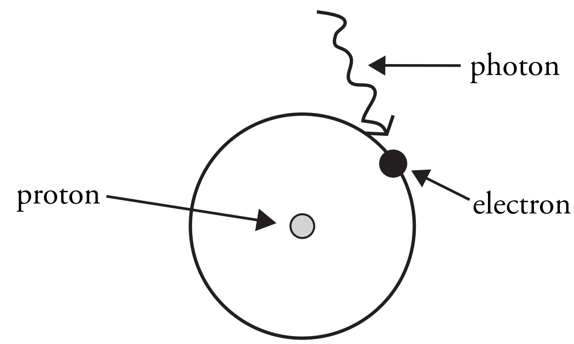
## Model 2 – A Hydrogen Atom




6. Refer to Model 2.

   *a.* What force of attraction holds the electron in the hydrogen atom?

   *b.* Which type of energy needs to be overcome to remove an electron from the atom—potential or kinetic?

   *c.* What is supplying the energy to remove the electron from the atom in Model 2?

7. Fill in the table below to show how the hydrogen atom (Model 2) parallels the ball in the ditch analogy (Model 1).

| **Soccer Ball in the Ditch** | **Hydrogen Atom** |
|---|---|
| Gravity | |
| Ball | |
| Player's kick | |

8. Consider the atom in Model 2.
   *a.* If the photon has less than the minimum energy needed to eject the electron from the atom, what will happen to the electron?

   *b.* If the photon has exactly the minimum energy needed to eject the electron from the atom, what will happen to the electron?

   *c.* If the photon has more than the minimum energy needed to eject the electron from the atom, what will happen to the electron?

9. The amount of energy necessary to remove an electron from an atom is called the **ionization energy** of that electron. What part of the analogy in Model 1 represents the ionization energy?

10. What is the relationship between the ionization energy of an electron and the net attractive force that holds an electron in an atom?

11. The electrons that escape the atom after bombardment by a photon are called **photoelectrons**. Why might this be an appropriate name for these electrons?

## Read This!

**Photoelectron spectroscopy (PES)** allows scientists to determine the ionization energy of not only valence electrons, but all electrons in an atom. In PES, a gaseous sample of atoms is bombarded by X-rays or ultraviolet light (photons) of known energy. The kinetic energies of the photoelectrons that are ejected from the atoms are measured. The number of photoelectrons with the same kinetic energies is noted. Although only one electron is removed from each atom, several atoms are ionized in the experiment. The electron that is removed will differ from atom to atom. The collective result provides information about all the electrons in an atom of the sample.

12. Construct an algebraic equation that shows the relationship between the energy of the photon ($KE_{photon}$), the ionization energy (IE) and the kinetic energy of the photoelectron ($KE_{electron}$) as it leaves the atom.

13. If the kinetic energy of the photon is exactly equal to the ionization energy, the kinetic energy of the photoelectron should be zero. Verify that your equation is consistent with this idea. If not, revise your equation.

14. Consider the equation you wrote in Question 12. What pieces of data do you need to know to calculate the ionization energy of a given electron?

15. A photoelectron experiment is performed on a sample of silicon using photons with an energy of $1.43 \times 10^5$ kJ/mole. Photoelectrons are generated that have a kinetic energy of $1.34 \times 10^5$ kJ/mole. What was the ionization energy of these electrons?

16. In the previous question, was only one atom of silicon involved, or were many atoms involved? What evidence do you have from the question to support your answer?

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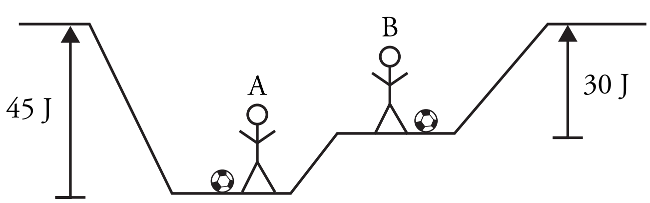
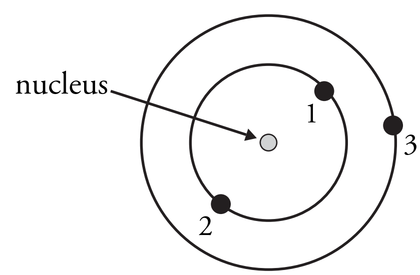
## Model 3 – Multiple Energy Levels

**Soccer Balls in a Ditch**




**Lithium Atom**



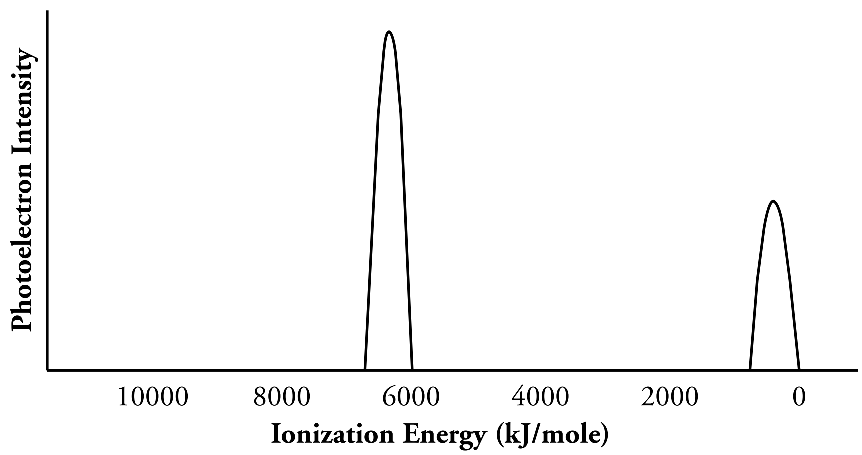

17. In the ditch diagram in Model 3, which player (A or B) will need to put more energy into their soccer ball to get it out of the ditch? Explain your answer in terms of both depth and potential energy.

18. Consider the electrons in an atom of lithium as diagrammed in Model 3. Which electron, 1 or 3, will require more energy to be removed? Support your answer by discussing the attractive forces in the atom and how they might be different for electrons 1 and 3.

19. Compare electrons 1, 2 and 3 in terms of their ionization energy. Explain your reasoning.

20. If a large number of lithium atoms are ionized in a PES experiment, each losing one randomly chosen electron, which ionization energy will be recorded more often, the lower IE or the higher IE? Justify your answer.

## Model 4 – Photoelectron Spectra of Lithium




21. Refer to the graph in Model 4.
    *a.* What are the units of the *x*-axis?

    *b.* What is unusual about the way the *x*-axis values are graphed?

    *c.* Which of the peaks in the graph represents electrons that are more tightly held by the nucleus? Explain your reasoning.

22. How many atoms of lithium were ionized (theoretically) in order to obtain the data for the spectrum above?

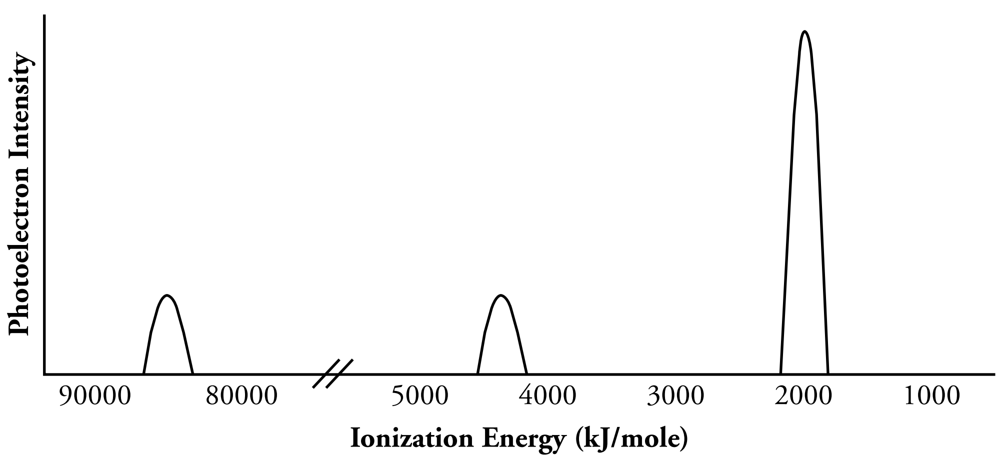
23. Based on the energy values of the peaks, label each peak with the electrons in a lithium atom (see Model 3) to which they correspond.

24. Why are there only two peaks and not three in the lithium spectrum in Model 4?

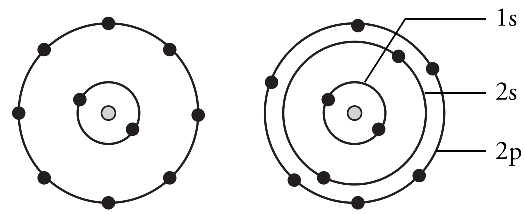
25. Why is the higher energy peak about twice as high as the lower energy peak?

26. What does the number of peaks in a PES spectrum reveal about the energy sublevels occupied by electrons in an atom?

27. If the photoelectric spectrum of Ne is:




Which shell model below best matches this spectrum? Explain your reasoning in one or two complete sentences.

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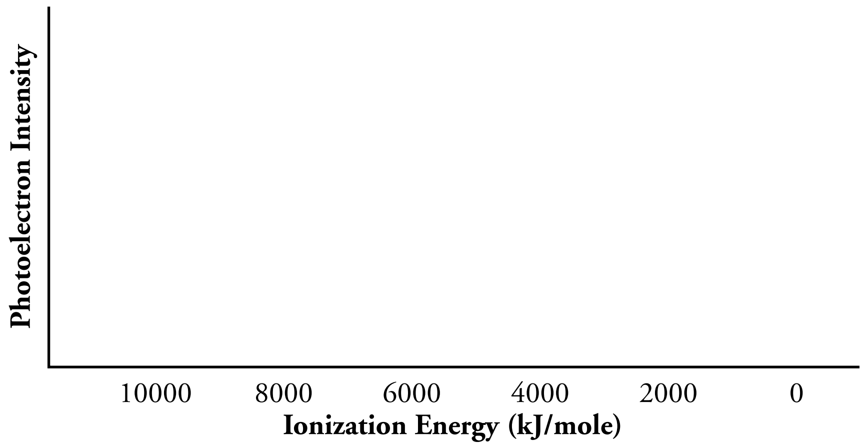
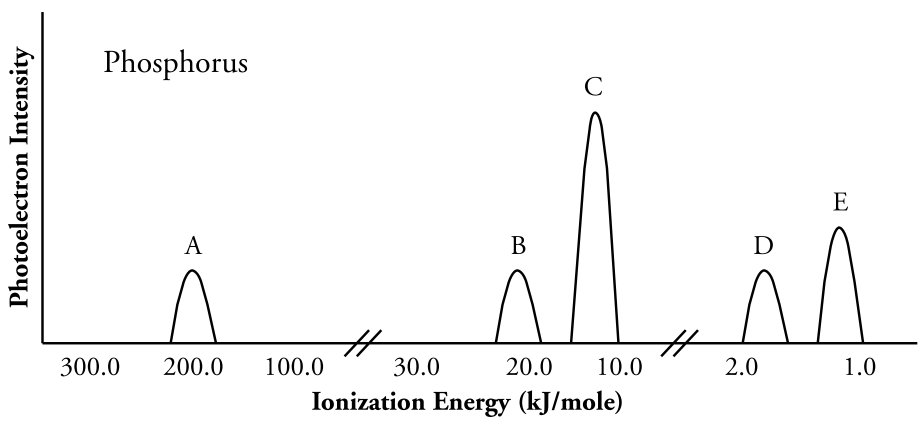
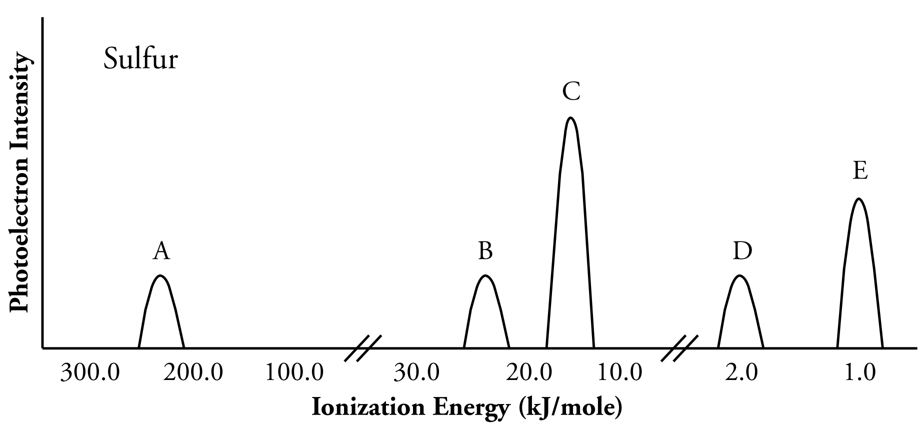
28. Look back at Model 4. Using the lithium PES spectrum as a starting point, show how the spectrum of the next larger element (beryllium) might be different. (Recall that Be will have one more proton in its nucleus and one more electron in its sublevels.)




## Model 5 – Sulfur and Phosphorus



29. Refer to Model 5.

    *a.* The atomic structure of which atoms are represented by the PES spectra shown?

    *b.* List the number of protons and electrons in each atom.

    *c.* Draw a shell model for each atom based on the PES spectrums below. Label each shell in your models with the corresponding PES peak from Model 5.

30. Consider the attractive and repulsive forces in the atoms of sulfur and phosphorus.

    *a.* Explain why most of the peaks in the sulfur spectrum are shifted to the left relative to the peaks in the phosphorus spectrum.

    *b.* Explain why peak E in the sulfur spectrum is shifted slightly right compared to peak E in the phosphorus spectrum.

31. Sketch the PES spectrum for chlorine using the spectra in Model 5 as a guide.

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## Extension Questions

32. PES experiments frequently use an X-ray wavelength of 0.8340 nm. Recall that the energy of a photon can be calculated using the equation $E = hc/\lambda$.

    *a.* Calculate the energy of the X-ray photon used in the PES experiment described.

    *b.* Calculate the ionization energy of a photoelectron with a kinetic energy of $2.372 \times 10^{-16}$ J. Include appropriate units.

    *c.* The value you have calculated is the ionization energy of a single electron. Generally we express the ionization energy of a mole of electrons. What would be the ionization energy of a mole of the electrons from part *a*? Include appropriate units and significant figures.

33. How are photoelectron spectroscopy and the photoelectric effect related?

34. What is the maximum wavelength of light that could be used to eject an electron with an ionization energy of 340 kJ/mole?

35. Photoelectron spectroscopy experiments must be performed under ultra-high vacuum conditions. Propose a reason for these extreme conditions.