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?
      *Gravity is keeping the soccer ball in the ditch.*
   b. Which type of energy must be overcome to get the ball out of the ditch—potential or kinetic?
      *Gravity is potential energy.*
   c. Which type of energy must the ball have to get out of the ditch—potential or kinetic?
      *The ball must have kinetic energy to get out of the ditch.*

2. How much energy must be given to the ball by kicking it to get it out of the ditch?
   *The ball needs at least 45 J of energy to leave 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.
      *The ball would not reach the top of the ditch and would roll back down to the bottom.*
   b. 45 J of energy to the soccer ball in the ditch.
      *The ball will get to the top of the ditch and stop.*
   c. 60 J of energy to the soccer ball in the ditch.
      *The ball will leave the ditch and keep moving.*
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.
   
a. The ball does not leave the ditch.
   
c. The ball leaves the ditch and has zero KE at the top.
   
d. The ball leaves the ditch and has 15 J of KE at the top.

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 ($KE_{roll}$).

$$KE_{kick} = PE + KE_{roll}$$

Model 2 – A Hydrogen Atom

6. Refer to Model 2.
   
a. What force of attraction holds the electron in the hydrogen atom?
   
   There is Coulombic attraction between the positively-charged nucleus and the electron.
   
b. Which type of energy needs to be overcome to remove an electron from the atom—potential or kinetic?
   
   Coulombic attraction is potential energy.
   
c. What is supplying the energy to remove the electron from the atom in Model 2?
   
   The photon is supplying the energy to remove the electron.
   
7. Fill in the table below to show how the hydrogen atom (Model 2) parallels the ball in the ditch analogy (Model 1).

<table>
<thead>
<tr>
<th>Soccer Ball in the Ditch</th>
<th>Hydrogen Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity</td>
<td>Coulombic Attraction</td>
</tr>
<tr>
<td>Ball</td>
<td>Electron</td>
</tr>
<tr>
<td>Player's kick</td>
<td>Photon</td>
</tr>
</tbody>
</table>
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?
      
      The electron will stay in the atom.
   
   b. If the photon has exactly the minimum energy needed to eject the electron from the atom, what will happen to the electron?
      
      The electron will be removed from the atom, but will have zero KE after being removed.
   
   c. If the photon has more than the minimum energy needed to eject the electron from the atom, what will happen to the electron?
      
      The electron will be removed from the atom and will have some KE after being removed.
   
9. The amount of energy necessary to remove an electron from an atom is called the **ionization energy**. What part of the analogy in Model 1 represents the ionization energy?

   The ionization energy in Model 2 is analogous to the 45 J of energy needed to get the ball out of the ditch in Model 1.

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

    The ionization energy is equal to, but opposite in sign to the Coulombic attraction 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?

    Photoelectrons is an appropriate name because they are electrons that have been removed from an atom by high energy photons.

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**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.

    $$KE_{photon} = IE + KE_{electron}$$

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Photoelectron Spectroscopy
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.

Example: \[ KE_{\text{photon}} = 30 \text{ kJ/mole}; \ IE = 30 \text{ kJ/mole} \]
\[ 30 \text{ kJ/mole} = 30 \text{ kJ/mole} + 0 \text{ kJ/mole} \]

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?

*To calculate the ionization energy of a given electron, you need to know the energy of the photons used in the experiment and the kinetic energy of the electrons after they are removed from the atom.*

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

\[ IE = 1.43 \times 10^5 \text{ kJ/mole} - 1.34 \times 10^5 \text{ kJ/mole} = 9 \times 10^3 \text{ kJ/mole} \]

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?

*Theoretically, a mole of electrons was removed because the units on the energies are “per mole.”*

### 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.

*Player A will need to kick the ball harder (put in more energy) to get it out of the ditch. Player A’s ball is deeper in the ditch and therefore has a greater attraction to the Earth, meaning it is attracted with more 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.

*Electron 1 will need more energy to be removed from the atom because it is closer to the nucleus, meaning it has a greater attraction.*
19. Compare electrons 1, 2 and 3 in terms of their ionization energy. Explain your reasoning.

*Electrons 1 and 2 have the same ionization energy because they are equidistant from the nucleus. Electron 3 has an ionization energy lower than electrons 1 or 2 because it is farther from the nucleus.*

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.

*The higher ionization energy (for electrons 1 and 2) would be recorded more often because there is a greater probability that one of those electrons is ejected compared to the one electron (electron 3) that has the lower ionization energy.*

**Model 4 – Photoelectron Spectra of Lithium**

![Photoelectron Spectra of Lithium](image)

21. Refer to the graph in Model 4.

   a. What are the units of the x-axis?

   *kJ/mole*

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

   *The lower IE values are on the right, the higher values are on the left.*

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

   *The peak on the left represents electrons with larger ionization energy values, so they are held more tightly by the nucleus of the atom.*

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

   *A mole of lithium atoms was ionized (theoretically) to get these data.*

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.

   *See Model 4.*
24. Why are there only two peaks and not three in the lithium spectrum in Model 4?
   *Two of the electrons in lithium have the same ionization energy, so there are only two peaks.*

25. Why is the higher energy peak about twice as high as the lower energy peak?
   *The higher energy peak represents two electrons (1 and 2), while the lower energy peak represents only one electron (3). The higher energy peak has a higher photoelectron intensity because it represents ejection and detection of two electrons.*

26. What does the number of peaks in a PES spectrum reveal about the energy sublevels occupied by electrons in an atom?
   *The number of peaks in a spectrum is equal to the number of sublevels for electrons in the atom.*

27. If the photoelectric spectrum of Ne is:

   ![Photoelectric Spectrum Image]

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

*The shell model on the right best matches the spectrum above because the spectrum has three peaks and the shell model on the right has three energy sublevels. Moreover, the low energy peak has a higher intensity attributable to the larger number of valence electrons compared to core electrons.*
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.)

Exact placement of peaks is not expected here, but students should know that the IE for both peaks will increase and that both peaks will be the same height.

Model 5 – Sulfur and Phosphorus
29. Refer to Model 5.
   a. The atomic structure of which atoms are represented by the PES spectra shown?
      *Sulfur* and *phosphorus*.
   b. List the number of protons and electrons in each atom.
      *Phosphorus*: 15 protons and 15 electrons.
      *Sulfur*: 16 protons and 16 electrons.
   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.
      *The sulfur atom has one more proton in the nucleus than the phosphorus atom. Therefore the pull of coulombic attraction from the nucleus is stronger, increasing the ionization energy of (almost) all the electrons.*
   b. Explain why peak E in the sulfur spectrum is shifted slightly right compared to peak E in the phosphorus spectrum.
      *Sulfur has four electrons in the outermost shell, compared to three electrons in that shell for phosphorus. Electrons repel each other so there is a slight reduction in ionization energy because of the repulsion effects of the surrounding electrons. The additional sulfur electron occupies a half-filled 3p orbital, thus causing electron–electron repulsion.*

31. Sketch the PES spectrum for chlorine using the spectra in Model 5 as a guide.
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 $E = \frac{hc}{\lambda}$.

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

      \[
      KE_{\text{photon}} = (6.626 \times 10^{-34} \text{ J s})(3.000 \times 10^8 \text{ m/s})/(0.8340 \times 10^{-9} \text{ m})
      = 2.383 \times 10^{-16} \text{ J}
      \]

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

      \[
      IE = 2.383 \times 10^{-16} \text{ J} - 2.372 \times 10^{-16} \text{ J}
      = 0.011 \times 10^{-16} \text{ J} = 1.1 \times 10^{-18} \text{ J}
      \]

   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.

      \[
      (1.1 \times 10^{-18} \text{ J/electron})(6.02 \times 10^{23} \text{ electrons/mole}) = 6.6 \times 10^5 \text{ J/mole} = 660 \text{ kJ/mole}
      \]

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

   The photoelectric effect discovered by Heinrich Rudolf Hertz and later explained by Einstein, is the phenomenon observed when incident electromagnetic waves with sufficient energy ionize the atoms on the surface of a metal and release electrons. Photoelectron spectroscopy is an application of the photoelectric effect that is used to determine the internal electronic structure of atoms.

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

   The photon's energy would need to at least equal the ionization energy of a single electron.

   \[
   IE_{\text{electron}} = 3.40 \times 10^5 \text{ J/mole} \left( \frac{1 \text{ mole}}{6.022 \times 10^{23} \text{ electrons}} \right) = 5.65 \times 10^{-18} \text{ J/electron}
   \]

   \[
   E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{E}
   \]

   \[
   \lambda = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{5.65 \times 10^{-18} \text{ J/electron}} = 3.5 \times 10^{-8} \text{ m} = 35 \text{ nm}
   \]

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

   The high energy electrons that are ejected from the sample must travel to a detector. If air was present, the electrons would surely bump into other atoms or molecules, gain or lose kinetic energy and/or be deflected away from the detector. The ultra-high vacuum conditions allow the high energy electrons a free path to the detector after being ejected from the sample.

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