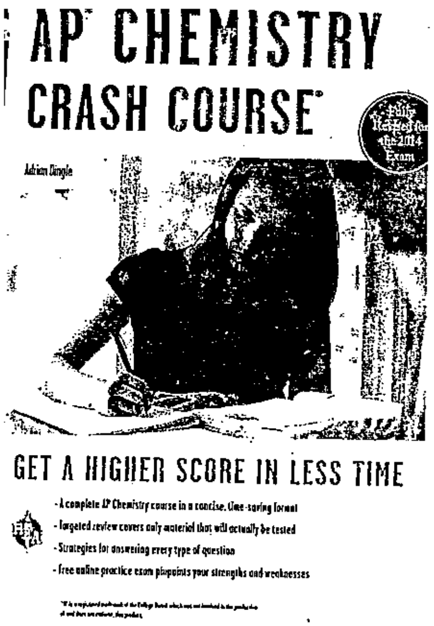


C. Photoelectron Spectroscopy (PES)—Evidence for the Shell Model and Orbitals

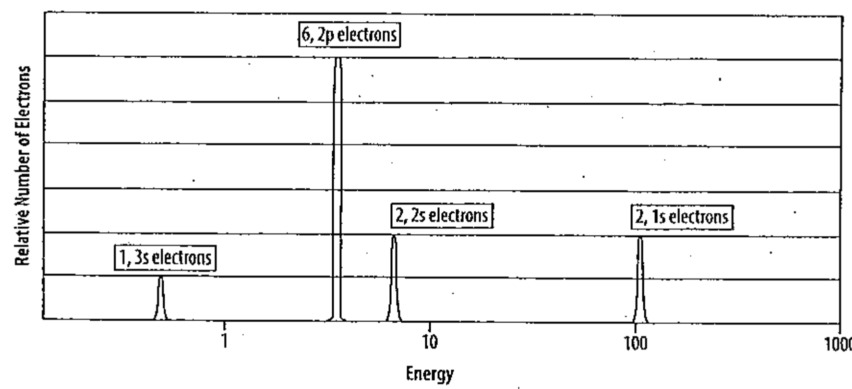
1. High energy X-rays or UV photons can be used to eject electrons from atoms. This is called the photoelectric effect. The energy applied can be calculated using

$$E = h\upsilon$$

where h = Planck's constant and υ = frequency.

2. The electrons that are ejected can be analyzed using PES to produce a spectrum that shows peaks that correspond to the energy (*x*-axis) and the relative number of electrons in any given sub-level (*y*-axis).
3. Electrons that are close to the nucleus, therefore with a greater attraction for the nucleus based upon Coulomb's law, will require larger energies to eject them.
4. Analysis of PES data leads to evidence for the shell model. For example, knowing the electronic configuration of sodium to be $1s^2\ 2s^2\ 2p^6\ 3s^1$, we would expect;
   i. Four peaks on the PES plot corresponding to the four different energies required to remove electrons from different sub-shells, with increasing energies as one approaches the nucleus, and
   ii. Peaks with heights (intensities) relative to the number of electrons in each sub-shell, i.e., for Na in the ratio, 2:2:6:1.

A simulated PES spectrum for sodium is shown below. Note that the scale on the *x*-axis is not linear, that electrons in different sub-shells but the *same* shells tend to be close together in terms of energy, and that electrons in *different* shells are often widely separated in terms of energy. Also note that the relative size (height) of each peak corresponds to the relative number of electrons in each sub-shell.



Practice Questions

1. Aluminum has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$.
   (a) How many unique peaks are expected in aluminum's PES spectrum? Explain.
   (b) Which electrons correspond to the largest energies? Explain.
   (c) Which peak in the spectrum will have the greatest intensity (i.e., be the largest)? Explain your answer.
   (d) Explain why the peaks corresponding to the 3s and the 3p electrons are relatively close together, and why they are distinctly different to the electrons in the 2s and 2p orbitals.

2. An element in the third period of the periodic table produces a PES spectrum that has only three peaks, in the ratio 2:2:1. Identify the element.
   (A) Aluminum
   (B) Boron
   (C) Carbon
   (D) Sodium

Answers

1. (a) Five, since there are five distinct sub-shells present in an Al atom.

   (b) The 1s electrons. They are closest to the nucleus (positive charge) and experience the greatest force of attraction according to Coulomb's law. They will be the most difficult to remove and will require the greatest energy.

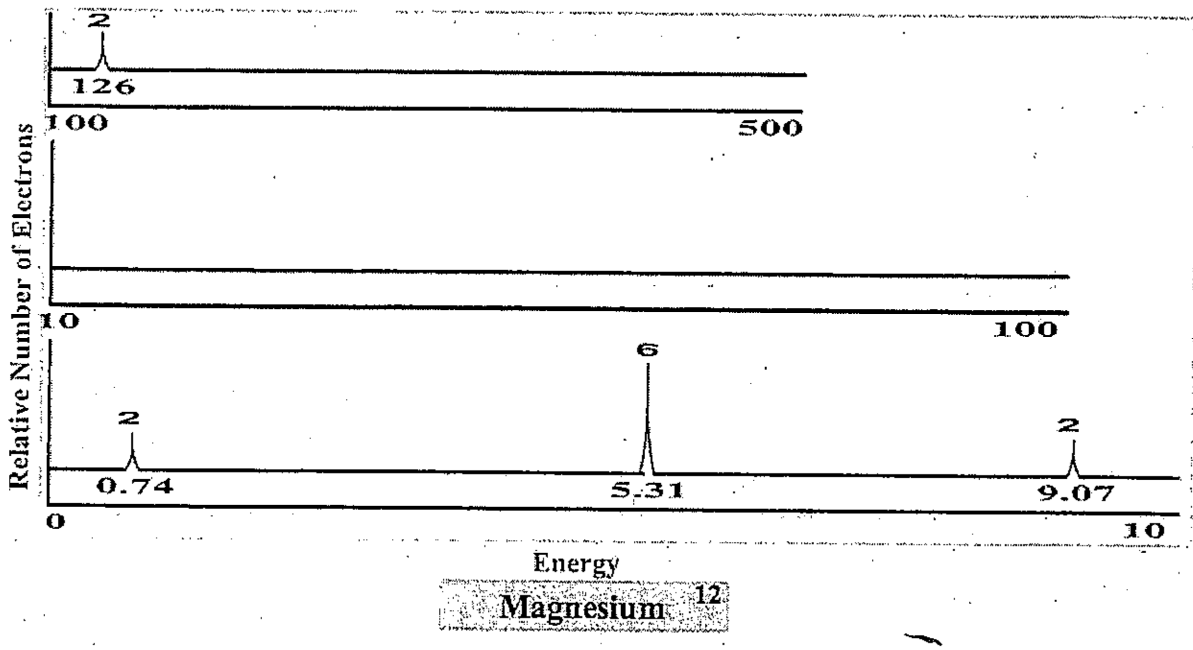
   (c) The peak corresponding to the 2p electrons. The intensity of the peak is relative to the number of electrons in the orbital. The 6, 2p electrons create a peak with the greatest intensity.

   (d) Even though the 3s and 3p electrons are in distinct orbitals that correspond to different energies, they are both in the third shell, at similar distances from the nucleus, and thus have similar energies. The 2s and 2p electrons on the other hand are a whole shell closer to the nucleus, and as such are much more difficult to remove and require distinctly higher energies.

2. **(B)** Boron

   Boron has an electronic configuration of $1s^2\ 2s^2\ 2p^1$ that would produce a PES spectrum with three peaks in the ratio 2:2:1.

PES Photoelectron Spectroscopy (PES).



Generated by the simulation at; http://www.chem.arizona.edu/chemt/Flash/photoelectron.html

I'm guessing that questions could take all kinds of different tacks, a few of which are listed below.

If the question flagged Mg as the element in question.

a. Which peak in the spectrum represents electrons that are closest to the nucleus?
b. What is the relevance of the relative height of the peaks at 5.31 eV and 9.07 eV?
c. Why is there such a large difference in energy between the peaks at 0.74, 5.31 and 9.07 eV, and the peak at 126 eV?

If the question did not flag Mg as the element in question.

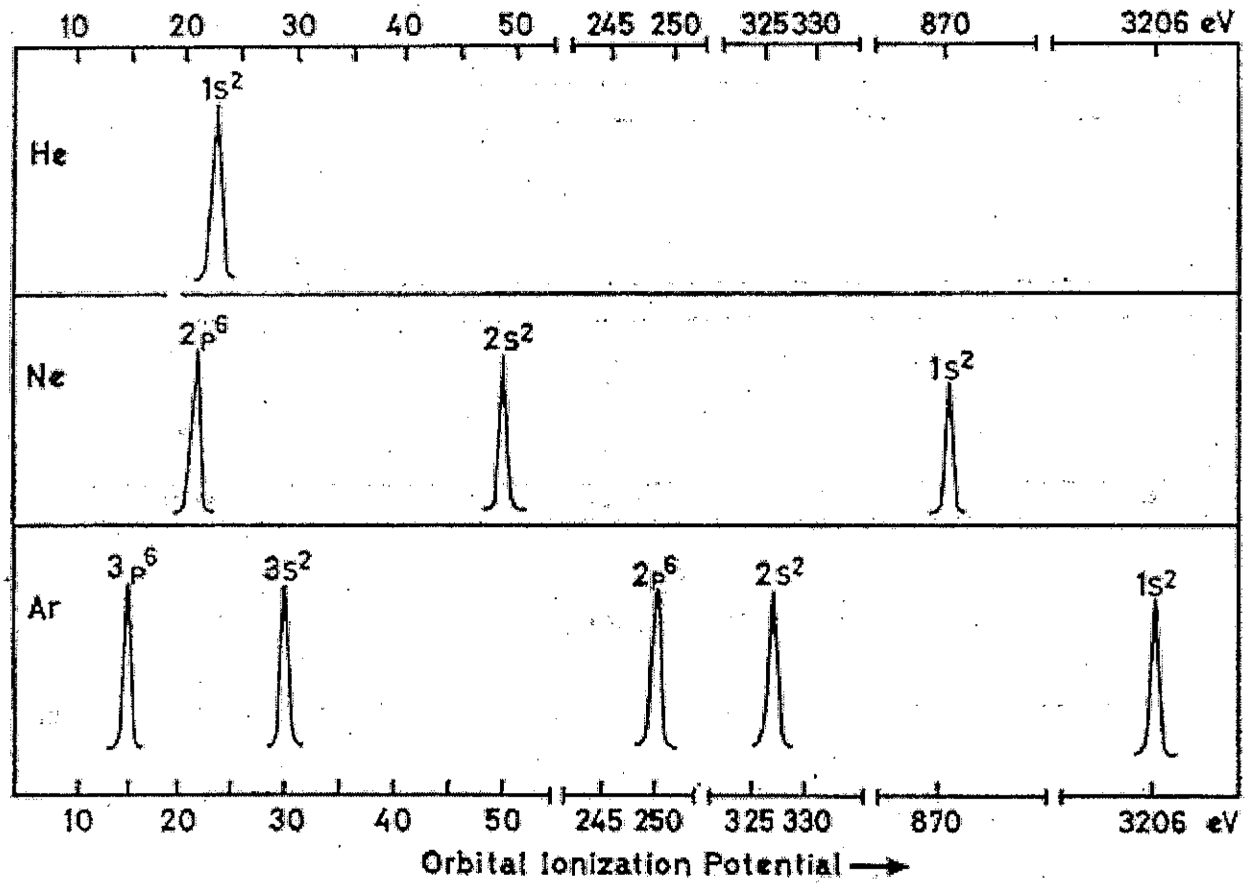
a. Assuming that the PES data shows ALL of the electrons present in the atom, identify the element.
b. Still applying the assumption in a., which specific electrons are associated with the peak at 126 eV?
c. What does a relatively low value of energy tell you about the relative position of the electrons within *any* atom?

The second half of the sentence might induce a question like;

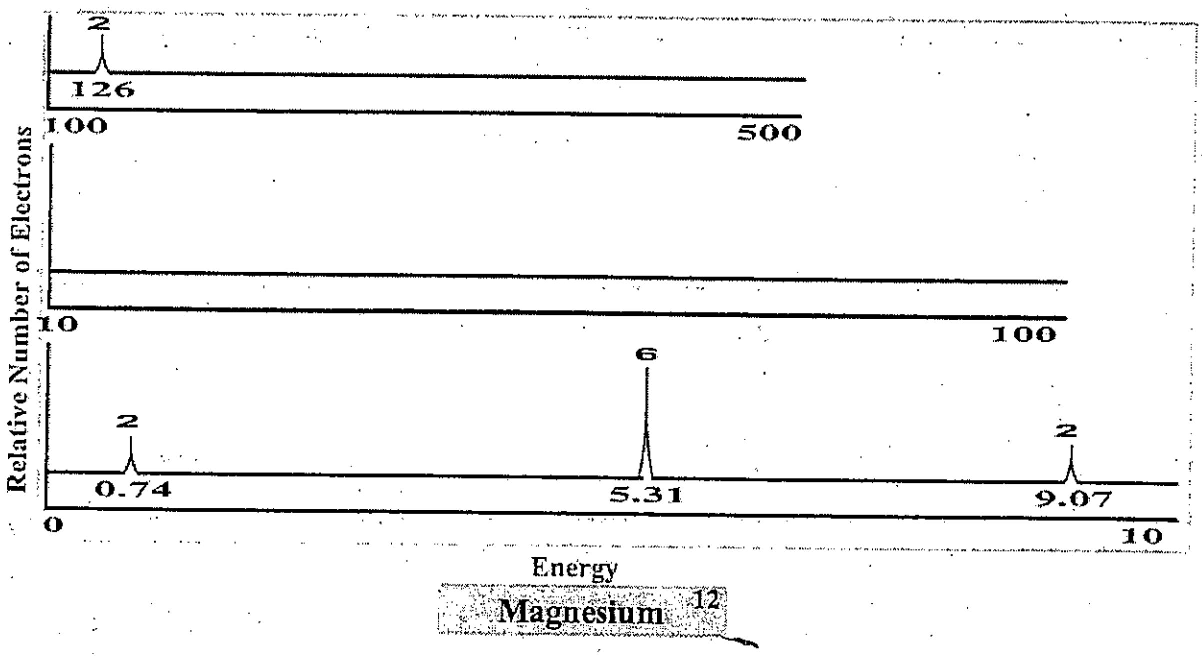
Mg is found in group 2 and period 3 of the periodic table. Use this information to answer the questions that follow.

a. Predict the full electronic configuration of Mg atoms using s, p, d, f notation.
b. Use your answer in a, to predict the relative height of the four peaks found in the PES plot for Mg.

The student also should be able to translate between various representations, such as reading photoelectron spectroscopy data and then writing an electron configuration consistent with the data, or using the periodic table to predict either the photoelectron spectrum or the electron configuration (SP 1.5).


10
20
30
40
50
245 250
325 330
870
3206 eV
He
1s²
Ne
2p⁶
2s²
1s²
Ar
3p⁶
3s²
2p⁶
2s²
1s²
Orbital Ionization Potential

PES Photoelectron Spectroscopy (PES).



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