❑ EXPERIMENTAL TECHNIQUES FOR ATOMIC ORBITALS

❖ Photoelectron Spectra (PES) Support the Existence of Atomic Orbitals

➢ The energies of orbitals are **calculated today by solving the Schrödinger equation** with computer software. The commercial software available is now so sophisticated that this approach can be as easy as typing in the name of the molecule or drawing it on screen. But these values are theoretical.

▪ **How do we determine *orbital energies experimentally*?**

➢ It so happens that the **electron configurations of atoms can be demonstrated experimentally**. The *approach used is very similar to the photoelectric effect*.

➢ Most of what we know about the structure of atoms and molecules has been obtained *by studying the interaction of electromagnetic radiation with matter*.

➢ **Line spectra reveal** the *existence of shells of different energy where electrons are held in atoms*.

➢ From the study of molecules by means of **infrared** and **microwave** spectroscopies we obtain information about *vibrational* and *rotational* states of molecules. The **types of bonds** present, the **geometry of the molecule**, and even **bond lengths** may be determined in specific cases.

❑ **Photoelectron Spectra (PES) Support the Existence of Atomic Orbitals**

➢ The spectroscopic technique known as *photoelectron spectroscopy (PES) has been of enormous importance* **in determining how electrons are bound in atoms/molecules**. This technique *provides direct information on the energies of atomic/molecular orbitals*.

❖ **Photoelectron spectroscopy** (PES) *utilizes photo-ionization and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample*.

• **Ultraviolet Photoelectron Spectroscopy** (UPS) using vacuum UV radiation (with a photon energy of 10-45 eV) to examine electrons in *valence* levels.

• **X-ray Photoelectron Spectroscopy** (XPS) uses soft x-rays (with a photon energy of 200-2000 eV) to examine electrons in *core*-levels. The idea of atomic orbitals and molecular orbitals is rather abstract and sometimes appears far removed from reality.
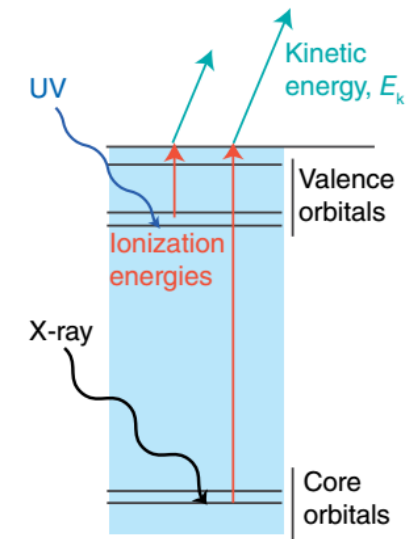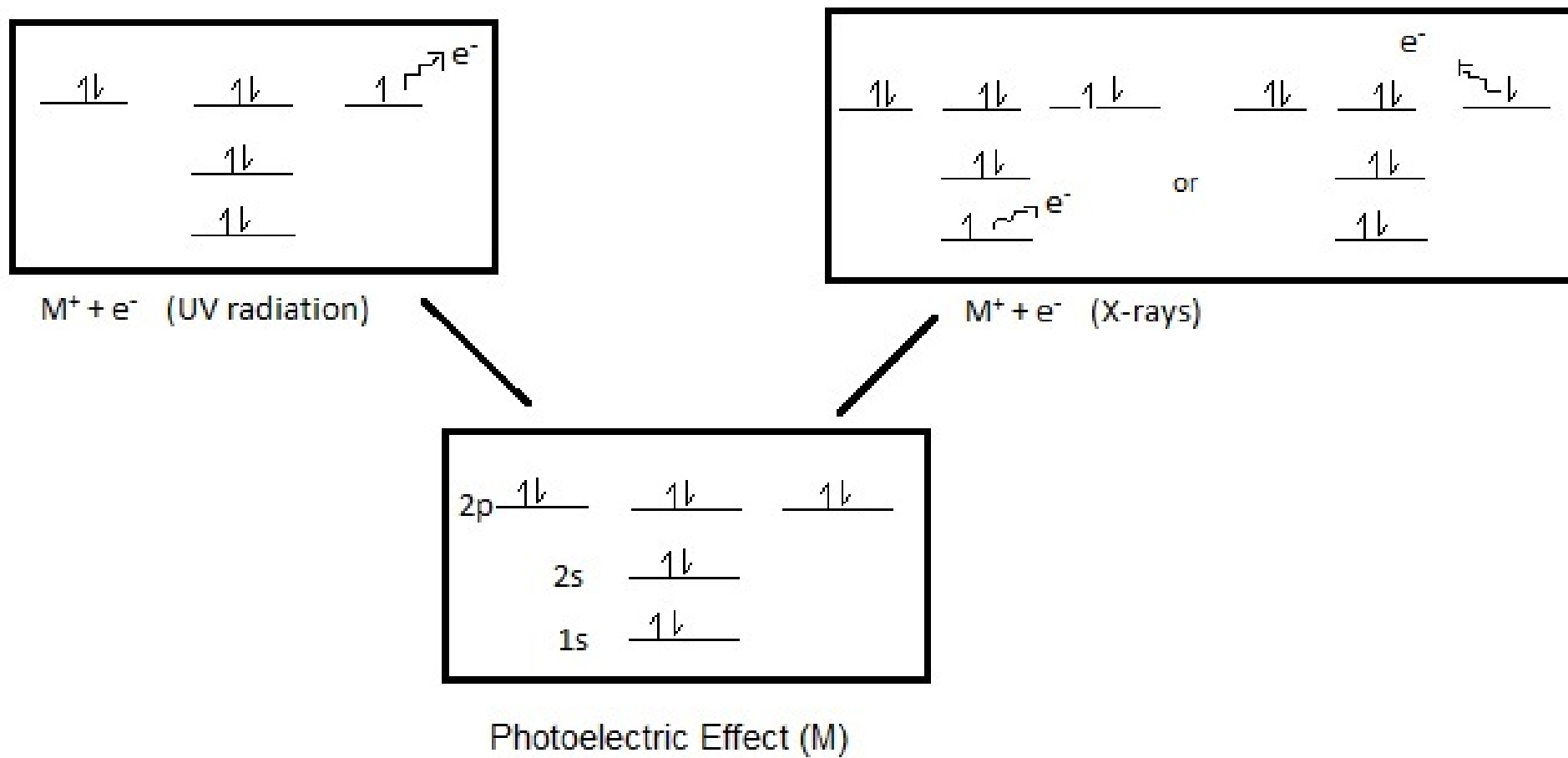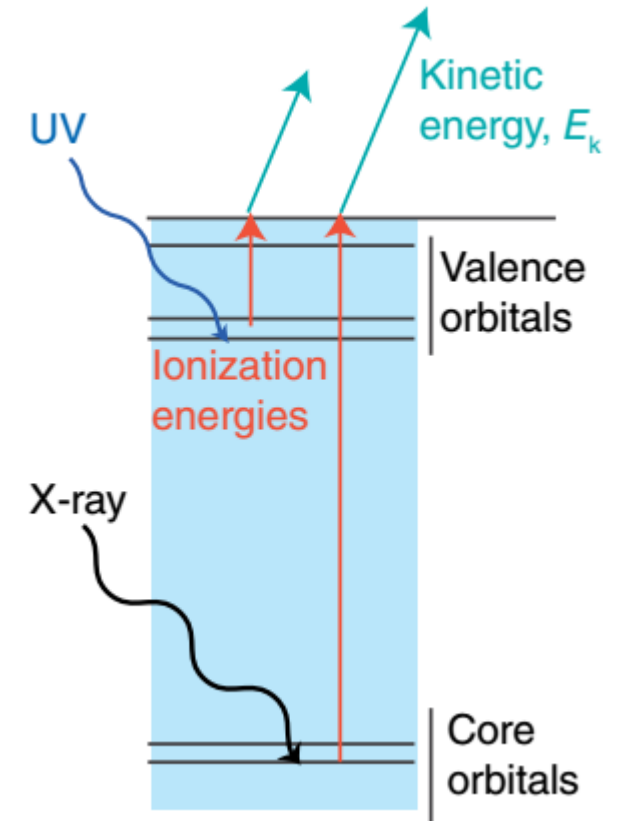
Figure 1. Scheme for UPS and XPS. Illustrates the ejection of electrons from respectively the valence electrons and core electrons.

- Both photoelectron spectroscopies are based upon a single photon in/electron out process. The energy of a photon of all types of electromagnetic radiation is given by the Planck–Einstein relation: $E = hv$ (10.4.1)
  where h is Planck constant and v is the frequency (Hz) of the radiation. UPS is a powerful technique to exam molecular electron structure since we are interested in the molecular orbitals from polyatomic molecules (especially the valence orbitals) and is the present topic.
- Photoelectron spectroscopy uses monochromatic sources of radiation (i.e. photons of fixed energy).
- In UPS the photon interacts with valence levels of the atom, molecule or solid, leading to ionization by removal of one of these valence electrons.
- The *kinetic energy distribution of the emitted photoelectrons* (i.e. *the number of emitted photoelectrons as a function of their kinetic energy*) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

detector

exit slit

sample

⊕ ⊖

energy
analyzer

He LAMP SOURCE

entrance slit

vacuum pumps

Electrostatic
analyzer

Electron
beam

Detector

Radiation source

Sample
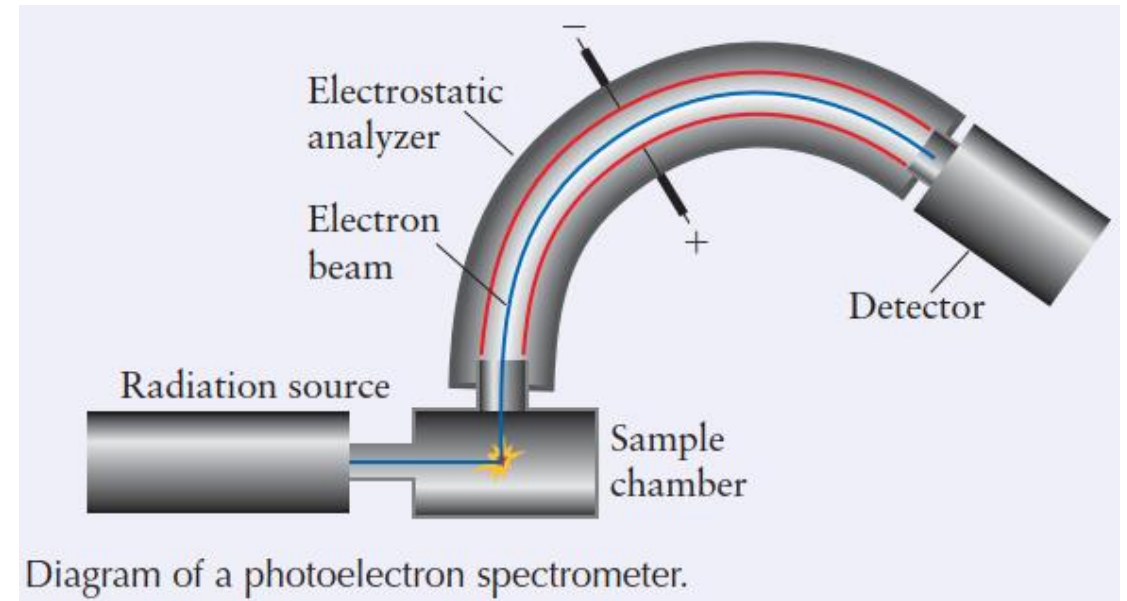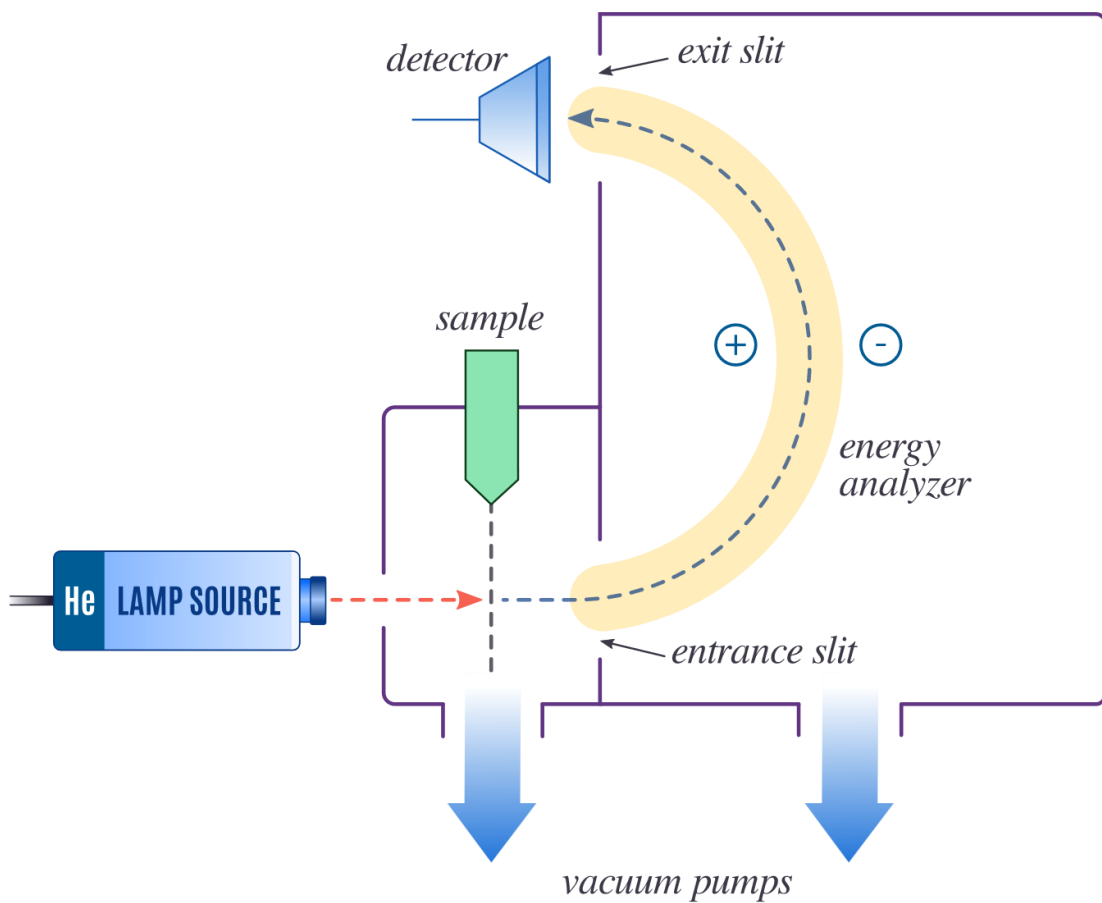chamber

Diagram of a photoelectron spectrometer.

Figure 10.4.1 : Diagram of a basic, typical PES instrument used in UPS, where the radiation source is an UV light source. When the sample is irradiated, the released photoelectrons pass through the lens system which slows them down before they enter the energy analyzer. The analyzer shown is a spherical deflection analyzer which the photoelectrons pass through before they are collected at the collector slit.

- A photoelectron spectrometer contains a source of high-frequency, short-wavelength radiation.
- ***Ultraviolet radiation is used (for PES) most often for molecules***, but
- ***x-rays are used (for ESCA)*** *to explore orbitals buried* ***deeply inside solids***.

Photons in both frequency ranges have so much energy that they can eject electrons from the molecular orbitals they occupy. Photoelectron spectroscopy may be used to study ***orbital energies of either core*** *or* ***valence electrons***.

Applying a source that produces x-rays (the source is high energy X-rays: 1000-1500 eV), the photon energy suffices to remove electrons from inner shells of atoms. **Electron spectroscopy for chemical analysis** (ESCA) or **X-PES** (or, even shorter, **XPS**) is an analytical technique founded on this process. As the ***energy of inner shell electrons is almost independent from the molecular surroundings***, X-PES spectra ***contain information on the elements present*** in a sample; a feature that led to the name "... for chemical analysis".

If ultraviolet radiation is used, we speak of **UV-PES** (or simply **UPS** which uses the energy of ultraviolet rays <41 eV). Here, the photon represents an energy quantum that allows the removal or ***ionization of valence electrons*** from a *valence shell or molecular orbitals*. Therefore, from UV-PES spectra, information on the energy of such orbitals is gained.

➤ **Helium gas is the most common UV radiation source** used for the ***photoelectron spectroscopy*** of molecules. The photon source that is frequently employed is the **He(I) source** that emits photons having an energy of 21.22 eV as the excited state $2s^1 2p^1$ relaxes to the $1s^2$ ground state. (When electronically excited, He atoms emit nearly monochromatic (single wavelength) radiation at a wavelength of 58.4 nm.) The ionization potential for the hydrogen atom is 13.6 eV, and the first ionization potential for many molecules is of comparable magnitude. The energy of these photons is above the threshold required to eject electrons from many valence shell molecular orbitals.

➤ *If high-energy electromagnetic radiation is directed into a gas, electrons are ejected from the molecules in the gas.*

➤ *The **energy required to eject an electron from a molecule**, called the **ionization energy**, is **a direct measure of how strongly bound the electron** is within the molecule.*

➢ The ionization energy of an electron within a molecule depends upon the molecular orbital the electron occupies; *the lower the energy of the molecular orbital, the more energy needed to remove,* or *ionize,* an electron from that molecular orbital.

➢ *The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules is called* **photoelectron spectroscopy (PES).**

➢ **Photoelectron Spectra (PES) Support the Existence of Atomic and Molecular Orbitals.**
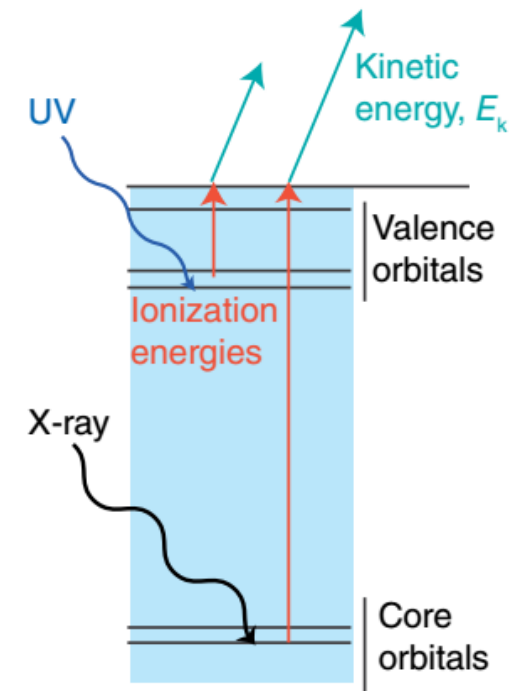
Photoelectron Spectra (PES) Support the Existence of Molecular Orbitals

Photoelectron spectroscopy is an instrumental technique that enables the measurement of **orbital energies** in atoms and molecules. In this technique gas phase atoms or molecules are ionized by high-energy radiation. For a molecule (M), the process is as follows:

$$M + h\nu \rightarrow M^+ + e^-$$

A photon with sufficient energy (*hv*) can cause an electron to be ejected from the atom or molecule. If the photon has energy that is above the threshold required for ionization, the excess energy is imparted as kinetic energy to the ejected electron. The ionization energy (***orbital energy***), the energy of the absorbed photon, and the kinetic energy of the ejected electron are related by the equation.

$$IE = h\nu - KE(electron)$$

We know *v*, the frequency of the radiation being used to bombard the molecules; so, if we could measure the kinetic energy of the ejected electron, KE, we could solve this expression to find the orbital energy.
The kinetic energy of an ejected electron depends on its speed, V, because $KE = mV^2/2$. A photoelectron spectrometer acts like a mass spectrometer in that it measures V for electrons just as a mass spectrometer can measure V for ions. In this method, the electrons pass through a region of electric or magnetic field, which deflects their path. As the strength of the field is changed, the paths of the electrons change, too, until they fall on a detector and generate a signal. From the strength of the field required to obtain a signal, we can work out the speed (and hence the kinetic energy) of electrons ejected from a given orbital and so obtain the energy of the orbital from which they came.

➢ Electrons that are ejected are passed through an analyzer and by means of a variable voltage, electrons having different energies can be detected. ***The number of electrons having specific energies is counted, and a spectrum showing the number of electrons emitted (intensity) versus energy is produced***.

Steps to Relate the Relationship between the Photoelectron Spectrum and the Electron Configuration of the Species

➢ A photoelectron count vs. binding energy graph is called a PES spectrum.

➢ The ***ionization energy defines the position of each peak***, whereas *the **height identifies** the ratio of **electrons in each level or orbital***.

➢ ***PES peaks represent electrons in various subshells*** of an atom.

Step 1: Write the electron configuration of the element or ion provided in the question.

Step 2: The number of subshells should equal the number of peaks provided in the PES.

Step 3: Assign each subshell with an individual peak from the photoelectron spectrum. The graph is constructed to have the highest binding energy closest to the left and the lowest binding energy to the right, so ***the lowest subshell is assigned to the leftmost peak***, followed by each subsequent subshell.

Step 4: Determine the **number of electrons** associated with each peak. ***The height (area) of each peak provides the relative number of electrons***, and ***the height (area) ratio provides how many electrons***.
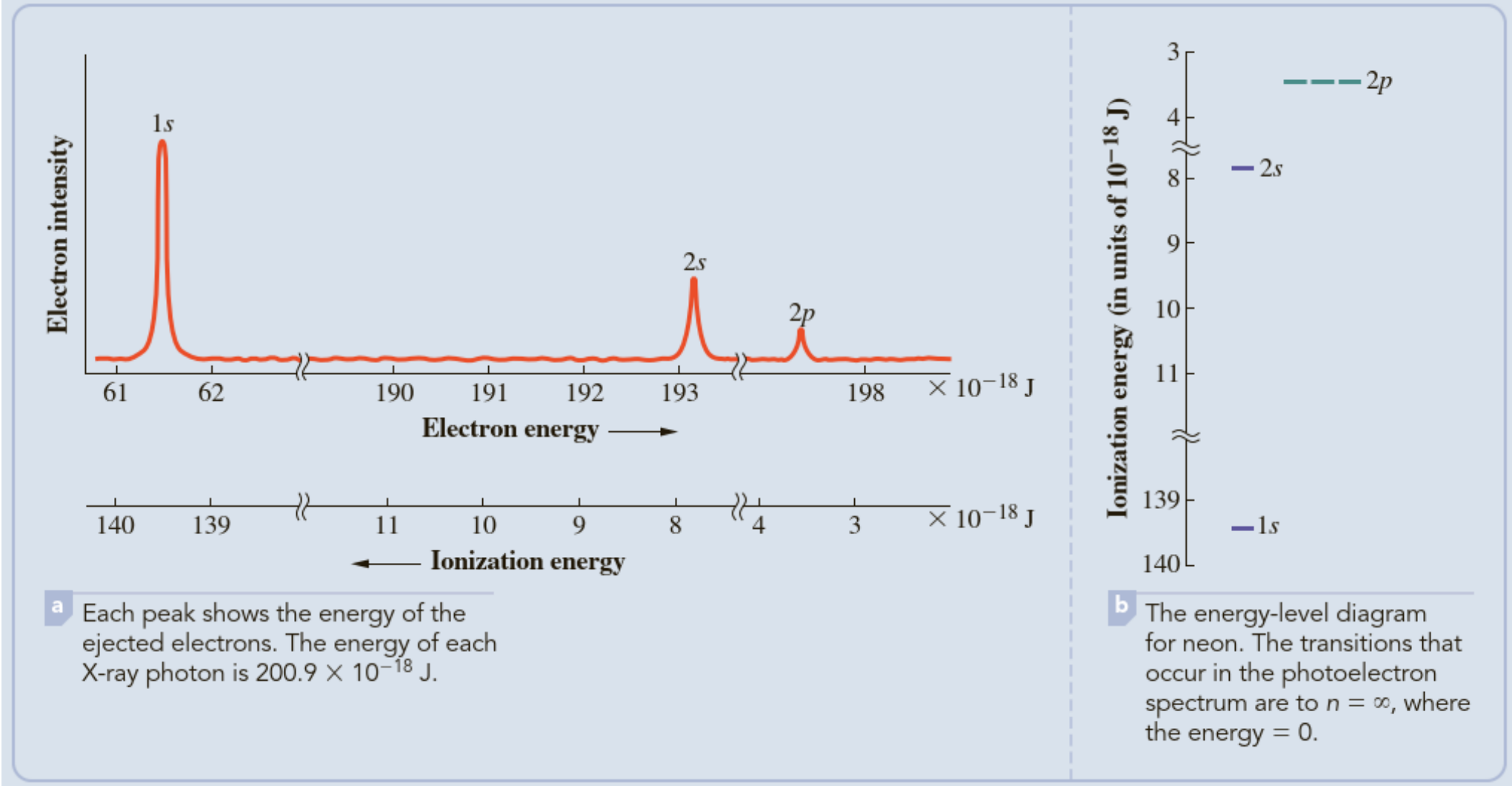
Photoelectron spectrum of neon (simulation)
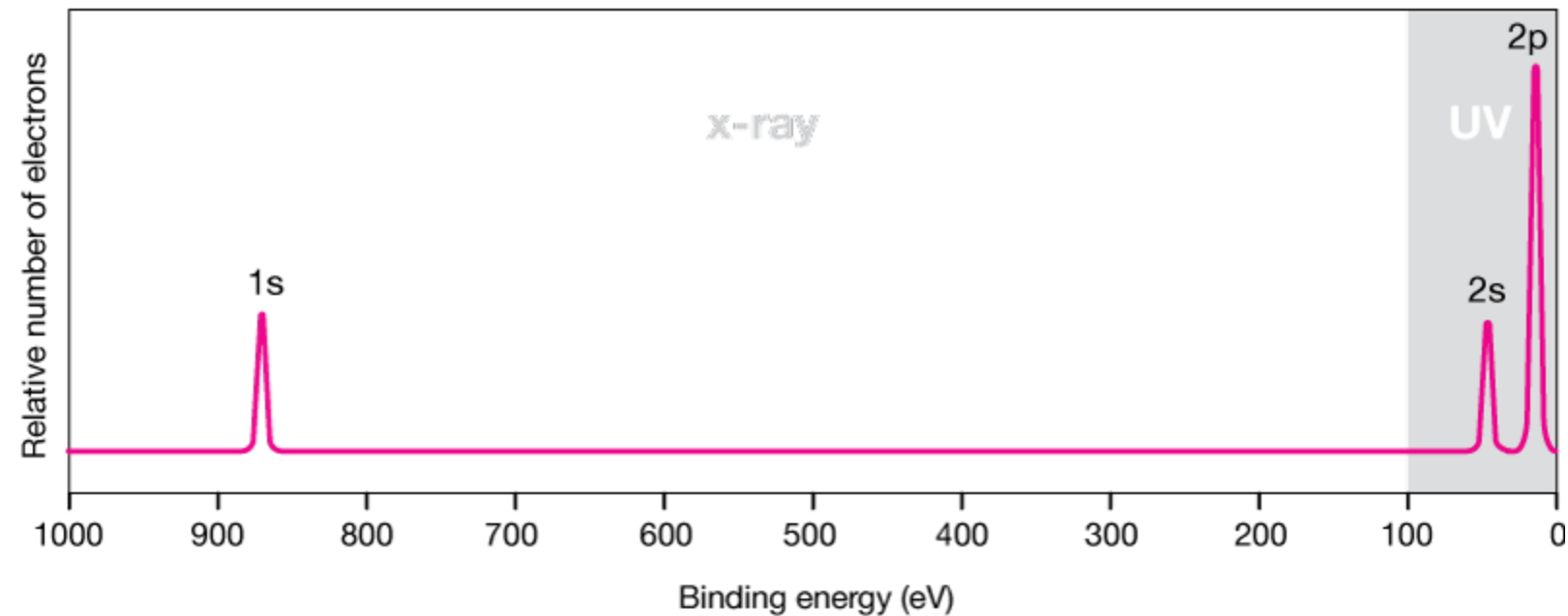
The inner-shell electrons are the most tightly bound, and require the most energy to ionize. The small peak at about 875 eV represents the two 1s electrons of Ne. The 8 electrons of the n = 2 shell are more weakly bound because they are farther from the nucleus and shielded from it by the 1s electrons. They ionize at much lower energies. Notice that the height of the peaks is proportional to the number of electrons in the orbital. The 2p peak is three times the height of the 2s peak; it represents six electrons to the two in the 2s orbital.

If you look at the electrons ejected from neon, you find that they have kinetic energies related to the ionization energies from all possible orbitals (1s, 2s, and 2p) in the atom. *When you scan the various kinetic energies of ejected electrons, you see a spectrum with peaks corresponding to the different occupied orbitals* (see Figure 8.11a). These ionization energies are *approximately equal to the positive values of the orbital energies (Figure 8.11b), so this spectrum provides direct experimental verification of the discrete energy levels associated with the electrons of the atom/molecule.*

Figure 8.11. X-ray photoelectron spectrum of neon

a Each peak shows the energy of the ejected electrons. The energy of each X-ray photon is 200.9×10^{-18} J.

b The energy-level diagram for neon. The transitions that occur in the photoelectron spectrum are to $n = \infty$, where the energy $= 0$.

Example
See if you can identify the chemical element depicted by this PES spectrum.
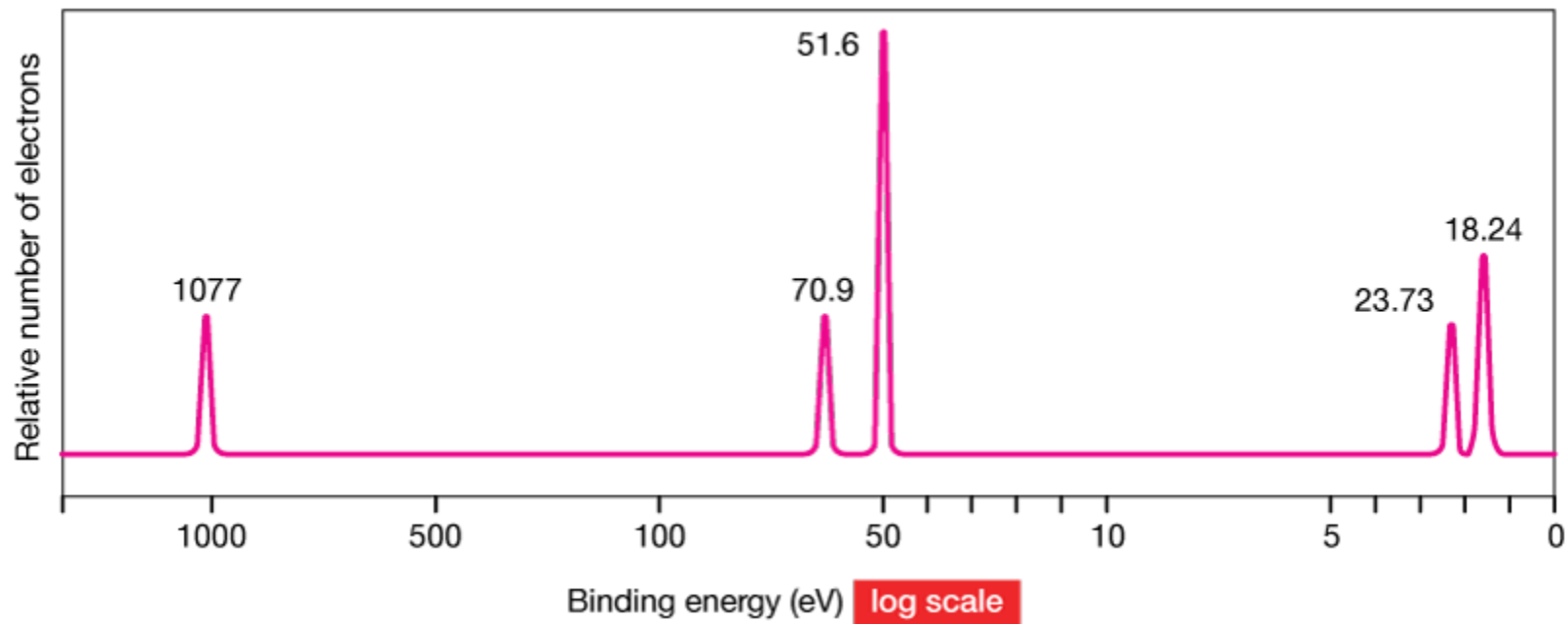
Solution : The most strongly bound electrons (highest binding energy) are those nearest to the positively-charged nucleus. Those are on the left side. As we move to the right in this figure, the binding energies (in eV) decrease. If you tap/roll over the figure, some rulers are placed next to each peak, and you can see that the 51.6 eV peak is about three times as intense and the 1077 eV and 0.9 eV peaks, therefore we conclude that the orbital it represents has three times the electrons, the difference we'd expect between **s** and **p** orbitals. Next, the lowest-energy peak, at 18.24 eV, must represent the outermost electron(s). Its intensity is about 1.5 times the 23.73 eV peak, a 3:2 ratio. From this we conclude that the electron configuration represented in this spectrum is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$, the ground-state configuration of **phosphorus (P)**.

➤ These experimental results for neon are consistent with the electron configuration Ne: $1s^2 2s^2 2p^6$ predicted by the aufbau principle. Ionization energies measured in this way are used to construct the energy-level diagram for atoms and to show explicitly the value of the ground-state energy.

➤ This method has been used to determine the energy levels for orbitals in most neutral atoms (Fig. 5.26). The energies are reported in units of rydbergs and plotted on a logarithmic scale. These **data confirm the existence of sub-shells**, which are grouped into shells having similar energies. However, there are significant exceptions. The ***3d subshell for elements 21 through 29 (scandium through copper) lies substantially higher than 3s and 3p and only slightly lower than 4s.*** This is consistent with the chemical observation that the 3d electrons participate as valence electrons in these transition metals. As Z goes above 30, the energy of the 3d subshell decreases rapidly, so the **3d electrons are not valence electrons for zinc and higher elements**. The 4d, 5d, 4f, and 5f subshells all behave similarly, so electrons in filled d and f subshells are not valence electrons. We can develop an approximate criterion for distinguishing valence and core electrons by examining the noble gases (elements 2, 10, 18, 36, 54, and 86), which participate poorly or not at all in chemical bonding. The highest-energy subshell for each of them lies below -1 rydberg. Therefore, -1 rydberg is a reasonable approximate boundary for the difference between valence and core electrons.

Figure 5.26 The energies of different subshells in the first 97 elements, as determined by photoelectron spectroscopy. Negative values on the vertical axis correspond to the bound state orbital energies. Subshells having the same principal quantum number n, such as 2s and 2p, have similar energies and are well separated from orbitals of different n. Significant exceptions do exist, as explained in the text. Note the logarithmic energy scale. One rydberg is 2.18 × 10^{-18} J.