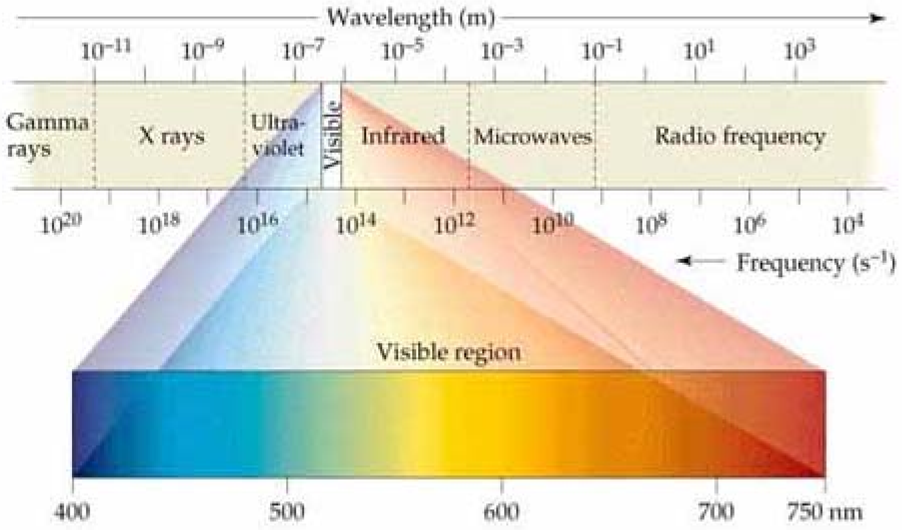
AP Chemistry

Chapter 6

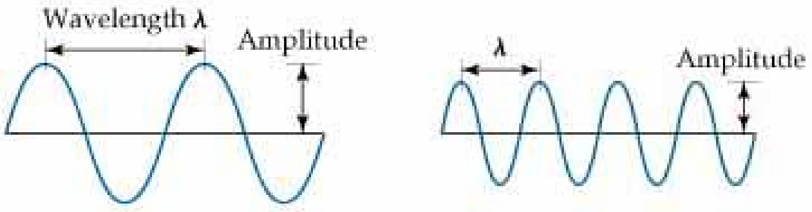
Electronic Structure of Atoms

Section 6.1 – Wave Nature of Light

- When we say "light," we generally are referring to visible light—a type of **electromagnetic radiation**
- But actually Visible light constitutes a very small segment of the electromagnetic spectrum, which is composed of various types of electromagnetic radiation in order of increasing wavelength

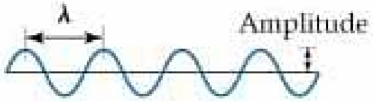


Characteristics of Light



(a) Two complete cycles of wavelength λ

(b) Wavelength half of that in (a); frequency twice as great as in (a)



(c) Same frequency as (b), smaller amplitude

Section 6.1

Characteristics of Light

- All types of electromagnetic radiation share certain characteristics.
- All have wavelike characteristics—similar to those of waves moving through water—including frequency and wavelength
- All move through a vacuum at the "speed of light," which is 3.00×10^8 m/s

$\nu\lambda = c$ or $c = f\lambda$

- Where v (nu) is the frequency of the radiation in reciprocal seconds (s^{-1}), λ (lambda) is the wavelength in meters, and c is the speed of light in meters per second

Types of Radiation

- Different types of electromagnetic radiation have some very different properties
- Visible light is visible because is has the characteristic wavelengths required to trigger the chemical reactions and subsequent sensations that constitute vision
- X rays have much shorter wavelengths than those of visible light and are useful diagnostically because they penetrate flesh but not bone.

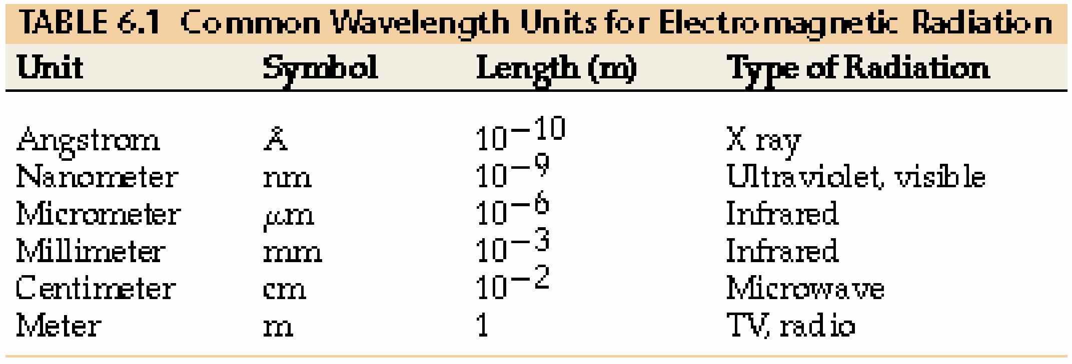
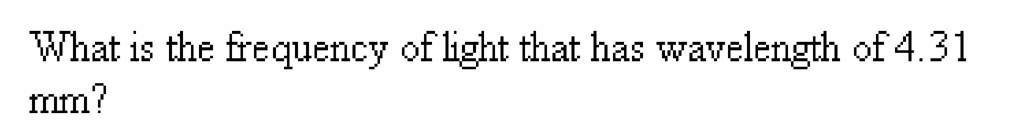


TABLE 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Infrared
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	TV, radio

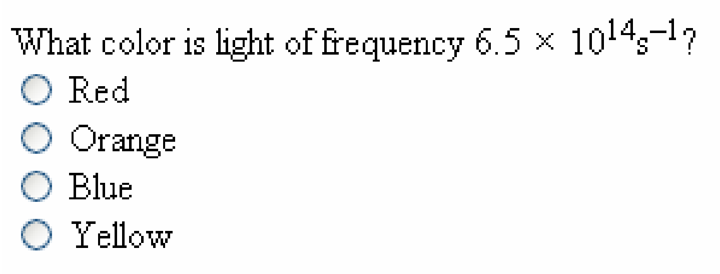
Practice problems

1.



What is the frequency of light that has wavelength of 4.31 mm?

2.



What color is light of frequency $6.5 \times 10^{14} s^{-1}$?

- ○ Red
- ○ Orange
- ○ Blue
- ○ Yellow

Section 6.1

6.2 Quantized Energy and Photons

- When solids are heated, they emit radiation, as seen in the red glow of an electric stove burner and the bright white light of a tungsten lightbulb
- The wavelength distribution of the radiation depends on temperature, a "red-hot" object being cooler than a "white-hot" one
- 1900 a German physicist named Max Planck (1858-1947): He assumed that energy can be released (or absorbed) by atoms only in "chunks" of some minimum size.
- Planck gave the name **quantum** (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation. He proposed that the energy, *E,* of a single quantum equals a constant times its frequency:

$$E = h\nu$$

Or

$$E = hf$$

Section 6.2

Planck’s Contribution

- The constant *h,* known as **Planck's constant,** has a value of 6.63 x 10^{-34} joule-seconds (J-s).
- According to Planck's theory, energy is always emitted or absorbed in whole-number multiples of *h* , for example, *h* , 2*h* , 3*h* , and so forth.
- We say that the allowed energies are quantized; that is, their values are restricted to certain quantities.
- Planck's revolutionary proposal was proved correct, and he was awarded the 1918 Nobel Prize in physics for his work on the quantum theory.

$$E = h\nu$$

Practice problem

- Calculate the smallest increment of energy, that is, the quantum of energy, that an object can absorb from yellow light whose wavelength is 589 nm.

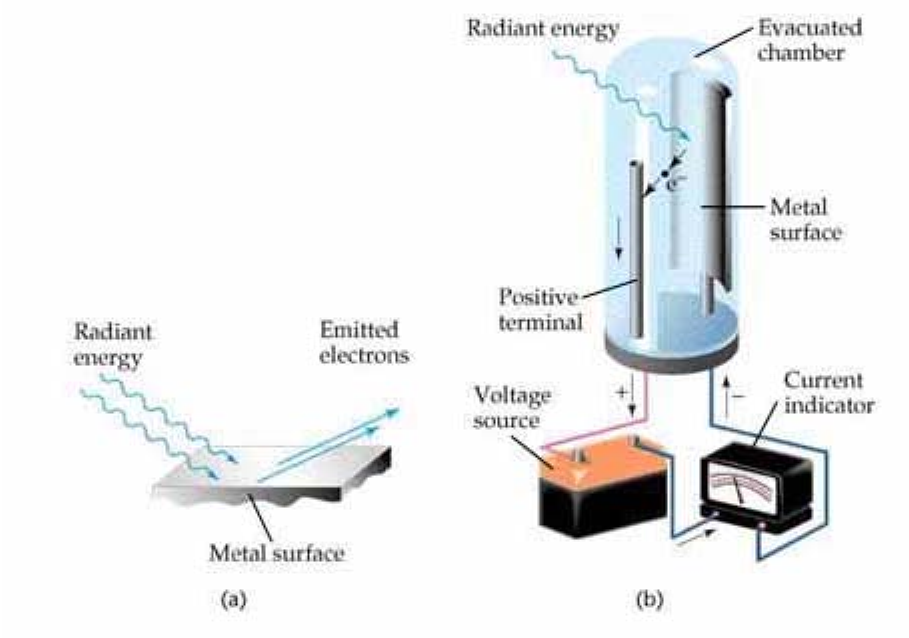
The Photoelectric Effect

- In 1905 Albert Einstein (1879-1955) used Planck's quantum theory to explain the *photoelectric effect*
- Experiments had shown that light shining on a clean metal surface causes the surface to emit electrons.
- For each metal, there is a minimum frequency of light below which no electrons are emitted.
- For example, light with a frequency of 4.60×10^{14} s^{-1} or greater will cause cesium metal to eject electrons, but light of lower frequency has no effect.

The Photoelectric Effect

- *The photoelectric effect. When photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal, as in (a).*
- *The photoelectric effect is the basis of the photocell shown in (b).*
- *The emitted electrons are drawn toward the positive terminal. As a result, current flows in the circuit. Photocells are used in photographic light meters as well as in numerous other electronic devices.*

Active Photoelectric Device – click HERE



Section 6.2

Photoelectric Effect - *explained*

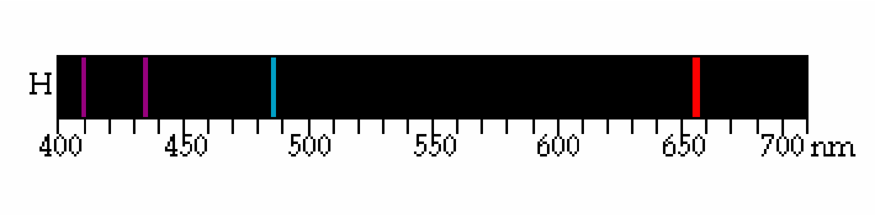
- To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface is a stream of tiny energy packets. Each energy packet behaves like a tiny particle of light and is called a **photon.** Extending Planck's quantum theory, Einstein deduced that each photon must have an energy proportional to the frequency of the light: $E = h$. Thus, radiant energy itself is quantized.
- When a photon strikes the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. If the photons of the radiation have less energy than this energy threshold, the electron cannot escape from the metal surface, even if the light beam is intense.
- If a photon does have sufficient energy, the electron is emitted. If a photon has more than the minimum energy required to free an electron, the excess appears as the kinetic energy of the emitted electron.

Section 6.2

6.3 Bohr's Model of the Hydrogen Atom

- Scientists have used flame tests to verify the presence of certain elements in compounds
- For example, Sodium gives off a characteristic yellow color when burned. Potassium burns with a violet flame.
- The colored light of a flame separates into a **line spectrum**, which consists of only a few specific wavelengths.

- **The line spectrum of hydrogen contains four visible lines.**



Bohr’s Contribution

- Bohr proposed that the electron in a hydrogen atom could circle the nucleus only in specific orbits designated by a quantum number *n*.
- The quantum number can have integer values, with $n = 1$ corresponding to the orbit closest to the nucleus.
- He showed the relationship between the value of *n* and the energy of an electron is

$$E_n = (-R_H)\left(\frac{1}{n^2}\right) \qquad \text{where} \quad n = 1, 2, 3, 4, \ldots$$

- R_H is the Rydberg constant ($2.18 \times 10^{-18} J$). The energy of an electron is, by convention, a negative number.
- **Ground State** is n = 1
- **Excited State** is n > 1

Section 6.3

Energy Changes

- Using his equation for the energy of an electron, Bohr calculated the energy *change* and the *frequency* associated with changing values of the quantum number *n*.

$$\Delta E = E_{\mathrm{final}} - E_{\mathrm{initial}} = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

- Using this relationship, Bohr was able to show that the visible line spectrum of hydrogen was due to the transitions of electrons in hydrogen atoms from *n* = 6 to *n* = 2, *n* = 5 to *n* = 2, *n* = 4 to *n* = 2, and *n* = 3 to *n* = 2.

For Example

- Calculate the frequency of an electron that undergoes a transition from *n* = 5 to *n* = 2
- Use the Equation:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

What does the negative sign mean?

$\Delta E = 2.18 \times 10^{-18}$ J

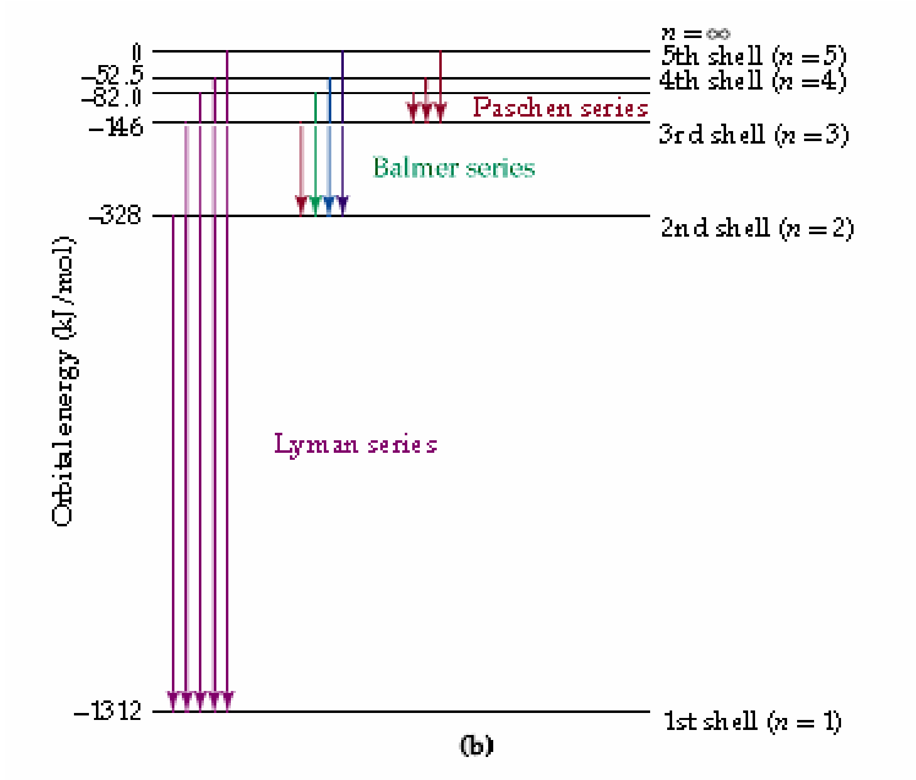
$h = 6.63 \times 10^{-34}$ J·s

Section 6.3

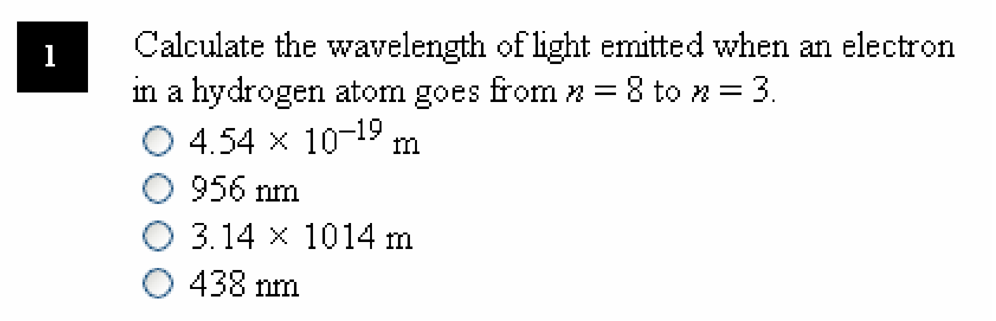
Electron transitions in the Bohr Model

- The visible lines in the hydrogen line spectrum are known as the Balmer series, in honor of Johann Balmer who first developed an equation by which their frequencies could be calculated.

- Electron transitions ending in *n* = 1 and *n* = 3 are called the Lyman and the Paschen series, respectively.



Practice problems



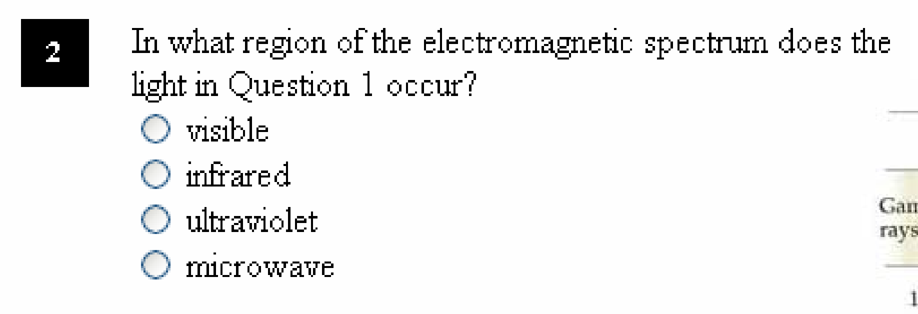
1 Calculate the wavelength of light emitted when an electron in a hydrogen atom goes from $n = 8$ to $n = 3$.

- ○ 4.54×10^{-19} m
- ○ 956 nm
- ○ 3.14 × 1014 m
- ○ 438 nm

Use the equation:

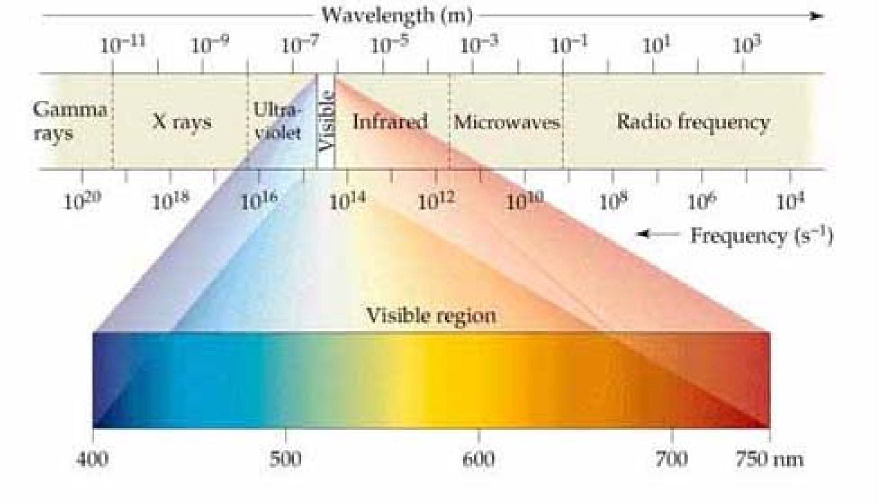
$$\Delta E = E_{\text{final}} - E_{\text{initial}} = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



2 In what region of the electromagnetic spectrum does the light in Question 1 occur?

- ○ visible
- ○ infrared
- ○ ultraviolet
- ○ microwave



Section 6.3

6.4 The Wave Behavior of Matter

- Curiously, the quantum theory seemed to suggest that energy had matterlike properties, that under appropriate conditions radiant energy could behave as though it were a stream of particles.
- Louis de Broglie took this concept and proposed that matter, under appropriate conditions, could exhibit properties of a wave—properties once associated only with energy.
- He used the term **matter waves** to describe these properties. And he proposed that objects have wavelengths associated with them that depend on their **momentum**.

Watch the Duality of Light Video

de Broglie’s Theorem

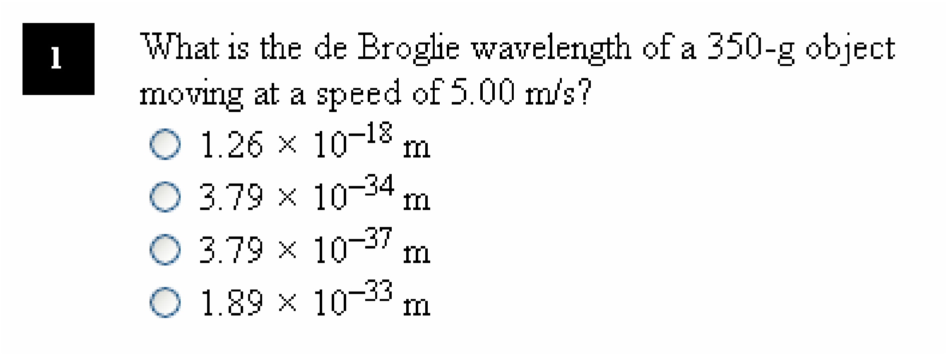
$$\lambda = \frac{h}{mv}$$

- Planck's constant is expressed in base SI units, kg-m^2/s^2, and mass is expressed in kg.
- This allows unit cancellation to give wavelength in meters.
- Inspection of this equation reveals that only extremely small objects, such as subatomic particles, have wavelengths sufficiently large as to be observable.
- In other words, the wavelength associated with a golf ball, for example, is so tiny as to be completely out of the range of any visible observation.
- Not long after de Broglie proposed that tiny particles should have observable wavelengths, scientists proved experimentally that electrons are diffracted by crystalline solids. Diffraction is a wavelike behavior.

Uncertainty…

- On the heels of de Broglie's theory, Werner Heisenberg concluded that there is a fundamental limitation on how precisely we can simultaneously measure the location and the momentum of an object small enough to have an observable wavelength.
- This limitation is known as the Heisenberg **uncertainty principle**.
- When applied to the electrons in an atom, this principle states *that it is inherently impossible to know simultaneously both the exact momentum of the electron and its exact location in space.*

For Example…



1 What is the de Broglie wavelength of a 350-g object moving at a speed of 5.00 m/s?

○ 1.26×10^{-18} m

○ 3.79×10^{-34} m

○ 3.79×10^{-37} m

○ 1.89×10^{-33} m

$$\lambda = \frac{h}{mv}$$

$h = 6.63 \times 10^{-34}$ J·s

Section 6.4

End

6.5 Quantum Mechanics and Atomic Orbitals

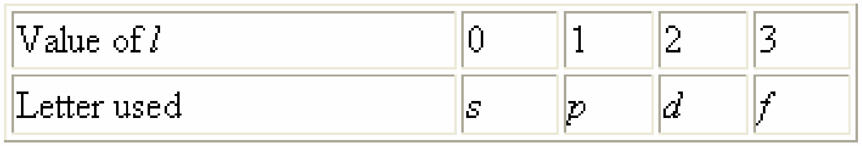
- Quantum theory and the uncertainty principle paved the way for scientists to describe the electrons in an atom in terms of wave properties
- Schrödinger developed an equation to incorporate both the wave and particle properties of the electron.
- The square of a wave function (ψ^2) is the **probability density**, or the probability that an electron will be found at a given point in space (also called **electron density**).
- <u>Regions where there is a high probability of finding the electron are regions of high electron density.</u>

Great video
On yahoo link

Section 6.5

Orbitals

- In the quantum mechanical model of the atom, *three* quantum numbers are required to describe what is now called an **orbital**.
  - 1. The principal quantum number, *n*, can have positive integer values. (1, 2, 3, . . .). The principal quantum number determines the *size of the orbital.*
  - 2. The second or azimuthal quantum number, *l*, can have integer values from 0 to *n*–1. The value of *l* determines the *shape of the orbital*. Each value of *l* has a letter associated with it to designate orbital shape.



Value of *l*	0	1	2	3
Letter used	*s*	*p*	*d*	*f*

  - 3. The magnetic quantum number, m_l, can have integer values from –*l* through +*l*. The magnetic quantum number determines the orbital's orientation in space.

Section 6.5

Orbitals

- Each value of *n* defines an electron shell.
- Within a shell, each value of *l* defines a subshell.
- Within a subshell, each value of m_l defines an individual orbital.
- The total number of orbitals in a shell is n^2, where *n* is the principal quantum number of the shell. The resulting number of orbitals for the shells—1, 4, 9, 16—has a special significance with regard to the periodic table: We see that the number of elements in the rows of the periodic table—2, 8, 18, and 32—are equal to twice these numbers.

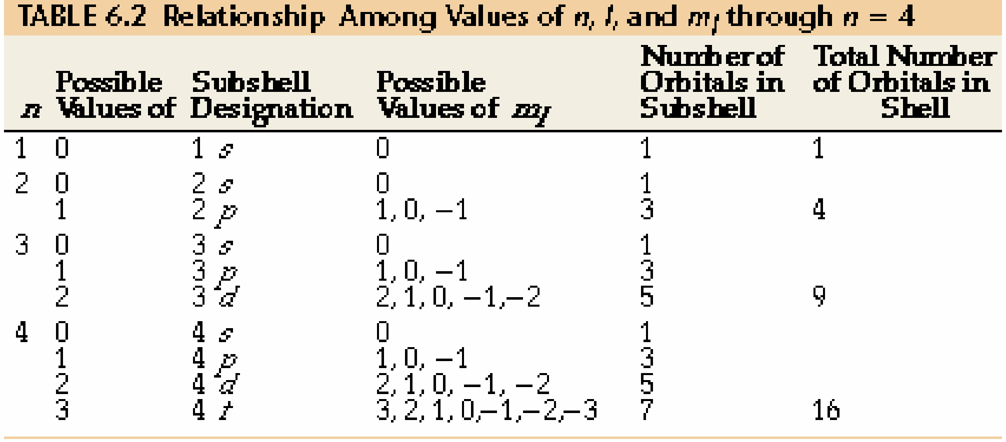


TABLE 6.2 Relationship Among Values of *n*, *l*, and m_l through $n = 4$

n	Possible Values of	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

Orbital Energy Level Diagram

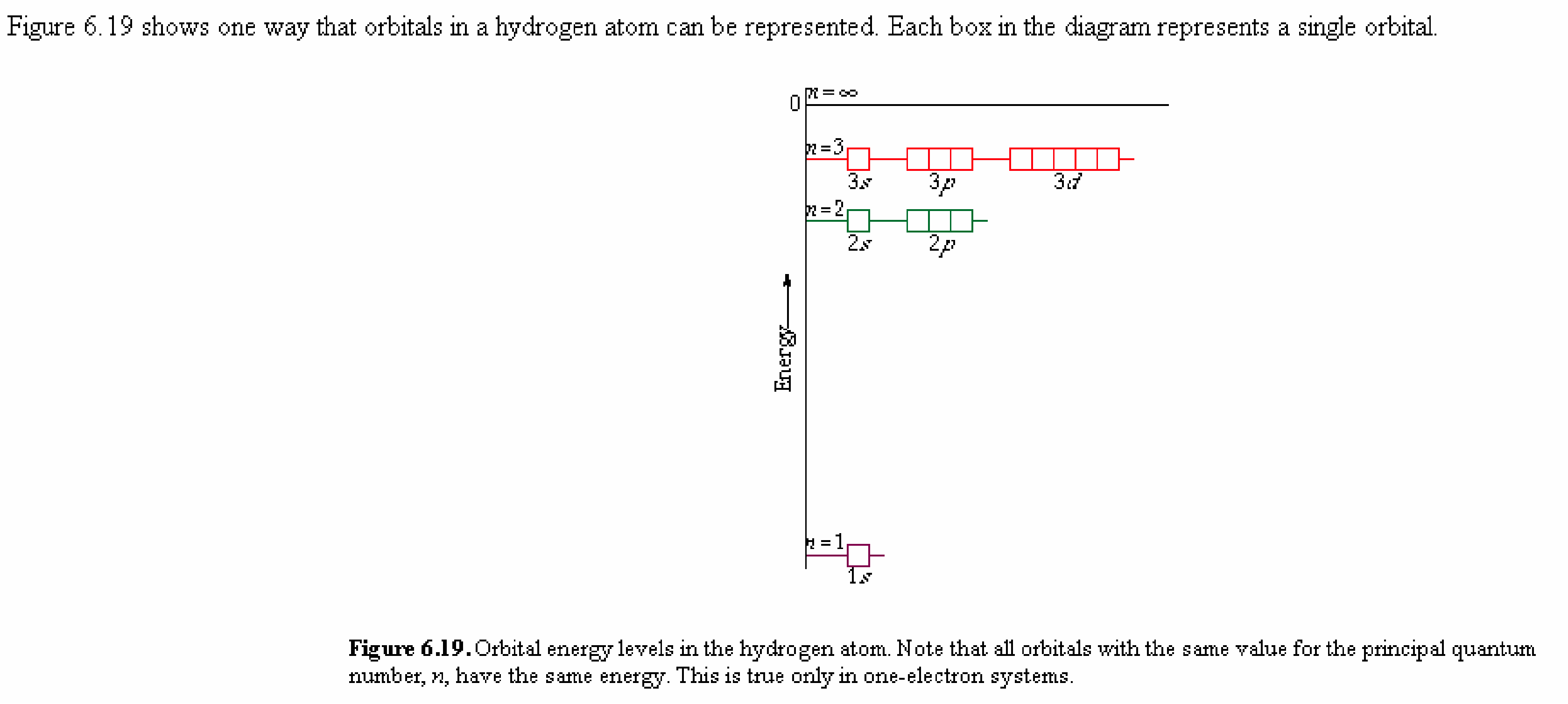


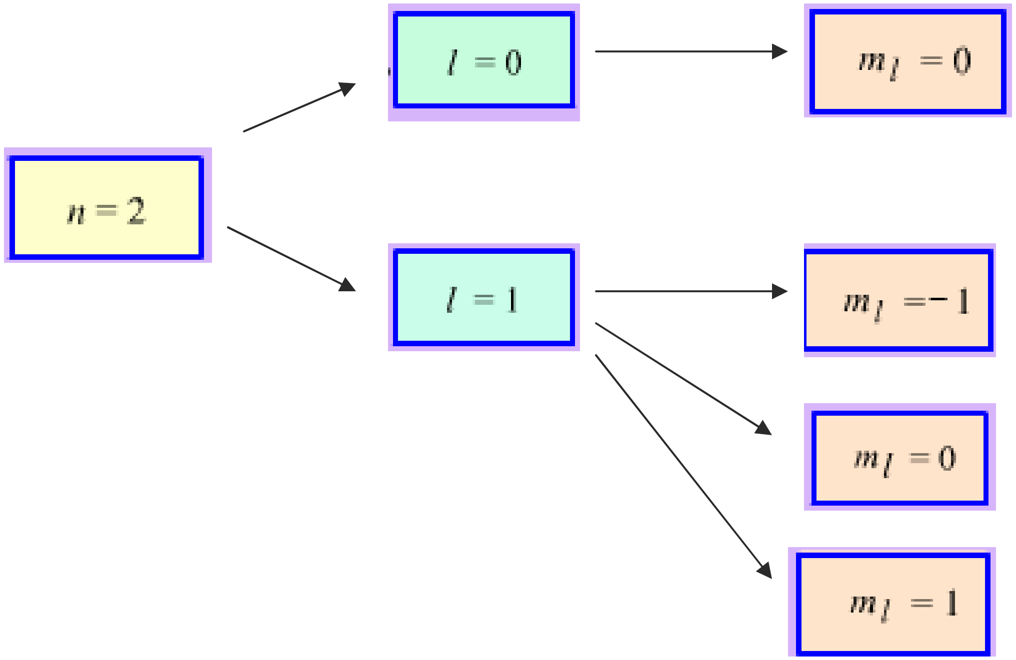
Figure 6.19 shows one way that orbitals in a hydrogen atom can be represented. Each box in the diagram represents a single orbital.

Figure 6.19. Orbital energy levels in the hydrogen atom. Note that all orbitals with the same value for the principal quantum number, *n*, have the same energy. This is true only in one-electron systems.

Section 6.5

Practice Question

How many orbitals are there in the $n=2$ shell?



$n = 2$

$l = 0$

$m_l = 0$

$l = 1$

$m_l = -1$

$m_l = 0$

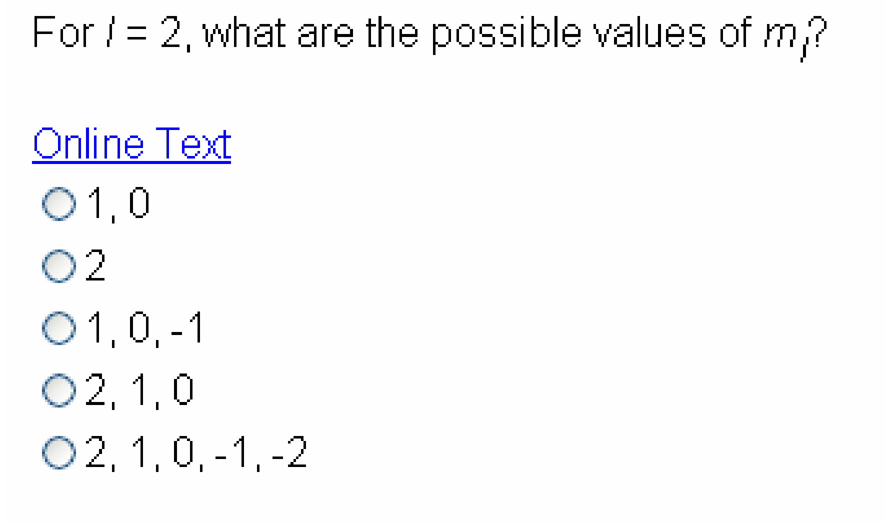
$m_l = 1$

orbitals
n, l, m_l

- 2, 0, 0
- 2, 1, 1
- 2, 1, 1
- 2, 1,− 1

Section 6.5

Practice Question



For $l = 2$, what are the possible values of m_l?

Online Text

○ 1, 0

○ 2

○ 1, 0, -1

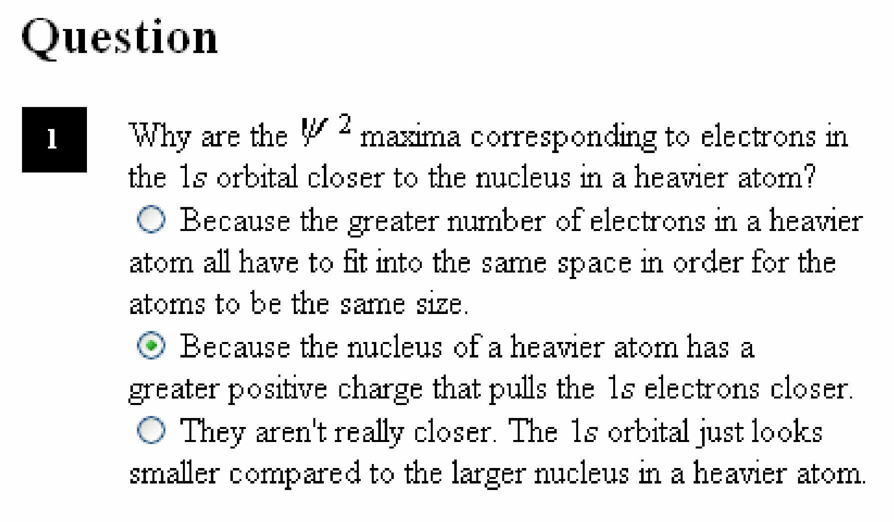
○ 2, 1, 0

○ 2, 1, 0, -1, -2

Section 6.5

6.6 Representations of Orbitals

- A graph of ψ^2 as a function of distance from the nucleus provides a way for us to picture the orbitals' shapes. For the *s* orbitals, a graph of ψ^2 ndicates spherical symmetry.
- For values of *n* greater than one, there are regions where the electron density drops to zero. A region of zero electron density between regions of nonzero electron density is called a **node**.



Question

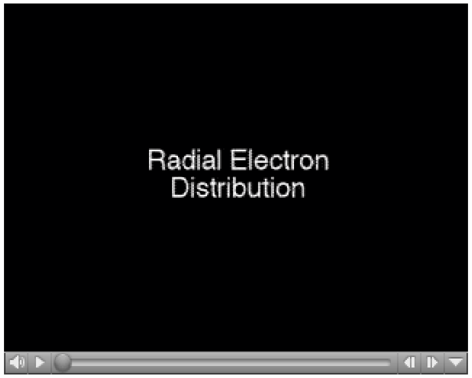
1 Why are the ψ^2 maxima corresponding to electrons in the 1*s* orbital closer to the nucleus in a heavier atom?

○ Because the greater number of electrons in a heavier atom all have to fit into the same space in order for the atoms to be the same size.

● Because the nucleus of a heavier atom has a greater positive charge that pulls the 1*s* electrons closer.

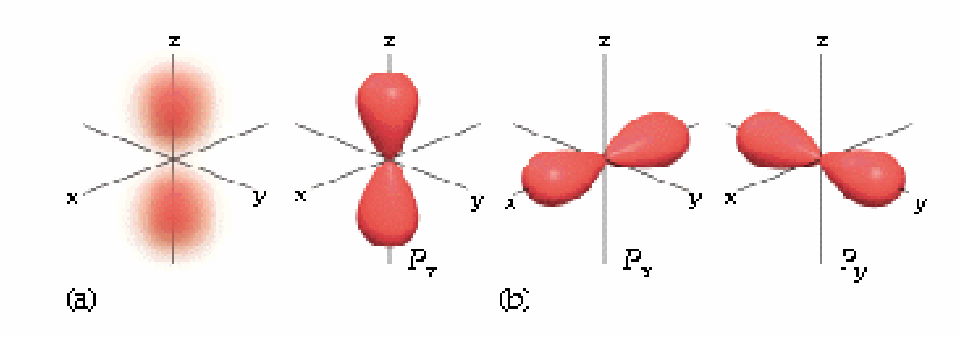
○ They aren't really closer. The 1*s* orbital just looks smaller compared to the larger nucleus in a heavier atom.

Radial Electron Distribution



Orbital Shape and Orientation

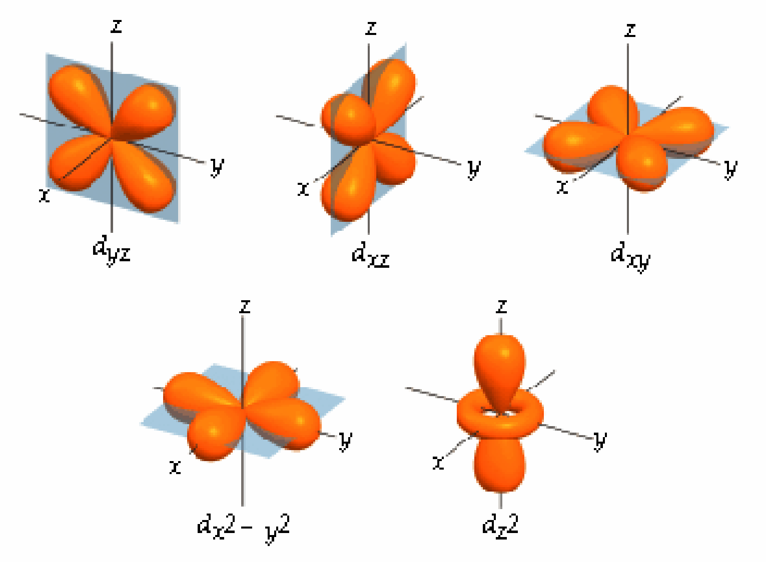
- The *p* orbitals have electron density distributed in dumbbell-shaped regions. The three *p* orbitals lie along the *x, y*, and *z* axes and are distinguished by the labels *px, py*, and *pz*.



Section 6.6

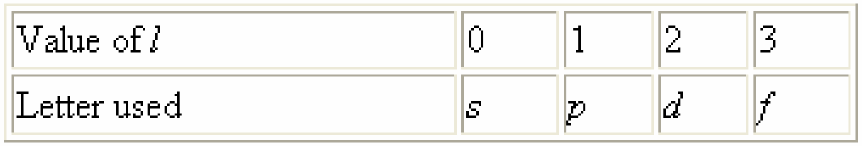
Orbital Shape and Orientation

- Four of the *d* orbitals have double dumbbell shapes that lie in planes defined by the *x*, *y*, and *z* axes. The fifth *d* orbital has two distinct components: a dumbbell shape lying along the *z* axis and a doughnut shape that encircles the *z* axis.

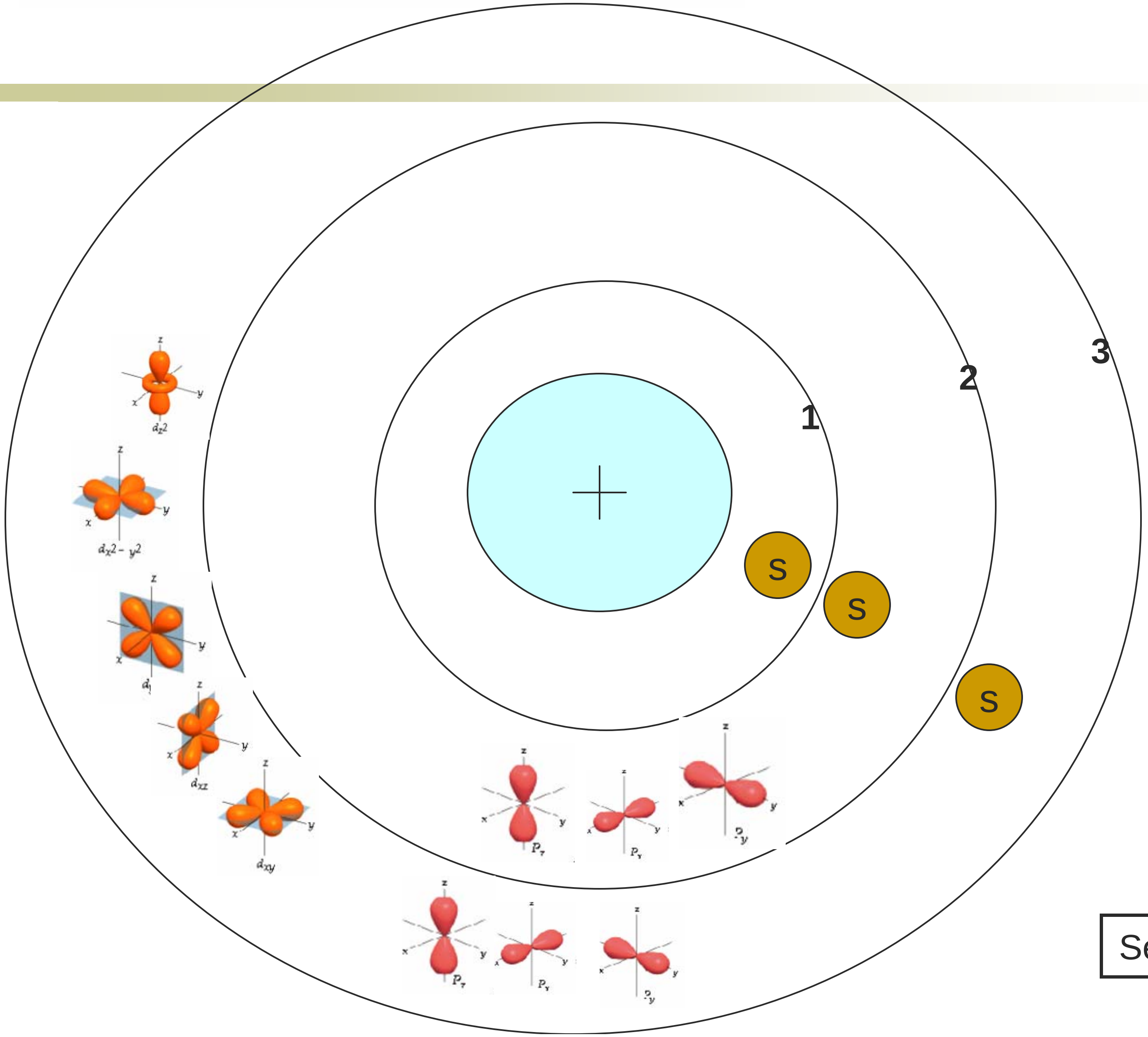


The shapes of *f* orbitals are somewhat complex, and we'll not show them here.

Section 6.6

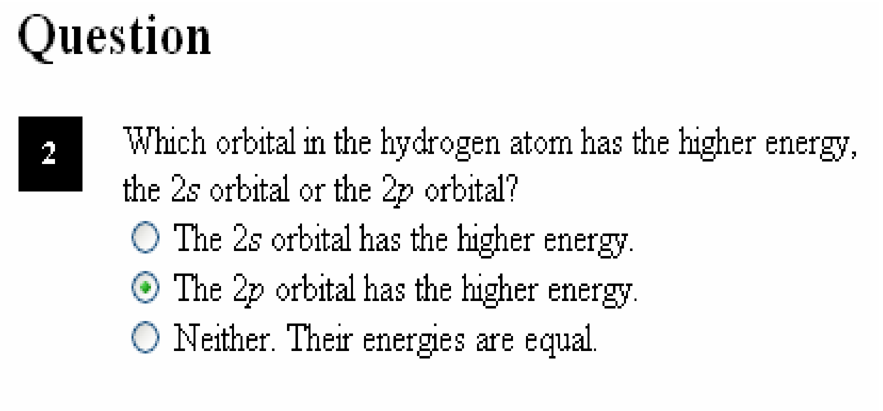


Value of *l*	0	1	2	3
Letter used	*s*	*p*	*d*	*f*



Section 6.6

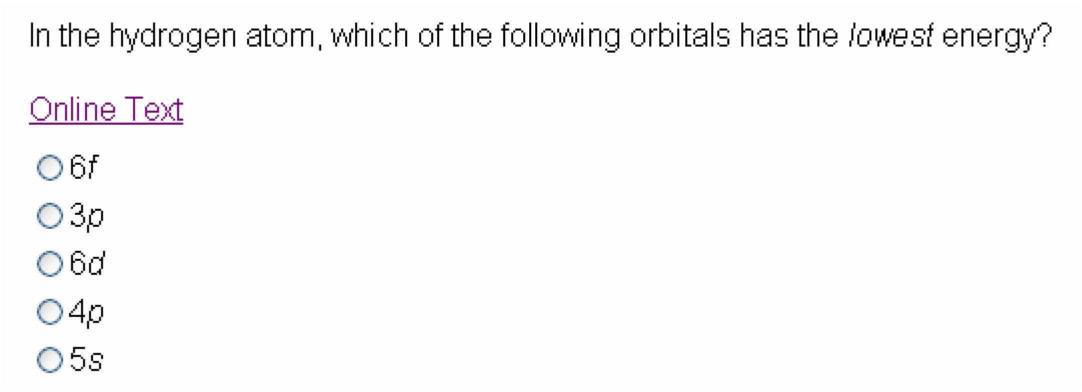
Practice Questions



Question

2 Which orbital in the hydrogen atom has the higher energy, the 2*s* orbital or the 2*p* orbital?

○ The 2*s* orbital has the higher energy.
● The 2*p* orbital has the higher energy.
○ Neither. Their energies are equal.



In the hydrogen atom, which of the following orbitals has the *lowest* energy?

Online Text

○ 6*f*
○ 3*p*
○ 6*d*
○ 4*p*
○ 5*s*

Section 6.6

End

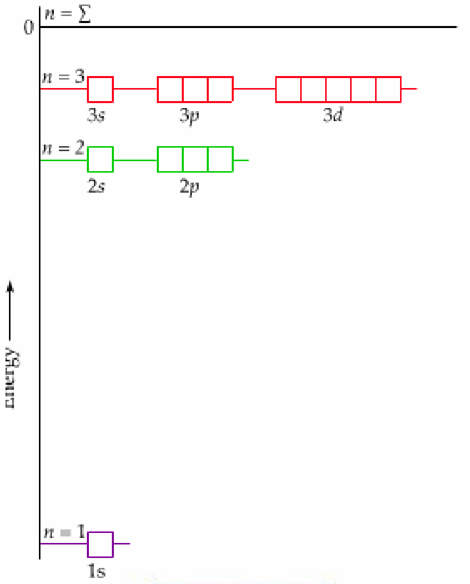
6.7 Orbitals in Many-Electron Atoms

- In a many-electron atom, repulsions between electrons result in differences in orbital energies within an electron shell.
- In effect, electrons are shielded from the nucleus by other electrons. The attraction between an electron and the nucleus is diminished by the presence of other electrons.
- Instead of the magnitude of attraction being determined by the nuclear charge, in a many-electron system the magnitude of attraction is determined by the **effective nuclear charge** Z_{eff}.
- This is the diminished nuclear charge that is felt by the electrons in orbitals with principal quantum number 2 and higher.

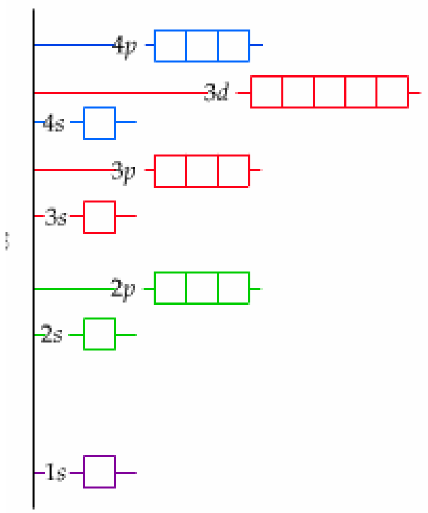
$$Z_{\text{eff}} = Z - S$$

- Z is the nuclear charge (atomic number), and S is the average number of electrons between the nucleus and the electron in question. The result is that orbital energies in many-electron atoms depend not only on the value of *n*, but also on the value of *l*. Within a shell, subshells of higher *l* value have higher energies.

Orbital Energy Level Diagram



One electron

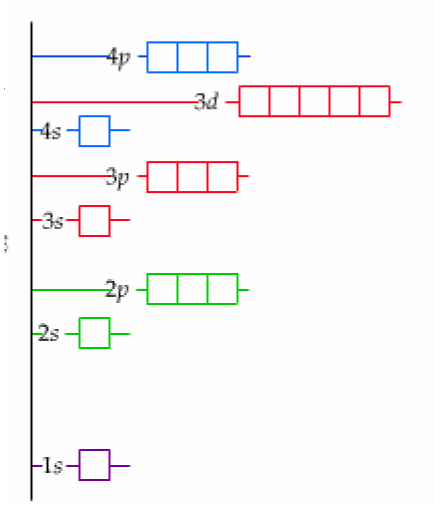


Many-electron

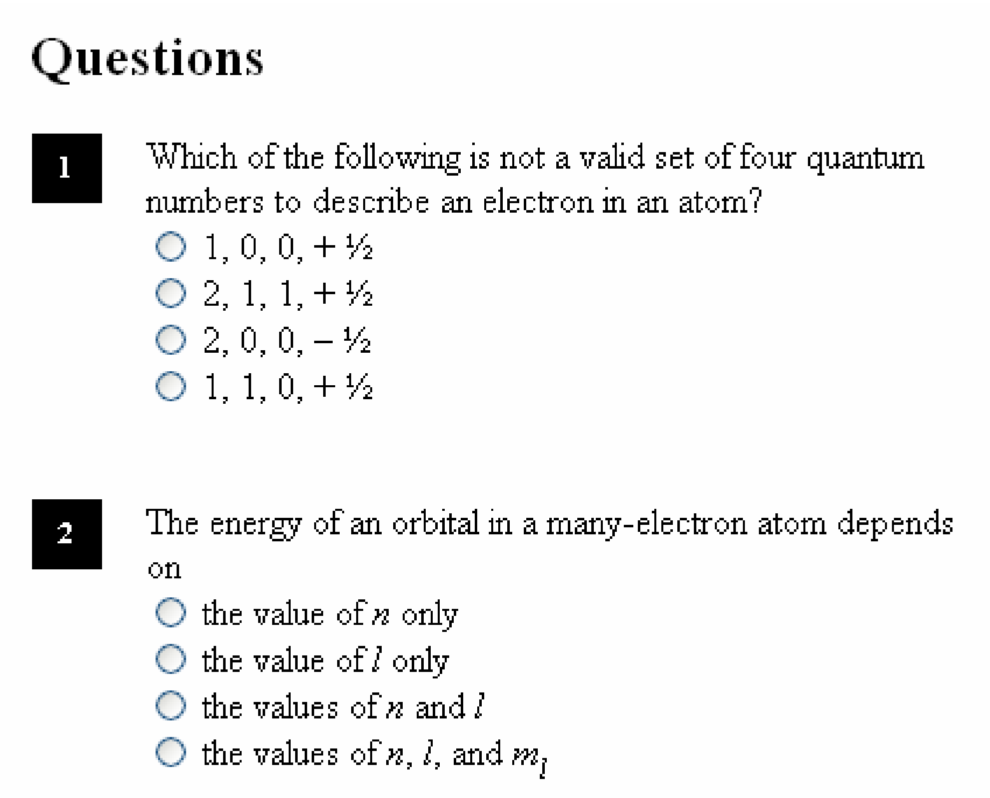
Section 6.7

Electron Spin

- In the quantum mechanical model of the atom, each orbital can accommodate two electrons. Electrons possess an intrinsic property known as **electron spin**. In order to distinguish the two electrons in a single orbital, we must use a fourth quantum number, the **electron spin quantum number**.
- The *electron spin quantum number*, *ms*, can have value of + ½ and – ½.
- The **Pauli exclusion principle** states that no two electrons in an atom can have the same set of four quantum numbers: *n*, *l*, *ml*, and *ms.* Thus, for two electrons to occupy the same orbital, one must have $m_s = +\frac{1}{2}$ and the other must have $m_s = -\frac{1}{2}$.



Practice Questions



Questions

1 Which of the following is not a valid set of four quantum numbers to describe an electron in an atom?

○ 1, 0, 0, + ½
○ 2, 1, 1, + ½
○ 2, 0, 0, – ½
○ 1, 1, 0, + ½

2 The energy of an orbital in a many-electron atom depends on

○ the value of n only
○ the value of l only
○ the values of n and l
○ the values of n, l, and m_l

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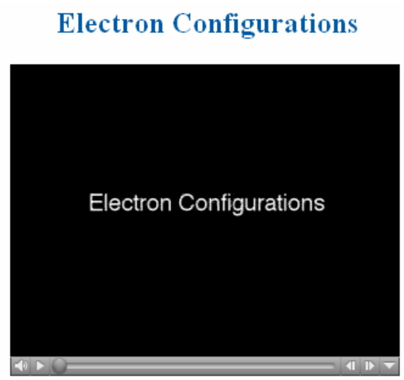
end

6.8 Electron Configurations

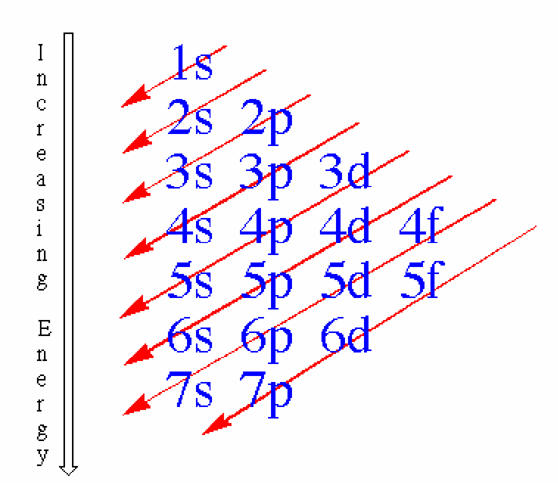
- The arrangement of electrons within the orbitals of an atom is known as the **electron configuration**.
- The most stable arrangement is called the *ground-state electron* configuration. This is the configuration where all of the electrons in an atom reside in the lowest energy orbitals possible.
- Bearing in mind that each orbital can accommodate a maximum of two electrons, we are able to predict the electron configurations of elements using the periodic table.

Section 6.8



6.8 Electron Configurations

- In its ground-state electron configuration, a hydrogen atom has one electron in its 1*s* orbital.
- A helium atom has two electrons, both of which are in the 1*s* orbital.
- A lithium atom has three electrons. Two of them are in the 1*s* orbital, the third one is in the next lowest energy orbital, the 2*s* orbital.
- Table 6.3 gives the ground-state electron configurations for the elements lithium through sodium.



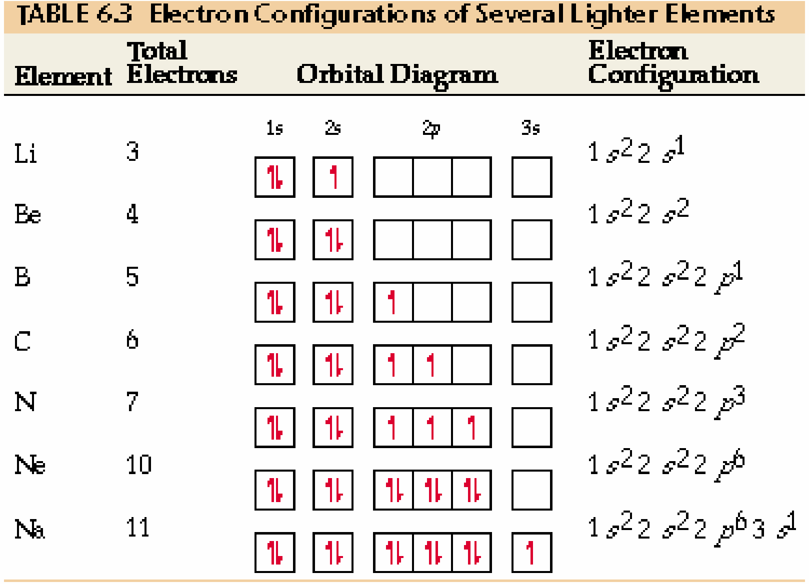


TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1*s*	2*s*	2*p*	3*s*	
Li	3	↑↓	↑			$1s^2 2s^1$
Be	4	↑↓	↑↓			$1s^2 2s^2$
B	5	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^2 2s^2 2p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Section 6.8

Hund’s Rule

- Note that when electrons begin to occupy the 2*p* subshell, they occupy all three *p* orbitals singly before pairing in a single orbital. This is the phenomenon that is described by **Hund's rule**.
- This rule states that for orbitals with the same energy, the lowest energy is attained when the number of electrons with the same spin is maximized.

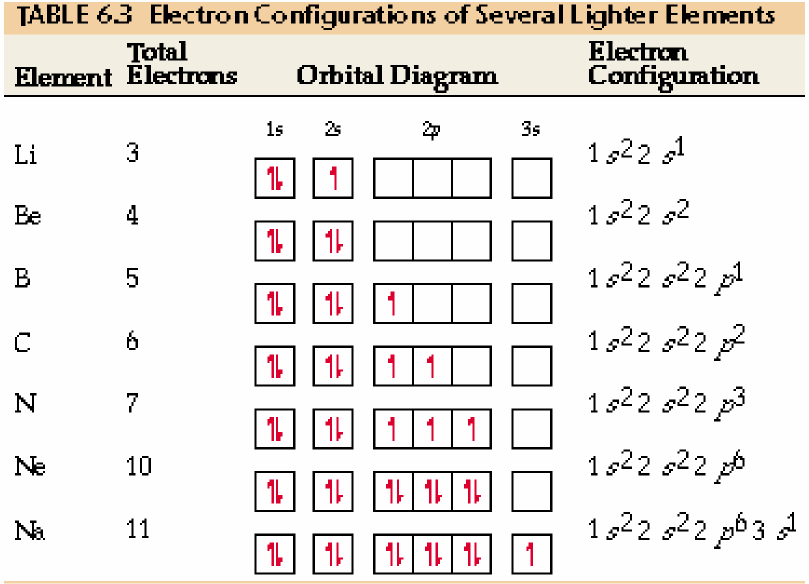


TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3	↑↓	↑			$1s^22s^1$
Be	4	↑↓	↑↓			$1s^22s^2$
B	5	↑↓	↑↓	↑		$1s^22s^22p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^22s^22p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^22s^22p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^22s^22p^63s^1$

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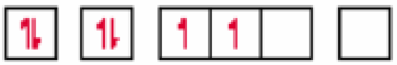
Writing Electron Configurations

- Electron configurations are commonly written using *spectroscopic notation* with superscripted numbers to denote how many electrons are in the orbital or subshell.
- For example, the electron configuration for Carbon is $1s^2 2s^2 2p^2$
- Orbital Diagram



$1s^2 2s^2 2p^2$

- For configurations with large amount of electrons:
- For Example, Sodium can be written as: $1s^2 2s^2 2p^6 3s^1$
- But more easily represented as: $[\mathrm{Ne}]\,3s^1$

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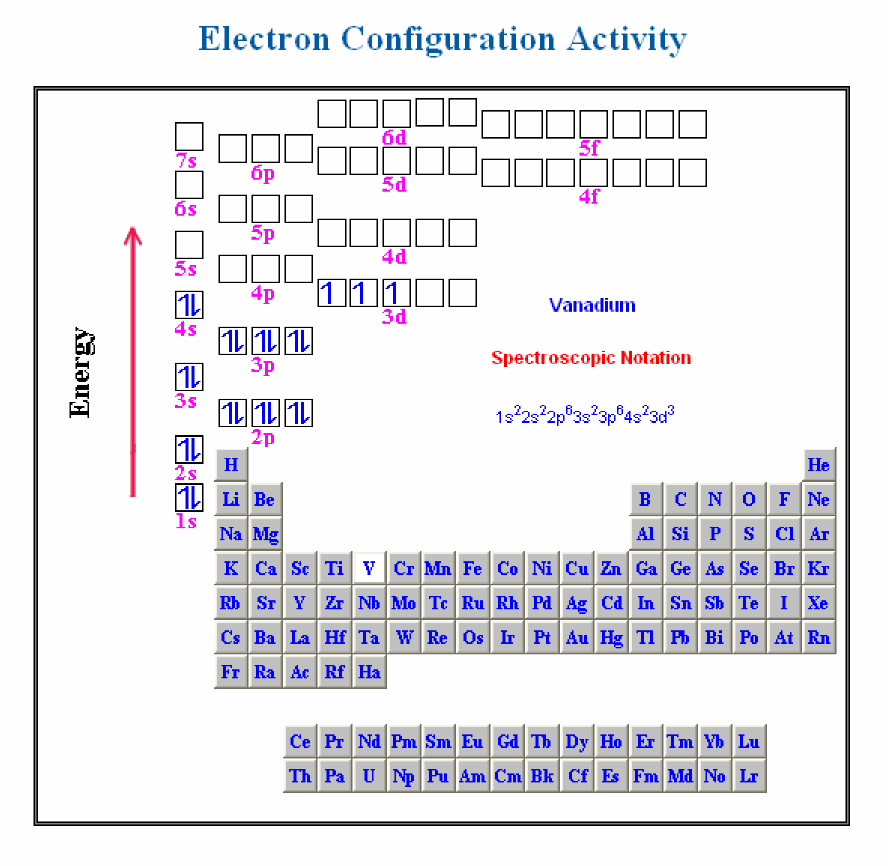
Practice



Electron Configuration Activity

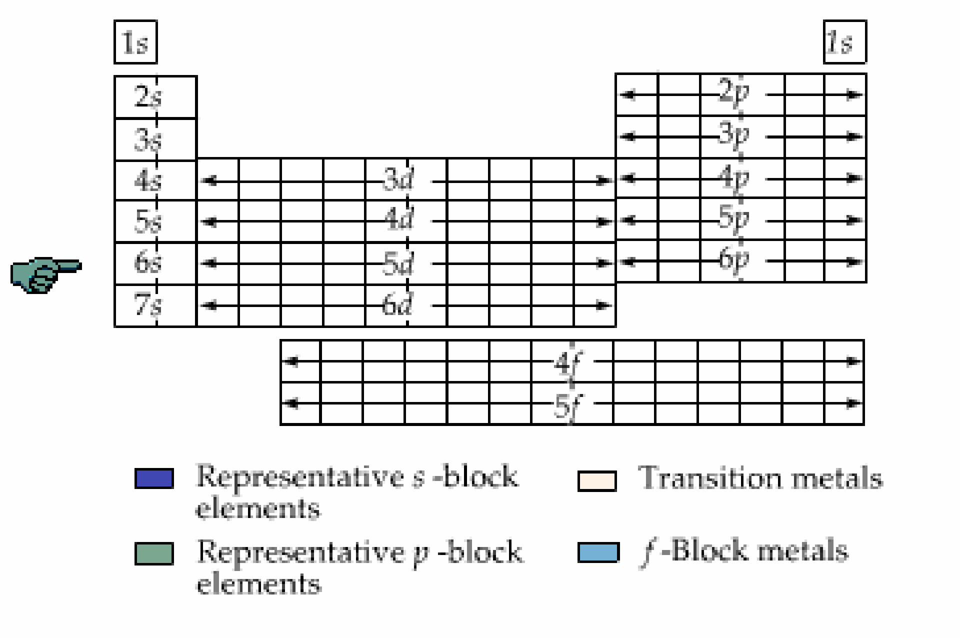
Vanadium

Spectroscopic Notation

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

6.9 Electron Configurations and the Periodic Table

- An easy way to view the table



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