

## Chapter 5

### Quantum Theory of the Hydrogen Atom

*The hydrogen atom, a problem we can solve exactly, is the theoretical seed from which our picture of molecules and complex atoms will soon sprout. The exercises in this chapter offer a thorough workout in the basics of quantum numbers, orbital patterns, and one-electron energies.*

*Pressing the analogy first made in Chapter 4, the set opens with a review of standing waves. See pages 130-133, R4.4, and 148-149 of PoC.*

1. Only one quantum number is needed to describe a standing wave in one dimension. A positive integer ( $n = 1, 2, \dots, \infty$ ), this single value specifies the number of half-wavelengths confined between the two endpoints. There are  $n - 1$  nodes present in a particular mode of vibration.
2. Since an integral number of half-wavelengths must fit into the interval  $L$ ,

$$n \frac{\lambda}{2} = L \quad (n = 1, 2, \dots, \infty)$$

we have the following restriction on the wavelength  $\lambda$ :

$$\lambda = \frac{2L}{n} \quad (n = 1, 2, \dots, \infty)$$

When  $L = 0.72$  m, as specified, the first five modes range in wavelength from 1.44 m (lowest frequency,  $n = 1$ ) to 0.288 m (highest frequency,  $n = 5$ ):

$n$	$\lambda_n = \frac{2L}{n}$	NODES ( $n - 1$ )
1	1.44	0
2	0.72	1
3	0.48	2
4	0.36	3
5	0.288	4

For a drawing of these first **five** standing waves, see Figure 5-1 on page 149 of *PoC* (and substitute the values  $L = 0.72$  m and  $\lambda_n = 1.44/n$ ).

3. Standing waves in one dimension are characterized by a single quantum number:

$$n = 1, 2, 3, \dots \infty$$

Each pattern of vibration contains  $n$  half-wavelengths and  $n - 1$  nodes.

(a) In principle, a string can support an infinite number of harmonics:  $n$  ranges from 1 to  $\infty$ .

(b) See Figure 5-1 on page 149 of *PoC* and take note: One additional half-cycle of oscillation is fitted into the same space for each increment of  $n$  by one unit. The second harmonic, for example, varies in space twice as fast as the first harmonic. The third harmonic varies three times as fast as the first. The fourth, four times. And so on:

$n$	FREQUENCY
1	$v$
2	$2v$
3	$3v$
4	$4v$
$n$	$nv$

The spatial frequency of the  $n$ th harmonic is  $nv$ .

4. A standing wave develops when two waves traveling in opposite directions—one disturbance moving at velocity  $u$  and the other at velocity  $-u$ —interfere constructively to produce a stationary pattern. Confined along a distance  $L$  are  $n$  half-wavelengths,

$$n \frac{\lambda}{2} = L$$

with the wavelength of each mode directly proportional to  $L$ :

$$\lambda_n = \frac{2L}{n}$$

The corresponding modal frequency

$$\nu_n = n \frac{u}{2L}$$

is thus inversely proportional to the wavelength:

$$\lambda_n \nu_n = u$$

Each frequency, moreover, is a multiple of some fundamental frequency  $\nu$ , which itself is inversely proportional to the string length:

$$\nu \equiv \nu_1 = \frac{u}{2L} \quad (n = 1)$$

(a) We have just established that the fundamental frequency is inversely proportional to the length of the string:

$$\nu = \frac{u}{2L}$$

A longer string will vibrate at a lower fundamental frequency. Its fundamental wavelength ( $2L$ ) will be longer.

(b) If a 100-cm string has a fundamental frequency of 440 Hz, then a 50-cm string (half the length) will vibrate at 880 Hz—twice as fast.

(c) By the same reasoning, a string of double the length (200 cm) will vibrate at half the fundamental frequency, or 220 Hz.

5. Write the frequency of the  $n$ th harmonic as

$$\nu_n = n\nu$$

and calculate the fractional change between  $\nu_{n+1}$  and  $\nu_n$ :

$$\frac{\nu_{n+1} - \nu_n}{\nu_n} = \frac{(n+1)\nu - n\nu}{n\nu} = \frac{1}{n}$$

Then, to obtain the percentage change, multiply by 100%:

$$\frac{1}{n} \times 100\%$$

A sample calculation for, say,  $n = 4$  yields the value 25%:

$$\frac{5v - 4v}{4v} \times 100\% = \frac{1}{4} \times 100\% = 25\%$$

The full set is displayed below:

	$n$	$\frac{1}{n} \times 100\%$
(a)	4	25
(b)	5	20
(c)	7	14
(d)	100	1
(e)	1,000,000	0.0001

At high frequencies, the change from one standing wave to the next is relatively small. See Figure 5.1 for a visual comparison.

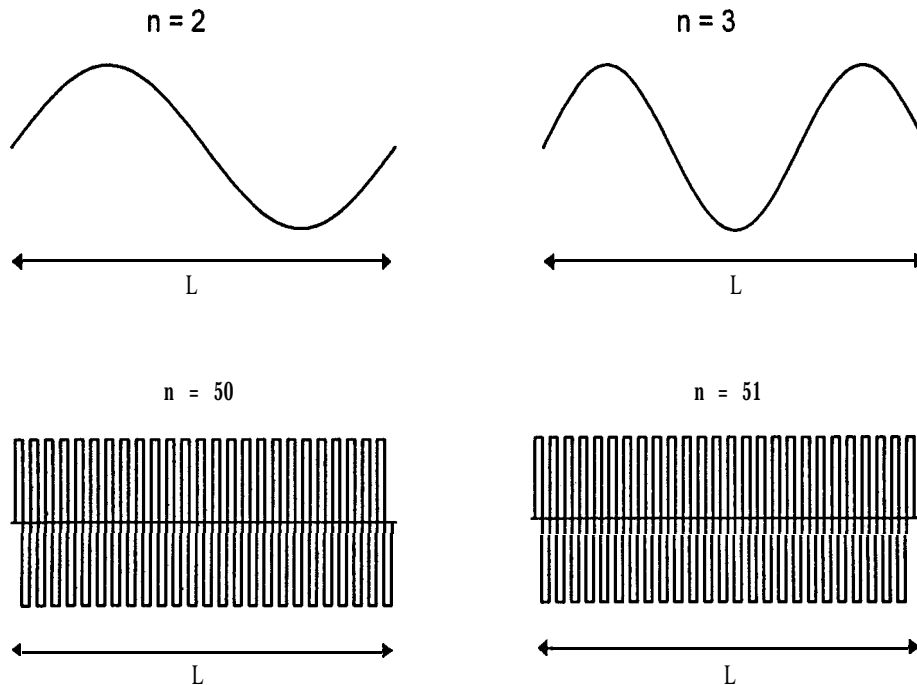


FIGURE 5.1 Standing waves. Top: Successive modes are easily distinguished at low quantum numbers, where relatively few half-wavelengths span the interval. The difference between  $n = 2$  and  $n = 3$ , for example, is clear. Wavelength decreases from  $L$  to  $\frac{2}{3}L$ , and frequency increases accordingly. Crests and troughs are well separated. Bottom: Going from one arbitrarily high mode ( $n = 50$ ) to the next ( $n = 51$ ), the crests and troughs lie close together and the incremental changes in frequency and wavelength are less pronounced. For the sake of clarity, the high-frequency oscillations are sampled twice per cycle and represented here as square waves.

From standing waves on a string to the quantized solutions of Schrödinger's equation. Relevant material is found in Sections 4-5, 4-6, 5-2, and 5-3 of PoC.

6. Presumably the proportional spacing between atomic energy levels should decrease as the principal quantum number increases. At sufficiently high values, too, we expect the levels to blend together into a *continuum*—a regime where the energies are spaced so closely as to appear unquantized.

In a hydrogen atom, for example, orbital energies are proportional to  $n^{-2}$  and thus become quasi-continuous at quantum numbers lower than those for string vibrations.

7. Quantum numbers of the one-electron atom are discussed on pages 148-152 and R5.2–R5.3 of PoC.

(a) Three quantum numbers correspond to the three spatial dimensions of a one-electron atom: a radial quantum number ( $n$ ) and two angular quantum numbers ( $\ell$  and  $m_\ell$ ).

(b) The principal quantum number,  $n$ , fixes the energy and radius of an electronic orbital. The angular momentum (or azimuthal) quantum number,  $\ell$ , determines the shape of the orbital and fixes the magnitude of the electronic angular momentum. The magnetic quantum number,  $m_\ell$ , establishes the orientation of the orbital and fixes its direction in a magnetic field.

(c) The principal quantum number  $n$  of a one-electron orbital is most like the single quantum number  $n$  used to describe a standing wave. The total number of nodes in both systems is equal to  $n - 1$ .

8. According to the uncertainty principle (Section 4-6), exact knowledge of an electron's position ( $\Delta x = 0$ ) precludes any definite knowledge of its momentum ( $\Delta p = \infty$ ):

$$\Delta p \Delta x > \approx h$$

If we know precisely where the electron is at some instant, then we have no idea where it is going or when it will get there.

9. A one-electron orbital ( $\psi$ ) is a solution to the Schrödinger equation for a single electron moving in the Coulomb potential of a single nucleus. It represents one of the allowed quantum states, carrying with it a certain energy and angular momentum.

Evaluated at some point in space ( $x, y, z$ ), the wave function  $\psi(x, y, z)$  provides a probability *amplitude* for finding the electron at that particular location. Its square,  $\psi^2(x, y, z)$ , is proportional to the probability itself, just as the intensity of an ordinary wave is proportional to its own particular amplitude. The wave function  $\psi$ , also like a wave, combines with other such functions and undergoes interference.

Quantum numbers and orbitals. See pages 148–152 and R5.2–R5.3 of PoC, together with Examples 5-1 through 5-4.

10. The general designation is  $n\ell$ , where  $\ell$  is assigned the code letters  $s$  (for  $\ell = 0$ ),  $p$  (for  $\ell = 1$ ),  $d$  (for  $\ell = 2$ ),  $f$  (for  $\ell = 3$ ),  $g$  (for  $\ell = 4$ ), and so forth.

	SUBSHELL	$n$	$\ell$
(a)	$3p$	3	1
(b)	$2s$	2	0
(c)	$4p$	4	1
(d)	$1s$	1	0
(e)	$2p$	2	1

11. More of the same:

	SUBSHELL	$n$	$\ell$
(a)	$3d$	3	2
(b)	$4d$	4	2
(c)	$3s$	3	0
(d)	$4s$	4	0
(e)	$4f$	4	3

12. Similar to the two preceding exercises. Azimuthal quantum numbers  $\ell = 0, 1, 2, 3, 4, 5 \dots$  correspond to the letters  $s, p, d, f, g, h \dots$

	$n$	$\ell$	SUBSHELL
(a)	3	2	$3d$
(b)	2	1	$2p$
(c)	4	3	$4f$
(d)	1	0	$1s$

13. Same idea:

	$n$	$\ell$	SUBSHELL
(a)	2	0	$2s$
(b)	6	5	$6h$
		1	$3p$
(e)	3	0	$3s$

14. For a given value of  $n$ , the quantum number  $\ell$  ranges from 0 to  $n - 1$ :

$$\ell = 0, 1, 2, \dots, n-1$$

Each shell  $n$  therefore supports  $n$  subshells:

$n$	$\ell$	LETTER CODE
1	0	<i>s</i>
2	0, 1	<i>s, p</i>
3	0, 1, 2	<i>s, p, d</i>
4	0, 1, 2, 3	<i>s, p, d, f</i>
5	0, 1, 2, 3, 4	<i>s, p, d, f, g</i>

See pages 152-153 (and particularly Figure 5-3) of *PoC*.

15. For a given value of  $\ell$ , the quantum number  $m_\ell$  ranges from  $-\ell$  to  $+\ell$  in steps of 1:

$$m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$$

Each subshell supports  $2\ell + 1$  magnetic sublevels:

	SUBSHELL	$n$	$\ell$	$m_\ell$
(a)	1 <i>s</i>	1	0	0
(b)	2 <i>s</i>	2	0	0
(c)	2 <i>p</i>	2	1	-1 0 1
(d)	3 <i>s</i>	3	0	0
(e)	3 <i>p</i>	3	1	-1 0 1

16. Similar:

	SUBSHELL	$n$	$\ell$	$m_\ell$
(a)	3 <i>d</i>	3	2	-2 -1 0 1 2
	4 <i>s</i>	4	0	0
(c)	4 <i>p</i>	4	1	-1 0 1
(d)	4 <i>d</i>	4	2	-2 -1 0 1 2
(e)	4 <i>f</i>	4	3	-3 -2 -1 0 1 2 3

17. The subshells are distributed as follows:

$$\begin{array}{l} 1s \\ 2s \ 2p \\ 3s \ 3p \ 3d \end{array}$$

Spherically symmetric, the *angular* wave function representing an s orbital is everywhere positive (and constant, too). See Figure 5-9 on page 162 of *PoC* for a sketch.

The *p* orbitals come in groups of three ( $m_\ell = -1, 0, 1$ ), and the corresponding angular wave functions can be combined to produce both real and complex functions—all equivalent in a free atom. Chemists typically represent the three *p* orbitals as dumbbells along three perpendicular axes, with each dumbbell bisected by a nodal plane. See Figure 5-11 on page 166 (in which the  $p_x$  and  $p_y$  functions are linear combinations of states having  $m_\ell = +1$  and  $m_\ell = -1$ ).

The *d* orbitals come five to a set. In common practice they are generally portrayed as four cloverleaf patterns and one “dumbbell in a doughnut,” with nodal planes and phases as shown in Figure 5-12 of *PoC* (page 167).

18. Here we take a closer look at the three magnetic sublevels of the  $3p$  subshell ( $m_\ell = -1, 0, 1$ ). Our conclusions pertain equally well, however, to any other set of *p* orbitals in a one-electron atom (where  $n = 2, 3, \dots, \infty$ ) and indeed to *any* subshell  $\ell$  within any shell  $n$  (where  $m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$ ).

(a) In the absence of a magnetic field, the states  $m_\ell = -1$ ,  $m_\ell = 0$ , and  $m_\ell = 1$  all have the same energy. The *p* subshell is threefold degenerate in the free atom.

Further, in a one-electron atom this single value of energy is equal to that of the  $3s$  and  $3d$  subshells. Energy depends only on  $n$ , not  $\ell$  or  $m_\ell$  (*PoC*, page 155).

(b) The electron, a charged particle, generates angular momentum and thus its own magnetic field while moving about the nucleus. Imposition of *an external* magnetic field then destroys the equivalence of the  $3p_x$ ,  $3p_y$ , and  $3p_z$  orbitals. The self-generated field of an electron interacts with the external field, leading to a different energy for each of the three quantized orientations ( $m_\ell = -1, 0, 1$ ). The degeneracy of the *p* subshell is broken, and the  $3s$  orbital lies lower in energy than the  $3p$ .

(c) An orbital splits further into two *spin* states, which develop from an intrinsic electronic angular momentum—and associated magnetic field—unrelated to any overt bodily rotation. Interacting with an external magnetic field, the spin-endowed electron has an “up” state ( $m_s = \frac{1}{2}$ ) and a “down” state ( $m_s = -\frac{1}{2}$ ). Each produces a different energy.

There are, in all, six distinct  $3p$  energies in a magnetic field:

$$\text{space (3) } \times \text{ spin (2) } = 6 \text{ states}$$



19. Electron spin. See pages 173-176, R5.4–R5.5, and A171 of *PoC*.

(a) The electron is thought to be a point particle lacking any discernible structure and therefore unable to spin like a top. Quantum mechanical “spin” produces an anomalous magnetic moment inconsistent with a classical rotation.

(b) The quantum number  $m_s$  measures the component of spin angular momentum along an axis established by an external magnetic field.

(c) Electron spin arises from an angular momentum inherent in the particle itself, not attributable to any obvious rotational motion. The fourth quantum number appears naturally in Dirac’s relativistic theory of the one-electron atom.

(d) Spin angular momentum is described by two quantum numbers— $s$  and  $m_s$ —just as orbital angular momentum is described by the two analogous quantum numbers  $\ell$  and  $m_\ell$ . The same rules apply: (1) The magnitude of an orbital angular momentum (in units of  $h/2\pi$ ) is  $\sqrt{\ell(\ell+1)}$ . The magnitude of a spin angular momentum is  $\sqrt{s(s+1)}$ . (2) The component of orbital angular momentum along an external field measures  $m_\ell$  in units of  $h/2\pi$ . Similarly, the corresponding component of spin angular momentum is  $m_s$ . (3) The allowed values of  $m_\ell$  run from  $-\ell$  to  $+\ell$  in steps of 1. The allowed values of  $m_s$  run from  $-s$  to  $+s$ , also in steps of 1.

For electrons, where  $s$  is always equal to  $\frac{1}{2}$ , the component  $m_s$  is restricted accordingly to the two values  $-\frac{1}{2}$  and  $+\frac{1}{2}$ .

20. The quantum number  $\ell$  ( $= 0, 1, 2, \dots, n-1$ ) must be a positive integer less than  $n$ :

	SUBSHELL	$n$	$\ell$	COMMENT
(a)	1d	1	2	forbidden ( $\ell > n$ )
(b)	5d	5	2	allowed
(c)	5f	5	3	allowed
(d)	5h	5	5	forbidden ( $\ell = n$ )
(e)	6h	6	5	allowed
(f)	8d	8	2	allowed

21. See Exercises 10 through 13. Subshells are defined by  $n$  and  $\ell$  alone, not  $m_\ell$ :

	$n$	$\ell$	SUBSHELL
(a)	3	2	3d
(b)	2	1	2p
(c)	4	3	4f
(d)	1	0	1s

22. Similar:

	$n$	$\ell$	SUBSHELL
(a)	2	0	2s
(b)	6	5	6h
(c)	3	1	3p
(d)	3	0	3s

23. The rules are as follows:

$$n = 1, 2, 3, \dots, \infty$$

$$\ell = 0, 1, 2, \dots, n-1$$

$$m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$$

$$m_s = \pm \frac{1}{2}$$

Violations are cited in the table below:

	$n$	$\ell$	$m_\ell$	$m_s$	COMMENT
(a)	4	2	1	0	forbidden ( $m_s \neq \pm \frac{1}{2}$ )
(b)	2	1	2	$\frac{1}{2}$	forbidden ( $ m_\ell  > \ell$ )
(c)	5	5	-2	$-\frac{1}{2}$	forbidden ( $\ell = n$ )
(d)	1	0	-1	$\frac{1}{2}$	forbidden ( $ m_\ell  > \ell$ )

24. Similar:

	$n$	$\ell$	$m_\ell$	$m_s$	COMMENT
(a)	3	2	2	1	forbidden ( $m_s \neq \pm \frac{1}{2}$ )
(b)	6	-1	5	$\frac{3}{2}$	forbidden ( $\ell < 0$ ; $m_s \neq \pm \frac{1}{2}$ )
(c)	3	0	1	4	forbidden ( $ m_\ell  > \ell$ )
(d)	3	$\frac{1}{2}$	0	$-\frac{1}{2}$	forbidden ( $\ell \neq 0, 1, 2, \dots, n-1$ )

25. The total number of nodes is  $n - 1$ , and the number of angular nodes is  $\ell$ :

$$\begin{array}{ccccccc} \text{RADIAL} & + & \text{ANGULAR} & = & \text{TOTAL} \\ n - \ell - 1 & & \ell & & n - 1 \end{array}$$

See Examples 5-3 and 5-4 in *PoC*. Nodal patterns for the fourth shell are as follows:

SUBSHELL	$n$	$\ell$	RADIAL NODES + ANGULAR NODES = TOTAL		
4s	4	0	3	0	3
4p	4	1	2	1	3
4d	4	2	1	2	3
4f	4	3	0	3	3

26. The radius of an orbital increases as  $n$  increases, enhancing the probability that the electron will be found farther from the nucleus. A hydrogen atom therefore expands when the electron moves out of the ground state ( $n = 1$ ). Its radial wave function persists over a greater distance from the nucleus.

**Energy calculations.** See pages 153-1 56 and Examples 5-5 through 5-7.

27. The orbital energies of a one-electron atom are quantized according to the formula introduced on pages 153-1 56 of *PoC*:

$$E_n = -R_\infty \frac{Z^2}{n^2}$$

Here the symbol  $n$  denotes the principal quantum number, and the symbol  $Z$  denotes the atomic number (the positive nuclear charge). The Rydberg constant,  $R_\infty$ , corresponds to the ionization energy of a hydrogen atom: the difference in energy between the levels  $n = 1$  and  $n = \infty$  when  $Z = 1$ .

For an arbitrary transition from an initial level  $n_i$  to a final level  $n_f$ , the difference in energy is thus

$$\Delta E = E_f - E_i = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

for any one-electron atom with atomic number  $Z$ . See Example 5-7 in *PoC* (page R5.9).

Note, in passing, that the full value of the Rydberg constant is given as

$$R_\infty = 2.1798741 \times 10^{-18} \text{ J}$$

in Table C-5 of *PoC* (page A65). Like most of the physical constants, it is a number known to very high precision. Our customary practice, however, will be to use only three or four digits for  $L$ -except in cases, as in this exercise, where round-off error proves to be an issue.

(a) Substitute the values  $n_i = 1$ ,  $n_f = 2$ , and  $Z = 1$  to obtain  $\Delta E$  between the ground state and first excited orbital of a hydrogen atom:

$$\begin{aligned}
 \Delta E &= -R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\
 &= -R_{\infty} (1)^2 \times \left( \frac{1}{2^2} - \frac{1}{1^2} \right) \\
 &= \frac{3R_{\infty}}{4} = \frac{3(2.1798741 \times 10^{-18} \text{ J})}{4} = 1.6349056 \times 10^{-18} \text{ J}
 \end{aligned}$$

Rounded to three digits, the energy ( $\frac{3}{4}R_{\infty}$ ) is  $1.63 \times 10^{-18} \text{ J}$ .

(b) To compute the wavelength associated with a photon having  $E = \frac{3}{4}R_{\infty}$ , rearrange the Planck-Einstein formula

$$E = h\nu = \frac{hc}{\lambda}$$

to isolate  $\lambda$ :

$$\begin{aligned}
 \lambda &= \frac{hc}{E} \\
 &= \frac{4hc}{3R_{\infty}} = \frac{4(6.6260755 \times 10^{-34} \text{ J s})(2.99792458 \times 10^8 \text{ m s}^{-1})}{3(2.1798741 \times 10^{-18} \text{ J})} \\
 &= 1.2150227 \times 10^{-7} \text{ m} \approx 122 \text{ nm}
 \end{aligned}$$

Visible light, which falls roughly in the range 400-700 nm (equivalently, 4000-7000 Å), is therefore **insufficiently** energetic to bring about the transition. The requisite energy must be provided by ultraviolet light-radiation with a shorter wavelength.

For additional examples of this kind of calculation, see Exercises 14 through 24 in Chapter 4. Related material is found in Section 4-4 and Example 4-5.

(c) Use the equation

$$E_k = \frac{1}{2}mv^2$$

to calculate the kinetic energy of a helium atom. If the mass  $m$  is in kilograms and the velocity  $v$  is in meters per second, then the energy  $E_k$  appears in joules (equivalent to  $\text{kg m}^2 \text{ s}^{-2}$ ):

$$m = \frac{4.0026 \text{ g}}{\text{mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times 6.022 \times 10^{23} \text{ atoms} = 6.647 \times 10^{-27} \text{ kg (per atom)}$$

$$v = 1000 \text{ m s}^{-1}$$

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}(6.647 \times 10^{-27} \text{ kg})(1000 \text{ m s}^{-1})^2 = 3.323 \times 10^{-21} \text{ J}$$

This energy is also less—by a factor of 500—than the difference between the first and second shells of hydrogen. A helium atom moving at  $1000 \text{ m s}^{-1}$  does not have enough energy to excite a hydrogen atom in the ground state.

For assorted calculations involving kinetic energy, see Exercises 15, 16, 17, 20, 21, and 24 in Chapter 1, as well as Exercises 23, 25, 28, 29, 33, 34, and 35 in Chapter 4. The subject is covered on pages 30-31, 39-40, and R1.4-R1.5 of *PoC*, along with Examples 1-1, 1-2, 1-6, 4-5, and 5-6.

28. Refer back to Exercise 27 for a brief review of energy quantization in a one-electron atom:

$$E_n = -R_\infty \frac{Z^2}{n^2}$$

We calculate  $\Delta E_{4 \rightarrow 5}$  for H and then compare it with the equivalent value for He<sup>+</sup>.

Hydrogen ( $Z = 1$ ,  $n_i = 4$ ,  $n_f = 5$ ):

$$\begin{aligned} \Delta E &= -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -R_\infty (1)^2 \times \left( \frac{1}{5^2} - \frac{1}{4^2} \right) \\ &= 0.0225 R_\infty = 4.90 \times 10^{-20} \text{ J} \end{aligned}$$

Helium ion ( $Z = 2$ ,  $n_i = 4$ ,  $n_f = 5$ ):

$$\begin{aligned} \Delta E &= -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -R_\infty (2)^2 \times \left( \frac{1}{5^2} - \frac{1}{4^2} \right) \\ &= 4 \times 0.0225 R_\infty = 1.96 \times 10^{-19} \text{ J} \end{aligned}$$

The levels in He<sup>+</sup> are more widely spaced, by a factor of 4:

$$\left(\frac{Z_{\text{He}^+}}{Z_{\text{H}}}\right)^2 = \left(\frac{2}{1}\right)^2 = 4$$

29. Given the frequency of the transition,

$$\nu = 6.169 \times 10^{14} \text{ s}^{-1}$$

we calculate the corresponding photon energy:

$$E = h\nu = (6.626 \times 10^{-34} \text{ J s})(6.169 \times 10^{14} \text{ s}^{-1}) = 4.088 \times 10^{-19} \text{ J}$$

We then insert this value into the energy equation for hydrogen (implicitly,  $Z = 1$ ),

$$\Delta E = E_f - E_i = -R_\infty \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

and thereby establish a relationship between  $n_i$  and  $n_f$ :

$$\left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = \frac{|\Delta E|}{R_\infty} = \frac{4.088 \times 10^{-19} \text{ J}}{2.1799 \times 10^{-18} \text{ J}} = 0.1875$$

Trial and error yields two solutions, one for absorption ( $n_f > n_i$ ) and one for emission ( $n_f < n_i$ ).

Absorption ( $n_i = 2$ ,  $n_f = 4$ )

$$\left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = 0.1875$$

$$\left| \frac{1}{4^2} - \frac{1}{2^2} \right| = \left| \frac{1}{16} - \frac{1}{4} \right| = |-0.1875| = 0.1875$$

Emission ( $n_i = 4$ ,  $n_f = 2$ )

$$\left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = 0.1875$$

$$\left| \frac{1}{2^2} - \frac{1}{4^2} \right| = \left| \frac{1}{4} - \frac{1}{16} \right| = |0.1875| = 0.1875$$

QUESTION: A correct result, but how do we arrive at it?

ANSWER: We need take only two false steps. (1) Absorption or emission between the first and second shells ( $1 \rightleftharpoons 2$ ) yields a magnitude 0.7500 for the difference in  $1/n^2$ : larger than 0.1875, and hence too energetic. Moreover, any other transition involving  $n = 1$  will produce an even larger number. We must go on to the next shell,  $n = 2$ . (2) The transition  $2 \rightleftharpoons 3$  yields an absolute value of 0.1389: too small, but a step in the right direction. Our very next choice ( $2 \rightleftharpoons 4$ ) yields 0.1875: just right.

30. The energy of any orbital in a one-electron atom depends only on the quantum number  $n$ , not  $\ell$  or  $m_\ell$ .

Thus for the  $1s \rightarrow 2p$  transition in hydrogen ( $Z=1$ ), we simply calculate  $\Delta E$  between  $n_i = 1$  and  $n_f = 2$ :

$$\begin{aligned} \Delta E &= -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -R_\infty (1)^2 \times \left( \frac{1}{2^2} - \frac{1}{1^2} \right) \\ &= \frac{3R_\infty}{4} = \frac{3(2.1798741 \times 10^{-18} \text{ J})}{4} \\ &= 1.6349056 \times 10^{-18} \text{ J} \end{aligned}$$

The associated wavelength follows directly from the Planck-Einstein relationship:

$$\begin{aligned}
 |\Delta E| &= h\nu = \frac{hc}{\lambda} \\
 \lambda &= \frac{hc}{|\Delta E|} \\
 &= \frac{4hc}{3R_\infty} = \frac{4(6.6260755 \times 10^{-34} \text{ J s})(2.99792458 \times 10^8 \text{ m s}^{-1})}{3(2.1798741 \times 10^{-18} \text{ J})} \\
 &= 1.2150227 \times 10^{-7} \text{ m} \approx 122 \text{ nm}
 \end{aligned}$$

See Exercise 27 and Example 5-7 for additional details. Results (rounded to three digits) are summarized in the table below:

TRANSITION	$n_i$	$n_f$	$\Delta E (R_\infty)$	$\Delta E (\text{J})$	$\lambda (\text{m})$	COMMENT
(a) $1s \rightarrow 2p$	1	2	0.7500	$1.63 \times 10^{-18}$	$1.22 \times 10^{-7}$	absorption
(b) $5f \rightarrow 4d$	5	4	-0.0225	$-4.90 \times 10^{-20}$	$4.05 \times 10^{-6}$	emission
(c) $3d \rightarrow \infty$	3	$\infty$	0.1111	$2.42 \times 10^{-19}$	$8.20 \times 10^{-7}$	absorption
(d) $\infty \rightarrow 1s$	$\infty$	1	-1.0000	$-2.18 \times 10^{-18}$	$9.11 \times 10^{-8}$	emission

Absorptive transitions occur when the final state,  $n_f$ , lies higher than the initial state,  $n_i$ . The atom takes up energy from the electromagnetic field, and  $\Delta E$  (for the atom) is positive.

Emissive transitions arise when  $n_f < n_i$ . Falling from a higher state to a lower state, the atom gives up energy to the electromagnetic field. The atomic  $\Delta E$  is negative.

Note that our convention is to state the wavelength as *a positive* quantity, even if  $\Delta E$  happens to be negative:

$$\lambda = \frac{hc}{|\Delta E|}$$

31. For calculations involving  $\text{He}^+$ , we use  $Z = 2$  in the one-electron energy formula:

$$\Delta E = E_f - E_i = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Compared with hydrogen ( $Z = 1$ ), the energy of each transition is therefore four times the value calculated in the preceding exercise ( $2^2 = 4$ ):



$$\text{H: } \Delta E = -R_{\infty}(1)^2 \times \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\text{He}^+: \Delta E = -R_{\infty}(2)^2 \times \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The wavelengths are reduced by the same factor:

$$\text{H: } \lambda = \frac{hc}{|\Delta E_{\text{H}}|}$$

$$\text{He}^+: \lambda = \frac{hc}{|\Delta E_{\text{He}^+}|} = \frac{hc}{4|\Delta E_{\text{H}}|}$$

Results are given in the following table:

TRANSITION	$n_i$	$n_f$	$\Delta E (R_{\infty})$	$\Delta E (\text{J})$	$\lambda (\text{m})$	COMMENT
(a) $1s \rightarrow 2p$	1	2	3.0000	$6.54 \times 10^{-18}$	$3.04 \times 10^{-8}$	absorption
(b) $5f \rightarrow 4d$	5	4	-0.0900	$-1.96 \times 10^{-19}$	$1.01 \times 10^{-6}$	emission
(c) $3d \rightarrow \infty$	3	$\infty$	0.4444	$9.69 \times 10^{-19}$	$2.05 \times 10^{-7}$	absorption
(d) $\infty \rightarrow 1s$	$\infty$	1	-4.0000	$-8.72 \times 10^{-18}$	$2.28 \times 10^{-8}$	emission

32. Similar to Examples 4-5 and 5-6. First, calculate the ionization energy of hydrogen in its ground state:

$$\begin{aligned} \mathbf{AE}_{1 \rightarrow \infty} &= -R_{\infty}(1)^2 \times \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right) \\ &= R_{\infty} \\ &= 2.18 \times 10^{-18} \text{ J} \end{aligned}$$

Next, calculate the energy of an ionizing photon with a wavelength of  $827 \text{ \AA}$  (equal to  $8.27 \times 10^{-8} \text{ m}$ ):

$$\begin{aligned} E = h\nu &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{8.27 \times 10^{-8} \text{ m}} \\ &= 2.40 \times 10^{-18} \text{ J} \end{aligned}$$

(a) The kinetic energy of the ejected electron is the difference between the photon energy ( $h\nu$ ) and the ground-state ionization energy of the atom ( $\Delta E_{1 \rightarrow \infty}$ ):

$$\begin{aligned} E_k &= h\nu - \Delta E_{1 \rightarrow \infty} \\ &= (2.40 - 2.18) \times 10^{-18} \text{ J} \\ &= 0.22 \times 10^{-18} \text{ J} \\ &= 2.2 \times 10^{-19} \text{ J} \quad (2 \text{ sig fig}) \end{aligned}$$

(b) Use the defining equation

$$E_k = \frac{1}{2}mv^2$$

to obtain the velocity:

$$v = \sqrt{\frac{2E_k}{m}} = \sqrt{\frac{2(2.2 \times 10^{-19} \text{ kg m}^2 \text{ s}^{-2})}{9.109 \times 10^{-31} \text{ kg}}} = 7.0 \times 10^5 \text{ m s}^{-1}$$

The mass of an electron,  $9.1093897 \times 10^{-31}$  kg, is available in Table C-5 of *PoC* (page A65). Note that 1 J is equal to  $1 \text{ kg m}^2 \text{ s}^{-2}$ .

33. Assume, contrary to fact, that the electron is initially at rest—with zero velocity and hence zero kinetic energy. We then calculate the energy it gives up while falling from infinity ( $E = 0$ ) “down” to the  $n$ th shell of a hydrogen atom:

$$\Delta E_{\infty \rightarrow n} = -R_{\infty}(1)^2 \times \left( \frac{1}{n^2} - \frac{1}{\infty^2} \right) = -\frac{R_{\infty}}{n^2}$$

These values, determined solely by the principal quantum number  $n$ , are independent of the angular momentum quantum number  $\ell$ . It makes no difference whether the transition terminates in an  $s$ ,  $p$ , or  $d$  subshell:

$$\Delta E_{\infty \rightarrow 1} = -\frac{R_{\infty}}{1^2} = -2.18 \times 10^{-18} \text{ J} \quad (1s)$$

$$\Delta E_{\infty \rightarrow 2} = -\frac{R_{\infty}}{2^2} = -5.45 \times 10^{-19} \text{ J} \quad (2s, 2p)$$

$$\Delta E_{\infty \rightarrow 3} = -\frac{R_{\infty}}{3^2} = -2.42 \times 10^{-19} \text{ J} \quad (3s, 3p, 3d),$$

Next we compute the initial kinetic energy,

$$\begin{aligned} E_k &= \frac{1}{2}mv^2 \\ &= \frac{1}{2}(9.109 \times 10^{-31} \text{ kg})(1.00 \times 10^6 \text{ m s}^{-1})^2 = 4.555 \times 10^{-19} \text{ kg m}^2 \text{ s}^{-2} \\ &= 4.555 \times 10^{-19} \text{ J} \end{aligned}$$

and subtract it from  $\Delta E_{\infty \rightarrow n}$  to obtain the total energy released:

$$(a) \text{ To } 3d: \Delta E_{\infty \rightarrow 3} - E_k = (-2.42 - 4.555) \times 10^{-19} \text{ J} = -6.98 \times 10^{-19} \text{ J}$$

$$(b) \text{ To } 3p: \Delta E_{\infty \rightarrow 3} - E_k = (-2.42 - 4.555) \times 10^{-19} \text{ J} = -6.98 \times 10^{-19} \text{ J}$$

$$(c) \text{ To } 3s: \Delta E_{\infty \rightarrow 3} - E_k = (-2.42 - 4.555) \times 10^{-19} \text{ J} = -6.98 \times 10^{-19} \text{ J}$$

$$(d) \text{ To } 2p: \Delta E_{\infty \rightarrow 2} - E_k = (-5.45 - 4.555) \times 10^{-19} \text{ J} = -1.00 \times 10^{-18} \text{ J}$$

$$(e) \text{ To } 2s: \Delta E_{\infty \rightarrow 2} - E_k = (-5.45 - 4.555) \times 10^{-19} \text{ J} = -1.00 \times 10^{-18} \text{ J}$$

$$(f) \text{ To } 1s: \Delta E_{\infty \rightarrow 1} - E_k = (-2.18 - 0.456) \times 10^{-18} \text{ J} = -2.64 \times 10^{-18} \text{ J}$$

See also Example 5-6.

34. Transition energies for the  $\text{Li}^{2+}$  ion ( $Z = 3$ ),

$$\Delta E_{\infty \rightarrow n} = -R_{\infty} \frac{Z^2}{n^2} = \frac{9R_{\infty}}{n^2}$$

are nine times greater than those for the H atom:

$$\text{H: } \Delta E_{\infty \rightarrow 1} = -R_{\infty}$$

$$\text{Li}^{2+}: \Delta E_{\infty \rightarrow 1} = -9R_{\infty} = -1.96 \times 10^{-17} \text{ J}$$

$$\Delta E_{\infty \rightarrow 2} = -\frac{1}{4}R_{\infty}$$

$$\Delta E_{\infty \rightarrow 2} = -\frac{9}{4}R_{\infty} = -4.90 \times 10^{-18} \text{ J}$$

$$\Delta E_{\infty \rightarrow 3} = -\frac{R_{\infty}}{9}$$

$$\Delta E_{\infty \rightarrow 3} = -R_{\infty} = -2.18 \times 10^{-18} \text{ J}$$

The kinetic energy of the free electron, calculated in the previous exercise, is  $4.555 \times 10^{-19} \text{ J}$ . See the tabulation at the top of the next page:

(a) To 3d:  $\Delta E_{\infty \rightarrow 3} - E_k = -2.18 \times 10^{-18} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -2.64 \times 10^{-18} \text{ J}$

(b) To 3p:  $\Delta E_{\infty \rightarrow 3} - E_k = -2.18 \times 10^{-18} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -2.64 \times 10^{-18} \text{ J}$

(c) To 3s:  $\Delta E_{\infty \rightarrow 3} - E_k = -2.18 \times 10^{-18} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -2.64 \times 10^{-18} \text{ J}$

(d) To 2p:  $\Delta E_{\infty \rightarrow 2} - E_k = -4.90 \times 10^{-18} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -5.36 \times 10^{-18} \text{ J}$

(e) To 2s:  $\Delta E_{\infty \rightarrow 2} - E_k = -4.90 \times 10^{-18} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -5.36 \times 10^{-18} \text{ J}$

(f) To 1s:  $\Delta E_{\infty \rightarrow 1} - E_k = -1.96 \times 10^{-17} \text{ J} - 4.555 \times 10^{-19} \text{ J} = -2.01 \times 10^{-17} \text{ J}$

35. Once again, we use the equation

$$\Delta E = E_f - E_i = -R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

to determine the difference in energy between two states of a hydrogen atom ( $Z = 1$ ), this time taking  $n_f = 3$  and  $n_i = 4, 5, 6, 7$ . Then, with energy in hand, we go on to calculate the wavelength of the emitted photon:

$$|\Delta E| = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{|\Delta E|}$$

One sample calculation ( $n_i = 4 \rightarrow n_f = 3$ ) should suffice.

Energy:

$$\begin{aligned} \Delta E &= -R_{\infty} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -(2.18 \times 10^{-18} \text{ J}) \times (1)^2 \times \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = -1.06 \times 10^{-19} \text{ J} \end{aligned}$$

Wavelength:

$$\lambda = \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{1.06 \times 10^{-19} \text{ J}} = 1.87 \times 10^{-6} \text{ m} \quad (1.87 \mu\text{m})$$

The transitions, all with micron wavelengths ( $1 \mu\text{m} = 10^{-6} \text{ m}$ ), fall into the infrared portion of the electromagnetic spectrum:

$n_i$	$\Delta E \text{ (J)}$	$\lambda \text{ (}\mu\text{m)}$
4	$-1.06 \times 10^{-19}$	1.87
5	$-1.55 \times 10^{-19}$	1.28
6	$-1.82 \times 10^{-19}$	1.09
7	$-1.98 \times 10^{-19}$	1.00

36. Since all emissions in the Paschen series terminate at  $n_f = 3$ , the most energetic transition is from  $n_i = \infty$  to  $n_f = 3$ :

$$\Delta E = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_\infty Z^2 \left( \frac{1}{3^2} - \frac{1}{\infty^2} \right) = -R_\infty \frac{Z^2}{9}$$

The wavelength, in turn, is inversely proportional to the energy:

$$|\Delta E| = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{|\Delta E|}$$

For  $\text{He}^+$  ( $Z = 2$ ):

$$\Delta E = -\frac{4R_\infty}{9} = -9.69 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{9hc}{4R_\infty} = 2.05 \times 10^{-7} \text{ m} \quad (205 \text{ nm})$$

For H ( $Z = 1$ ):

$$\Delta E = -\frac{R_\infty}{9} = -2.42 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{9hc}{R_\infty} = 8.20 \times 10^{-7} \text{ m} \quad (820 \text{ nm})$$

Energies in the helium ion are four times greater than those in the hydrogen atom.

37. The least energetic transition in the Paschen series (Exercise 35) is from  $n_i = 4$  to  $n_f = 3$ :

$$\Delta E = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_\infty Z^2 \left( \frac{1}{3^2} - \frac{1}{4^2} \right)$$

$$\lambda = \frac{hc}{|\Delta E|}$$

For He<sup>+</sup> ( $Z = 2$ ):

$$\Delta E = -(2.18 \times 10^{-18} \text{ J}) \times (2)^2 \times \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = -4.24 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{4.24 \times 10^{-19} \text{ J}} = 4.69 \times 10^{-7} \text{ m} \quad (469 \text{ nm})$$

For H ( $Z = 1$ ):

$$\Delta E = -(2.18 \times 10^{-18} \text{ J}) \times (1)^2 \times \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = -1.06 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{1.06 \times 10^{-19} \text{ J}} = 1.87 \times 10^{-6} \text{ m} \quad (1.87 \text{ } \mu\text{m})$$

Energies in the helium ion are four times greater than those in the hydrogen atom:

$$\left( \frac{Z_{\text{He}^+}}{Z_{\text{H}}} \right)^2 = \left( \frac{2}{1} \right)^2 = 4$$

38. The most energetic transition is from  $n_i = \infty$  to the lowest shell in the series ( $n_f$ , to be determined):

$$\Delta E_{\text{max}} = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{\infty^2} \right) = -R_\infty \frac{Z^2}{n_f^2}$$

We equate the magnitude of  $\Delta E_{\max}$  to the energy carried away by the emitted photon,

$$|\Delta E_{\max}| = h\nu = \frac{hc}{\lambda}$$

and then solve for  $n_f$ :

$$\frac{hc}{\lambda} = \frac{Z^2 R_{\infty}}{n_f^2}$$

$$n_f^2 = \frac{Z^2 R_{\infty} \lambda}{hc}$$

$$n_f = Z \sqrt{\frac{R_{\infty} \lambda}{hc}}$$

Given a wavelength of  $2.279 \times 10^{-6}$  m (or 2.279  $\mu\text{m}$ ) when  $Z = 1$ , we determine finally that the transition terminates in the fifth shell,  $n_f = 5$ :

$$n_f = \sqrt{\frac{(2.18 \times 10^{-18} \text{ J})(2.279 \times 10^{-6} \text{ m})}{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}} = \sqrt{25.0} = 5.00$$

39. The Pfund emissions (see Exercise 38) correspond to transitions from  $n_i = 6, 7, 8, \dots$  to  $n_f = 5$ :

$$\Delta E = -R_{\infty} Z^2 \left( \frac{1}{5^2} - \frac{1}{n_i^2} \right)$$

Substituting  $Z = 4$  for the nuclear charge of  $\text{Be}^{3+}$ , we can compute energy and wavelength for emission from any initial state  $n_i > 5$ . The sample calculation below is for  $n_i = 6$ :

$$\Delta E = -R_{\infty} (4)^2 \times \left( \frac{1}{5^2} - \frac{1}{6^2} \right) = -0.1956 \times (2.18 \times 10^{-18} \text{ J}) = -4.26 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{4.26 \times 10^{-19} \text{ J}} = 4.66 \times 10^{-7} \text{ m}$$

Values for the first four transitions are presented in the following table:

$n_i$	$\Delta E$ (J)	$\lambda$ (nm)	COMMENT
6	$-4.26 \times 10^{-19}$	466	visible
7	$-6.83 \times 10^{-19}$	291	ultraviolet
8	$-8.50 \times 10^{-19}$	234	ultraviolet
9	$-9.65 \times 10^{-19}$	206	ultraviolet

40. Use the same general method as in the preceding exercises, here with  $n_f = 4$ :

	Z	$n_i$	$\Delta E$ (J)	$\lambda$ (m)	COMMENT
H	1	5	$-4.90 \times 10^{-20}$	$4.05 \times 10^{-6}$	infrared (4.05 $\mu\text{m}$ )
		6	$-7.57 \times 10^{-20}$	$2.62 \times 10^{-6}$	infrared (2.62 $\mu\text{m}$ )
		7	$-9.18 \times 10^{-20}$	$2.16 \times 10^{-6}$	infrared (2.16 $\mu\text{m}$ )
		8	$-1.02 \times 10^{-19}$	$1.94 \times 10^{-6}$	infrared (1.94 $\mu\text{m}$ )
He+	2	5	$-1.96 \times 10^{-19}$	$1.01 \times 10^{-6}$	infrared (1.01 $\mu\text{m}$ )
		6	$-3.03 \times 10^{-19}$	$6.56 \times 10^{-7}$	visible (656 nm)
		7	$-3.67 \times 10^{-19}$	$5.41 \times 10^{-7}$	visible (541 nm)
		8	$-4.09 \times 10^{-19}$	$4.86 \times 10^{-7}$	visible (486 nm)
Li <sup>2+</sup>	3	5	$-4.41 \times 10^{-19}$	$4.50 \times 10^{-7}$	visible (450 nm)
		6	$-6.81 \times 10^{-19}$	$2.92 \times 10^{-7}$	ultraviolet (292 nm)
		7	$-8.26 \times 10^{-19}$	$2.41 \times 10^{-7}$	ultraviolet (241 nm)
		8	$-9.20 \times 10^{-19}$	$2.16 \times 10^{-7}$	ultraviolet (216 nm)

Since  $Z^2 = 4$  for He+, each energy is quadrupled and each wavelength is cut by one-fourth relative to hydrogen. The scaling factor  $Z^2$  for Li<sup>2+</sup> is 9.

41. Ionization strips the atom of its electron. Accordingly, we calculate the energy and wavelength corresponding to an absorption from  $n_i = 1$  (the ground state) to  $n_f = \infty$ , just as in Example 5-5:

$$\Delta E = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_\infty Z^2 \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right) = R_\infty Z^2$$

$$\lambda = \frac{hc}{\Delta E}$$



The three ionization energies scale according to the value of  $Z^2$ , whereas the wavelengths go as  $1/Z^2$ :

	$Z$	$\Delta E (R_\infty)$	$\Delta E (J)$	$\lambda (m)$	$\lambda (nm)$
H	1	1	$2.18 \times 10^{-18}$	$9.11 \times 10^{-8}$	91.1
He+	2	4	$8.72 \times 10^{-18}$	$2.28 \times 10^{-8}$	22.8
Li <sup>2+</sup>	3	9	$1.96 \times 10^{-17}$	$1.01 \times 10^{-8}$	10.1

42. Conservation of energy. First, we calculate the energy needed to promote the electron from the ground state of hydrogen ( $n_i = 1$ ;  $Z = 1$ ) to the level  $n_f = 3$ :

$$\Delta E_{1 \rightarrow 3} = -R_\infty (1)^2 \times \left( \frac{1}{3^2} - \frac{1}{1^2} \right) = \frac{8R_\infty}{9}$$

Second, we subtract  $\Delta E_{1 \rightarrow 3}$  from the initial kinetic energy of the xenon atom (given as  $E_k = 2.28 \times 10^{-18} \text{ J}$ ). Doing so, we obtain the kinetic energy  $E'_k$  of Xe after the collision:

$$E'_k = E_k - \Delta E_{1 \rightarrow 3}$$

Third, we solve for the speed  $v'$  consistent with this final kinetic energy:

$$E'_k = \frac{1}{2} m (v')^2 = E_k - \Delta E_{1 \rightarrow 3}$$

$$v' = \sqrt{\frac{2(E_k - \Delta E_{1 \rightarrow 3})}{m}} = \sqrt{\frac{2(E_k - \frac{8}{9}R_\infty)}{m}}$$

Substituting the mass of a xenon atom,

$$m = \frac{131.29 \text{ g Xe}}{\text{mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 2.180 \times 10^{-25} \text{ kg (per atom)}$$

we have our answer:

$$v' = \sqrt{\frac{2(2.28 - \frac{8}{9} \times 2.18) \times 10^{-18} \text{ kg m}^2 \text{ s}^{-2}}{2.180 \times 10^{-25} \text{ kg}}} = 1.8 \times 10^3 \text{ m s}^{-1}$$

Note that the subtraction in the numerator limits  $v'$  to two significant figures:

$$\text{Numerator: } 2.28 - \frac{8}{9} \times 2.18 = 2.28 - 1.938 = 0.34 \quad (2 \text{ sig fig})$$

43. Ionization corresponds to a transition from  $n_i = 1$  (the ground state) to  $n_f = \infty$  (zero potential energy):

$$\Delta E = -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -R_\infty Z^2 \left( \frac{1}{\infty^2} - \frac{1}{1^2} \right) = R_\infty Z^2 \equiv I$$

Expressing the Rydberg constant in kilojoules per mole,

$$\frac{2.1798741 \times 10^{-18} \text{ J}}{\text{atom}} \times \frac{6.0221367 \times 10^{23} \text{ atoms}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.3127500 \times 10^3 \text{ kJ mol}^{-1}$$

we solve for the nuclear charge (from  $R_\infty Z^2 = I$ ) and determine that  $Z = 5$ :

$$Z = \sqrt{\frac{I}{R_\infty}} = \sqrt{\frac{3.28 \times 10^4 \text{ kJ mol}^{-1}}{1.31 \times 10^3 \text{ kJ mol}^{-1}}} = \sqrt{25.0} = 5.00$$

The nucleus of the formerly unknown monatomic ion,  $B^{4+}$ , contains five protons.

44. The emission series terminates in shell  $n_f = n$ , as yet undetermined:

$n_i$	$n_f$	$\nu$ ( $s^{-1} \equiv \text{Hz}$ )
$n+1$	$n$	$3.93 \times 10^{14}$
$n+2$	$n$	$6.63 \times 10^{14}$
$n+3$	$n$	$8.56 \times 10^{14}$

Our task is to establish  $n$  from just these few frequencies.

(a) We begin with symbolic expressions for the first two emission energies,

$$A E_{n+1 \rightarrow n} = h\nu_{n+1 \rightarrow n} = -R_\infty Z^2 \left[ \frac{1}{n^2} - \frac{1}{(n+1)^2} \right] \quad (n_i = n+1, n_f = n)$$

$$A E_{n+2 \rightarrow n} = h\nu_{n+2 \rightarrow n} = -R_\infty Z^2 \left[ \frac{1}{n^2} - \frac{1}{(n+2)^2} \right] \quad (n_i = n+2, n_f = n)$$

and use them to obtain the ratio of frequencies:

$$\frac{\nu_{n+1 \rightarrow n}}{\nu_{n+2 \rightarrow n}} = \frac{n^{-2} - (n+1)^{-2}}{n^{-2} - (n+2)^{-2}}$$

Then, comparing the possible theoretical ratios (calculated for  $n = 1, 2, 3, \dots$ ) with the experimentally determined ratio of 0.593,

$$\frac{\nu_{n+1 \rightarrow n}}{\nu_{n+2 \rightarrow n}} = \frac{3.93 \times 10^{14} \text{ s}^{-1}}{6.63 \times 10^{14} \text{ s}^{-1}} = 0.593$$

we eventually arrive at  $n$  by trial and error:

$n$	$\frac{\nu_{n+1 \rightarrow n}}{\nu_{n+2 \rightarrow n}}$
1	0.844
2	0.741
3	0.684
4	0.648
5	0.624
6	0.606
→ 7	0.593 ←

The emissions terminate in the seventh shell,  $n = 7$ .

(b) The transition in question-fourth in the series-is from  $n_i = 11$  to  $n_f = 7$ . We know further, from Exercise 43, that  $Z = 5$ . All that remains is to substitute the numbers.

Energy:

$$\begin{aligned} \Delta E &= -R_\infty Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= -(2.18 \times 10^{-18} \text{ J}) \times (5)^2 \times \left( \frac{1}{7^2} - \frac{1}{11^2} \right) \\ &= -6.62 \times 10^{-19} \text{ J} \end{aligned}$$

Frequency:

$$\nu = \frac{|\Delta E|}{h} = \frac{6.62 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 9.99 \times 10^{14} \text{ s}^{-1}$$

Wavelength:

$$\lambda = \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1})}{6.62 \times 10^{-19} \text{ J}} = 3.00 \times 10^{-7} \text{ m}$$

45. We know, from Example 5-5 in *PoC*, that the ionization energy for a one-electron atom depends solely on a positive integer, the nuclear charge  $Z$ :

$$I = R_{\infty} Z^2 \quad (Z = 1, 2, 3, \dots)$$

Values of  $I$  are thus limited to  $R_{\infty}$  (when  $Z = 1$ ),  $4R_{\infty}$  (when  $Z = 2$ ),  $9R_{\infty}$  (when  $Z = 3$ ), and so forth.

Accordingly, we must determine whether

$$I = 3.28 \times 10^3 \text{ kJ mol}^{-1}$$

can meet this requirement for some integral value of  $Z$ :

$$Z^2 = \frac{I}{R_{\infty}} = \frac{3.28 \times 10^3 \text{ kJ mol}^{-1}}{1.31 \times 10^3 \text{ kJ mol}^{-1}} = 2.50 = 1, 4, 9, 16, \dots$$

Our answer is *no*:  $Z^2 = 2.50$  does not belong to the series 1, 4, 9, 16, . . . , and

$$Z = \sqrt{2.50} = 1.58$$

proves not to be an integer. The atom contains more than one electron.

Note that this calculation is valid only if  $I$  and  $R_{\infty}$  are expressed in the same units. See Exercise 43 for the conversion of  $R_{\infty}$  from joules per atom into kilojoules per mole.