Chapter 36
Atoms

Conceptual Problems

***1** •

Determine the Concept Examination of Figure 35-4 indicates that as *n* increases, the spacing of adjacent energy levels decreases**.**

2 •

Picture the Problem The energy of an atom of atomic number *Z*, with exactly one electron in its *n*th energy state is given by $E_n = -Z^2 \frac{E_0^2}{n^2}, n = 1, 2, 3, \ldots$.

Express the energy of an atom of atomic number *Z*, with exactly one electron, in its *n*th energy state:

$$E_n = -Z^2 \frac{E_0^2}{n^2}, n = 1, 2, 3, \ldots$$

where E_0 is the atom's ground state energy.

For lithium (*Z* = 3) in its first excited state (*n* = 1) this expression becomes:

$$E_2 = -(3)^2 \frac{E_0}{1^2} = -9E_0$$

and $\boxed{(a) \text{ is correct.}}$

3 •

Determine the Concept Bohr's postulates are 1) the electron in the hydrogen atom can move only in certain non-radiating, circular orbits called *stationary states*, 2) if E_i and E_f are the initial and final energies of the atom, the frequency *f* of the emitted radiation during a transition is given by $f = [E_\text{i} - E_\text{f}]/h$, and 3) the angular momentum of a circular orbit is constrained by $mvr = n\hbar$. $\boxed{(a) \text{ is correct.}}$

4 ••

Picture the Problem We can express the kinetic energy of the orbiting electron as well as its total energy as functions of its radius *r*.

Express the total energy of an orbiting electron:

$$E = K + U$$

Express the orbital kinetic energy of an electron:

$$K = \frac{kZe^2}{2r} \qquad (1)$$

Express the potential energy of an orbiting electron:

$$U = -\frac{kZe^2}{r}$$

Substitute and simplify to obtain:

$$E = \frac{kZe^2}{2r} - \frac{kZe^2}{r} = \frac{kZe^2}{2r} - \frac{2kZe^2}{2r}$$
$$= -\frac{kZe^2}{2r}$$

$$\boxed{\text{Thus, as } r \text{ increases, } E \text{ becomes less negative and therefore } \textit{increases}.}$$

$$\boxed{\text{Examination of the expression for } K \text{ makes it clear that if } r \text{ increases, } K \text{ decreases.}}$$

5 •

Picture the Problem We can relate the kinetic energy of the electron in the *n* = 2 state to its total energy using $E_2 = K_2 + U_2$.

Express the total energy of the hydrogen atom in its *n* = 2 state:

$$E_2 = K_2 + U_2 = K_2 - 2K_2 = -K_2$$

or

$$K_2 = -E_2$$

Express the energy of hydrogen in its *n*th energy state:

$$E_n = -Z^2 \frac{E_0^2}{n^2} = -(1)^2 \frac{E_0^2}{n^2} = -\frac{E_0^2}{n^2}$$

where E_0 is hydrogen's ground state energy and $Z = 1$.

Substitute to obtain:

$$K_n = \frac{E_0^2}{n^2} \text{ and } K_2 = \frac{E_0}{2^2} = \frac{E_0}{4}$$

$$\boxed{(d) \text{ is correct.}}$$

6 •

Picture the Problem The orbital radius *r* depends on the *n* = 1 orbital radius a_0, the atomic number *Z*, and the orbital quantum number *n* according to $r = n^2a_0/Z$.

The radius of the *n* = 5 orbit is:

$$r_5 = 5^2 \frac{a_0}{1} = 25a_0$$

because $Z = 1$ for hydrogen.

$$\boxed{(b) \text{ is correct.}}$$

*7 •

Determine the Concept We can find the possible values of ℓ by using the constraints on the quantum numbers *n* and ℓ.

The allowed values for the orbital quantum number ℓ for *n* = 1, 2, 3, and 4 are summarized in table shown to the right:

n	ℓ
1	0
2	0, 1
3	0, 1, 2
4	0, 1, 2, 3

From the table it is clear that ℓ can have 4 values.

$$\boxed{(a) \text{ is correct.}}$$

8 •

Picture the Problem We can find the number of different values m_ℓ can have by enumerating the possibilities when the principal quantum number n = 4.

The allowed values for the orbital quantum number ℓ and the magnetic quantum number m_ℓ for n = 4 are summarized to the right:

$$\ell = 0, 1, 2, 3$$

and

$$m_\ell = -3, -2, -1, 0, 1, 2, 3$$

From this enumeration we can see that m can have 7 values.

$$\boxed{(c) \text{ is correct.}}$$

9 •

Picture the Problem We can visualize the relationship between the quantum number ℓ and the electronic configuration as shown in the table below.

	s	p	d	f	g	h
ℓ value	0	1	2	3	4	5

Because the p state corresponds to ℓ = 1, $\boxed{(c) \text{ is correct.}}$

***10** ••

Determine the Concept The s state, with ℓ = 0, is a ″penetrating″ state in which the probability density near the nucleus is significant. Consequently, the 3s electron in sodium is in a region of low potential energy for a significant portion of the time. In the state ℓ = 1, the probability density at the nucleus is zero, so the 2p electron of sodium is shielded from the nuclear charge by the 1s electrons. In hydrogen, the 3s and 2p electrons experience the same nuclear potential.

11 ••

Determine the Concept In conformity with the exclusion principle, the total number of electrons that can be accommodated in states of quantum number n is n^2 (see Problem 48). The fact that closed shells correspond to $2n^2$ electrons indicates that there is another quantum number that can have two possible values.

12 ••

Picture the Problem We can group these elements by using Table 35-1 to look for a common outer electronic configuration in the ground states.

The following elements have an outer $4s^2$ configuration in the ground state:

$$\boxed{\text{titanium, manganese, and calcium}}$$

The following elements have an outer 4s configuration in the ground state: $\boxed{\text{potassium, chromium, and copper.}}$

Remarks: It is to be expected that atoms of the first group will have similar properties, and, likewise, that atoms of the second group will have similar properties.

13 •

Picture the Problem We can use the fact that the sum of the exponents in the electronic configuration representation is the atomic number to identify these two elements.

(*a*) Adding the exponents yields a sum of 15. Because this sum is the atomic number, *Z*, the element must be $\boxed{\text{phosphorus.}}$

(*b*) Adding the exponents yields a sum of 24. Because this sum is the atomic number, *Z*, the element must be $\boxed{\text{chromium.}}$

Remarks: Checking the electronic configurations in Table 35-1 further confirms these conclusions.

***14** •

Picture the Problem We can apply the constraints on the quantum numbers ℓ and m_ℓ to find the possible values for each when $n = 3$.

Express the constraints on the quantum numbers n, ℓ, and m_ℓ:

$$n = 1, 2, 3, \ldots,$$
$$\ell = 0, 1, 2, \ldots, n-1,$$

and

$$m_\ell = -\ell, -\ell + 1, \ldots, \ell$$

So, for $n = 3$, the constraints on ℓ limit it to the values:

$$\ell = \boxed{0, 1, \text{and } 2.}$$

m_ℓ can take on the values:

$$m_\ell = \boxed{-2, -1, 0, 1, 2}$$

15 •

Determine the Concept The correspondence between the letter designations K, L, M, N, O, and P for the shells and the principal quantum number *n* is summarized in the table below.

Shell designation	K	L	M	N	O	P	Q
n	1	2	3	4	5	6	7
ℓ	0	0	0	0	0	0	0
		1	1	1	1	1	1
			2	2	2	2	2
				3	3	3	3
					4	4	4
						5	5
							6

While $n = 2$ for the L shell, ℓ can be either 0 or 1. $\boxed{(d)\text{ is correct.}}$

16 ••

Picture the Problem The strengths and weaknesses of each model are summarized in the following table.

	Bohr Theory	**Schrödinger Theory**
Ease of application	Easy	Difficult
Prediction of stationary state energies	Correct predictions	Correct predictions
Prediction of angular momenta	Predicts incorrect results	Predicts correct results
Spatial distribution of electrons	Predicts incorrect results	Predicts correct probabilistic distribution

17 ••

Determine the Concept The optical spectrum of any atom is due to the configuration of its outer-shell electrons. Ionizing the next atom in the periodic table gives you an ion with the same number of outer-shell electrons, and almost the same nuclear charge. Hence, the spectra should be very similar.

***18** ••

Determine the Concept The Ritz combination principle is due to the quantization of energy levels in the atom. We can use the relationship between the wavelength of the emitted photon and the difference in energy levels within the atom that results in the emission of the photon to express each of the wavelengths and then the sum of the reciprocals of the first and second wavelengths and the sum of the reciprocals of the third and fourth wavelengths.

Express the wavelengths of the spectral lines λ_1, λ_2, λ_3, and λ_4 in terms of the corresponding energy transitions:

$$\lambda_1 = \frac{hc}{E_3 - E_2}$$

$$\lambda_2 = \frac{hc}{E_2 - E_0}$$

$$\lambda_3 = \frac{hc}{E_3 - E_1}$$

and

$$\lambda_4 = \frac{hc}{E_1 - E_0}$$

Add the reciprocals of λ_1 and λ_2 to obtain:

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{E_3 - E_2}{hc} + \frac{E_2 - E_0}{hc} = \frac{E_3 - E_0}{hc} \qquad (1)$$

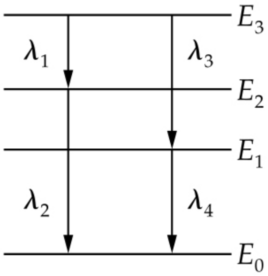
Add the reciprocals of λ_3 and λ_4 to obtain:

$$\frac{1}{\lambda_3} + \frac{1}{\lambda_4} = \frac{E_3 - E_1}{hc} + \frac{E_1 - E_0}{hc} = \frac{E_3 - E_0}{hc} \qquad (2)$$

Because the right-hand sides of equations (1) and (2) are equal:

$$\boxed{\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3} + \frac{1}{\lambda_4}}$$

One possible set of energy levels is shown to the right:



19 •

Determine the Concept An allowed transition must satisfy the selection rules $\Delta m_\ell = 0$ or ±1 and $\Delta\ell = \pm1$.

(*a*) $\Delta\ell = -1$ and $\Delta m_\ell = 0$:

$\boxed{\text{The transition is allowed.}}$

(*b*) (3,0,1) does not exist.

$\boxed{\text{The transition is not allowed.}}$

(*c*) $\Delta\ell = -1$ and $\Delta m_\ell = 2$:

$\boxed{\text{The transition is not allowed.}}$

(*d*) $\Delta\ell = +1$ and $\Delta m_\ell = 1$:

$\boxed{\text{The transition is allowed.}}$

(*e*) $\Delta\ell = -1$ and $\Delta m_\ell = 0$:

$$\boxed{\text{The transition is allowed.}}$$

Estimation and Approximation

***20** ••

Picture the Problem The number of photons need to stop a ^{85}Rb atom traveling at 300 m/s is the ratio of its momentum to that of a typical photon.

(*a*) The number *N* of photon-atom collisions needed to bring an atom to rest is the ratio of the change in the momentum of the atom as it stops to the momentum brought to the collision by each photon:

$$N=\frac{\Delta p_{\text{atom}}}{p_{\text{photon}}}=\frac{mv}{\frac{E}{c}}=\frac{mvc}{E}$$

where *m* is the mass of the atom.

The kinetic energy of an atom whose temperature is *T* is:

$$\tfrac{1}{2}mv^2=\tfrac{3}{2}kT \Rightarrow v=\sqrt{\frac{3kT}{m}}$$

Substitute for *v* to obtain:

$$N=\frac{mc}{E}\sqrt{\frac{3kT}{m}}=\frac{c}{E}\sqrt{3mkT}$$

For an atom use mass is 50 u:

$$N=\frac{3\times10^{8}\text{ m/s}}{1\,\text{eV}\times\frac{1.6\times10^{-19}\text{ J}}{\text{eV}}}\sqrt{3\left(50\,\text{u}\times\frac{1.66\times10^{-27}\text{ kg}}{\text{u}}\right)\left(1.38\times10^{-23}\text{ J/K}\right)\left(500\,\text{K}\right)}\approx\boxed{10^{5}}$$

(*b*) The number *N* of ping-pong ball-bowling ball collisions needed to bring the bowling ball to rest is the ratio of the change in the momentum of the bowling ball as it stops to the momentum brought to the collision by each ping-pong ball:

$$N=\frac{\Delta p_{\text{bowling ball}}}{p_{\text{ping-pong ball}}}=\frac{m_{\text{bb}}v_{\text{bb}}}{m_{\text{ppb}}v_{\text{ppb}}}$$

Provided the speeds of the approaching bowling ball and ping-pong ball are approximately the same:

$$N=\frac{\Delta p_{\text{bowling ball}}}{p_{\text{ping-pong ball}}}\approx\frac{m_{\text{bb}}}{m_{\text{ppb}}}\approx\frac{6\,\text{kg}}{4\,\text{g}}\approx\boxed{10^{3}}$$

(*c*) The number of photons *N* needed to stop a ^{85}Rb atom is the ratio of the change in the momentum of the atom to the momentum brought to the collision by each photon:

$$N=\frac{\Delta p_{\text{atom}}}{p_{\text{photon}}}=\frac{mv}{\frac{h}{\lambda}}=\frac{mv\lambda}{h}$$

Substitute numerical values and evaluate *N*:

$$N=\frac{85\left(1.66\times10^{-27}\text{ kg}\right)\left(300\text{ m/s}\right)\left(780.24\text{ nm}\right)}{6.63\times10^{-34}\text{ J}\cdot\text{s}}=\boxed{4.98\times10^{4}}$$

21 ••

Picture the Problem We can use the relationship between the kinetic energy of an atom and its momentum, together with the de Broglie equation, to derive the expression for the thermal de Broglie wavelength. In Part (*b*), we can use the definition of the number density of atoms and the result from Part (*a*), with the interatomic spacing set equal to the thermal de Broglie wavelength, to estimate the temperature needed to create a Bose condensate.

(*a*) Express the kinetic energy of an atom in terms of its momentum:

$$K=\frac{p^2}{2m}$$

Use the de Broglie relationship to express the atom's momentum in terms of its de Broglie wavelength:

$$p=\frac{h}{\lambda_T}$$

where λ_T is the thermal de Broglie wavelength.

Substitute for p to obtain:

$$K=\frac{h^2}{2m\lambda_T^2}$$

The kinetic energy of an atom is also a function of its temperature T:

$$K=\frac{3}{2}kT$$

Equate these expressions for K to obtain:

$$\frac{3}{2}kT=\frac{h^2}{2m\lambda_T^2}$$

Solve for λ_T:

$$\lambda_T=\boxed{\sqrt{\frac{h^2}{3mkT}}}$$

(*b*) The number density of atoms ρ is given by:

$$\rho=\frac{N}{V}$$

where N is the number of atoms and V is the volume they occupy.

Assume that the atoms are arrayed on a cubic lattice of lattice spacing d to obtain:

$$V=Nd^3 \text{ and } \rho=\frac{N}{Nd^3}=\frac{1}{d^3}$$

Solve for d to obtain:

$$d=\rho^{-1/3}$$

Setting $d=\lambda_T$ yields:

$$\rho^{-1/3}=\sqrt{\frac{h^2}{3mkT}}$$

Solve for T to obtain:

$$T = \frac{h^2 \rho^{2/3}}{3mk}$$

Substitute numerical values and evaluate T:

$$T = \frac{\left(6.63\times10^{-34}\ \text{J}\cdot\text{s}\right)^2\left(10^{12}\ \frac{\text{atoms}}{\text{cm}^3}\times\frac{10^6\ \text{cm}^3}{\text{m}^3}\right)^{2/3}}{3(85\,\text{u})\left(1.66\times10^{-27}\ \frac{\text{kg}}{\text{u}}\right)\left(1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}\right)} = \boxed{75.2\,\text{nK}}$$

The Bohr Model of the Hydrogen Atom

22 •

Picture the Problem The radius of the first Bohr orbit is given by $a_0 = \frac{\hbar^2}{mke^2}$.

Equation 36-12 is:

$$a_0 = \frac{\hbar^2}{mke^2}$$

Substitute numerical values and evaluate a_0:

$$a_0 = \frac{\left(1.05\times10^{-34}\ \text{J}\cdot\text{s}\right)^2}{\left(9.11\times10^{-31}\text{kg}\right)\left(8.99\times10^9\ \text{N}\cdot\text{m}^2/\text{kg}^2\right)\left(1.60\times10^{-19}\ \text{C}\right)^2} = 5.26\times10^{-11}\ \text{m}$$

$$= \boxed{0.0526\,\text{nm}}$$

23 •

Picture the Problem We can use the equation relating the wavelength of the radiation emitted during a transition between two energy states to find the wavelengths for the transitions specified in the problem statement.

Express the wavelength of the radiation emitted during an energy transformation from one energy state to another:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} = \frac{1240\,\text{eV}\cdot\text{nm}}{E_\text{i} - E_\text{f}}$$

provided the energies are expressed in eV. Note that this relationship tells us that the longest wavelength corresponds to the smallest energy difference.

Because $E_\text{f} = -13.6$ eV:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{E_\text{i} + 13.6\,\text{eV}}$$

Express the energy of the *n*th energy state of the atom:

$$E_n=-\frac{E_0}{n^2}=-\frac{13.6\,\text{eV}}{n^2}$$

Substitute to obtain:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{-\frac{13.6\,\text{eV}}{n^2}+13.6\,\text{eV}}=\frac{1240\,\text{eV}\cdot\text{nm}}{13.6\,\text{eV}\left(1-\frac{1}{n^2}\right)} \qquad (1)$$

(*a*) Evaluate equation (1) for $n = n_1 = 3$:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{13.6\,\text{eV}\left(1-\frac{1}{3^2}\right)}=\boxed{103\,\text{nm}}$$

(*b*) Evaluate equation (1) for $n = n_1 = 4$:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{13.6\,\text{eV}\left(1-\frac{1}{4^2}\right)}=\boxed{97.3\,\text{nm}}$$

24 •

Picture the Problem For the Balmer series, $E_f = E_2 = -3.40$ eV. The wavelength associated with each transition is related to the difference in energy between the states by $\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{E_i-E_f}$.

Express the wavelength of the radiation emitted during an energy transformation from one energy state to another:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} \qquad (1)$$

provided the energies are expressed in eV. Note that this relationship tells us that the longest wavelength corresponds to the smallest energy difference.

Evaluate ΔE for the transition $n = 3$ to $n = 2$:

$$\Delta E_{n\to 2}=E_n-E_2=\frac{E_0}{n^2}-E_2$$

Because $E_f = E_2 = -3.40$ eV and $E_0 = -13.6$ eV:

$$\Delta E_{n\to 2}=-\frac{13.6\,\text{eV}}{n^2}+3.40\,\text{eV} \qquad (2)$$

Evaluate equation (2) for $n = 3$:

$$\Delta E_{3\to 2}=-\frac{13.6\,\text{eV}}{3^2}+3.40\,\text{eV}=\boxed{1.89\,\text{eV}}$$

Substitute in equation (1) to obtain:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{1.89\,\text{eV}}=\boxed{656\,\text{nm}}$$

Evaluate equation (2) for n = 4:

$$\Delta E_{4\to 2}=-\frac{13.6\,\text{eV}}{4^2}+3.40\,\text{eV}=\boxed{2.55\,\text{eV}}$$

Substitute in equation (1) to obtain:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{2.55\,\text{eV}}=\boxed{486\,\text{nm}}$$

Evaluate equation (2) for n = 5:

$$\Delta E_{5\to 2}=-\frac{13.6\,\text{eV}}{5^2}+3.40\,\text{eV}=\boxed{2.86\,\text{eV}}$$

Substitute in equation (1) to obtain:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{2.86\,\text{eV}}=\boxed{434\,\text{nm}}$$

25 ••

Picture the Problem We can use Bohr's second postulate to relate the photon energy to its frequency and use $\lambda=\dfrac{1240\,\text{eV}\cdot\text{nm}}{E_\text{i}-E_\text{f}}$ to find the wavelengths of the three longest wavelengths in the Paschen series.

(*a*) Use Bohr's second postulate to express the energy of the photons in the Paschen series:

$$hf=\Delta E=E_\text{i}-E_\text{f}$$

For the series limit:

$$n=\infty \text{ and } E_\text{i}=0$$

Substitute to obtain:

$$\Delta E=-E_\text{f}=-\left(-\frac{E_0}{n_2^2}\right)=\frac{E_0}{n_2^2} \qquad (1)$$

Evaluate the photon energy for n_2 = 3:

$$hf=\frac{13.6\,\text{eV}}{3^2}=\boxed{1.51\,\text{eV}}$$

Express the wavelength of the radiation resulting from an energy transition $\Delta E = hf$:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} \qquad (2)$$

provided the energies are expressed in eV.

Evaluate λ_{min} for the transition $n = \infty$ to $n_2 = 3$:

$$\lambda_{\text{min}} = \frac{1240\,\text{eV}\cdot\text{nm}}{1.51\,\text{eV}} = \boxed{821\,\text{nm}}$$

(*b*) For the three longest wavelengths:

$$n_{\text{i}} = 4, 5, \text{and } 6$$

Equation (1) becomes:

$$\begin{aligned} hf = E_{\text{i}} - E_{\text{f}} &= -\frac{E_0}{n_{\text{i}}^2} - \left(-\frac{E_0}{n_2^2}\right) \\ &= E_0\left(\frac{1}{n_2^2} - \frac{1}{n_{\text{i}}^2}\right) = E_0\left(\frac{1}{9} - \frac{1}{n_{\text{i}}^2}\right) \end{aligned} \qquad (3)$$

Evaluate equation (3) for $n = 4$:

$$\Delta E_{4\to3} = (13.6\,\text{eV})\left(\frac{1}{9} - \frac{1}{16}\right) = \boxed{0.661\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 0.661$ eV:

$$\lambda_{4\to3} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.661\,\text{eV}} = \boxed{1876\,\text{nm}}$$

Evaluate equation (3) for $n = 5$:

$$\Delta E_{5\to3} = (13.6\,\text{eV})\left(\frac{1}{9} - \frac{1}{25}\right) = \boxed{0.967\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 0.967$ eV:

$$\lambda_{5\to3} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.967\,\text{eV}} = \boxed{1282\,\text{nm}}$$

Evaluate equation (3) for $n = 6$:

$$\Delta E_{6\to3} = (13.6\,\text{eV})\left(\frac{1}{9} - \frac{1}{36}\right) = \boxed{1.13\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 1.13$ eV:

$$\lambda_{6\to3} = \frac{1240\,\text{eV}\cdot\text{nm}}{1.13\,\text{eV}} = \boxed{1097\,\text{nm}}$$

The positions of these lines on a horizontal linear scale are shown below with the wavelengths and transitions indicated.

```
   6→3       5→3                               4→3
 ---|-------------|-------------------------------------------|-----
1097 nm    1282 nm                            1876 nm
```

***26 ••**

Picture the Problem We can use Bohr's second postulate to relate the photon energy to its frequency and use $\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{E_\text{i} - E_\text{f}}$ to find the wavelengths of the three longest wavelengths in the Brackett series.

(*a*) Use Bohr's second postulate to express the energy of the photons in the Paschen series:

$$hf = \Delta E = E_\text{i} - E_\text{f}$$

For the series limit:

$$n = \infty \text{ and } E_\text{i} = 0$$

Substitute to obtain:

$$\Delta E = -E_\text{f} = -\left(-\frac{E_0}{n_2^2}\right) = \frac{E_0}{n_2^2} \qquad (1)$$

Evaluate the photon energy for $n_2 = 4$:

$$hf = \frac{13.6\,\text{eV}}{4^2} = \boxed{0.850\,\text{eV}}$$

Express the wavelength of the radiation resulting from an energy transition $\Delta E = hf$:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} \qquad (2)$$

provided the energies are expressed in eV.

Evaluate λ_min for the transition $n = \infty$ to $n_2 = 4$:

$$\lambda_\text{min} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.850\,\text{eV}} = \boxed{1459\,\text{nm}}$$

(*b*) For the three longest wavelengths:

$$n_\text{i} = 5, 6, \text{and } 7$$

Equation (1) becomes:

$$\Delta E = E_\text{i} - E_\text{f} = -\frac{E_0}{n_\text{i}^2} - \left(-\frac{E_0}{n_2^2}\right)$$
$$= E_0\left(\frac{1}{n_2^2} - \frac{1}{n_\text{i}^2}\right) = E_0\left(\frac{1}{16} - \frac{1}{n_\text{i}^2}\right) \qquad (3)$$

Evaluate equation (3) for $n = 5$:

$$\Delta E_{5\to4} = (13.6\,\text{eV})\left(\frac{1}{16} - \frac{1}{25}\right) = \boxed{0.306\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 0.306$ eV:

$$\lambda_{5\to4} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.306\,\text{eV}} = \boxed{4052\,\text{nm}}$$

Evaluate equation (3) for $n = 6$:

$$\Delta E_{6\to 4} = (13.6\,\text{eV})\left(\frac{1}{16} - \frac{1}{36}\right) = \boxed{0.472\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 0.472$ eV:

$$\lambda_{6\to 4} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.472\,\text{eV}} = \boxed{2627\,\text{nm}}$$

Evaluate equation (3) for $n = 7$:

$$\Delta E_{7\to 4} = (13.6\,\text{eV})\left(\frac{1}{16} - \frac{1}{49}\right) = \boxed{0.572\,\text{eV}}$$

Evaluate equation (2) for $\Delta E = 0.572$ eV:

$$\lambda_{7\to 4} = \frac{1240\,\text{eV}\cdot\text{nm}}{0.572\,\text{eV}} = \boxed{2168\,\text{nm}}$$

The positions of these lines on a horizontal linear scale are shown below with the wavelengths and transitions indicated.

```
  7→4    6→4                                        5→4
---|---------|--------------------------------------------|-----
2168 nm 2627 nm                                   4052 nm
```

27 ••

Picture the Problem We can use the grating equation to find the wavelength of the given spectral line and the Rydberg-Ritz formula to evaluate *R*.

(*a*) The grating equation is:

$$m\lambda = d\sin\theta$$

where $m = 1, 2, 3, \ldots$

Solve for λ:

$$\lambda = \frac{d\sin\theta}{m}$$

Substitute numerical values and evaluate λ for $m = 1$:

$$\lambda = \frac{(3.377\,\mu\text{m})\sin 11.233^\circ}{1} = \boxed{657.8\,\text{nm}}$$

(*b*) The Rydberg-Ritz formula is:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Solve for R to obtain:

$$R=\frac{1}{\lambda}\left(\frac{1}{\frac{1}{n_2^2}-\frac{1}{n_1^2}}\right)$$

Substitute numerical values and evaluate R:

$$R=\frac{1}{0.6578\,\mu\text{m}}\left(\frac{1}{\frac{1}{2^2}-\frac{1}{3^2}}\right)$$

$$=10.946\,\mu\text{m}^{-1}=\boxed{1.0946\times10^{7}\,\text{m}^{-1}}$$

Remarks: The data used here came from a real experiment. The value for *R* differs by approximately 0.2% from the commonly accepted value.

28 •••

Picture the Problem This is an extreme value problem in which we need to identify the relationship between E and r, differentiate it with respect to r, and set that derivative equal to zero. Solving the latter expression for r will give us r_m.

Express the total energy of the electron:

$$E=\frac{\hbar^2}{2mr^2}-\frac{ke^2}{r}$$

Differentiate this expression with respect to r to obtain:

$$\frac{dE}{dr}=\frac{d}{dr}\left[\frac{\hbar^2}{2mr^2}-\frac{ke^2}{r}\right]$$

$$=\frac{d}{dr}\left[\frac{\hbar^2}{2mr^2}\right]-\frac{d}{dr}\left[\frac{ke^2}{r}\right]$$

$$=-\frac{\hbar^2}{mr^3}+\frac{ke^2}{r^2}$$

$$=0\text{ for extreme values}$$

Solve for r to obtain:

$$r=\frac{\hbar^2}{ke^2m}$$

Differentiate E a second time to obtain:

$$\frac{d^2E}{dr^2}=\frac{3\hbar^2}{mr^4}-\frac{2ke^2}{r^3}$$

Evaluate d^2E/dr^2 at r to obtain:

$$\left.\frac{d^2E}{dr^2}\right|_{r=\frac{\hbar^2}{ke^2m}}=\frac{k^4e^8m^3}{\hbar^6}>0$$

Therefore, our extreme value is a minimum and the value for r that minimizes the energy is $r = \boxed{\dfrac{\hbar^2}{ke^2 m}}$

Note that this is just the Bohr radius a_0. Consequently, the energy is the ground state energy of the hydrogen atom and:

$$E_{\text{min}} = \boxed{13.6\,\text{eV}}$$

***29 •••**

Picture the Problem We can express the total kinetic energy of the electron-nucleus system as the sum of the kinetic energies of the electron and the nucleus. Rewriting these kinetic energies in terms of the momenta of the electron and nucleus will lead to $K = p^2/2m_r$.

(*a*) Express the total kinetic energy of the electron-nucleus system:

$$K = K_e + K_n$$

Express the kinetic energies of the electron and the nucleus in terms of their momenta:

$$K_e = \frac{p^2}{2m_e} \text{ and } K_n = \frac{p^2}{2M}$$

Substitute to obtain:

$$K = \frac{p^2}{2m_e} + \frac{p^2}{2M} = \frac{p^2}{2}\left(\frac{1}{m_e} + \frac{1}{M}\right)$$

$$= \frac{p^2}{2}\left(\frac{M + m_e}{m_e M}\right) = \frac{p^2}{2\left(\dfrac{m_e M}{M + m_e}\right)}$$

$$= \boxed{\frac{p^2}{2m_r}}$$

provided we define $\mu = m_e M/(M + m_e)$.

(*b*) From Equation 36-14 we have:

$$R = \frac{m_r k^2 e^4}{4\pi c\hbar^3} = C\left(\frac{m_e}{1 + \dfrac{m_e}{M}}\right) \qquad (1)$$

where

$$C = \frac{k^2 e^4}{4\pi c\hbar^3}$$

Use the Table of Physical Constants at the end of the text to obtain:

$$C = 1.204663 \times 10^{37}\ \text{m}^{-1}/\text{kg}$$

For H:

$$R_{\mathrm{H}} = C\left(\frac{m_{\mathrm{e}}}{1+\dfrac{m_{\mathrm{e}}}{m_{\mathrm{p}}}}\right)$$

Substitute numerical values and evaluate R_{H}:

$$R_{\mathrm{H}} = \left(1.204663\times10^{37}\ \mathrm{m}^{-1}/\mathrm{kg}\right)\left(\frac{9.11\times10^{-31}\ \mathrm{kg}}{1+\dfrac{9.11\times10^{-31}\ \mathrm{kg}}{1.67\times10^{-27}\ \mathrm{kg}}}\right) = \boxed{1.096850\times10^{7}\ \mathrm{m}^{-1}}$$

Let $M\to\infty$ in equation (1) to obtain $R_{\mathrm{H,approx}}$:

$$R_{\mathrm{H,approx}} = Cm_{\mathrm{e}}$$

Substitute numerical values and evaluate $R_{\mathrm{H,approx}}$:

$$R_{\mathrm{H,approx}} = \left(1.204663\times10^{37}\ \mathrm{m}^{-1}/\mathrm{kg}\right)\left(9.11\times10^{-31}\ \mathrm{kg}\right) = \boxed{1.097448\times10^{7}\ \mathrm{m}^{-1}}$$

$$\boxed{R_{\mathrm{H}}\ \text{and}\ R_{\mathrm{H,approx}}\ \text{agree to three significant figures.}}$$

(*c*) Express the ratio of the kinetic energy K of the electron in its orbit about a stationary nucleus to the kinetic energy of the reduced-mass system K':

$$\frac{K}{K'} = \frac{\dfrac{p^2}{2m_{\mathrm{e}}}}{\dfrac{p^2}{2m_{\mathrm{r}}}} = \frac{\mu}{m_{\mathrm{e}}} = \frac{1}{m_{\mathrm{e}}}\left(\frac{m_{\mathrm{p}}m_{\mathrm{e}}}{m_{\mathrm{p}}+m_{\mathrm{e}}}\right)$$

$$= \frac{m_{\mathrm{p}}}{m_{\mathrm{p}}+m_{\mathrm{e}}} = \frac{1}{1+\dfrac{m_{\mathrm{e}}}{m_{\mathrm{p}}}}$$

Substitute numerical values and evaluate the ratio of the kinetic energies:

$$\frac{K}{K'} = \frac{1}{1+\dfrac{9.11\times10^{-31}\ \mathrm{kg}}{1.67\times10^{-27}\ \mathrm{kg}}}$$

$$= 0.999455$$

or

$$K = 0.999455K'$$

and the correction factor is the ratio of the masses or $\boxed{0.0545\%}$

Remarks: **The correct energy is slightly less than that calculated neglecting the motion of the nucleus.**

***30** ••

Picture the Problem We can use Equation 36-15 with $Z = 2$ to explain how it is that every other line of the Pickering series is very close to a line in the Balmer series. We can use the relationship between the energy difference between two quantum states and the wavelength of the photon emitted during a transition from the higher state to the lower state to find the wavelength of the photon corresponding to a transition from the $n = 6$ to the $n = 4$ level of He^+.

(*a*) From Equation 36-15, the energy levels of an atom are given by:

$$E_n = -Z^2 \frac{E_0}{n^2}$$

where E_0 is the Rydberg constant (13.6 eV).

For He^+, $Z = 2$ and:

$$E_n = -4\frac{E_0}{n^2}$$

Because of this, an energy level with even principal quantum number n in He^+ will have the same energy as a level with quantum number $n/2$ in H. Therefore, a transition between levels with principal quantum numbers $2m$ and $2p$ in He^+ will have almost the same energy as a transition between level m and p in H. In particular, transitions from $2m$ to $2p = 4$ in He^+ will have the same energy as transitions from m to $n = 2$ in H (the Balmer series).

(*b*) Transitions between these energy levels result in the emission or absorption of a photon whose wavelength is given by:

$$\lambda = \frac{hc}{E_6 - E_4} \qquad (1)$$

Evaluate E_6 and E_4:

$$E_6 = -4\left(\frac{13.6\,\text{eV}}{6^2}\right) = -1.51\,\text{eV}$$

and

$$E_4 = -4\left(\frac{13.6\,\text{eV}}{4^2}\right) = -3.40\,\text{eV}$$

Substitute for E_6 and E_4 in equation (1) and evaluate λ:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{-1.51\,\text{eV} - (-3.40\,\text{eV})} = \boxed{656\,\text{nm}}$$

which is the same as the $n = 3$ to $n = 2$ transition in H.

Quantum Numbers in Spherical Coordinates

31 •

Picture the Problem We can use the expression relating L to ℓ to find the magnitude of the angular momentum and the constraints on the quantum numbers to determine the allowed values for *m*.

(*a*) Express the angular momentum as a function of ℓ:

$$L=\sqrt{\ell(\ell+1)}\hbar$$

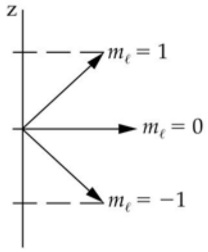
Substitute numerical values and evaluate *L*:

$$L=\sqrt{1(1+1)}\hbar=\sqrt{2}\hbar$$
$$=\sqrt{2}\left(1.055\times10^{-34}\ \text{J}\cdot\text{s}\right)$$
$$=\boxed{1.49\times10^{-34}\ \text{J}\cdot\text{s}}$$

(*b*) Because $m_\ell=-\ell,\ \ldots,\ 0,\ \ldots,\ \ell$ the allowed values for ℓ = 1 are:

$$m_\ell=\boxed{-1,0,+1}$$

(*c*) The vector diagram is shown on the right. Note that because $L_z=m_\ell\hbar$ and $L=\sqrt{2}\hbar$, the vectors for $m_\ell=-1$ and $m_\ell=1$ must make angles of 45° with the *z* axis.



32 •

Picture the Problem We can use the expression relating *L* to ℓ to find the magnitude of the angular momentum and the constraints on the quantum numbers to determine the allowed values for *m*.

(*a*) Express the angular momentum as a function of ℓ:

$$L=\sqrt{\ell(\ell+1)}\hbar$$

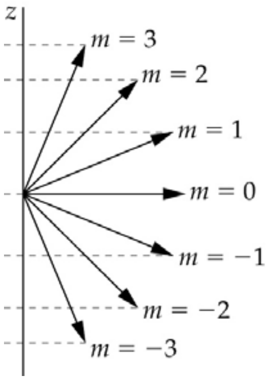
Substitute numerical values and evaluate *L*:

$$L=\sqrt{3(3+1)}\hbar=2\sqrt{3}\hbar$$
$$=2\sqrt{3}\left(1.055\times10^{-34}\ \text{J}\cdot\text{s}\right)$$
$$=\boxed{3.65\times10^{-34}\ \text{J}\cdot\text{s}}$$

(*b*) Because $m_\ell=-\ell,\ \ldots,\ 0,\ \ldots,\ \ell$ the allowed values for ℓ = 1 are:

$$m_\ell=\boxed{-3,-2,-1,0,+1,+2,+3}$$

(*c*) The vector diagram is shown on the right. Note that because $L_z = m_\ell \hbar$ and $L = 2\sqrt{3}\hbar$, the angles between the vectors and the *z* axis are determined by $\cos\theta_m = m_\ell / 2\sqrt{3}$. Thus $\theta_3 = 30°$, $\theta_2 = 54.7°$, and $\theta_1 = 73.2°$. The spacing between the allowed values of L_z is constant and equal to $\hbar$.



33 •

Picture the Problem We can find the possible values of ℓ by using the constraints on the quantum numbers. A more analytical solution is to first derive the number of electron states for an arbitrary value of *n* and then substitute the specific value of *n*.

(*a*) When *n* = 3: $\ell = \boxed{0,1,2}$

(*b*) For $\ell = 0$: $m_\ell = \boxed{0}$

For $\ell = 1$: $m_\ell = \boxed{-1,0,+1}$

For $\ell = 2$: $m_\ell = \boxed{-2,-1,0,+1,+2}$

(*c*) We can find the total number of electron states by enumerating the possibilities as shown in the table.

n	ℓ	m_ℓ
3	0	0
3	1	–1
3	1	0
3	1	1
3	2	–2
3	2	–1
3	2	0
3	2	1
3	2	2

$$\boxed{\begin{array}{l}\text{Note that there are 9 } m \text{ states. Because } N\text{, the number of electron states is}\\ \text{twice the number of } m_\ell \text{ states, the number of electron states is 18.}\end{array}}$$

Alternatively, we can derive an expression for the number of electron states for an arbitrary value of *n* and then substitute specific values of *n*:

The number of m_ℓ states for a given *n* is given by:

$$N_m = \sum_{\ell=0}^{n-1}(2\ell+1) = 2\sum_{\ell=0}^{n-1}\ell + \sum_{\ell=0}^{n-1}(1)$$

Express the sum of all integers from 0 to p:

$$\sum_{\ell=0}^{p}\ell = \tfrac{1}{2}p(p+1)$$

Use this result to evaluate $2\sum_{\ell=0}^{n-1}\ell$:

$$2\sum_{\ell=0}^{n-1}\ell = 2\left[\tfrac{1}{2}(n-1)n\right] = n^2 - n$$

Evaluate the second term to obtain:

$$\sum_{\ell=0}^{n-1}(1) = n$$

Substitute to obtain:

$$N_m = n^2 - n + n = n^2$$

and, because N, the number of electron states is twice the number of m states, the number of electron states is $N = 2n^2$.

Hence, for $n = 3$, the number of electron states is:

$$N = 2n^2 = 2(3)^2 = \boxed{18}$$

34 •

Picture the Problem While we could find the number of electron states by finding the possible values of ℓ from the constraints on the quantum numbers and then enumerating the states, we'll take a more analytical approach by deriving an expression for the number of electron states for an arbitrary value of n and then substitute specific values of n.

The number of m states for a given n is given by:

$$N_m = \sum_{\ell=0}^{n-1}(2\ell+1) = 2\sum_{\ell=0}^{n-1}\ell + \sum_{\ell=0}^{n-1}(1)$$

Express the sum of all integers from 0 to p:

$$\sum_{\ell=0}^{p}\ell = \tfrac{1}{2}p(p+1)$$

Use this result to evaluate $2\sum_{\ell=0}^{n-1}\ell$:

$$2\sum_{\ell=0}^{n-1}\ell = 2\left[\tfrac{1}{2}(n-1)n\right] = n^2 - n$$

Evaluate the second term to obtain:

$$\sum_{\ell=0}^{n-1}(1) = n$$

Substitute to obtain:

$$N_m = n^2 - n + n = n^2$$

and, because N, the number of electron states is twice the number of m states, the number of electron states is $N = 2n^2$.

(*a*) For n = 4, the number of electron states is:

$$N = 2n^2 = 2(4)^2 = \boxed{32}$$

(*b*) For n = 2, the number of electron states is:

$$N = 2n^2 = 2(2)^2 = \boxed{8}$$

***35** ••

Picture the Problem The minimum angle between the z axis and $\vec{L}$ is the angle between the $\vec{L}$ vector for $m = \ell$ and the z axis.

Express the angle θ as a function of L_z and L:

$$\theta = \cos^{-1}\left(\frac{L_z}{L}\right)$$

Relate the z component of $\vec{L}$ to m_ℓ and ℓ:

$$L_z = m_\ell \hbar = \ell\hbar$$

Express the angular momentum L:

$$L = \sqrt{\ell(\ell+1)}\hbar$$

Substitute to obtain:

$$\theta = \cos^{-1}\left(\frac{\ell\hbar}{\sqrt{\ell(\ell+1)}\hbar}\right) = \cos^{-1}\left(\sqrt{\frac{\ell}{\ell+1}}\right)$$

(*a*) For ℓ = 1:

$$\theta = \cos^{-1}\left(\sqrt{\frac{1}{1+1}}\right) = \boxed{45.0°}$$

(*b*) For ℓ = 4:

$$\theta = \cos^{-1}\left(\sqrt{\frac{4}{4+1}}\right) = \boxed{26.6°}$$

(*c*) For ℓ = 50:

$$\theta = \cos^{-1}\left(\sqrt{\frac{50}{50+1}}\right) = \boxed{8.05°}$$

36 ••

Picture the Problem We can use constraints on the quantum numbers in spherical coordinates to find the possible values of n and m_ℓ for each of the values of ℓ.

The constraints on n, m_ℓ, and ℓ are:

n = 1, 2, 3, ...
ℓ = 0, 1, 2, ..., $n - 1$
$m_\ell = -\ell$, $(-\ell + 1)$, ... 0, 1, 2, ... ℓ

(*a*) For $\ell = 3$:

$$\boxed{n \geq 4 \text{ and } m_\ell = -3, -2, -1, 0, 1, 2, 3}$$

(*b*) For $\ell = 4$:

$$\boxed{n \geq 5 \text{ and } m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4}$$

(*c*) For $\ell = 0$:

$$\boxed{n \geq 1 \text{ and } m_\ell = 0}$$

37 ••

Picture the Problem The magnitude of the orbital angular momentum L of an electron is related to orbital quantum number ℓ by $L = \sqrt{\ell(\ell+1)}\hbar$ and the z component of the angular momentum of the electron is given by $L_z = m\hbar$.

(*a*) For the $\ell = 2$ state, the square magnitude of the angular momentum is:

$$L^2 = 2(2+1)\hbar^2 = \boxed{6\hbar^2}$$

(*b*) For the $\ell = 2$ state, the maximum value of L_z^2 is:

$$L_z^2 = 2^2\hbar^2 = \boxed{4\hbar^2}$$

(*c*) The smallest value of $L_x^2 + L_y^2$ is given by:

$$L_x^2 + L_y^2 = L^2 - L_z^2 = 6\hbar^2 - 4\hbar^2 = \boxed{2\hbar^2}$$

Quantum Theory of the Hydrogen Atom

38 •

Picture the Problem We can use $\psi(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$ to evaluate the normalized ground-state wave function and its square at $r = a_0$ and $P(r) = 4\pi r^2|\psi|^2$ to find the radial probability density at the same location.

(*a*) Noting that $Z = 1$ for hydrogen, evaluate $\psi(a_0)$ to obtain:

$$\psi(a_0) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-a_0/a_0}$$

$$= \boxed{\frac{1}{ea_0\sqrt{\pi a_0}}}$$

(*b*) Square $\psi(a_0)$ to obtain:

$$\psi^2(a_0) = \left(\frac{1}{ea_0\sqrt{\pi a_0}}\right)^2 = \boxed{\frac{1}{e^2 a_0^3 \pi}}$$

(*c*) Use the result from part (*b*) to evaluate $P(a_0)$:

$$P(a_0) = 4\pi a_0^2 |\psi|^2 = 4\pi a_0^2 \left(\frac{1}{e^2 a_0^3 \pi}\right)$$

$$= \boxed{\frac{4}{e^2 a_0}}$$

***39** •

Picture the Problem We can use the constraints on *n*, ℓ, and *m* to determine the number of different wave functions, excluding spin, corresponding to the first excited energy state of hydrogen.

For $n = 2$:

$$\ell = 0 \text{ or } 1$$

(*a*) For $\ell = 0$, $m_\ell = 0$ and we have:

1 state

For $\ell = 1$, $m_\ell = -1, 0, +1$ and we have:

3 states

Hence, for $n = 2$ we have:

$$\boxed{4 \text{ states}}$$

(*b*) The four wave functions are summarized to the right.

n	ℓ	m_ℓ	(n, ℓ, m_ℓ)
2	0	0	(2,0,0)
2	1	–1	(2,1,–1)
2	1	0	(2,1,0)
2	1	1	(2,1,1)

40 ••

Picture the Problem We can use $\psi(r) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$ to evaluate the normalized ground-state wave function and its square and $P(r) = 4\pi r^2 |\psi|^2$ to find the radial probability density at the same location. Because the range Δ*r* is so small, the variation in the radial probability density *P(r*) can be neglected. The probability of finding the electron in some small range Δ*r* is then *P*(*r*) Δ*r*.

Express the probability of finding the electron in the range Δ*r*:

$$\text{Probability} = \int P(r)\,dr \qquad (1)$$

where *P*(*r*) is the radial probability density function.

The radial probability density function is:

$$P(r) = 4\pi r^2 |\psi|^2 \qquad (2)$$

Express the normalized ground-state wave function:

$$\psi(r)=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$$

Evaluate the normalized ground-state wave function evaluated at $r = a_0$ to obtain:

$$\psi(a_0)=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-a_0/a_0}=\frac{1}{ea_0\sqrt{\pi a_0}}$$

Square $\psi(a_0)$ to obtain:

$$\psi^2(a_0)=\left(\frac{1}{ea_0\sqrt{\pi a_0}}\right)^2=\frac{1}{e^2a_0^3\pi}$$

Substitute in equation (2) to obtain:

$$P(a_0)=4\pi a_0^2|\psi|^2=4\pi a_0^2\left(\frac{1}{e^2a_0^3\pi}\right)=\frac{4}{e^2a_0}$$

(*a*) Substitute in equation (1) to find the probability of finding the electron in the small range $\Delta r = 0.03a_0$:

$$\text{Probability}=\int P(a_0)dr\approx P(a_0)\Delta r$$

$$=\frac{4}{e^2a_0}(0.03a_0)=\boxed{0.0162}$$

(*b*) Evaluate the normalized ground-state wave function at $r = 2a_0$ to obtain:

$$\psi(2a_0)=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}e^{-2a_0/a_0}=\frac{1}{e^2a_0\sqrt{\pi a_0}}$$

Square $\psi(2a_0)$ to obtain:

$$\psi^2(2a_0)=\left(\frac{1}{e^2a_0\sqrt{\pi a_0}}\right)^2=\frac{1}{e^4a_0^3\pi}$$

Substitute in equation (2) to obtain:

$$P(2a_0)=4\pi(2a_0)^2|\psi|^2=16\pi a_0^2\left(\frac{1}{e^4a_0^3\pi}\right)$$

$$=\frac{16}{e^4a_0}$$

Substitute in equation (1) to find the probability of finding the electron in some small range $\Delta r = 0.03a_0$:

$$\text{Probability}=\int P(2a_0)dr\approx P(2a_0)\Delta r$$

$$=\frac{16}{e^4a_0}(0.03a_0)=\boxed{0.00879}$$

Remarks: There is about a 2% chance of finding the electron in this range at $r = a_0$, but at $r = 2a_0$, the chance is only about 0.9%.

41 ••

Picture the Problem We can use Equation 36-36 and the given expression for $C_{2,0,0}$ to evaluate the spherically symmetric wave function ψ for $n = 2$, $\ell = 0$, $m_\ell = 0$, and $Z = 1$ and then use this result to evaluate ψ^2 and $P(r)$ for $r = a_0$.

(*a*) Express the spherically symmetric wave function for $n = 2$, $\ell = 0$, $m_\ell = 0$, and $Z = 1$ (Equation 35-36):

$$\psi_{2,0,0} = C_{2,0,0}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$
$$= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

Evaluate this expression for $r = a_0$:

$$\psi_{2,0,0}(a_0) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{a_0}{a_0}\right)e^{-a_0/2a_0}$$
$$= \frac{1}{4\sqrt{2e\pi}\,a_0^{3/2}} = \boxed{\frac{0.0605}{a_0^{3/2}}}$$

(*b*) Square $\psi_{2,0,0}(a_0)$ to obtain:

$$\left[\psi_{2,0,0}(a_0)\right]^2 = \left(\frac{0.0605}{a_0^{3/2}}\right)^2 = \boxed{\frac{0.00366}{a_0^3}}$$

(*c*) Express the radial probability density:

$$P(r) = 4\pi r^2\psi^2(r)$$

Substitute to obtain:

$$P(a_0) = 4\pi a_0^2\,\frac{0.00366}{a_0^3} = \boxed{\frac{0.0460}{a_0}}$$

42 •••

Picture the Problem We can use the definition of the radial probability density and the wave function (Equation 35-37) for the state (2, 1, 0) to obtain the result given in the problem statement.

Using Equation 35-37, express the wave function for the state (2, 1, 0):

$$\psi_{2,1,0}(r) = C_{2,1,0}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta$$

Square $\psi_{2,1,0}(r)$ to obtain:

$$\left[\psi_{2,1,0}(r)\right]^2 = \left(C_{2,1,0}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta\right)^2$$
$$= C_{2,1,0}^2\frac{Z^2r^2}{a_0^2}e^{-Zr/a_0}\cos^2\theta$$

Express the radial probability density:

$$P(r) = 4\pi r^2 \psi^2(r)$$

Substitute and simplify to obtain:

$$P(r) = 4\pi r^2 C_{2,1,0}^2 \frac{Z^2 r^2}{a_0^2} e^{-Zr/a_0} \cos^2\theta$$

$$= \boxed{Ar^4 \cos^2\theta \; e^{-Zr/a_0}}$$

where

$$A == \boxed{\frac{4\pi C_{2,1,0}^2 Z^2}{a_0^2}}$$

43 •••

Picture the Problem In this instance, $\int P(r)dr$ extends over a sufficiently narrow interval $\Delta r << 0.02a_0$ that we can neglect the dependence of $P(r)$ on r. Hence, we can set $\int P(r)dr = P(r)\Delta r$ and use the wave function (Equation 36-36) for the state (2, 0, 0) and the expression for $C_{2,0,0}$ from Problem 41 to find $\psi_{2,0,0}$, $\psi_{2,0,0}^2$, $P(r)$, and the probability of finding the electron in the range specified at $r = a_0$ and
$r = 2a_0$.

(*a*) Express the probability of finding the electron in the range Δr:

$$\text{Probability} = \int P(r)dr \qquad (1)$$

where $P(r)$ is the radial probability density function.

The radial probability density function is:

$$P(r) = 4\pi r^2 |\psi|^2 \qquad (2)$$

The normalized wave function for the (2, 0, 0) state of hydrogen is given by Equation 36-36:

$$\psi_{2,0,0}(r) = C_{2,0,0}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

From Problem 41 we have, for hydrogen:

$$C_{2,0,0} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}$$

Substitute to obtain:

$$\psi_{2,0,0}(r) = C_{2,0,0}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$= \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

Evaluate the normalized ground-state wave function at $r = a_0$ to obtain:

$$\psi_{2,0,0}(a_0) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-a_0/2a_0}$$
$$= \frac{1}{4\sqrt{2\pi e}\,a_0^{3/2}} = \frac{0.0605}{a_0^{3/2}}$$

Square $\psi_{2,0,0}(a_0)$ to obtain:

$$\left[\psi_{2,0,0}(a_0)\right]^2 = \left(\frac{0.0605}{a_0^{3/2}}\right)^2 = \frac{0.00366}{a_0^3}$$

Substitute in equation (2) to obtain:

$$P(a_0) = 4\pi a_0^2\psi^2(a_0) = 4\pi a_0^2\left(\frac{0.00366}{a_0^3}\right)$$
$$= \frac{4\pi(0.00366)}{a_0} = \frac{0.0460}{a_0}$$

Substitute in equation (1) to find the probability of finding the electron in some small range $\Delta r = 0.02\,a_0$:

$$\text{Probability} = \int P(a_0)dr \approx P(a_0)\Delta r$$
$$= \frac{0.0460}{a_0}(0.02a_0)$$
$$= \boxed{9.20\times10^{-4}}$$

(*b*) Evaluate the normalized ground-state wave function at $r = 2a_0$ to obtain:

$$\psi_{2,0,0}(2a_0) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{2a_0}{a_0}\right)e^{-2a_0/2a_0} = 0$$

Square $\psi_{2,0,0}(2a_0)$ to obtain:

$$\left[\psi_{2,0,0}(a_0)\right]^2 = 0$$

Substitute in equation (2) to obtain:

$$P(2a_0) = 0$$

Substitute in equation (1) to find the probability of finding the electron in some small range $\Delta r = 0.02\,a_0$:

$$\text{Probability} = \int P(2a_0)dr \approx P(2a_0)\Delta r$$
$$= \boxed{0}$$

***44** ••

Picture the Problem We wish to show that $\psi_{1,0,0} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} = Ce^{-Zr/a_0}$ is a solution to $-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + U(r)\psi = E\psi$, where $U(r) = -\frac{kZe^2}{r}$. Because the ground state is spherically symmetric, we do not need to consider the angular partial derivatives in Equation 36-21.

The normalized ground-state wave function is:

$$\psi_{1,0,0}=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}=Ce^{-Zr/a_0}$$

Differentiate this expression with respect to *r* to obtain:

$$\frac{\partial\psi_{1,0,0}}{\partial r}=C\frac{\partial}{\partial r}\left[e^{-Zr/a_0}\right]=-C\frac{Z}{a_0}e^{-Zr/a_0}$$

Multiply both sides of this equation by r^2:

$$r^2\frac{\partial\psi_{1,0,0}}{\partial r}=-C\frac{Z}{a_0}r^2e^{-Zr/a_0}$$

Differentiate this expression with respect to *r* to obtain:

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_{1,0,0}}{\partial r}\right)=-C\frac{Z}{a_0}\frac{\partial}{\partial r}\left(r^2e^{-Zr/a_0}\right)=\left[-\frac{2Zr}{a_0}+r^2\left(\frac{Z}{a_0}\right)^2\right]Ce^{-Zr/a_0}$$

Substitute in Schrödinger’s equation to obtain:

$$-\frac{\hbar^2}{2mr^2}\left[-\frac{2Zr}{a_0}+r^2\left(\frac{Z}{a_0}\right)^2\right]Ce^{-Zr/a_0}-\frac{kZe^2}{r}Ce^{-Zr/a_0}=ECe^{-Zr/a_0}$$

Solve for *E*:

$$E=-\frac{\hbar^2}{2mr^2}\left[-\frac{2Zr}{a_0}+r^2\left(\frac{Z}{a_0}\right)^2\right]-\frac{kZe^2}{r}$$

Because $a_0=\dfrac{\hbar^2}{mke^2}$:

$$E=-\frac{\hbar^2}{2mr^2}\left[-\frac{2mke^2Zr}{\hbar^2}+r^2\left(\frac{Zmke^2}{\hbar^2}\right)^2\right]-\frac{kZe^2}{r}=\frac{kZe^2}{r}-\frac{Z^2k^2e^4m}{2\hbar^2}-\frac{kZe^2}{r}$$

$$=\boxed{-\frac{Z^2k^2e^4m}{2\hbar^2}}$$

Because this is the correct ground state energy, we have shown that Equation 36-33, is a solution to Schrödinger’s Equation 36-21 with the potential energy function Equation 36-26.

45 ••

Picture the Problem We can substitute the dimensions of the physical quantities for the physical quantities in Equation 36-28 and simplify the resulting expression to show that it has dimensions of energy.

Equation 36-28 is:

$$E_0 = \frac{mk^2e^4}{2\hbar^2}$$

The units of this equation are:

$$\frac{[\text{kg}]\left[\frac{\text{N}\cdot\text{m}^2}{\text{C}^2}\right]^2[\text{C}]^4}{[\text{J}\cdot\text{s}]^2} = \frac{[\text{kg}][\text{N}\cdot\text{m}^2]^2}{[\text{N}\cdot\text{m}\cdot\text{s}]^2} = \frac{[\text{kg}][\text{m}]^2}{[\text{s}]^2} = \boxed{[\text{J}]}$$

46 ••

Picture the Problem The Bohr radius is $a_0 = \frac{\hbar^2}{mke^2}$. We can substitute the dimensions of the physical quantities for the physical quantities in this equation and simplify the resulting expression to show that it has dimensions of length.

Because the SI units of $\hbar$ are J·s, its dimensions are:

$$\frac{\text{M}\cdot\text{L}^2}{\text{T}^2}\cdot\text{T} = \frac{\text{M}\cdot\text{L}^2}{\text{T}}$$

Because the SI units of k are N·m^2/C^2, its dimensions are:

$$\frac{\text{M}\cdot\text{L}}{\text{T}^2}\cdot\text{L}^2\cdot\frac{1}{\text{Q}^2} = \frac{\text{M}\cdot\text{L}^3}{\text{T}^2\cdot\text{Q}^2}$$

where Q is the dimension of charge.

Substitute the dimensions in $a_0 = \frac{\hbar^2}{mke^2}$ to obtain:

$$\frac{\left[\frac{\text{M}\cdot\text{L}^2}{\text{T}}\right]^2}{\text{M}\cdot\left[\frac{\text{M}\cdot\text{L}^3}{\text{T}^2\cdot\text{Q}^2}\right]\cdot\text{Q}^2} = \frac{\frac{\text{M}^2\cdot\text{L}^4}{\text{T}^2}}{\frac{\text{M}^2\cdot\text{L}^3}{\text{T}^2}} = \boxed{\text{L}}$$

47 ••

Picture the Problem This is an extreme value problem. We'll begin its solution with the radial probability distribution function, differentiate it with respect to its independent variable r, set this derivative equal to zero, and solve for the value for an extreme value for r. We can show that this value corresponds to a maximum by evaluating the second derivative of $P(r)$ at the location found from the first derivative.

Differentiate the radial probability distribution function with respect to *r* to obtain:

$$\frac{dP(r)}{dr} = C\frac{d}{dr}\left[r^2 e^{-2Zr/a_0}\right]$$
$$= C\left[2re^{-2Zr/a_0} - \frac{2Zr^2}{a_0}e^{-2Zr/a_0}\right]$$
$$= \frac{2CZr}{a_0}e^{-2Zr/a_0}\left(\frac{a_0}{Z} - r\right)$$
$$= 0 \text{ for extrema}$$

Solve for *r* to obtain:

$$r = \frac{a_0}{Z}$$

To show that this value for *r* corresponds to a maximum, differentiate *dP*(*r*)/*dr* to obtain:

$$\frac{d^2P(r)}{dr^2} = -\frac{2CZr}{a_0}e^{-2Zr/a_0} + \left(\frac{a_0}{Z} - r\right) \times \left(-\frac{4CZ^2}{a_0^2} + \frac{2CZ}{a_0}\right)e^{-2Zr/a_0}$$

Evaluate this derivative at $r = a_0/Z$:

$$\left.\frac{d^2P(r)}{dr^2}\right|_{r=\frac{a_0}{Z}} = -2Ce^{-2} < 0$$

because *C* is a positive constant. Hence, *P*(*r*) has its maximum value at $r = \boxed{\dfrac{a_0}{Z}}$

48 •••

Picture the Problem We can double the sum of the number of *m* states for a given *n* to show that the number of states in the hydrogen atom for a given *n* is $2n^2$.

The number of m_ℓ states for a given *n* is:

$$N_{m_\ell} = \sum_{\ell=0}^{n-1}(2\ell+1) = 2\sum_{\ell=0}^{n-1}\ell + \sum_{\ell=0}^{n-1}(1)$$

The sum of all integers from 0 to *p* is:

$$\sum_{\ell=0}^{p}\ell = \tfrac{1}{2}p(p+1)$$

and

$$2\sum_{\ell=0}^{n-1}\ell = 2\left(\tfrac{1}{2}\right)(n-1)(n) = n^2 - n$$

The second term is:

$$\sum_{\ell=0}^{n-1}(1) = n$$

Substitute to obtain:

$$N_{m_\ell} = n^2 - n + n = n^2$$

Because N, the number of electron states, is twice the number of m_ℓ states, the number of electron states is:

$$N = 2N_{m_\ell} = \boxed{2n^2}$$

49 •••

Picture the Problem The ground state of a hydrogen atom is the state described by $n = 1$, $\ell = 0$, $m_\ell = 0$. We can calculate the probability that the electron in the ground state of the hydrogen atom is in the region $0 < r < a_0$ by evaluating the integral $\int_0^{a_0} 4\pi r^2 \psi_{1,0,0}^2(r)dr$.

Express the probability that the electron in the ground state of a hydrogen atom is in the region $0 < r < a_0$:

$$\text{Probability} = \int_0^{a_0} 4\pi r^2 \psi_{1,0,0}^2(r)dr$$

Express the ground-state wave function for hydrogen:

$$\psi_{1,0,0}(r) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

Square the wave function to obtain:

$$\psi_{1,0,0}^2(r) = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

Substitute to obtain:

$$\text{Probability} = \int_0^{a_0} 4\pi r^2 \left(\frac{1}{\pi a_0^3} e^{-2r/a_0}\right)dr$$

$$= \frac{4}{a_0^3}\int_0^{a_0} r^2 e^{-2r/a_0} dr$$

Use a table of integrals to find:

$$\int x^2 e^{bx} dx = \frac{e^{bx}}{b^3}\left(b^2x^2 - 2bx + 2\right)$$

Use this integral to show that:

$$\text{Probability} = -e^{-2r/a_0}\left(\frac{2r^2}{a_0^2} + \frac{2r}{a_0} + 1\right)\Bigg|_0^{a_0}$$

$$= 1 - 5e^{-2} = \boxed{0.323}$$

The Spin-Orbit Effect and Fine Structure

***50** •

Picture the Problem The energy difference between the two possible orientations of an electron in a magnetic field is $2\mu B$ and the wavelength of the photons required to induce a spin-flip transition can be found from $hc/\Delta E$. The magnetic moment μ_B associated with the spin of an electron is 5.79×10^{-5} eV/T.

(*a*) Relate the difference in energy between the two spin orientations in terms of the difference in the potential energies of the two states:

$$\Delta E = 2\mu B = 2\left(5.79\times10^{-5}\text{ eV/T}\right)\left(0.6\text{ T}\right) = \boxed{6.95\times10^{-5}\text{ eV}}$$

(*b*) Relate the wavelength of the photon needed to induce such a transition to the energy required:

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

Substitute numerical values and evaluate λ:

$$\lambda = \frac{1240\text{ eV}\cdot\text{nm}}{6.95\times10^{-5}\text{ eV}} = 1.78\times10^{7}\text{ nm} = \boxed{1.78\text{ cm}}$$

51 •

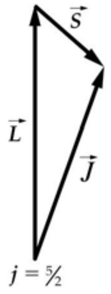
Determine the Concept j and ℓ are constrained according to $j = \ell \pm \frac{1}{2}$. For $j = ½$, $\ell = \frac{1}{2} \pm \frac{1}{2}$ or $\ell = \boxed{0 \text{ or } 1}$.

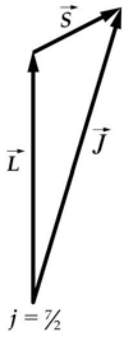
52 •

Determine the Concept j and ℓ are constrained according to $j = \ell \pm \frac{1}{2}$. For $\ell = 2$, $j = 2 \pm \frac{1}{2}$, or $j = \boxed{\frac{3}{2} \text{ or } \frac{5}{2}}$

53 •

Picture the Problem The total angular momentum vector $\vec{J}$ is the sum of the orbital momentum vector $\vec{L}$ and the spin orbital angular momentum vector $\vec{S}$. The quantum number j can be either $\ell + \frac{1}{2}$ or $\ell - \frac{1}{2}$, where $\ell \neq 0$. Hence, j can take on the values 3 + 1/2 = 7/2 and 3 – 1/2 = 5/2. The scaled vector diagrams are shown to the right.





The Periodic Table

54 •

Determine the Concept The total number of quantum states of hydrogen with quantum number n is $2n^2$. For n =4, we have $2(4)^2 = 32$. $\boxed{(c)\text{ is correct.}}$

55 •

Determine the Concept From Table 36-1, oxygen's electronic configuration is $1s^22s^22p^4$. Because there are 4 electrons in the p state, $\boxed{(c)\text{ is correct.}}$

***56** •

Determine the Concept We can use the atomic numbers of carbon and oxygen to determine the sum of the exponents in their electronic configurations and then use the rules for the filling of the shells to find their electronic configurations.

(*a*) The atomic number Z of carbon is 6. So we must fill the subshells of the electronic configuration until we have placed its 6 electrons. This is accomplished by writing:

$$\boxed{1s^2 2s^2 2p^2}$$

(*b*) The atomic number Z of oxygen is 8. So we must fill the subshells of the electronic configuration until we have placed its 8 electrons. This is accomplished by writing:

$$\boxed{1s^2 2s^2 2p^4}$$

57 •

Determine the Concept We can find the z component of the orbital angular momentum using $L_z = m\hbar$ and the relationship between the quantum numbers ℓ (which we know from the state of the electrons) and m_ℓ (which is related to ℓ through $m_\ell = -\ell, (-\ell + 1), \ldots, 0, 1, 2, \ldots \ell$).

(*a*) For a p electron $\ell = 1$. For $\ell = 1$, $m_\ell = -1, 0,$ or 1. Because $L_z = -m\hbar, \ldots, m\hbar$:

$$L_z = \boxed{-2\hbar, -\hbar, 0, \hbar, 2\hbar}$$

(*b*) For an f electron, $\ell = 4$. For $\ell = 4$, $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$. Because $L_z = -m\hbar, \ldots, m\hbar$:

$$L_z = \boxed{-4\hbar, -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar, 4\hbar}$$

Optical Spectra and X-Ray Spectra

58 •

Determine the Concept Lithium, sodium, potassium, chromium, and cesium have one outer s electron and hence belong in the same group. Beryllium, magnesium, calcium, nickel, and barium have two outer s electrons and, hence, belong in the same group.

59 •

Determine the Concept We can use Table 35-1 to find the electronic configurations for the first excited states of these elements.

(*a*) For H, E depends only on n and the lowest excited state is: $\boxed{\text{2s or 2p}}$

(*b*) For Na, the 3p state is higher energy than the 3s state and the lowest excited state is: $\boxed{1s^2 2s^2 2p^6 3p}$

(*c*) For He, the lowest excited state has one electron in the 2s state and the lowest excited state is: $\boxed{\text{1s2s}}$

60 •

Determine the Concept Atoms with one outer electron have spectra similar to H: Li, Rb, Ag, Fr. Atoms with two outer electrons have spectra similar to He: Ca, Ti, Hg, Cd, Ba, Ra. Therefore, the table should be completed as shown below:

Optical Spectra Similar to Hydrogen	Optical Spectra Similar to Helium
Li, Rb, Ag, Fr	Ca, Ti, Hg, Cd, Ba, Ra

***61 •**

Picture the Problem When an electron from state n drops into a vacated state in the n = 1 shell, a photon of energy $\Delta E = E_n - E_1$ is emitted. We can find the wavelength of this photon using $\lambda = hc/\Delta E$. The second and third longest wavelengths in the K series correspond to transitions from n = 3 to n = 1 and n = 4 to n = 1 and the shortest wavelength to the transition from $n = \infty$ to n = 1.

Express the wavelength of the emitted photon in terms of the energy transition within the atom:

$$\lambda = \frac{hc}{E_n - E_1} = \frac{1240\,\text{eV}\cdot\text{nm}}{E_n - E_1}$$

Express the energy of the *n*th energy state:

$$E_n = -(Z-1)^2\frac{E_0}{n^2}$$

where n = 1, 2, …

Substitute to obtain:

$$\lambda = \frac{hc}{E_n - E_1} = \frac{1240\,\text{eV}\cdot\text{nm}}{-(Z-1)^2\frac{E_0}{n^2} - \left(-(Z-1)^2\frac{E_0}{1^2}\right)} = \frac{1240\,\text{eV}\cdot\text{nm}}{(Z-1)^2E_0\left(1-\frac{1}{n^2}\right)}$$

(*a*) Evaluate this expression with n = 3 and Z = 42 to obtain:

$$\lambda_3 = \frac{1240\,\text{eV}\cdot\text{nm}}{(42-1)^2(13.6\,\text{eV})\left(1-\frac{1}{3^2}\right)} = \boxed{0.0610\,\text{nm}}$$

Use n = 4 and Z = 42 to obtain:

$$\lambda_4 = \frac{1240\,\text{eV}\cdot\text{nm}}{(42-1)^2(13.6\,\text{eV})\left(1-\frac{1}{4^2}\right)} = \boxed{0.0578\,\text{nm}}$$

(*b*) The shortest wavelength in the series corresponds to the largest energy difference between the initial and final states. Repeat the calculation in part (*a*) with $n = \infty$ to obtain:

$$\lambda_\infty = \frac{1240\,\text{eV}\cdot\text{nm}}{(42-1)^2(13.6\,\text{eV})(1-0)} = \boxed{0.0542\,\text{nm}}$$

62 •

Picture the Problem When an electron from state n drops into the vacated state in the n = 1 shell, a photon of energy $E_n - E_1$ is emitted. The wavelength of this photon is $\lambda = \dfrac{hc}{(Z-1)^2(13.6\,\text{eV})\left(1-\frac{1}{n^2}\right)}$. Hence, if we know the wavelength of the K_α line we can solve for the atomic number of the element and use its value to identify the element.

Express the wavelength of the K_α line as a function of the atomic number of the element:

$$\lambda = \frac{hc}{(Z-1)^2(13.6\,\text{eV})\left(1-\dfrac{1}{n^2}\right)}$$

Solve for *Z*:

$$Z = 1 + \sqrt{\frac{hc}{\lambda(13.6\,\text{eV})\left(1-\dfrac{1}{n^2}\right)}}$$

Substitute numerical values and evaluate *Z*:

$$Z = 1 + \sqrt{\frac{1240\,\text{eV}\cdot\text{nm}}{(0.3368\,\text{nm})(13.6\,\text{eV})\left(1-\dfrac{1}{2^2}\right)}}$$
$$= 20$$

$$\boxed{\text{The element whose atomic number is 20 is calcium.}}$$

63 •

Picture the Problem The K_α corresponds to a transition from $n = 2$ to $n = 1$. Equation 36-16 relates the atomic number *Z* to the wavelength of the emitted photon When an electron from state *n* drops into a vacated state in the $n = 1$ shell, a photon of energy $E_n - E_1$ is emitted. We can find the wavelength of this photon using $\lambda = hc/(E_n - E_1)$ and E_n from $E_n = -Z^2(E_0/n^2)$.

Express the wavelength of the K_α line:

$$\lambda = \frac{hc}{E_n - E_1} = \frac{1240\,\text{eV}\cdot\text{nm}}{E_n - E_1}$$

Express the energy of the atom's *n*th energy state:

$$E_n = -Z^2\frac{E_0}{n^2}$$

Substitute and simplify to obtain:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{-Z^2\dfrac{E_0}{n^2} + Z^2E_0} = \frac{1240\,\text{eV}\cdot\text{nm}}{Z^2E_0\left(1-\dfrac{1}{n^2}\right)}$$

(*a*) Substitute $n = 2$, $Z = 12$, and $E_0 = 13.6$ eV to obtain:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{11^2(13.6\,\text{eV})\left(1-\dfrac{1}{2^2}\right)} = \boxed{1.00\,\text{nm}}$$

(*b*) Substitute $n = 2$, $Z = 29$, and $E_0 = 13.6$ eV to obtain:

$$\lambda = \frac{1240\,\mathrm{eV\cdot nm}}{28^2(13.6\,\mathrm{eV})\left(1-\frac{1}{2^2}\right)}$$

$$= \boxed{0.155\,\mathrm{nm}}$$

General Problems

64 •

Picture the Problem The energy associated with a transition from an initial state to some final state is given by $\Delta E = E_\mathrm{i} - E_\mathrm{f}$ and the wavelength λ of a photon emitted in such a transition is given by $\lambda = hc/\Delta E$. Hence, the shortest wavelength corresponds to the largest energy difference.

Express the wavelength of the emitted photon in terms of the energy difference ΔE between the atom's initial and final states:

$$\lambda = \frac{hc}{\Delta E} \quad \text{or} \quad \Delta E = \frac{hc}{\lambda}$$

For λ_min, ΔE will be the energy required to ionize a hydrogen atom:

$$\Delta E_\mathrm{max} = \frac{hc}{\lambda_\mathrm{min}} = \boxed{13.6\,\mathrm{eV}}$$

65 •

Picture the Problem This spectral line is due to a transition from some initial state n_i to a final state n_f (we're given that the final state is the ground state). The wavelength of the spectral line is related to the difference in energy ΔE between these states according to $\lambda = 1240\,\mathrm{eV\cdot nm}/\Delta E$ and the energy of the nth state is given (for hydrogen, $Z = 1$) by $E_n = (1^2)(-13.6\ \mathrm{eV})/n^2$.

Relate the wavelength of a spectral line to the energy transition within the atom:

$$\lambda = \frac{1240\,\mathrm{eV\cdot nm}}{\Delta E} \qquad (1)$$

Express the energy difference ΔE in a transition:

$$\Delta E = E_\mathrm{i} - E_\mathrm{f} = -\frac{Z^2E_0}{n_\mathrm{i}^2} + \frac{Z^2E_0}{n_\mathrm{f}^2}$$

$$= Z^2E_0\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right)$$

For $Z = 1$ and $E_0 = 13.6$ eV:

$$\Delta E = (13.6\,\mathrm{eV})\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right)$$

Substitute in equation (1) to obtain:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{(13.6\,\text{eV})\left(\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}\right)} = \frac{91.2\,\text{nm}}{\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}}$$

or

$$\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2} = \frac{91.2\,\text{nm}}{\lambda}$$

For λ = 97.254 nm and n_f = 1 this expression simplifies to:

$$1-\frac{1}{n_\text{i}^2} = \frac{91.2\,\text{nm}}{97.254\,\text{nm}} = 0.938$$

Solve for n_i to obtain:

$$n_\text{i} = 4$$

$$\boxed{\text{The transition that produced the given wavelength was from } n_\text{i} = 4 \text{ to } n_\text{f} = 1.}$$

66 •

Picture the Problem This spectral line is due to a transition from some initial state n_i to a final state n_f (we're given that the final state is the ground state). The wavelength of the spectral line is related to the difference in energy ΔE between these states according to $\lambda = 1240\,\text{eV}\cdot\text{nm}/\Delta E$ and the energy of the nth state is given (for hydrogen, Z = 1) by $E_\text{n} = (1^2)(-13.6\text{ eV})/n^2$.

Relate the wavelength of a spectral line to the energy transition within the atom:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} \qquad (1)$$

Express the energy difference ΔE in a transition:

$$\Delta E = E_\text{i} - E_\text{f} = -\frac{Z^2E_0}{n_\text{i}^2}+\frac{Z^2E_0}{n_\text{f}^2} = Z^2E_0\left(\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}\right)$$

For Z = 1 and E_0 = 13.6 eV:

$$\Delta E = (13.6\,\text{eV})\left(\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}\right)$$

Substitute in equation (1) to obtain:

$$\lambda=\frac{1240\,\text{eV}\cdot\text{nm}}{(13.6\,\text{eV})\left(\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}\right)}$$

$$=\frac{91.2\,\text{nm}}{\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}}$$

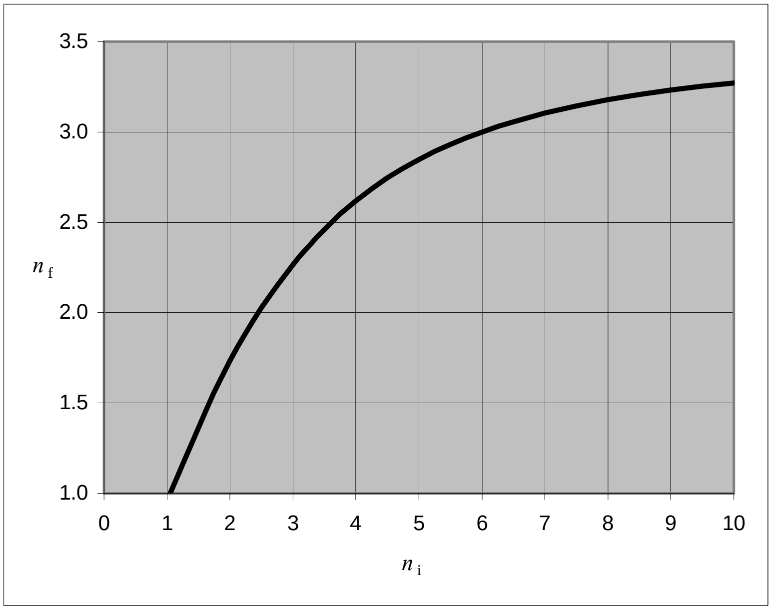
or

$$\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}=\frac{91.2\,\text{nm}}{\lambda}$$

For λ = 1093.8 nm this expression simplifies to:

$$\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}=\frac{91.2\,\text{nm}}{1093.8\,\text{nm}}=0.0834$$

Because the only constraints on n_f and n_i are that they be integers, we can solve this equation by trial and error. One way to do this is to plot a graph of n_i as a function of n_f and look for integer solutions visually or with a trace of the trajectory of the curve. The following graph was plotted using a spreadsheet program. Note that a solution to our equation is n_i = 6 and n_f = 3.



$$\boxed{\text{Thus, the transition that produces the given wavelength is from } n_\text{i}=6 \text{ to } n_\text{f}=3.}$$

67 •

Picture the Problem These spectral lines are due to transitions in singly ionized helium from some initial state n_i to a final state n_f. The wavelengths of the spectral lines are related to the difference in energy ΔE between these states according to $\lambda = 1240\,\text{eV}\cdot\text{nm}/\Delta E$ and the energy of the nth state is given (for helium, $Z = 2$) by $E_n = (2^2)(-13.6\text{ eV})/n^2$.

Relate the wavelength of a spectral line to the energy transition within the atom:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E} \qquad (1)$$

Express the energy difference ΔE in a transition:

$$\Delta E = E_\text{i} - E_\text{f} = -\frac{Z^2E_0}{n_\text{i}^2} + \frac{Z^2E_0}{n_\text{f}^2} = Z^2E_0\left(\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2}\right)$$

For $Z = 2$ and $E_0 = 13.6$ eV:

$$\Delta E = 2^2(13.6\,\text{eV})\left(\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2}\right) = (54.4\,\text{eV})\left(\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2}\right)$$

Substitute in equation (1) to obtain:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{(54.4\,\text{eV})\left(\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2}\right)} = \frac{22.8\,\text{nm}}{\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2}}$$

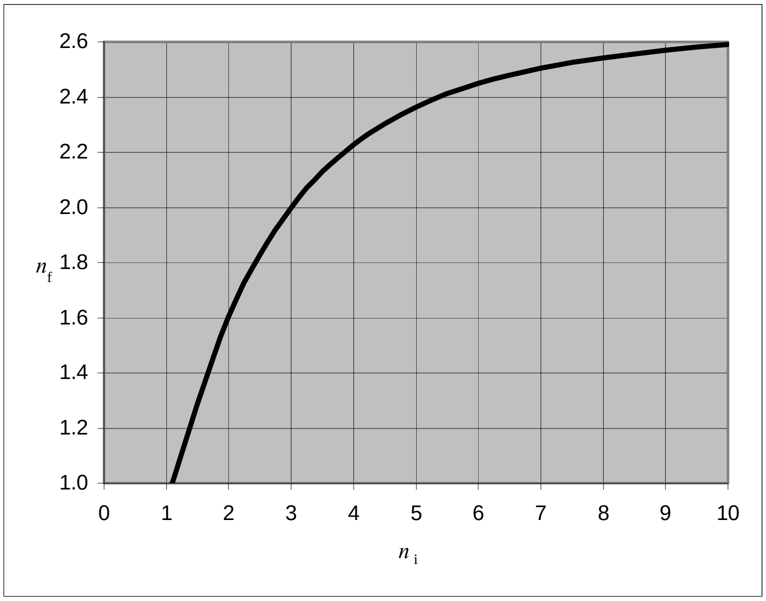
or

$$\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2} = \frac{22.8\,\text{nm}}{\lambda}$$

For $\lambda = 164$ nm this expression becomes:

$$\frac{1}{n_\text{f}^2} - \frac{1}{n_\text{i}^2} = \frac{22.8\,\text{nm}}{164\,\text{nm}} = 0.139$$

Because the only constraints on n_f and n_i are that they be integers, we can solve this equation by trial and error. One way to do this is to plot a graph of n_i as a function of n_f and look for integer solutions visually or with a trace of the trajectory of the curve. The following graph was plotted using a spreadsheet program. Note that a solution to our equation is $n_\text{i} = 3$ and $n_\text{f} = 2$.



$\boxed{\text{Thus, the transition that produces the given wavelength is from } n_i = 3 \text{ to } n_f = 2.}$

Similarly, for λ = 230.6 nm:

$\boxed{\text{The transition that produces the given wavelength is from } n_i = 9 \text{ to } n_f = 3.}$

For λ = 541 nm:

$\boxed{\text{The transition that produces the given wavelength is from } n_i = 7 \text{ to } n_f = 4.}$

***68 ••**

Picture the Problem We can show that ke^2 = 1.44 eV·nm by solving the equation for the ground state energy of an atom for ke^2.

Express the ground state energy of an atom as a function of k, e, and a_0:

$$E_0 = \frac{ke^2}{2a_0}$$

Solve for ke^2:

$$ke^2 = 2E_0 a_0$$

Substitute for E_0 and a_0 to obtain:

$$ke^2 = 2(13.6\,\text{eV})(0.0529\,\text{nm}) = \boxed{1.44\,\text{eV}\cdot\text{nm}}$$

69 ••

Picture the Problem Because the energies of the photons emitted by potassium during these transitions are related to their wavelengths through $hf = (1240\text{ eV}\cdot\text{nm}/\lambda)$ eV where λ is in nm, we can use this relationship to find the energies of the given photons. The difference in energy between these states can be found using its definition and is related to the magnetic field through $\Delta E = 2\mu_B B$.

(*a*) For λ = 766.41 nm:

$$hf = \frac{1240\,\text{eV}\cdot\text{nm}}{766.41\,\text{nm}} = \boxed{1.6179\,\text{eV}}$$

For λ = 769.90 nm:

$$hf = \frac{1240\,\text{eV}\cdot\text{nm}}{769.90\,\text{nm}} = \boxed{1.6106\,\text{eV}}$$

(*b*) Using its definition, express the difference in energy between these two states:

$$\Delta E = 1.6179\,\text{eV} - 1.6106\,\text{eV}$$
$$= \boxed{0.00730\,\text{eV}}$$

(*c*) Relate the energy difference between these states ΔE to the magnetic field B and the quantum unit of magnetic moment (a Bohr magneton) μ_B:

$$\Delta E = 2\mu_B B$$

Solve for B:

$$B = \frac{\Delta E}{2\mu_B}$$

Substitute numerical values and evaluate B:

$$B = \frac{0.0073\,\text{eV}}{2\left(5.79\times10^{-5}\,\text{eV/T}\right)} = \boxed{63.0\,\text{T}}$$

Remarks: This magnetic field is about 42 times that of commercial magnetic resonance imagers.

70 ••

Picture the Problem One 1s electron must be released from the atom. It is shielded from the nuclear charge Z by one other 1s electron. Thus, the effective charge is $Z - 1$, and the ionization energy for that 1s electron is $E_{\text{min}} = (Z-1)^2E_0$.

(*a*) For tungsten, Z = 74, and:

$$E_{\text{min}} = 73^2(13.6\,\text{eV}) = \boxed{72.5\,\text{keV}}$$

(*b*) For molybdenum, Z = 42, and:

$$E_{\text{min}} = 41^2(13.6\,\text{eV}) = \boxed{22.9\,\text{keV}}$$

(*c*) For copper, Z = 29, and:

$$E_{\text{min}} = 28^2(13.6\,\text{eV}) = \boxed{10.7\,\text{keV}}$$

***71 ••**

Picture the Problem We can show that α is dimensionless by showing that it has no units. In part (*b*) we can use Bohr's 3rd postulate and the expression for the radii of the Bohr orbits, together with the definition of α, to show that the speed of the electron in a stationary state of quantum number n is related to α according to $v_{\text{n}} = c\alpha/n$.

(*a*) Express the units of α:

$$\frac{\text{C}^2\left(\dfrac{\text{N}\cdot\text{m}^2}{\text{C}^2}\right)}{(\text{J}\cdot\text{s})\dfrac{\text{m}}{\text{s}}} = \frac{\text{N}\cdot\text{m}^2}{\text{J}\cdot\text{m}} = 1$$

$$\boxed{\text{Because } \alpha \text{ is unitless, it is also dimensionless.}}$$

(*b*) Apply the quantization of angular momentum postulate to obtain:

$$v_n = \frac{n\hbar}{mr_n}$$

The radii of the Bohr orbits are given by:

$$r_n = n^2\frac{\hbar^2}{mkZe^2}$$

or, because Z = 1 for hydrogen,

$$r_n = n^2\frac{\hbar^2}{mke^2}$$

Substitute and simplify to obtain:

$$v_n = \frac{n\hbar}{mn^2\dfrac{\hbar^2}{mke^2}} = \frac{ke^2}{n\hbar}$$

Divide this expression by the definition of α to obtain:

$$\frac{v_n}{\alpha} = \frac{\dfrac{ke^2}{n\hbar}}{\dfrac{e^2k}{\hbar c}} = \frac{c}{n}$$

Solve for v_n:

$$v_n = \boxed{\frac{\alpha c}{n}}$$

72 ••

Picture the Problem We can use Problem 29 to express the energy levels of positronium in terms of the reduced mass of the electron-positron system. In part (*b*) we can find the energies corresponding to 400 nm and 700 nm to decide whether the transitions between any of the levels found in (*a*) fall in the visible range of wavelengths

Express the energy of positronium as a function of the quantum number *n*:

$$E_n = -\frac{m_r k^2 e^4}{2\hbar^2}\frac{Z^2}{n^2}$$

From Problem 29 we have:

$$m_r = \frac{m_\text{e} m_\text{pos}}{m_\text{e} + m_\text{pos}}$$

Because $m_\text{e} = m_\text{pos}$:

$$m_r = \frac{m_\text{e} m_\text{e}}{m_\text{e} + m_\text{e}} = \frac{m_\text{e}}{2}$$

Substitute and simplify to obtain:

$$E_n = -\frac{m_\text{e} k^2 e^4}{4\hbar^2}\frac{1}{n^2} = -\frac{E_0}{2n^2}$$

(*a*) Evaluate E_n for n = 1, 2, 3, 4, and 5 to obtain:

n	E_n
	(eV)
1	–6.80
2	–1.70
3	–0.756
4	–0.425
5	–0.272

Relate the wavelength of the emitted photons to the energy-level differences:

$$\lambda = \frac{hc}{\Delta E} = \frac{1240\ \text{eV}\cdot\text{nm}}{\Delta E}$$

Solve for ΔE:

$$\Delta E = \frac{1240\ \text{eV}\cdot\text{nm}}{\lambda}$$

Evaluate ΔE for λ = 400 nm and λ = 700 nm:

$$\Delta E_{400\ \text{nm}} = \frac{1240\ \text{eV}\cdot\text{nm}}{400\ \text{nm}} = 3.10\ \text{eV}$$

and

$$\Delta E_{700\ \text{nm}} = \frac{1240\ \text{eV}\cdot\text{nm}}{700\ \text{nm}} = 1.77\ \text{eV}$$

$$\boxed{\begin{array}{c}\text{Because none of the energies in the table shown above are in the interval}\\ \text{1.77 eV to 3.10 eV, no transitions are in the visible range of wavelengths.}\end{array}}$$

73 •

Picture the Problem We can use $E = hf$ to find the frequency of the photon and $\lambda = hc/E$ to find its wavelength.

(*a*) The energy of the photon whose energy is equal to the Lamb shift energy is given by:

$$E = hf$$

Solve for f to obtain:

$$f = \frac{E}{h}$$

Substitute numerical values and evaluate f:

$$f = \frac{4.372\times10^{-6}\text{ eV}}{4.14\times10^{-15}\text{ eV}\cdot\text{s}} = \boxed{1.06\,\text{GHz}}$$

(*b*) The wavelength of this photon is given by:

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

Substitute numerical values and evaluate λ:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{4.372\times10^{-6}\text{ eV}} = \boxed{28.4\,\text{cm}}$$

$$\boxed{\text{This wavelength is in the microwave portion of the electromagnetic spectrum.}}$$

***74** •

Picture the Problem The ionization energy of the electron is the magnitude of the energy of the atom in the given state. We can use $E = -E_0/n^2$, where E_0 is the ground-state energy, to find the energy levels in the 44th and 45th states and, hence, the energy level separation between the states. The wavelength of a photon resonant with this transition can be found from $\lambda = hc/\Delta E$. We'll approximate the size of the atom in the $n = 45$ state by finding the radius of the outer-shell electron.

(*a*) The energy of the atom in its *n*th state is:

$$E_n = -\frac{E_0}{n^2}$$

The energy of the atom in the $n = 45$ state is:

$$E_{45} = -\frac{13.6\,\text{eV}}{(45)^2} = -6.72\,\text{meV}$$

The ionization energy is the negative of the energy in the state $n = 45$:

$$E_{\text{ionizing}} = -E_{45} = \boxed{6.72\,\text{meV}}$$

(*b*) The energy level separation between the $n = 45$ and $n = 44$ state is:

$$E_{45\to44} = -\left(\frac{13.6\text{ eV}}{(45)^2} - \frac{13.6\text{ eV}}{(44)^2}\right)$$

$$= \boxed{3.09\times10^{-4}\text{ eV}}$$

(*c*) The photon wavelength is:

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

Substitute numerical values and evaluate λ:

$$\lambda = \frac{1240\,\text{eV}\cdot\text{nm}}{3.09\times10^{-4}\,\text{eV}} = \boxed{4.01\times10^{6}\ \text{nm}}$$

(*d*) The radii of the Bohr orbits are given by:

$$r = n^2\frac{a_0}{Z}$$

Substitute numerical values and evaluate the radius of the 45th Bohr orbit:

$$r = (45)^2\frac{0.0529\,\text{nm}}{1} = \boxed{107\,\text{nm}}$$

75 ••

Picture the Problem We can use the definition of the Rydberg constant and the equation for the reduced mass from Problem 29 to calculate the Rydberg constant for hydrogen and for deuterium. We can find the wavelength difference between the longest wavelength Balmer lines of hydrogen and deuterium by finding the longest wavelengths from the Rydberg-Ritz equation, using the appropriate value for *R*, and taking their difference.

(*a*) From Equation 36-14 we have:

$$R = \frac{m_r k^2 e^4}{4\pi c\hbar^3} = C\left(\frac{m_e}{1+\dfrac{m_e}{M}}\right)$$

where

$$C = \frac{k^2e^4}{4\pi c\hbar^3} = 1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}$$

For H:

$$R_H = C\left(\frac{m_e}{1+\dfrac{m_e}{m_p}}\right)$$

Substitute numerical values and evaluate R_H:

$$R_H = \left(1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}\right)\times\left(\frac{9.109390\times10^{-31}\ \text{kg}}{1+\dfrac{9.109390\times10^{-31}\ \text{kg}}{1.672623\times10^{-27}\ \text{kg}}}\right) = \boxed{1.096776\times10^{7}\ \text{m}^{-1}}$$

For deuterium:

$$R_D = C\left(\frac{m_e}{1+\frac{m_e}{2m_p}}\right)$$

Substitute numerical values and evaluate R_D:

$$R_D = \left(1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}\right)\times\left(\frac{9.109390\times10^{-31}\ \text{kg}}{1+\frac{9.109390\times10^{-31}\ \text{kg}}{2\left(1.672623\times10^{-27}\ \text{kg}\right)}}\right) = \boxed{1.097075\times10^{7}\ \text{m}^{-1}}$$

(*b*) Express the wavelength difference between the longest wavelength Balmer lines of hydrogen and deuterium:

$$\Delta\lambda = \lambda_{\text{longest, H}} - \lambda_{\text{longest, D}}$$

Use the Rydberg-Ritz formula to express the reciprocal wavelength:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2}-\frac{1}{n_1^2}\right)$$

where n_1 and n_2 are integers and $n_1 > n_2$.

Solve for λ to obtain:

$$\lambda = \frac{n_1^2 n_2^2}{R\left(n_1^2-n_2^2\right)}$$

The longest wavelength in the Balmer series corresponds to a transition from $n_1 = 3$ to $n_2 = 2$. Use $R = R_H$ to evaluate $\lambda_{\text{longest, H}}$:

$$\lambda_{\text{longest, H}} = \frac{3^2\left(2^2\right)}{\left(1.096776\times10^{7}\ \text{m}^{-1}\right)\left(3^2-2^2\right)} = 656.470\ \text{nm}$$

Find $\lambda_{\text{longest,D}}$ using $R = R_D$:

$$\lambda_{\text{longest, D}} = \frac{3^2\left(2^2\right)}{\left(1.097075\times10^{7}\ \text{m}^{-1}\right)\left(3^2-2^2\right)} = 656.291\ \text{nm}$$

Substitute to obtain:

$$\Delta\lambda = 656.470\ \text{nm} - 656.291\ \text{nm} = \boxed{0.179\ \text{nm}}$$

76 ••

Picture the Problem We can use Problem 29 to express the energy levels of muonium in terms of the reduced mass of the muonium-proton system. In Part (*b*) we can find the energies corresponding to 400 nm and 700 nm to decide whether the transitions between any of the levels found in (*a*) fall in the visible range of wavelengths

Express the energy of muonium as a function of the quantum number *n*:

$$E_n = -\frac{m_r k^2 e^4}{2\hbar^2}\frac{Z^2}{n^2} \qquad (1)$$

From Equation 35-47 in Problem 17 we have:

$$m_r = \frac{m_\text{p} m_{\mu^{-1}}}{m_\text{p} + m_{\mu^{-1}}}$$

Because $m_{\mu^{-1}} = 207 m_\text{e}$:

$$m_r = \frac{207 m_\text{p} m_\text{e}}{m_\text{p} + 207 m_\text{e}} = \frac{207 m_\text{e}}{1 + 207\dfrac{m_\text{e}}{m_\text{p}}}$$

Because $m_\text{p} = 1836 m_\text{e}$:

$$m_r = \frac{207 m_\text{e}}{1 + \dfrac{207}{1836}} = 186 m_\text{e}$$

Substitute in equation (1) and simplify to obtain:

$$E_n = -\frac{186 m_\text{e} k^2 e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{186 E_0}{n^2}$$

(*a*) Evaluate E_n for n = 1, 2, 3, 4, and 5 to obtain:

n	E_n
	(keV)
1	–2.53
2	–0.633
3	–0.281
4	–0.158
5	–0.101

Relate the wavelength of the emitted photons to the energy-level differences:

$$\lambda = \frac{hc}{\Delta E} = \frac{1240\,\text{eV}\cdot\text{nm}}{\Delta E}$$

Solve for ΔE:

$$\Delta E = \frac{1240\,\text{eV}\cdot\text{nm}}{\lambda}$$

Evaluate ΔE for λ = 400 nm and λ = 700 nm:

$$\Delta E_{400\,\text{nm}} = \frac{1240\,\text{eV}\cdot\text{nm}}{400\,\text{nm}} = 3.10\,\text{eV}$$

and

$$\Delta E_{700\,\text{nm}} = \frac{1240\,\text{eV}\cdot\text{nm}}{700\,\text{nm}} = 1.77\,\text{eV}$$

$$\boxed{\begin{array}{c}\text{Because none of the energies in the table shown above are in the interval}\\ \text{1.77 eV to 3.10 eV, no transitions are in the visible range of wavelengths.}\end{array}}$$

77 ••

Picture the Problem We can use the definition of the Rydberg constant and the equation for the reduced mass from Problem 29 to calculate the Rydberg constant for hydrogen, tritium, and deuterium. We can find the wavelength difference between the longest wavelength Balmer lines of tritium and deuterium and tritium and hydrogen by finding the longest wavelengths from the Rydberg-Ritz equation, using the appropriate value for *R*, and taking their difference.

(*a*) From Problem 29 we have:

$$R = \frac{m_\text{r}k^2e^4}{4\pi c\hbar^3} = C\left(\frac{m_\text{e}}{1+\frac{m_\text{e}}{M}}\right)$$

where

$$C = \frac{k^2e^4}{4\pi c\hbar^3} = 1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}$$

For tritium:

$$R_\text{T} = C\left(\frac{m_\text{e}}{1+\frac{m_\text{e}}{m_\text{p}+2m_\text{n}}}\right)$$

Evaluate the expression in parentheses to obtain:

$$m_r = 9.107738\times10^{-31}\ \text{kg}$$

Substitute numerical values and evaluate R_T:

$$\begin{aligned}R_\text{T} &= \left(1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}\right)\\ &\quad\times\left(9.107738\times10^{-31}\ \text{kg}\right)\\ &= \boxed{1.097175\times10^{7}\ \text{m}^{-1}}\end{aligned}$$

For deuterium:

$$R_\text{D} = C\left(\frac{m_\text{e}}{1+\frac{m_\text{e}}{2m_\text{p}}}\right)$$

Substitute numerical values and evaluate R_D:

$$R_D = \left(1.204662\times10^{37}\ \text{m}^{-1}/\text{kg}\right) \times \left(\frac{9.109390\times10^{-31}\ \text{kg}}{1+\dfrac{9.109390\times10^{-31}\ \text{kg}}{2\left(1.672623\times10^{-27}\ \text{kg}\right)}}\right) = 1.097075\times10^{7}\ \text{m}^{-1}$$

(*b*) Express the wavelength difference between the longest wavelength Balmer lines of hydrogen and deuterium:

$$\Delta\lambda = \lambda_{\text{longest, D}} - \lambda_{\text{longest, T}}$$

Use the Rydberg-Ritz formula to express the reciprocal wavelength:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

where n_1 and n_2 are integers and $n_1 > n_2$.

Solve for λ to obtain:

$$\lambda = \frac{n_1^2 n_2^2}{R\left(n_1^2 - n_2^2\right)}$$

The longest wavelength in the Balmer series corresponds to a transition from $n_1 = 3$ to $n_2 = 2$. Use $R = R_T$ to evaluate $\lambda_{\text{longest, T}}$:

$$\lambda_{\text{longest, T}} = \frac{3^2\left(2^2\right)}{\left(1.097175\times10^{7}\ \text{m}^{-1}\right)\left(3^2 - 2^2\right)} = 656.231\,\text{nm}$$

Find $\lambda_{\text{longest,D}}$ using $R = R_D$:

$$\lambda_{\text{longest, D}} = \frac{3^2\left(2^2\right)}{\left(1.097075\times10^{7}\ \text{m}^{-1}\right)\left(3^2 - 2^2\right)} = 656.291\,\text{nm}$$

Substitute to obtain:

$$\Delta\lambda = 656.291\,\text{nm} - 656.231\,\text{nm} = \boxed{0.0600\,\text{nm}}$$

Proceed similarly to show that for hydrogen and hydrogen:

$$\Delta\lambda = 656.4695\,\text{nm} - 656.2314\,\text{nm} = \boxed{0.238\,\text{nm}}$$