

CHAPTER 29

ANSWERS TO QUESTIONS

- Q29.1** Neon signs do not emit light in a continuous spectrum. There are many discrete wavelengths which correspond to transitions among the various energy levels of neon. This also accounts for the particular color of the light emitted from a neon sign. You can see the separate colors if you look at a section of the sign through a diffraction grating, or at its reflection in a compact disk. A spectroscope lets you read their wavelengths.
- Q29.2** No. An atom need only be in a high-energy state. When the atom falls to a lower energy state, a quantum of light is emitted.
- Q29.3** The term *electron clouds* refers to the probabilistic location of electrons about an atom. Electrons in an *s* subshell have a spherical probability distribution. Electrons in *p*, *d*, and *f* subshells have directionality to their distribution. It is shape of these electron clouds that determines how atoms form molecules and chemical compounds.
- Q29.4** If the exclusion principle were not valid, all electrons would descend to the *1s* energy state. There would be no chemical compounds or molecules or any chemical difference between elements. Such a universe, without life, would be extremely boring.
- Q29.5** Fundamentally, three quantum numbers describe an orbital wave function because we live in three-dimensional space. They arise mathematically from boundary conditions on the wave function, expressed as a product of a function of *r*, a function of θ , and a function of ϕ .
- Q29.6** The deflecting force on an atom with a magnetic moment is proportional to the *gradient* of the magnetic field. Thus, atoms with oppositely directed magnetic moments would be deflected in *opposite* directions in an inhomogeneous magnetic field.
- Q29.7** Practically speaking, no. Ions have a net charge and the magnetic force $q(\mathbf{v} \times \mathbf{B})$ would deflect the beam, making it difficult to separate the atoms with different orientations of magnetic moments.
- Q29.8** The Stern-Gerlach experiment with hydrogen atoms. Electron spin resonance on atoms with one unpaired electron.
- Q29.9** If the exclusion principle were not valid, the elements and their chemical behavior would be grossly different because every electron would end up in the lowest energy level of the atom. All matter would be nearly alike in its chemistry and composition, since the shell structures of all elements would be identical. Most materials would have a much higher density. The spectra of atoms and molecules would be very simple, and there would be very little color in the world.
- Q29.10** The three elements have similar electronic configurations. Each has filled inner shells plus one electron in an *s* orbital. Their single outer electrons largely determine their chemical interactions with other atoms.
- Q29.11** All these elements have a single valence electron in an *s* state. The outermost electron is relatively loosely bound, so the ionization energies of these metals are low compared to other atoms. Comparing these elements with one another, we may attribute the decrease in ionization energy with increasing atomic number to this: As atomic number increases atomic size increases slightly. As the outer electron is farther from the center of the positively charged cloud below it, it interacts less strongly and the ionization energy decreases.
- Q29.12** At low density, the gas consists of essentially separate atoms. As the density increases, the atoms interact with each other. This has the effect of giving different atoms levels at slightly different energies, at any one instant. The collection of atoms can then emit photons in lines or bands, narrower or wider, depending on the density.

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Q29.13 An atom is a quantum system described by a wave function. The electric force of attraction to the nucleus imposes a constraint on the electrons. The physical constraint implies mathematical boundary conditions on the wave functions, with consequent quantization so that only certain wave functions are allowed to exist. The Schrödinger equation assigns a definite energy to each allowed wave function. Each wave function is spread out in space, describing an electron with no definite position.

Q29.14 Each of the electrons must have at least one quantum number different from the quantum numbers of each of the other electrons. They can differ (in m_s) by being spin-up or spin-down. They can also differ (in ℓ) in angular momentum and in the general shape of the wave function (Look at the $2s$ and $2p$ graphs in Figure 29.7). Those electrons with $\ell = 1$ can differ (in m_ℓ) in orientation of angular momentum – look at Figure QQAns29.4.

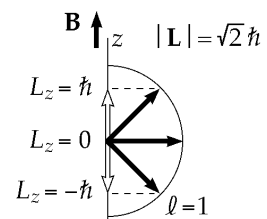


Fig. QQAns29.4

Q29.15 The Mosely graph shows that the reciprocal square root of the wavelength of K_α characteristic x-rays is a linear function of atomic number. Then measuring this wavelength for a new chemical element reveals its location on the graph, including its atomic number.

PROBLEM SOLUTIONS

- *29.1 (a) The point of closest approach is found when

$$E = K + U = 0 + \frac{k_e q_\alpha q_{\text{Au}}}{r}$$

or
$$r_{\min} = \frac{k_e (2e)(79e)}{E}$$

$$r_{\min} = \frac{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2 / \text{C}^2)(158)(1.60 \times 10^{-19} \text{ C})^2}{(4.00 \text{ MeV})(1.60 \times 10^{-13} \text{ J/MeV})} = \boxed{5.68 \times 10^{-14} \text{ m}}$$

- (b) The maximum force exerted on the alpha particle is

$$F_{\max} = \frac{k_e q_\alpha q_{\text{Au}}}{r_{\min}^2} = \frac{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2 / \text{C}^2)(158)(1.60 \times 10^{-19} \text{ C})^2}{(5.68 \times 10^{-14} \text{ m})^2} = \boxed{11.3 \text{ N}} \text{ away from the nucleus}$$

- 29.2 (a) Longest wavelength implies lowest frequency and smallest energy:

the atom falls from

$n = 3$

to

$n = 2$

losing energy

$$-\frac{13.6 \text{ eV}}{3^2} + \frac{13.6 \text{ eV}}{2^2} = \boxed{1.89 \text{ eV}}$$

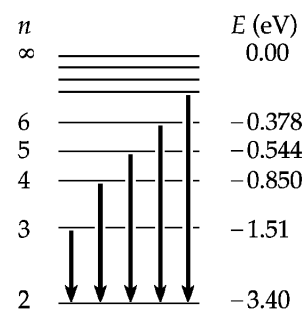
The photon frequency is

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

and its wavelength is

$$\lambda = \frac{c}{f} = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(1.89 \text{ eV})} \left(\frac{\text{eV}}{1.60 \times 10^{-19} \text{ J}} \right)$$

$$\lambda = \boxed{656 \text{ nm}}$$



Balmer Series

- (b) The biggest energy loss is for an atom to fall from an ionized configuration,

$n = \infty$

to the

$n = 2 \text{ state}$

It loses energy

$$-\frac{13.6 \text{ eV}}{\infty} + \frac{13.6 \text{ eV}}{2^2} = \boxed{3.40 \text{ eV}}$$

to emit light of wavelength

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(3.40 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} = \boxed{365 \text{ nm}}$$

29.3

The reduced mass of positronium is **less** than hydrogen, so the photon energy will be **less** for positronium than for hydrogen. This means that the wavelength of the emitted photon will be **longer** than 656.3 nm. On the other hand, helium has about the same reduced mass but more charge than hydrogen, so its transition energy will be **larger**, corresponding to a wavelength **shorter** than 656.3 nm.

All the factors in the given equation are constant for this problem except for the reduced mass and the nuclear charge. Therefore, the wavelength corresponding to the energy difference for the transition can be found simply from the ratio of mass and charge variables.

For hydrogen,
$$\mu = \frac{m_p m_e}{m_p + m_e} \approx m_e$$
 The photon energy is
$$\Delta E = E_3 - E_2$$

Its wavelength is
$$\lambda = 656.3 \text{ nm},$$
 where
$$\lambda = \frac{c}{f} = \frac{hc}{\Delta E}$$

(a) For positronium,
$$\mu = \frac{m_e m_e}{m_e + m_e} = \frac{m_e}{2}$$

so the energy of each level is one half as large as in hydrogen, which we could call "protonium". The photon energy is inversely proportional to its wavelength, so for positronium,

$$\lambda_{32} = 2(656.3 \text{ nm}) = \boxed{1.31 \mu\text{m}} \text{ (in the infrared region)}$$

(b) For He⁺,
$$\mu \approx m_e, \quad q_1 = e, \quad \text{and} \quad q_2 = 2e,$$

so the transition energy is $2^2 = 4$ times larger than hydrogen.

Then,
$$\lambda_{32} = \left(\frac{656}{4}\right) \text{ nm} = \boxed{164 \text{ nm}} \text{ (in the ultraviolet region)}$$

*29.4 (a) For a particular transition from n_i to n_f ,
$$\Delta E_H = -\frac{\mu_H k_e^2 e^4}{2\hbar^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{hc}{\lambda_H}$$

and
$$\Delta E_D = -\frac{\mu_D k_e^2 e^4}{2\hbar^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{hc}{\lambda_D}$$
 where
$$\mu_H = \frac{m_e m_p}{m_e + m_p}$$

and
$$\mu_D = \frac{m_e m_D}{m_e + m_D}$$
 By division,
$$\frac{\Delta E_H}{\Delta E_D} = \frac{\mu_H}{\mu_D} = \frac{\lambda_D}{\lambda_H}$$

or
$$\lambda_D = \left(\frac{\mu_H}{\mu_D} \right) \lambda_H$$
 Then,
$$\lambda_H - \lambda_D = \left(1 - \frac{\mu_H}{\mu_D} \right) \lambda_H$$

(b)
$$\frac{\mu_H}{\mu_D} = \left(\frac{m_e m_p}{m_e + m_p} \right) \left(\frac{m_e + m_D}{m_e m_D} \right) = \frac{(1.007276 \text{ u})(0.000549 \text{ u} + 2.013553 \text{ u})}{(0.000549 \text{ u} + 1.007276 \text{ u})(2.013553 \text{ u})} = 0.999728$$

$$\lambda_H - \lambda_D = (1 - 0.999728)(656.3 \text{ nm}) = \boxed{0.179 \text{ nm}}$$

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- 29.5 (a) The photon has energy 2.28 eV.

And $(13.6 \text{ eV}) / 2^2 = 3.40 \text{ eV}$ is required to ionize a hydrogen atom from state $n = 2$. So while the photon cannot ionize a hydrogen atom pre-excited to $n = 2$, it can ionize a hydrogen atom in the $n = \boxed{3}$ state, with energy

$$-\frac{13.6 \text{ eV}}{3^2} = -1.51 \text{ eV}$$

- (b) The electron thus freed can have kinetic energy $K_e = 2.28 \text{ eV} - 1.51 \text{ eV} = 0.769 \text{ eV} = \frac{1}{2} m_e v^2$

Therefore,

$$v = \sqrt{\frac{2(0.769)(1.60 \times 10^{-19}) \text{ J}}{9.11 \times 10^{-31} \text{ kg}}} = \boxed{520 \text{ km/s}}$$

- 29.6 (a) In the $3d$ subshell, $n = 3$ and $\ell = 2$,

| | | | | | | | | | | | |
|---------|----------|------|------|------|------|------|------|------|------|------|------|
| we have | n | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| | ℓ | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | m_ℓ | +2 | +2 | +1 | +1 | 0 | 0 | -1 | -1 | -2 | -2 |
| | m_s | +1/2 | -1/2 | +1/2 | -1/2 | +1/2 | -1/2 | +1/2 | -1/2 | +1/2 | -1/2 |

(A total of 10 states)

- (b) In the $3p$ subshell, $n = 3$ and $\ell = 1$,

| | | | | | | | |
|---------|----------|------|------|------|------|------|------|
| we have | n | 3 | 3 | 3 | 3 | 3 | 3 |
| | ℓ | 1 | 1 | 1 | 1 | 1 | 1 |
| | m_ℓ | +1 | +1 | +0 | +0 | -1 | -1 |
| | m_s | +1/2 | -1/2 | +1/2 | -1/2 | +1/2 | -1/2 |

(A total of 6 states)

*29.7 (a) $\int |\psi|^2 dV = 4\pi \int_0^\infty |\psi|^2 r^2 dr = 4\pi \left(\frac{1}{\pi a_0^3} \right) \int_0^\infty r^2 e^{-2r/a_0} dr$

Using integral tables, $\int |\psi|^2 dV = -\frac{2}{a_0^2} \left[e^{-2r/a_0} \left(r^2 + a_0 r + \frac{a_0^2}{2} \right) \right]_0^\infty = \left(-\frac{2}{a_0^2} \right) \left(-\frac{a_0^2}{2} \right) = \boxed{1}$

so the wave function as given is normalized.

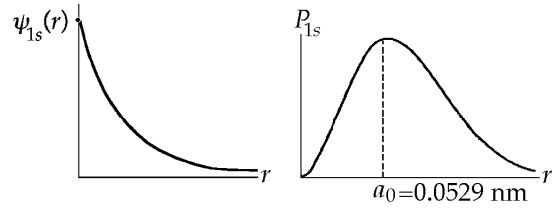
(b) $P_{a_0/2 \rightarrow 3a_0/2} = 4\pi \int_{a_0/2}^{3a_0/2} |\psi|^2 r^2 dr = 4\pi \left(\frac{1}{\pi a_0^3} \right) \int_{a_0/2}^{3a_0/2} r^2 e^{-2r/a_0} dr$

Again, using integral tables,

$$P_{a_0/2 \rightarrow 3a_0/2} = -\frac{2}{a_0^2} \left[e^{-2r/a_0} \left(r^2 + a_0 r + \frac{a_0^2}{2} \right) \right]_{a_0/2}^{3a_0/2} = -\frac{2}{a_0^2} \left[e^{-3} \left(\frac{17a_0^2}{4} \right) - e^{-1} \left(\frac{5a_0^2}{4} \right) \right] = \boxed{0.497}$$

29.8
$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (\text{Eq. 29.3})$$

$$P_{1s}(r) = \frac{4r^2}{a_0^3} e^{-2r/a_0} \quad (\text{Eq. 29.7})$$



29.9
$$\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\frac{d^2\psi}{dr^2} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} = \frac{1}{a_0^2} \psi$$

$$\frac{2}{r} \frac{d\psi}{dr} = \frac{-2}{r\sqrt{\pi a_0^3}} e^{-r/a_0} = \frac{2}{r a_0} \psi$$

$$-\frac{\hbar^2}{2m_e} \left(\frac{1}{a_0^2} - \frac{2}{r a_0} \right) \psi - \frac{e^2}{4\pi\epsilon_0 r} \psi = E \psi$$

But
$$a_0 = \frac{\hbar^2(4\pi\epsilon_0)}{m_e e^2}$$

so
$$-\frac{e^2}{8\pi\epsilon_0 a_0} = E$$

or
$$E = -\frac{k_e e^2}{2a_0}$$

This is true, so the Schrödinger equation is satisfied.

29.10
$$\psi = \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$

so
$$P_r = 4\pi r^2 |\psi|^2 = 4\pi r^2 \frac{r^2}{24 a_0^5} e^{-r/a_0}$$

Set
$$\frac{dP}{dr} = \frac{4\pi}{24 a_0^5} \left[4r^3 e^{-r/a_0} + r^4 \left(-\frac{1}{a_0} \right) e^{-r/a_0} \right] = 0$$

Solving for r , this is a maximum at
$$r = 4a_0$$
.

29.11 The hydrogen ground-state radial probability density is

$$P(r) = 4\pi r^2 |\psi_{1s}|^2 = \frac{4r^2}{a_0^3} \exp\left(-\frac{2r}{a_0}\right)$$

The number of observations at $2a_0$ is, by proportion

$$N = 1000 \frac{P(2a_0)}{P(a_0/2)} = 1000 \frac{(2a_0)^2}{(a_0/2)^2} \frac{e^{-4a_0/a_0}}{e^{-a_0/a_0}} = 1000(16)e^{-3} = \boxed{797 \text{ times}}$$

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29.12 (a) For the d state, $l = 2$, $L = \sqrt{6\hbar} = 2.58 \times 10^{-34} \text{ J}\cdot\text{s}$

(b) For the f state, $l = 3$, $L = \sqrt{12\hbar} = 3.65 \times 10^{-34} \text{ J}\cdot\text{s}$

29.13 $L = \sqrt{l(l+1)\hbar}$: $4.714 \times 10^{-34} = \sqrt{l(l+1)} \left(\frac{6.626 \times 10^{-34}}{2\pi} \right)$

$$l(l+1) = \frac{(4.714 \times 10^{-34})^2 (2\pi)^2}{(6.626 \times 10^{-34})^2} = 1.998 \times 10^1 \approx 20 = 4(4+1)$$

so $l = 4$

*29.14 In the N shell, $n = 4$. For $n = 4$, l can take on values of 0, 1, 2, and 3. For each value of l , m_l can be $-l$ to l in integral steps. Thus, the maximum value for m_l is 3. Since $L_z = m_l \hbar$, the maximum value for L_z is $L_z = 3\hbar$.

29.15 The 5th excited state has $n = 6$, energy $\frac{-13.6 \text{ eV}}{36} = -0.378 \text{ eV}$

The atom loses this much energy: $\frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(1090 \times 10^{-9} \text{ m})(1.60 \times 10^{-19} \text{ J/eV})} = 1.14 \text{ eV}$

to end up with energy $-0.378 \text{ eV} - 1.14 \text{ eV} = -1.52 \text{ eV}$

which is the energy in state 3: $-\frac{13.6 \text{ eV}}{3^2} = -1.51 \text{ eV}$

While $n = 3$, l can be as large as 2, giving angular momentum $\sqrt{l(l+1)\hbar} = \sqrt{6\hbar}$

29.16 For a $3d$ state, $n = 3$ and $l = 2$

Therefore, $L = \sqrt{l(l+1)\hbar} = \sqrt{6\hbar} = 2.58 \times 10^{-34} \text{ J}\cdot\text{s}$

m_l can have the values $-2, -1, 0, 1, \text{ and } 2$

so L_z can have the values $-2\hbar, -\hbar, 0, \hbar$ and $2\hbar$

Using the relation $\cos\theta = L_z / L$

we find the possible values of θ $145^\circ, 114^\circ, 90.0^\circ, 65.9^\circ, \text{ and } 35.3^\circ$

- 29.17 (a) $n = 1$: For $n = 1$, $\ell = 0$, $m_\ell = 0$, $m_s = \pm \frac{1}{2}$

| n | ℓ | m_ℓ | m_s |
|-----|--------|----------|--------|
| 1 | 0 | 0 | $-1/2$ |
| 1 | 0 | 0 | $+1/2$ |

Yields 2 sets; $2n^2 = 2(1)^2 = \boxed{2}$

- (b) $n = 2$: For $n = 2$,

we have

| n | ℓ | m_ℓ | m_s |
|-----|--------|----------|-----------|
| 2 | 0 | 0 | $\pm 1/2$ |
| 2 | 1 | -1 | $\pm 1/2$ |
| 2 | 1 | 0 | $\pm 1/2$ |
| 2 | 1 | 1 | $\pm 1/2$ |

yields 8 sets;

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

Note that the number is twice the number of m_ℓ values. Also, for each ℓ there are $(2\ell + 1)$ different m_ℓ values. Finally, ℓ can take on values ranging from 0 to $n - 1$.

So the general expression is

$$\text{number} = \sum_0^{n-1} 2(2\ell + 1)$$

The series is an arithmetic progression:

$$2 + 6 + 10 + 14 \dots$$

the sum of which is

$$\text{number} = \frac{n}{2} [2a + (n-1)d]$$

where

$$a = 2, d = 4:$$

$$\text{number} = \frac{n}{2} [4 + (n-1)4] = 2n^2$$

- (c) $n = 3$: $2(1) + 2(3) + 2(5) = 2 + 6 + 10 = 18$

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

- (d) $n = 4$: $2(1) + 2(3) + 2(5) + 2(7) = 32$

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

- (e) $n = 5$: $32 + 2(9) = 32 + 18 = 50$

$$2n^2 = 2(5)^2 = \boxed{50}$$

Chapter 29

- 29.18 (a) Density of a proton: $\rho = \frac{m}{V} = \frac{1.67 \times 10^{-27} \text{ kg}}{(4/3)\pi(1.00 \times 10^{-15} \text{ m})^3} = \boxed{3.99 \times 10^{17} \text{ kg/m}^3}$
- (b) Size of model electron: $r = \left(\frac{3m}{4\pi\rho}\right)^{1/3} = \left(\frac{3(9.11 \times 10^{-31} \text{ kg})}{4\pi(3.99 \times 10^{17} \text{ kg/m}^3)}\right)^{1/3} = \boxed{8.17 \times 10^{-17} \text{ m}}$
- (c) Moment of inertia: $I = \frac{2}{5}mr^2 = \frac{2}{5}(9.11 \times 10^{-31} \text{ kg})(8.17 \times 10^{-17} \text{ m})^2 = 2.43 \times 10^{-63} \text{ kg} \cdot \text{m}^2$
- $$L_z = I\omega = \frac{\hbar}{2} = \frac{Iv}{r}$$
- Therefore, $v = \frac{\hbar r}{2I} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(8.17 \times 10^{-17} \text{ m})}{2\pi(2 \times 2.43 \times 10^{-63} \text{ kg} \cdot \text{m}^2)} = \boxed{1.77 \times 10^{12} \text{ m/s}}$
- (d) This is $\boxed{5.91 \times 10^3}$ times larger than the speed of light.

*29.19 The 3d subshell has $\ell = 2$, and $n = 3$. Also, we have $s = 1$.

Therefore, we can have $n = 3, \ell = 2; m_\ell = -2, -1, 0, 1, 2; s = 1; \text{ and } m_s = -1, 0, 1$

leading to the following table:

| | | | | | | | | | | | | | | | |
|----------|----|----|----|----|----|----|----|---|---|----|---|---|----|---|---|
| n | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| ℓ | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| m_ℓ | -2 | -2 | -2 | -1 | -1 | -1 | 0 | 0 | 0 | 1 | 1 | 1 | 2 | 2 | 2 |
| s | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| m_s | -1 | 0 | 1 | -1 | 0 | 1 | -1 | 0 | 1 | -1 | 0 | 1 | -1 | 0 | 1 |

- 29.20 (a) $L = mvr = m \frac{2\pi r}{T} r = \sqrt{\ell(\ell+1)}\hbar = \sqrt{(\ell^2 + \ell)}\hbar \approx \ell\hbar$
- $$(5.98 \times 10^{24} \text{ kg}) \frac{2\pi(1.496 \times 10^{11} \text{ m})^2}{3.156 \times 10^7 \text{ s}} = \ell\hbar \quad \text{so} \quad \frac{2.66 \times 10^{40}}{1.055 \times 10^{-33} \text{ J} \cdot \text{s}} = \ell = \boxed{2.52 \times 10^{74}}$$

(b) $|E| = |-U + K| = |-K| = \frac{1}{2}mv^2 = \frac{1}{2} \frac{mr^2}{mr^2} mv^2 = \frac{1}{2} \frac{L^2}{mr^2} = \frac{1}{2} \frac{\ell(\ell+1)\hbar^2}{mr^2} \approx \frac{1}{2} \frac{\ell^2\hbar^2}{mr^2}$

$$\frac{dE}{d\ell} = \frac{1}{2} \frac{2\ell\hbar^2}{mr^2} \frac{\ell}{\ell} = 2 \frac{E}{\ell} \quad \text{so} \quad dE = 2 \frac{E}{\ell} d\ell = 2 \frac{\frac{1}{2}(5.98 \times 10^{24} \text{ kg}) \left(\frac{2\pi \times 1.496 \times 10^{11} \text{ m}}{3.156 \times 10^7 \text{ s}}\right)^2}{2.52 \times 10^{74}} d\ell \quad (1)$$

$$\Delta E = \frac{5.30 \times 10^{33} \text{ J}}{2.52 \times 10^{74}} = \boxed{2.10 \times 10^{-41} \text{ J}}$$

Chapter 29

29.21 (a) $1s^2 2s^2 2p^4$

- (b) For the 1s electrons, $n = 1, l = 0, m_l = 0, m_s = +1/2$ and $-1/2$
 For the two 2s electrons, $n = 2, l = 0, m_l = 0, m_s = +1/2$ and $-1/2$
 For the four 2p electrons, $n = 2; l = 1; m_l = -1, 0, \text{ or } 1; \text{ and } m_s = +1/2$ or $-1/2$

29.22

| | |
|-----------------------------------|------------------------------|
| Electronic configuration: | Sodium to Argon |
| $[1s^2 2s^2 2p^6] + 3s^1$ | $\rightarrow \text{Na}^{11}$ |
| $+ 3s^2$ | $\rightarrow \text{Mg}^{12}$ |
| $+ 3s^2 3p^1$ | $\rightarrow \text{Al}^{13}$ |
| $+ 3s^2 3p^2$ | $\rightarrow \text{Si}^{14}$ |
| $+ 3s^2 3p^3$ | $\rightarrow \text{P}^{15}$ |
| $+ 3s^2 3p^4$ | $\rightarrow \text{S}^{16}$ |
| $+ 3s^2 3p^5$ | $\rightarrow \text{Cl}^{17}$ |
| $+ 3s^2 3p^6$ | $\rightarrow \text{Ar}^{18}$ |
| $[1s^2 2s^2 2p^6 3s^2 3p^6] 4s^1$ | $\rightarrow \text{K}^{19}$ |

*29.23 The $4s$ subshell fills first, for potassium and calcium, before the $3d$ subshell starts to fill for scandium through zinc. Thus, we would first suppose that $[\text{Ar}]3d^4 4s^2$ would have lower energy than $[\text{Ar}]3d^5 4s^1$. But the latter has more unpaired spins, six instead of four, and Hund's rule suggests that this could give the latter configuration lower energy. In fact it must, for $[\text{Ar}]3d^5 4s^1$ is the ground state for chromium.

29.24 (a) For electron one and also for electron two, $n = 3$ and $l = 1$. The possible states are listed here in columns giving the other quantum numbers:

| | | | | | | | | | | | | | | | | |
|--------------|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| electron one | m_l | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | |
| | m_s | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ |
| electron two | m_l | 1 | 0 | 0 | -1 | -1 | 1 | 0 | 0 | -1 | -1 | 1 | 1 | 0 | -1 | -1 |
| | m_s | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ |
| electron one | m_l | 0 | 0 | 0 | 0 | 0 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 | -1 |
| | m_s | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ |
| electron two | m_l | 1 | 1 | 0 | -1 | -1 | 1 | 1 | 0 | 0 | -1 | 1 | 1 | 0 | 0 | -1 |
| | m_s | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ | $-\frac{1}{2}$ | $\frac{1}{2}$ |

There are thirty allowed states, since electron one can have any of three possible values for m_l for both spin up and spin down, amounting to six states, and the second electron can have any of the other five states.

- (b) Were it not for the exclusion principle, there would be 36 possible states, six for each electron independently.

Chapter 29

*29.25

| | | | | | | | | | | | | | | | | |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Shell | K | | L | | | | | M | | | | | N | | | |
| n | 1 | | 2 | | | | | 3 | | | | | 4 | | | |
| l | 0 | 0 | 1 | | | 0 | 1 | | 2 | | | 0 | | | | |
| m_l | 0 | 0 | 1 | 0 | -1 | 0 | 1 | 0 | -1 | 2 | 1 | 0 | -1 | -2 | 0 | |
| m_s | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ | |
| count | 1 | 2 | 3 | | | 4 | 10 | | 12 | 18 | | | 21 | 30 | | 20 |
| | He | | Be | | | Ne | | Mg | Ar | | | Zn | | Ca | | |

(a) zinc or copper

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ or $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

*29.26

In the table of electronic configurations in the text, or on a periodic table, we look for the element whose last electron is in a $3p$ state and which has three electrons outside a closed shell. Its electron configuration then ends in $3s^2 3p^1$. The element is aluminum.

29.27 (a)

| | | | | | | | |
|----------|----|----|--------|--------|------------|------------|----------------|
| $n + l$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| subshell | 1s | 2s | 2p, 3s | 3p, 4s | 3d, 4p, 5s | 4d, 5p, 6s | 4f, 5d, 6p, 7s |

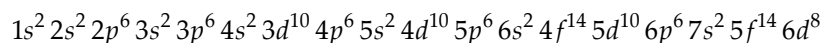
(b) $Z = 15$: Filled subshells: $1s, 2s, 2p, 3s$
 (12 electrons)
 Valence subshell: $3p$ subshell
 3 electrons in $3p$ subshell
 Prediction: Valence = +3 or -5
 Element is phosphorus, Valence = +3 or -5 (Prediction correct)

$Z = 47$: Filled subshells: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s$
 (38 electrons)
 Outer subshell: $4d$ subshell
 9 electrons in $4d$ subshell
 Prediction: Valence = -1
 Element is silver, (Prediction fails) Valence is +1

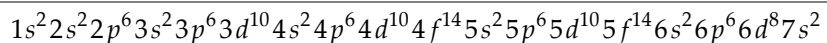
$Z = 86$: Filled subshells: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p$
 (86 electrons)
 Prediction: Outer subshell is full: inert gas
 Element is radon, inert (Prediction correct)

29.28

Listing subshells in the order of filling, we have for element 110,



In order of increasing principal quantum number, this is



Chapter 29

- *29.29** In the ground state of sodium, the outermost electron is in an s state. This state is spherically symmetric, so it generates no magnetic field by orbital motion, and has the same energy no matter whether the electron is spin-up or spin-down. The energies of the states $3p \uparrow$ and $3p \downarrow$ above $3s$ are $hf_1 = hc/\lambda_1$ and hc/λ_2 .

The energy difference is

$$2\mu_B B = hc \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

so
$$B = \frac{hc}{2\mu_B} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right) = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})}{2(9.27 \times 10^{-24} \text{ J/T})} \left(\frac{1}{588.995 \times 10^{-9} \text{ m}} - \frac{1}{589.592 \times 10^{-9} \text{ m}} \right)$$

$$B = \boxed{18.4 \text{ T}}$$

29.30 (a) $n = 3, \ell = 0, m_\ell = 0$

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

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

(b) ψ_{300} corresponds to $E_{300} = -\frac{Z^2 E_0}{n^2} = -\frac{2^2(13.6)}{3^2} = \boxed{-6.05 \text{ eV}}$

$\psi_{31-1}, \psi_{310}, \psi_{311}$ have the same energy since n is the same.

$\psi_{32-2}, \psi_{32-1}, \psi_{320}, \psi_{321}, \psi_{322}$ have the same energy since n is the same.

All states are degenerate.

29.31 $E = \frac{hc}{\lambda} = e\Delta V: \quad \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(10.0 \times 10^{-9} \text{ m})} = (1.60 \times 10^{-19})\Delta V$

$$\Delta V = \boxed{124 \text{ V}}$$

- *29.32** Some electrons can give all their kinetic energy $K_e = e\Delta V$ to the creation of a single photon of x-radiation, with

$$hf = \frac{hc}{\lambda} = e\Delta V$$

$$\lambda = \frac{hc}{e\Delta V} = \frac{(6.6261 \times 10^{-34} \text{ J}\cdot\text{s})(2.9979 \times 10^8 \text{ m/s})}{(1.6022 \times 10^{-19} \text{ C})\Delta V} = \boxed{\frac{1240 \text{ nm}\cdot\text{V}}{\Delta V}}$$

Chapter 29

29.33 Following Example 29.8 $E_\gamma = \frac{3}{4}(42-1)^2(13.6 \text{ eV}) = 1.71 \times 10^4 \text{ eV} = 2.74 \times 10^{-15} \text{ J}$

$$f = 4.14 \times 10^{18} \text{ Hz}$$

and

$$\lambda = \boxed{0.0725 \text{ nm}}$$

29.34 The K_β x-rays are emitted when there is a vacancy in the ($n = 1$) K shell and an electron from the ($n = 3$) M shell falls down to fill it. Then this electron is shielded by nine electrons originally and by one in its final state.

$$\frac{hc}{\lambda} = -\frac{13.6(Z-9)^2}{3^2} \text{ eV} + \frac{13.6(Z-1)^2}{1^2} \text{ eV}$$

$$\frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(0.152 \times 10^{-9} \text{ m})(1.60 \times 10^{-19} \text{ J/eV})} = (13.6 \text{ eV}) \left(-\frac{Z^2}{9} + \frac{18Z}{9} - \frac{81}{9} + Z^2 - 2Z + 1 \right)$$

$$8.17 \times 10^3 \text{ eV} = (13.6 \text{ eV}) \left(\frac{8Z^2}{9} - 8 \right)$$

so $601 = \frac{8Z^2}{9} - 8$

and $Z = 26$

Iron

***29.35 (a)** Suppose the electron in the M shell is shielded from the nucleus by two K plus seven L electrons. Then its energy is

$$\frac{(-13.6 \text{ eV})(83-9)^2}{3^2} = -8.27 \text{ keV}$$

Suppose, after it has fallen into the vacancy in the L shell, it is shielded by just two K-shell electrons. Then its energy is

$$\frac{(-13.6 \text{ eV})(83-2)^2}{2^2} = -22.3 \text{ keV}$$

Thus the electron's energy loss is the photon energy: $(22.3 - 8.27) \text{ keV} = \boxed{14.0 \text{ keV}}$

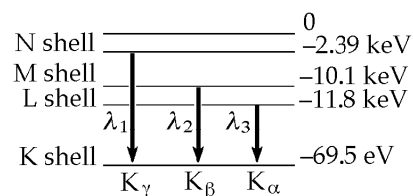
(b) $\Delta E = \frac{hc}{\lambda}$

so $\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(14.0 \times 10^3)(1.60 \times 10^{-19} \text{ J})} = \boxed{8.85 \times 10^{-11} \text{ m}}$

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29.36 $E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} = \frac{1.240 \text{ keV} \cdot \text{nm}}{\lambda}$

For $\lambda_1 = 0.0185 \text{ nm}, E = 67.11 \text{ keV}$
 $\lambda_2 = 0.0209 \text{ nm}, E = 59.4 \text{ keV}$
 $\lambda_3 = 0.0215 \text{ nm}, E = 57.7 \text{ keV}$



The ionization energy for the K shell is 69.5 keV, so the ionization energies for the other shells are:

L shell = 11.8 keV

M shell = 10.1 keV

N shell = 2.39 keV

29.37 (a) The configuration we may model as SN NS has higher energy than SN SN. The higher energy state has antiparallel magnetic moments, so it has parallel spins of the oppositely charged particles.

(b) $E = \frac{hc}{\lambda} = 9.42 \times 10^{-25} \text{ J} = \text{span style="border: 1px solid black; padding: 2px;">} 5.89 \mu\text{eV}$

(c) $\Delta E \Delta t \approx \frac{\hbar}{2}$ so $\Delta E \approx \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}{2(10^7 \text{ yr})(3.16 \times 10^7 \text{ s/yr})} \left(\frac{1.00 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} \right) = \text{span style="border: 1px solid black; padding: 2px;">} 1.04 \times 10^{-30} \text{ eV}$

***29.38** Section 24.3 says $f_{\text{observer}} = f_{\text{source}} \sqrt{\frac{1+v_a/c}{1-v_a/c}}$

The velocity of approach, v_a , is the negative of the velocity of mutual recession: $v_a = -v$.

Then, $\frac{c}{\lambda'} = \frac{c}{\lambda} \sqrt{\frac{1-v/c}{1+v/c}}$ and $\lambda' = \lambda \sqrt{\frac{1+v/c}{1-v/c}}$

29.39 (a) $\lambda' = \lambda \sqrt{\frac{1+v/c}{1-v/c}}$ $510 \text{ nm} = 434 \text{ nm} \sqrt{\frac{1+v/c}{1-v/c}}$

$$1.18^2 = \frac{1+v/c}{1-v/c} = 1.381$$

$$1 + \frac{v}{c} = 1.381 - 1.381 \frac{v}{c} \qquad 2.38 \frac{v}{c} = 0.381$$

$$\frac{v}{c} = 0.160 \qquad \text{or} \qquad v = \text{span style="border: 1px solid black; padding: 2px;">} 0.160c = 4.80 \times 10^7 \text{ m/s}$$

(b) $v = HR$: $R = \frac{v}{H} = \frac{4.80 \times 10^7 \text{ m/s}}{17 \times 10^{-3} \text{ m/s} \cdot \text{ly}} = \text{span style="border: 1px solid black; padding: 2px;">} 2.82 \times 10^9 \text{ ly}$

Chapter 29

- 29.40 (a) The energy difference between these two states is equal to the energy that is absorbed.

Thus,
$$E = E_2 - E_1 = \frac{(-13.6 \text{ eV})}{4} - \frac{(-13.6 \text{ eV})}{1} = 10.2 \text{ eV} = \boxed{1.63 \times 10^{-18} \text{ J}}$$

(b) $E = \frac{3}{2} k_B T$ or
$$T = \frac{2E}{3k_B} = \frac{2(1.63 \times 10^{-18} \text{ J})}{3(1.38 \times 10^{-23} \text{ J/K})} = \boxed{7.88 \times 10^4 \text{ K}}$$

29.41
$$r_{av} = \int_0^\infty rP(r)dr = \int_0^\infty \left(\frac{4r^3}{a_0^3}\right)(e^{-2r/a_0})dr$$

Make a change of variables with $\frac{2r}{a_0} = x$ and $dr = \frac{a_0}{2} dx$

Then
$$r_{av} = \frac{a_0}{4} \int_0^\infty x^3 e^{-x} dx = \frac{a_0}{4} \left[-x^3 e^{-x} + 3(-x^2 e^{-x} + 2e^{-x}(-x-1)) \right]_0^\infty = \boxed{\frac{3}{2} a_0}$$

- *29.42 The fermions are described by the exclusion principle. Two of them, one spin-up and one spin-down, will be in the ground energy level, with

$$d_{NN} = L = \frac{1}{2} \lambda, \quad \lambda = 2L = \frac{h}{p}, \quad \text{and} \quad p = \frac{h}{2L} \quad K = \frac{1}{2} mv^2 = \frac{p^2}{2m} = \frac{h^2}{8mL^2}$$

The third must be in the next higher level, with

$$d_{NN} = \frac{L}{2} = \frac{\lambda}{2}, \quad \lambda = L, \quad \text{and} \quad p = \frac{h}{L} \quad K = \frac{p^2}{2m} = \frac{h^2}{2mL^2}$$

The total energy is then

$$\frac{h^2}{8mL^2} + \frac{h^2}{8mL^2} + \frac{h^2}{2mL^2} = \boxed{\frac{3h^2}{4mL^2}}$$

- *29.43 The wave function for the 2s state is given by Eq. 29.8: $\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$

(a) Taking $r = a_0 = 0.529 \times 10^{-10} \text{ m}$

we find
$$\psi_{2s}(a_0) = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{0.529 \times 10^{-10} \text{ m}}\right)^{3/2} [2-1]e^{-1/2} = \boxed{1.57 \times 10^{14} \text{ m}^{-3/2}}$$

(b) $|\psi_{2s}(a_0)|^2 = (1.57 \times 10^{14} \text{ m}^{-3/2})^2 = \boxed{2.47 \times 10^{28} \text{ m}^{-3}}$

(c) Using Equation 29.5 and the results to (b) gives
$$P_{2s}(a_0) = 4\pi a_0^2 |\psi_{2s}(a_0)|^2 = \boxed{8.69 \times 10^8 \text{ m}^{-1}}$$

Chapter 29

***29.44** From Figure 29.12, a typical ionization energy is 8 eV. For internal energy to ionize most of the atoms we require

$$\frac{3}{2}k_B T = 8 \text{ eV}: \quad T = \frac{2 \times 8 (1.60 \times 10^{-19} \text{ J})}{3 (1.38 \times 10^{-23} \text{ J/K})} \quad \boxed{\sim \text{between } 10^4 \text{ K and } 10^5 \text{ K}}$$

29.45

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

By Equation 29.6, $P(r) = 4\pi r^2 \psi^2 = \frac{1}{8} \left(\frac{r^2}{a_0^3} \right) \left(2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}$

$$(a) \quad \frac{dP(r)}{dr} = \frac{1}{8} \left[\frac{2r}{a_0^3} \left(2 - \frac{r}{a_0} \right)^2 - \frac{2r^2}{a_0^3} \left(\frac{1}{a_0} \right) \left(2 - \frac{r}{a_0} \right) - \frac{r^2}{a_0^3} \left(2 - \frac{r}{a_0} \right)^2 \left(\frac{1}{a_0} \right) \right] e^{-r/a_0} = 0$$

$$\text{or} \quad \frac{1}{8} \left(\frac{r}{a_0^3} \right) \left(2 - \frac{r}{a_0} \right) \left[2 \left(2 - \frac{r}{a_0} \right) - \frac{2r}{a_0} - \frac{r}{a_0} \left(2 - \frac{r}{a_0} \right) \right] e^{-r/a_0} = 0$$

The roots of $\frac{dP}{dr} = 0$ at $r = 0$, $r = 2a_0$ and $r = \infty$ are minima with $P(r) = 0$

Therefore we require $[\dots] = 4 - (6r/a_0) + (r/a_0)^2 = 0$

with solutions $r = (3 \pm \sqrt{5})a_0$

We substitute the last two roots into $P(r)$ to determine the most probable value:

When $r = (3 - \sqrt{5})a_0 = 0.7639a_0$, $P(r) = 0.0519/a_0$

When $r = (3 + \sqrt{5})a_0 = 5.236a_0$, $P(r) = 0.191/a_0$

Therefore, the most probable value of r is $(3 + \sqrt{5})a_0 = \boxed{5.236a_0}$

$$(b) \quad \int_0^\infty P(r) dr = \int_0^\infty \frac{1}{8} \left(\frac{r^2}{a_0^3} \right) \left(2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} dr$$

Let $u = \frac{r}{a_0}$, $dr = a_0 du$,

$$\int_0^\infty P(r) dr = \int_0^\infty \frac{1}{8} u^2 (4 - 4u + u^2) e^{-u} dr = \int_0^\infty \frac{1}{8} (u^4 - 4u^3 + 4u^2) e^{-u} du = -\frac{1}{8} (u^4 + 4u^2 + 8u + 8) e^{-u} \Big|_0^\infty = 1$$

This is as desired.

$$29.46 \quad \Delta z = \frac{at^2}{2} = \frac{1}{2} \left(\frac{F_z}{m_0} \right) t^2 = \frac{\mu_z (dB_z/dz) \left(\frac{\Delta x}{v} \right)^2}{2m_0} \quad \text{and} \quad \mu_z = \frac{e\hbar}{2m_e}$$

$$\frac{dB_z}{dz} = \frac{2m_0(\Delta z)v^2(2m_e)}{\Delta x^2 e\hbar} = \frac{2(108)(1.66 \times 10^{-27} \text{ kg})(10^{-3} \text{ m})(10^4 \text{ m}^2/\text{s}^2)(2 \times 9.11 \times 10^{-31} \text{ kg})}{(1.00 \text{ m}^2)(1.60 \times 10^{-19} \text{ C})(1.05 \times 10^{-34} \text{ J} \cdot \text{s})}$$

$$\frac{dB_z}{dz} = \boxed{0.389 \text{ T/m}}$$

29.47 With one vacancy in the K shell, excess energy

$$\Delta E \approx -(Z-1)^2(13.6 \text{ eV}) \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = 5.40 \text{ keV}$$

We suppose the outermost 4s electron is shielded by 22 electrons inside its orbit:

$$E_{\text{ionization}} \approx \frac{2^2(13.6 \text{ eV})}{4^2} = 3.40 \text{ eV}$$

Note the experimental ionization energy is 6.76 eV.

$$K = \Delta E - E_{\text{ionization}} \approx \boxed{5.39 \text{ keV}}$$

$$29.48 \quad E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} = \Delta E$$

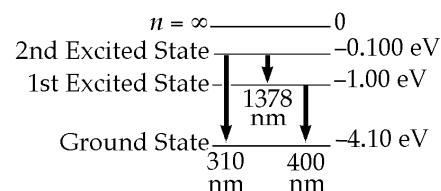
$$\lambda_1 = 310 \text{ nm}, \quad \text{so} \quad \Delta E_1 = 4.00 \text{ eV}$$

$$\lambda_2 = 400 \text{ nm}, \quad \Delta E_2 = 3.10 \text{ eV}$$

$$\lambda_3 = 1378 \text{ nm}, \quad \Delta E_3 = 0.900 \text{ eV}$$

and the ionization energy = 4.10 eV

The energy level diagram having the fewest levels and consistent with these energies is shown at the right.



29.49 (a) One molecule's share of volume

$$\text{Al: } V = \frac{\text{mass per molecule}}{\text{density}} = \left(\frac{27.0 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} \right) \left(\frac{1.00 \times 10^{-6} \text{ m}^3}{2.70 \text{ g}} \right) = 1.66 \times 10^{-29} \text{ m}^3$$

$$\sqrt[3]{V} = \boxed{2.55 \times 10^{-10} \text{ m} \sim 10^{-1} \text{ nm}}$$

$$\text{U: } V = \left(\frac{238 \text{ g}}{6.02 \times 10^{23} \text{ molecules}} \right) \left(\frac{1.00 \times 10^{-6} \text{ m}^3}{18.9 \text{ g}} \right) = 2.09 \times 10^{-29} \text{ m}^3$$

$$\sqrt[3]{V} = \boxed{2.76 \times 10^{-10} \text{ m} \sim 10^{-1} \text{ nm}}$$

(b) The outermost electron in any atom sees the nuclear charge screened by all the electrons below it. If we can visualize a single outermost electron, it moves in the electric field of net charge, $+Ze - (Z-1)e = +e$, the charge of a single proton, as felt by the electron in hydrogen. So the Bohr radius sets the scale for the outside diameter of every atom. An innermost electron, on the other hand, sees the nuclear charge unscreened, and the scale size of its (K-shell) orbit is a_0/Z .

$$29.50 \quad P = \int_{2.50a_0}^{\infty} \frac{4r^2}{a_0^3} e^{-2r/a_0} dr = \frac{1}{2} \int_{5.00}^{\infty} z^2 e^{-z} dz \quad \text{where } z \equiv \frac{2r}{a_0}$$

$$P = -\frac{1}{2}(z^2 + 2z + 2)e^{-z} \Big|_{5.00}^{\infty} = -\frac{1}{2}[0] + \frac{1}{2}(25.0 + 10.0 + 2.00)e^{-5} = \left(\frac{37}{2}\right)(0.00674) = \boxed{0.125}$$

29.51 (a) For a classical atom, the centripetal acceleration is

$$a = \frac{v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2 m_e}$$

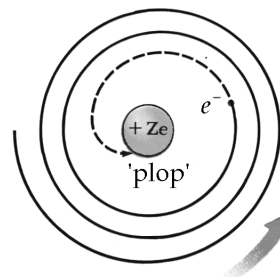
$$E = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{m_e v^2}{2} = -\frac{e^2}{8\pi\epsilon_0 r}$$

$$\text{so} \quad \frac{dE}{dt} = \frac{e^2}{8\pi\epsilon_0 r^2} \frac{dr}{dt} = \frac{-1}{6\pi\epsilon_0} \frac{e^2 a^2}{c^3} = \frac{-e^2}{6\pi\epsilon_0 c^3} \left(\frac{e^2}{4\pi\epsilon_0 r^2 m_e} \right)^2$$

$$\text{Therefore,} \quad \frac{dr}{dt} = -\frac{e^4}{12\pi^2 \epsilon_0^2 r^2 m_e^2 c^3}$$

$$(b) \quad -\int_{2.00 \times 10^{-10} \text{ m}}^0 12\pi^2 \epsilon_0^2 r^2 m_e^2 c^3 dr = e^4 \int_0^T dt$$

$$\frac{12\pi^2 \epsilon_0^2 m_e^2 c^3}{e^4} r^3 \Big|_0^{2.00 \times 10^{-10}} = T = \boxed{8.46 \times 10^{-10} \text{ s}}$$



Since atoms last a lot longer than 0.8 ns, the classical laws (fortunately!) do not hold for systems of atomic size.

Chapter 29

*29.52 $\Delta E = 2\mu_B B = hf$

so $2(9.27 \times 10^{-24} \text{ J/T})(0.350 \text{ T}) = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})f$

and $f = \boxed{9.79 \times 10^9 \text{ Hz}}$

29.53 $\psi = \frac{1}{4}(2\pi)^{-1/2} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} = A \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$

$$\frac{\partial^2 \psi}{\partial r^2} = \left(\frac{A e^{-r/2a_0}}{a_0^2}\right) \left(\frac{3}{2} - \frac{r}{4a_0}\right)$$

Substituting into Schrödinger's equation and dividing by ψ ,

$$\frac{1}{a_0^2} \left(\frac{1}{2} - \frac{r}{4a_0}\right) = -\frac{2m}{\hbar^2} [E - U] \left(2 - \frac{r}{a_0}\right)$$

Now $E - U = \left(\frac{1}{4}\right) \frac{\hbar^2}{2ma_0^2} - \frac{(ke^2/4a_0)(m/\hbar^2)}{(m/\hbar^2)} = -\frac{1}{4} \left(\frac{\hbar^2}{2ma_0^2}\right)$

and $\left(\frac{1}{a_0^2}\right) \left(\frac{1}{2} - \frac{r}{4a_0}\right) = \frac{1}{4a_0^2} \left(2 - \frac{r}{a_0}\right)$

$\therefore \psi$ is a solution.

- *29.54 (a) Suppose the atoms move in the $+x$ direction. The absorption of a photon by an atom is a completely inelastic collision, described by

$$mv_i \mathbf{i} + \frac{h}{\lambda} (-\mathbf{i}) = mv_f \mathbf{i} \quad \text{so} \quad v_f - v_i = -\frac{h}{m\lambda}$$

This happens promptly every time an atom has fallen back into the ground state, so it happens every $10^{-8} \text{ s} = \Delta t$. Then,

$$a = \frac{v_f - v_i}{\Delta t} = -\frac{h}{m\lambda\Delta t} \sim -\frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{(10^{-25} \text{ kg})(500 \times 10^{-9} \text{ m})(10^{-8} \text{ s})} \sim \boxed{-10^6 \text{ m/s}^2}$$

- (b) With constant average acceleration,

$$v_f^2 = v_i^2 + 2a\Delta x \quad 0 \sim (10^3 \text{ m/s})^2 + 2(-10^6 \text{ m/s}^2)\Delta x$$

so $\Delta x \sim \frac{(10^3 \text{ m/s})^2}{10^6 \text{ m/s}^2} \boxed{\sim 1 \text{ m}}$

$$29.55 \quad hf = \Delta E = \frac{4\pi^2 m k_e^2 e^4}{2h^2} \left(\frac{1}{(n-1)^2} - \frac{1}{n^2} \right)$$

$$f = \frac{2\pi^2 m k_e^2 e^4}{h^3} \left(\frac{2n-1}{(n-1)^2 n^2} \right)$$

29.56 As n approaches infinity, we have f approaching

$$\frac{2\pi^2 m k_e^2 e^4}{h^3} \frac{2}{n^3}$$

The classical frequency is

$$f = \frac{v}{2\pi r} = \frac{1}{2\pi} \sqrt{\frac{k_e e^2}{m}} \frac{1}{r^{3/2}}$$

where

$$r = \frac{n^2 h^2}{4\pi m k_e e^2}$$

Using this equation to eliminate r from the expression for f ,

$$f = \frac{2\pi^2 m k_e^2 e^4}{h^3} \frac{2}{n^3}$$

$$*29.57 \quad (a) \quad \Delta E = \frac{e\hbar B}{m_e} = \frac{1.60 \times 10^{-19} \text{ C} (6.63 \times 10^{-34} \text{ J}\cdot\text{s}) (5.26 \text{ T})}{2\pi (9.11 \times 10^{-31} \text{ kg})} \left(\frac{\text{N}\cdot\text{s}}{\text{T}\cdot\text{C}\cdot\text{m}} \right) \left(\frac{\text{kg}\cdot\text{m}}{\text{N}\cdot\text{s}^2} \right) = 9.75 \times 10^{-23} \text{ J} = \boxed{609 \mu\text{eV}}$$

$$(b) \quad k_B T = (1.38 \times 10^{-23} \text{ J/K}) (80 \times 10^{-3} \text{ K}) = 1.10 \times 10^{-24} \text{ J} = \boxed{6.90 \mu\text{eV}}$$

$$(c) \quad f = \frac{\Delta E}{h} = \frac{9.75 \times 10^{-23} \text{ J}}{6.63 \times 10^{-34} \text{ J}\cdot\text{s}} = \boxed{1.47 \times 10^{11} \text{ Hz}}$$

$$\lambda = \frac{c}{f} = \frac{3 \times 10^8 \text{ m/s}}{1.47 \times 10^{11} \text{ Hz}} = \boxed{2.04 \times 10^{-3} \text{ m}}$$

ANSWERS TO EVEN NUMBERED PROBLEMS

2. (a) 1.89 eV, 656 nm (b) 3.40 eV, 365 nm

4. (a) See the solution (b) 0.179 nm

| (a) | n | ℓ | m_ℓ | m_s |
|-----|-----|--------|----------|-------|
| | 3 | 2 | 2 | 1/2 |
| | 3 | 2 | 2 | -1/2 |
| | 3 | 2 | 1 | 1/2 |
| | 3 | 2 | 1 | -1/2 |
| | 3 | 2 | 0 | 1/2 |
| | 3 | 2 | 0 | -1/2 |
| | 3 | 2 | -1 | 1/2 |
| | 3 | 2 | -1 | -1/2 |
| | 3 | 2 | -2 | 1/2 |
| | 3 | 2 | -2 | -1/2 |

| (b) | n | ℓ | m_ℓ | m_s |
|-----|-----|--------|----------|-------|
| | 3 | 1 | 1 | 1/2 |
| | 3 | 1 | 1 | -1/2 |
| | 3 | 1 | 0 | 1/2 |
| | 3 | 1 | 0 | -1/2 |
| | 3 | 1 | -1 | 1/2 |
| | 3 | 1 | -1 | -1/2 |

8. See the solution

10. $4a_0$

12. (a) $\sqrt{6}\hbar$ (b) $\sqrt{12}\hbar$

14. $3\hbar$

16. $L = \sqrt{6}\hbar$; $L_z = -2\hbar, -\hbar, 0, \hbar, 2\hbar$; $\theta = 145^\circ, 114^\circ, 90.0^\circ, 65.9^\circ, \text{ and } 35.3^\circ$

18. (a) $3.99 \times 10^{17} \text{ kg/m}^3$ (b) 81.7 am
(c) 1.77 Tm/s (d) $5.91 \times 10^3 c$

20. (a) 2.52×10^{74} (b) $2.10 \times 10^{-41} \text{ J}$

22. See the solution

24. (a) See the solution (b) 36

26. Aluminum

28. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 6d^8 7s^2$

Chapter 29

30. (a) $\ell = 0$ and $m_\ell = 0$; or $\ell = 1$ and $m_\ell = -1, 0, \text{ or } 1$; or $\ell = 2$ and $m_\ell = -2, -1, 0, 1, \text{ or } 2$
 (b) -6.05 eV

32. See the solution

34. Iron

36. L shell = 11.8 keV; M shell = 10.1 keV; N shell = 2.39 keV; see the solution

38. See the solution

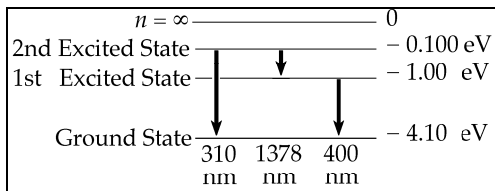
40. (a) $1.63 \times 10^{-18} \text{ J}$ (b) $7.88 \times 10^4 \text{ K}$

42. $3h^2 / 4mL^2$

44. between 10^4 K and 10^5 K

46. 0.389 T/m

48.



50. 0.125

52. 9.79 GHz

54. (a) $\sim -10^6 \text{ m/s}^2$ (b) $\sim 1 \text{ m}$

56. $4\pi^2 m_e k_e^2 e^4 / h^3 n^3$; see the solution