

Homework # 1

11.3 Calculate the energies for the Bohr orbits with $n = 2$ and 3 for atomic hydrogen.

The energy for a Bohr orbit is

$$E_n = -\frac{m_e e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2}$$

The collection of constants on the right side of the equation may be expressed in terms of the Rydberg constant:

$$\begin{aligned} R_H &= \frac{m_e e^4}{8ch^3 \epsilon_0^2} \\ \frac{m_e e^4}{8h^2 \epsilon_0^2} &= R_H ch \\ &= (109737.31534 \text{ cm}^{-1}) (2.99792458 \times 10^{10} \text{ cm s}^{-1}) (6.626075 \times 10^{-34} \text{ J s}) \\ &= 2.1798739 \times 10^{-18} \text{ J} \end{aligned}$$

Therefore,

$$E_n = -\left(2.1798739 \times 10^{-18} \text{ J}\right) \frac{1}{n^2}$$

For the Bohr orbits with $n = 2$ and 3,

$$E_2 = -\left(2.1798739 \times 10^{-18} \text{ J}\right) \frac{1}{4} = -5.449685 \times 10^{-19} \text{ J}$$

$$E_3 = -\left(2.1798739 \times 10^{-18} \text{ J}\right) \frac{1}{9} = -2.422082 \times 10^{-19} \text{ J}$$

11.5 What are the wavelengths associated with (a) an electron moving at $1.50 \times 10^6 \text{ cm s}^{-1}$, and (b) a 60-g tennis ball moving at 1500 cm s^{-1} ?

The wavelengths can be calculated using

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

$$(a) \quad \lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.109 \times 10^{-31} \text{ kg}) (1.50 \times 10^6 \text{ m s}^{-1})} = 4.85 \times 10^{-10} \text{ m} = 4.85 \text{ \AA}$$

$$(b) \quad \lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(60 \times 10^{-3} \text{ kg}) (1500 \times 10^{-2} \text{ m s}^{-1})} = 7.36 \times 10^{-34} \text{ m}$$

The wavelength of the tennis ball is too small to be of practical significance, whereas the wavelength of the electron is too large to be ignored.

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- 11.15** An electron in an excited state in a hydrogen atom can return to the ground state in two different ways: first, via a direct transition in which a photon of wavelength λ_1 is emitted and second, via an intermediate excited state reached by the emission of a photon of wavelength λ_2 . This intermediate excited state then decays to the ground state by emitting another photon of wavelength λ_3 . Derive an equation that relates λ_1 to λ_2 and λ_3 .
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The energy of the photon of wavelength λ_1 , E_1 , equals the sum of the energy of the photon of wavelength λ_2 , E_2 , and the energy of the photon of wavelength λ_3 , E_3 . That is,

$$\begin{aligned} E_1 &= E_2 + E_3 \\ \frac{hc}{\lambda_1} &= \frac{hc}{\lambda_2} + \frac{hc}{\lambda_3} \\ \frac{1}{\lambda_1} &= \frac{1}{\lambda_2} + \frac{1}{\lambda_3} \end{aligned}$$

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- 11.19** Scientists have found interstellar hydrogen atoms with quantum number n in the hundreds. Calculate the wavelength of light emitted when a hydrogen atom undergoes a transition from $n = 236$ to $n = 235$. In what region of the electromagnetic spectrum does this wavelength fall?
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The wavenumber of the emitted radiation is

$$\begin{aligned} \tilde{\nu} &= (109737 \text{ cm}^{-1}) \left| \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \right| \\ &= (109737 \text{ cm}^{-1}) \left| \left(\frac{1}{236^2} - \frac{1}{235^2} \right) \right| = 1.680406 \times 10^{-2} \text{ cm}^{-1} \end{aligned}$$

Therefore, the wavelength of this radiation is

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{1.680406 \times 10^{-2} \text{ cm}^{-1}} = 59.5094 \text{ cm}$$

This wavelength is in the radio frequency region.

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- 11.25** What is the probability of locating a particle in a one-dimensional box between $L/4$ and $3L/4$, where L is the length of the box? Assume the particle to be in the lowest level.
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The probability is

$$\begin{aligned}
 P &= \int_{L/4}^{3L/4} \psi^2 dx \\
 &= \int_{L/4}^{3L/4} \left(\frac{2}{L}\right) \sin^2 \frac{\pi}{L} x dx \\
 &= \frac{2}{L} \left(\frac{x}{2} - \frac{\sin \frac{2\pi x}{L}}{\frac{4\pi}{L}} \right)_{L/4}^{3L/4} \\
 &= \frac{2}{L} \left[\left(\frac{3L}{8} - \frac{\sin \frac{3\pi}{2}}{\frac{4\pi}{L}} \right) - \left(\frac{L}{8} - \frac{\sin \frac{\pi}{2}}{\frac{4\pi}{L}} \right) \right] \\
 &= \frac{2}{L} \left[\left(\frac{3L}{8} + \frac{L}{4\pi} \right) - \left(\frac{L}{8} - \frac{L}{4\pi} \right) \right] \\
 &= \frac{2}{L} \left(\frac{L}{4} + \frac{L}{2\pi} \right) \\
 &= \frac{1}{2} + \frac{1}{\pi} \\
 &= 0.82
 \end{aligned}$$

11.27 An important property of the wave functions of the particle in a one-dimensional box is that they are orthogonal; that is,

$$\int_0^L \psi_n \psi_m dx = 0 \quad m \neq n$$

Prove this statement using ψ_1 and ψ_2 and Equation 11.23.

Let $m = 1$ and $n = 2$.

$$\int_0^L \psi_2 \psi_1 dx = \frac{2}{L} \int_0^L \sin \frac{2\pi x}{L} \sin \frac{\pi x}{L} dx$$

A table of integrals gives, for $a^2 \neq b^2$,

$$\int \sin ax \sin bx dx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)}$$

Setting $a = 2\pi/L$ and $b = \pi/L$,

$$\begin{aligned}
 \int_0^L \psi_2 \psi_1 dx &= \frac{2}{L} \left[\frac{\sin \frac{\pi x}{L}}{\frac{2\pi}{L}} - \frac{\sin \frac{3\pi x}{L}}{\frac{6\pi}{L}} \right]_0^L \\
 &= \frac{2}{L} \left[\left(\frac{\sin \pi}{\frac{2\pi}{L}} - \frac{\sin 3\pi}{\frac{6\pi}{L}} \right) - \left(\frac{\sin 0}{\frac{2\pi}{L}} - \frac{\sin 0}{\frac{6\pi}{L}} \right) \right] \\
 &= \frac{2}{L} [(0 - 0) - (0 - 0)] \\
 &= 0
 \end{aligned}$$

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- 11.31 Use the 2s wave function given in Table 11.2 to calculate the value of r (other than $r = \infty$) at which this wave function becomes zero.

Only the radial portion of the 2s wave function depends on r , and ψ becomes zero when $R(r) = 0$.

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

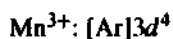
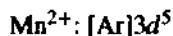
This requires (for $r \neq \infty$)

$$1 - \frac{r}{2a_0} = 0$$

$$r = 2a_0 = 2 (0.529 \text{ \AA}) = 1.058 \text{ \AA}$$

- 11.33 Explain, in terms of their electron configurations, why Fe^{2+} is more easily oxidized to Fe^{3+} than Mn^{2+} to Mn^{3+} .

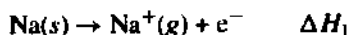
The electron configurations of the species being considered are



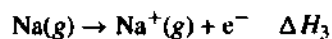
A half-filled subshell has extra stability. On oxidizing Fe^{2+} , the product has a half-filled d subshell. In oxidizing Mn^{2+} , a half-filled d subshell is being lost, which requires more energy.

- 11.39 The standard enthalpy of atomization of an element is the energy required to convert 1 mole of an element in its most stable form at 25°C to 1 mole of monatomic gas. Given that the standard enthalpy of atomization for sodium is 108.4 kJ mol⁻¹, calculate the energy in kilojoules required to convert 1 mole of sodium metal at 25°C to 1 mole of gaseous Na⁺ ions.

The equation



is a sum of the following two processes



Therefore,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

ΔH_3 represents the ionization energy of 1 mole of Na(g), which is 495.9 kJ (Table 11.4). Thus, the energy required to convert 1 mole of sodium metal to 1 mole of gaseous Na⁺ ions is

$$\Delta H_1 = 108.4 \text{ kJ mol}^{-1} + 495.9 \text{ kJ mol}^{-1} = 604.3 \text{ kJ mol}^{-1}$$

Last question.

Calculate mass of 1 atom of Carbon-12 in grams.

1 mole has a mass of 12.000 grams, 6.022×10^{23} atoms/mole.

$$\text{Mass of 1 atom} = \frac{12.000 \text{ grams}}{6.022 \times 10^{23}} = 1.993 \times 10^{-23} \text{ grams}$$