CHEM 544 Fall 2019 - Homework 3 solution
Total 38 pts

Problems
Chap. 2 [16 pts]
2.12 [2]
(a) \[ E = \frac{n^2 h^2}{8 m L^2}, \quad F = -\frac{dE}{dL} = \frac{n^2 h^2}{4 m L^3} \] .
(b) \[ L = \frac{n^2 h^2}{4 m F} \approx 4.9 \times 10^{-13} \text{ (m)}. \]

2.14 [4 pts]
In QM,
\[ \langle x^2 \rangle_{QM} = \int_0^L \psi_n^* x^2 \psi_n dx = \frac{2}{L} \int_0^L x^2 \sin \left( \frac{n \pi x}{L} \right)^2 dx \]
Defining \( x' = \frac{n \pi}{L} x \), thus \( dx' = \frac{n \pi}{L} dx \) and \( (x:0 \rightarrow L \rightarrow x':0 \rightarrow n \pi) \),
\[ \langle x^2 \rangle_{QM} = 2 \left( \frac{L}{n \pi} \right)^3 \int_0^{n \pi} x^2 \sin^2 (x') dx' = \frac{2 L^2}{n^3 \pi^3} \frac{1}{24} \left( 4n^3 \pi^3 - 6n \pi \right) = L^2 \left( \frac{1}{3} - \frac{1}{2n^2 \pi^2} \right). \]

Similarly, \( \langle x \rangle_{QM} = \frac{2}{L} \left( \frac{L}{n \pi} \right)^2 \int_0^{n \pi} x \sin (x') dx' = \frac{2 L^2}{n^2 \pi^2} \frac{1}{8} \left( 2n^2 \pi^2 \right) = \frac{L^2}{2} \).

Therefore, \( \Delta x_{QM} = \sqrt{L^2 \left( \frac{1}{3} - \frac{1}{2n^2 \pi^2} \right) - \left( \frac{L}{2} \right)^2} = \frac{L}{2} \sqrt{1 - \frac{2}{n^2 \pi^2}}. \)

In CM (\( \Psi_n = 1/\sqrt{L} \)),
\[ \langle x^2 \rangle_{CM} = \frac{1}{L} \int_0^L x^2 dx = \frac{1}{3L} \left( L^3 \right) = \frac{L^2}{3} \text{ and } \langle x \rangle_{CM} = \frac{1}{L} \int_0^L x dx = \frac{1}{2L} \left( L^2 \right) = \frac{L}{2}, \text{ so,} \]
\[ \Delta x_{CM} = \sqrt{\frac{L^2}{3} - \left( \frac{L}{2} \right)^2} = \frac{L}{2} \sqrt{\frac{1}{3}}. \]

Thus, \( \Delta x_{QM} \big|_{n \rightarrow \infty} = \Delta x_{CM} \)

2.18 [2 pts]
(a) Using \( H \Psi = E \Psi \) and \( \Psi = X(x)Y(y)Z(z) \),
\[- \frac{1}{X} \frac{\partial^2 X}{\partial x^2} - \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = \frac{2mE}{\hbar^2} \equiv \frac{2m(E_x + E_y + E_z)}{\hbar^2} \] .
(b) \( E_x = \frac{\hbar k_x}{2m} = \frac{\hbar^2 n_x^2}{8mL^2}, X = \left( \frac{2}{L} \right)^{1/2} \sin\left( \frac{n_x \pi}{L} x \right), \)

\( E_y = \frac{\hbar k_y}{2m} = \frac{\hbar^2 n_y^2}{8mL^2}, Y = \left( \frac{2}{L} \right)^{1/2} \sin\left( \frac{n_y \pi}{L} y \right), \)

\( E_z = \frac{\hbar k_z}{2m} = \frac{\hbar^2 n_z^2}{8mL^2}, Z = \left( \frac{2}{L} \right)^{1/2} \sin\left( \frac{n_z \pi}{L} z \right), \) then

\[ E = E_x + E_y + E_z \quad \text{and} \quad \Psi = \left( \frac{2}{L} \right)^{3/2} \sin\left( \frac{n_x \pi}{L} x \right)\sin\left( \frac{n_y \pi}{L} y \right)\sin\left( \frac{n_z \pi}{L} z \right). \]

\[ \iiint \Psi(n_x', n_y', n_z')^* \Psi(n_x, n_y, n_z) \, dx \, dy \, dz \]

(c) \[
\left( \frac{2}{L} \right)^3 \int_0^L \int_0^L \int_0^L \sin\left( \frac{n_x' \pi}{L} x \right) \sin\left( \frac{n_y' \pi}{L} y \right) \sin\left( \frac{n_z' \pi}{L} z \right) \sin\left( \frac{n_x \pi}{L} x \right) \sin\left( \frac{n_y \pi}{L} y \right) \sin\left( \frac{n_z \pi}{L} z \right) \, dx \, dy \, dz \]

\[ = \left( \frac{2}{L} \right)^3 \int_0^L \sin\left( \frac{n_x' \pi}{L} x \right) dx \int_0^L \sin\left( \frac{n_y \pi}{L} y \right) dy \int_0^L \sin\left( \frac{n_z \pi}{L} z \right) dz \]

where \( \frac{2}{L} \int_0^L \sin\left( \frac{n_x' \pi}{L} x \right) \cos\left( \frac{n_x \pi}{L} x \right) \, dx = \frac{L}{2} \left[ \cos\left( \frac{n_x'}{2} \pi \right) \right] - \frac{L}{2} \left[ \cos\left( \frac{n_x}{2} \pi \right) \right] = \delta_{n_x', n_x}. \]

because \( (n_x' - n_x) \) and \( (n_x + n_x) \) are integer numbers. Therefore,

\[ \iiint \Psi(n_x', n_y', n_z')^* \Psi(n_x, n_y, n_z) \, dx \, dy \, dz = \delta_{n_x', n_x} \delta_{n_y', n_y} \delta_{n_z', n_z}. \]

(d) The degeneracy is 6.

2.25 [2 pts] See the student’s solution manual (SSM; www.oxfordtectbooks.co.uk/orc/mqm5e).

2.26 [2 pts] \( \Delta E = \hbar \omega = \hbar \sqrt{\frac{k_f}{m}} = 4.55 \times 10^{-20} \) (J), thus \( \lambda = 4.35 \) (\( \mu \)m).

2.29 [2 pts] (a) \( \langle x \rangle = 0 \), (b) \( \langle x^2 \rangle = 1 \), (c) \( \langle p_x \rangle = 0 \), (d) \( \langle p_x^2 \rangle = \frac{\hbar^2 \alpha^2}{2} \), then \( \Delta x \Delta p_x = \frac{\hbar}{2} \).

2.31 [2 pts] See SSM.

2.32 [2 pts] (a) \( H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 \);

\[ b) \ E = \hbar \omega_x (n_x + \frac{1}{2}) + \hbar \omega_y (n_y + \frac{1}{2}), \]

(c) \( E_x = \frac{\hbar}{2} (\omega_x + \omega_y) \).
Chap. 3 [14 pts]

3.2 [6 pts]

\[ R_{1s} = \left( \frac{Z}{a} \right)^{3/2} 2e^{-\rho/2}, R_{2s} = \left( \frac{Z}{a} \right)^{3/2} \left( \frac{1}{8} \right)^{1/2} (2-\rho)e^{-\rho/2}, R_{3s} = \left( \frac{Z}{a} \right)^{3/2} \left( \frac{1}{243} \right)^{1/2} (6-6\rho+\rho^2)e^{-\rho/2} \]

where \( \rho = \frac{2Z}{na} r \).

(a) \[ \langle r \rangle_{1s} = \left( \frac{Z}{a} \right)^{3} 4 \int_{0}^{\infty} e^{-\rho} r^3 \, dr = \left( \frac{Z}{a} \right)^{3} 4 \left( \frac{a}{2Z} \right)^{4} \int_{0}^{\infty} e^{-\rho} \rho^3 \, d\rho = \frac{3a}{2Z} \]

(b) Similarly,

\[ \langle r^2 \rangle_{1s} = \left( \frac{Z}{a} \right)^{3} 4 \int_{0}^{\infty} e^{-\rho} r^4 \, dr = \left( \frac{Z}{a} \right)^{3} 4 \left( \frac{a}{2Z} \right)^{5} \int_{0}^{\infty} e^{-\rho} \rho^4 \, d\rho = 3 \left( \frac{a}{Z} \right)^2 \]

(c) The most probable radius is at \( r_{\text{max}} \) where \( \frac{\partial(P(r))}{\partial r} = 0 \) and \( P(r) = r^2 R(r)^2 \).

For 1s, \( \frac{\partial(P_{1s}(r))}{\partial r} \propto 2\rho e^{-\rho} - \rho^2 e^{-\rho} = -\rho(\rho-2)e^{-\rho} = 0 \Rightarrow \rho_{\text{max}} = 2 \Rightarrow r_{\text{max}} = a / Z \).

For 2s, \( \frac{\partial(P_{2s}(r))}{\partial r} \propto (\rho^2 - 6\rho + 4)(2-\rho)e^{-\rho} = 0 \Rightarrow \rho = 0.2, 3 \pm \sqrt{5} \). The largest \( \rho \) gives the maximum of \( P_{2s} \), thus \( r_{\text{max}} = a(3+\sqrt{5}) / Z \).

For 3s, \( \frac{\partial(P_{3s}(r))}{\partial r} \propto (\rho^3 - 12\rho^2 + 30\rho - 12)(\rho^2 - 6\rho + 6)e^{-\rho} = 0 \Rightarrow \rho = 0.3 \pm \sqrt{3.049}, 2.79, 8.72 \). The largest \( \rho \) gives the maximum of \( P_{2s} \), thus \( r_{\text{max}} = 8.72 * (3a) / (2Z) = 13.1a / Z \).

3.3 [4 pts]

\[ R_{3s} = \left( \frac{Z}{a} \right)^{3/2} \left( \frac{1}{243} \right)^{1/2} (6-6\rho+\rho^2)e^{-\rho/2}, R_{3p} = \left( \frac{Z}{a} \right)^{3/2} \left( \frac{1}{486} \right)^{1/2} (4-\rho)\rho e^{-\rho/2} \text{ and } \rho = \frac{2}{3a} r \]

(a) \[ P = \int_{0}^{a} R_{3s} r^2 \, dr = \left( \frac{1}{a} \right)^3 \frac{1}{243} \int_{0}^{a} (6-6\rho+\rho^2)^2 e^{-\rho} r^2 \, dr \]
\[
= \left( \frac{1}{a} \right)^3 \frac{1}{243} \left( \frac{3a}{2} \right)^{3/2} \int_0^2 (6 - 6 \rho + \rho^2)^2 e^{-\rho} \rho^2 d\rho = 9.86 \times 10^{-3}.
\]

(b) \( P = \int_0^a R_3 \rho^2 d\rho = \left( \frac{1}{a} \right)^3 \frac{1}{486} \left( \frac{3a}{2} \right)^{3/2} \int_0^2 (4 - \rho^2)^2 \rho^4 e^{-\rho} d\rho = 1.25 \times 10^{-3} \).

3.11 [2 pts]

\[\cos \theta|_{\text{min}} = \frac{\langle l_z \rangle_{\text{max}}}{\sqrt{\langle l^2 \rangle}} = \frac{4l}{\sqrt{l(l+1)}} \xrightarrow{l \to \infty} 0, \text{ thus } \theta \xrightarrow{l \to \infty} 0.\]

\[
\cos \theta = \frac{m_i}{\sqrt{l(l+1)}}
\]

L = 1: \(m_i = 1, \theta = 45^\circ;\)
\(m_i = 0, \theta = 90^\circ;\)
\(m_i = -1, \theta = 135^\circ;\)
L = 2: \(m_i = 2, \theta = 35.2^\circ;\)
\(m_i = 1, \theta = 65.9^\circ;\)
\(m_i = 0, \theta = 90^\circ;\)
\(m_i = -1, \theta = 114.1^\circ;\)
L = 3: \(m_i = 3, \theta = 30^\circ;\)
\(m_i = 2, \theta = 54.7^\circ;\)
\(m_i = 1, \theta = 73.2^\circ;\)
\(m_i = 0, \theta = 90^\circ;\)
\(m_i = -1, \theta = 106.8^\circ;\)
\(m_i = -2, \theta = 125.3^\circ;\)
\(m_i = -3, \theta = 150^\circ;\)

3.15 [2 pts]

For 1s state, \( R(r) = 2 \left( \frac{Z}{a} \right)^{3/2} e^{-Zr/a} \) where \( a = \frac{4\pi \varepsilon_0 \hbar^2}{\mu e^2} \).

Using \( \nabla^2 \Psi_1 \propto \nabla^2 e^{-Zr/a} = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{Z^2 - 2Za}{a^2} \right) e^{-Zr/a} \) and \( \int_0^\infty x^ne^{-ax}dx = \frac{n!}{b^{n+1}}. \)

\[
\langle T \rangle = -\frac{\hbar^2}{2\mu} \int_0^\infty r^2 dr R \nabla^2 R = -\frac{\hbar^2}{2\mu} \frac{4Z^3}{a^3} \left( \frac{Z^2}{a^2} - 2Z \frac{a^2}{a^2} \right) e^{-Zr/a} dr - \frac{2Z}{a} \int_0^\infty r e^{-2Zr/a} dr
\]

\[
= -\frac{\hbar^2}{2\mu} \frac{4Z^3}{a^3} \left( \frac{Z^2}{a^2} - 2Z \frac{a^2}{a^2} \right) = \frac{Z^2 \hbar^2}{2\mu a^3} = \frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}
\]

\[
\langle V \rangle = -\frac{Ze^2}{4\pi \varepsilon_0} \int_0^\infty r^2 dr R \left( \frac{1}{r} \right) R = -\frac{Ze^2}{4\pi \varepsilon_0} \frac{4Z^3}{a^3} \frac{a^2}{4Z^2} = -\frac{Z^2 e^2}{16\pi^2 \varepsilon_0^2 a} = -\frac{Z^2 \mu e^4}{16\pi^2 \varepsilon_0^2 \hbar^2}
\]

Thus, \( \langle T \rangle = -\frac{1}{2} \langle V \rangle. \)
Additional problems [8 pts]

Solution

(a) \( \mathbf{B} = \nabla \times \mathbf{A} = \frac{B}{2} \left( \begin{array}{c} \partial / \partial x \\ \partial / \partial y \\ \partial / \partial z \end{array} \right) \times \left( \begin{array}{c} -y \\ x \\ 0 \end{array} \right) = \left( \begin{array}{c} 0 \\ 0 \\ 2 \end{array} \right) = B \mathbf{k} \).

(b) \( H = \frac{1}{2m} (\mathbf{P} - e \mathbf{A})^2 = \frac{1}{2m} \left( \mathbf{P} \cdot \mathbf{P} - e \mathbf{P} \cdot e \mathbf{A} - e \mathbf{A} \cdot \mathbf{P} + e^2 \mathbf{A} \cdot \mathbf{A} \right)^2 \)

\[
= \frac{1}{2m} \left( P_x^2 + P_y^2 - \frac{eB}{2} (-P_x y + P_y x - yP_x + xP_y) + \left( \frac{eB}{2} \right)^2 (x^2 + y^2) \right) \\
= \frac{1}{2m} \left( P_x + \frac{eB}{2} y \right)^2 + \left( P_y - \frac{eB}{2} x \right)^2 \\
\]

(c) \([q, p] = \frac{1}{eB} \left[ (P_x + \frac{eB}{2} y)(P_y - \frac{eB}{2} x) - (P_y - \frac{eB}{2} x)(P_x + \frac{eB}{2} y) \right] \)

\[
= \frac{1}{eB} \left[ (P_x P_y - \frac{eB}{2} P_x y + \frac{eB}{2} yP_x - \left( \frac{eB}{2} \right)^2 yx) - (P_y P_x - \frac{eB}{2} P_y x + \frac{eB}{2} xP_y + \left( \frac{eB}{2} \right)^2 yx) \right] \\
= \frac{1}{2} \left[ [x, P_x] + [y, P_y] \right] = i\hbar \cdot \\
\]

(d) Using \( p = (P_y - \frac{eB}{2} x) \) and \( q = \frac{1}{eB} (P_x + \frac{eB}{2} y) \),

Hamiltonian is rewritten by \( H = \frac{1}{2m} p^2 + \frac{1}{2} \left( \frac{(eB)^2}{m} \right) q^2 \), thus the system is harmonic oscillator with the quantized energy of \( E = \hbar \omega (n + 1/2) \) where \( \omega = eB / m \) and \( n \) is the quantum number.