

Chapter 6

The Hydrogen Atom

Homework Solutions

1. $\text{He}^+ : Z = 2 \quad E_n = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{n^2}$

(a) $n_U = 6, n_L = 3$

$$\begin{aligned} \Delta E = E_U - E_L &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \cdot \frac{Z^2}{n_U^2} - \left[-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \cdot \frac{Z^2}{n_L^2} \right] = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \left[\frac{Z^2}{n_U^2} - \frac{Z^2}{n_L^2} \right] \\ &= -\frac{1}{2} (2625 \text{ kJ/mol}) \left[\frac{2^2}{6^2} - \frac{2^2}{3^2} \right] = 437.5 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} = 7.27 \times 10^{-19} \text{ J} \\ E_{\text{phot}} = \Delta E = \frac{hc}{\lambda} \rightarrow \lambda &= \frac{hc}{E_{\text{phot}}} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{7.27 \times 10^{-19} \text{ J}} \\ &= 2.74 \times 10^{-7} \text{ m} \cdot \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 274 \text{ nm} \end{aligned}$$

(b) Ionization: $n_U = \infty, n_L = 1$

$$\begin{aligned} \text{Ioniz. Energy} = \Delta E = E_U - E_L &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \left[\frac{Z^2}{n_U^2} - \frac{Z^2}{n_L^2} \right] \\ &= -\frac{1}{2} (2625 \text{ kJ/mol}) \left[0 - \frac{2^2}{1^2} \right] = 5250 \text{ kJ/mol} \times \frac{10^3 \text{ J}}{1 \text{ kJ}} \times \frac{1}{6.02 \times 10^{23} \text{ mol}^{-1}} \\ &= 8.72 \times 10^{-18} \text{ J} \cdot \frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} = 54.5 \text{ eV} \end{aligned}$$

2. $\psi_{1s} = A_{1s} e^{-Zr/a_0} \quad \psi_{2s} = A_{2s} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$

(a) Orthogonality

$$\begin{aligned} \langle \psi_{1s} | \psi_{2s} \rangle &= \iiint \psi_{1s} \psi_{2s} dV = \iiint \left[A_{1s} e^{-Zr/a_0} \right] \left[A_{2s} \left(1 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \right] \left[r^2 \sin \theta dr d\theta d\phi \right] \\ &= A_{1s} A_{2s} I_R I_\Theta I_\Phi \end{aligned}$$

The angular integrals are: $I_\Theta I_\Phi = 4\pi$. We'll focus on I_R

$$\begin{aligned} I_R &= \int_0^\infty \left[e^{-Zr/a_0} \right] \left[\left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0} \right] r^2 dr = \int_0^\infty \left\{ r^2 e^{-3Zr/2a_0} - \frac{Z}{2a_0} r^3 e^{-3Zr/2a_0} \right\} dr \\ &= \int_0^\infty r^2 e^{-br} dr - \frac{Z}{2a_0} \int_0^\infty r^3 e^{-br} dr \quad b = \frac{3Z}{2a_0} \end{aligned}$$

$$I_R = \left\{ \frac{2!}{\left(\frac{3Z}{2a_0}\right)^3} - \frac{Z}{2a_0} \frac{3!}{\left(\frac{3Z}{2a_0}\right)^4} \right\} = \frac{2(2a_0)^3}{(3Z)^3} - \frac{Z}{2a_0} \frac{6(2a_0)^4}{(3Z)^4}$$

$$= \frac{16a_0^3}{27Z^3} - \frac{Z}{2a_0} \frac{96a_0^4}{81Z^4} = \frac{16a_0^3}{27Z^3} - \frac{16a_0^3}{27Z^3} = 0$$

(b) Normalization

$$I_\Theta = \int_0^\pi \sin \theta d\theta = [-\cos \theta]_0^\pi = 2$$

$$I_\Phi = \int_0^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi$$

$$I_R = \int_0^\infty r^2 e^{-2Zr/a_0} dr = \int_0^\infty r^2 e^{-br} dr = \frac{2!}{\left(\frac{2Z}{a_0}\right)^3} = \frac{a_0^3}{4Z^3}$$

$$\langle \psi_{1s} | \psi_{1s} \rangle = 1 = A_{1s}^2 \cdot I_R \cdot I_\Theta \cdot I_\Phi = A_{1s}^2 \cdot \frac{a_0^3}{4Z^3} \cdot 2 \cdot 2\pi = A_{1s}^2 \pi \left(\frac{a_0}{Z}\right)^3$$

Therefore: $A_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2}$

(c) Most probable r: Maximum in the RDF

$$RDF = P(r) = Br^2 |R(r)|^2 = Br^2 [e^{-Zr/a_0}]^2 = Br^2 e^{-2Zr/a_0}$$

$d[P(r)]/dr = 0$ at maximum

$$\frac{dP(r)}{dr} = 0 = B \frac{d}{dr} [r^2 e^{-2Zr/a_0}] = B[r^2 e^{-2Zr/a_0} (-2Z/a_0) + e^{-2Zr/a_0} (2r)]$$

$$= B2re^{-2Zr/a_0} [-Zr/a_0 + 1]$$

Maximum when: $-\frac{Zr_{\max}}{a_0} + 1 = 0 \rightarrow r_{\max} = \frac{a_0}{Z}$

(d) $\langle r \rangle$: $\langle r \rangle = \int_0^\infty rP(r)dr = \int_0^\infty r [Br^2 e^{-2Zr/a_0}] dr$

Before we can use the above formula, we must calculate the normalization constant, B

$$\int_0^\infty P(r)dr = 1 = \int_0^\infty Br^2 e^{-2Zr/a_0} dr = B \cdot \frac{2!}{\left[\frac{2Z}{a_0}\right]^3} = B \cdot \frac{1}{4} \left(\frac{a_0}{Z}\right)^3 \rightarrow B = 4 \left(\frac{Z}{a_0}\right)^3$$

$$\begin{aligned}
\langle r \rangle &= \int_0^\infty r P(r) dr = \int_0^\infty r \left[B r^2 e^{-2Zr/a_0} \right] dr = B \int_0^\infty r^3 e^{-2Zr/a_0} dr \\
&= B \cdot \frac{3!}{\left(\frac{2Z}{a_0} \right)^4} = B \cdot \frac{3}{8} \cdot \left(\frac{a_0}{Z} \right)^4 = \left[4 \left(\frac{Z}{a_0} \right)^3 \right] \cdot \frac{3}{8} \cdot \left(\frac{a_0}{Z} \right)^4 \\
&= \frac{3}{2} \frac{a_0}{Z}
\end{aligned}$$

(e) $P(0 \leq r \leq 2a_0/Z)$

$$P(0 \leq r \leq 2a_0/Z) = \int_0^{2a_0/Z} P(r) dr = B \int_0^{2a_0/Z} r^2 e^{-2Zr/a_0} dr$$

To put it in the form where we can use a dimensionless numerical definite integral (see given data), let's define: $x = 2Zr/a_0 \rightarrow r = a_0 x / 2Z$, $dr = a_0 x / 2Z$, and $r = 2a_0/Z$ corresponds to $x = (2Z/a_0)(2a_0/Z) = 4$

$$\begin{aligned}
P(0 \leq r \leq 2a_0/Z) &= B \int_0^4 \left(\frac{a_0 x}{2Z} \right)^2 e^{-x} \left(\frac{a_0}{2Z} \right) dx = B \left(\frac{a_0}{2Z} \right)^3 \int_0^4 x^2 e^{-x} dx \\
&= \left[4 \left(\frac{Z}{a_0} \right)^2 \right] \cdot \frac{1}{8} \left(\frac{a_0}{Z} \right)^3 [1.524] = 0.762 \approx 0.76
\end{aligned}$$

(f) $P(a_0/Z \leq r \leq 4a_0/Z)$

$$P(a_0/Z \leq r \leq 4a_0/Z) = \int_{a_0/Z}^{4a_0/Z} P(r) dr = B \int_{a_0/Z}^{4a_0/Z} r^2 e^{-2Zr/a_0} dr$$

To put it in the form where we can use a dimensionless numerical definite integral (see given data), let's define: $x = 2Zr/a_0 \rightarrow r = a_0 x / 2Z$, $dr = a_0 x / 2Z$.

$r = a_0/Z$ corresponds to $x = (2Z/a_0)(a_0/Z) = 2$, $r = 4a_0/Z$ corresponds to $x = (2Z/a_0)(4a_0/Z) = 8$

$$\begin{aligned}
P\left(\frac{a_0}{Z} \leq r \leq \frac{4a_0}{Z} \right) &= B \int_2^8 \left(\frac{a_0 x}{2Z} \right)^2 e^{-x} \left(\frac{a_0}{2Z} \right) dx = B \left(\frac{a_0}{2Z} \right)^3 \int_2^8 x^2 e^{-x} dx \\
&= \left[4 \left(\frac{Z}{a_0} \right)^3 \right] \cdot \frac{1}{8} \left(\frac{a_0}{Z} \right)^3 \left[\int_2^8 x^2 e^{-x} dx \right] = \frac{1}{2} \left[\int_2^8 x^2 e^{-x} dx \right] \\
&= \frac{1}{2} \left[\int_0^8 x^2 e^{-x} dx - \int_0^2 x^2 e^{-x} dx \right] = \frac{1}{2} [1.972 - 0.647] = 0.66
\end{aligned}$$

$$\begin{aligned}
\text{(g)} \quad \langle V \rangle &= \left\langle -\frac{Ze^2}{4\pi\epsilon_0 r} \right\rangle = -\frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle \\
\left\langle \frac{1}{r} \right\rangle &= \int_0^\infty \frac{1}{r} P(r) dr = \int_0^\infty \frac{1}{r} \left[Br^2 e^{-2Zr/a_0} \right] dr = B \int_0^\infty r e^{-2Zr/a_0} dr \\
\psi_{n22}(r, \theta, \varphi) &= R_{12}\left(\frac{r}{a_0}\right) \cdot \sin^2\theta \cdot \frac{e^{2i\varphi}}{4} \left[\frac{Z}{a_0} \right]^3 \\
&= B \frac{\left(\frac{2Z}{a_0}\right)^2}{4} = B \frac{1}{4} \left(\frac{Z}{a_0}\right)^2 = \frac{Z}{a_0}
\end{aligned}$$

$$\langle V \rangle = \left\langle -\frac{Ze^2}{4\pi\epsilon_0 r} \right\rangle = -\frac{Ze^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Ze^2}{4\pi\epsilon_0} \frac{Z}{a_0} = -\frac{Z^2 e^2}{4\pi\epsilon_0} \cdot \frac{1}{a_0}$$

(h) Verify Solution of the Radial Equation

$$\begin{aligned}
R &= e^{-Zr/a_0} \quad \frac{dR}{dr} = \left(-\frac{Z}{a_0} \right) e^{-Zr/a_0} \quad \frac{d^2 R}{dr^2} = \left(\frac{Z}{a_0} \right)^2 e^{-Zr/a_0} \\
-\frac{\hbar^2}{2m} \left[\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{a_0 r} R \right] &= \\
-\frac{\hbar^2}{2m} \left[\left(\frac{Z}{a_0} \right)^2 e^{-Zr/a_0} + \frac{2}{r} \left(-\frac{Z}{a_0} \right) e^{-Zr/a_0} - 0 + \frac{2Z}{a_0 r} e^{-Zr/a_0} \right] &= \\
-\frac{\hbar^2}{2m} \left[\left(\frac{Z}{a_0} \right)^2 e^{-Zr/a_0} \right] &= \left(-\frac{\hbar^2 Z^2}{2ma_0^2} \right) R
\end{aligned}$$

3. $RDF = P(r) = Br^2 |R(r)|^2 = Br^2 \left[r e^{-2Zr/a_0} \right]^2 = Br^4 e^{-2Zr/a_0}$

(a) $r_{\max}$ (most probably distance from the nucleus)

$d[P(r)]/dr = 0$ at maximum

$$\begin{aligned}
\frac{dP(r)}{dr} = 0 &= B \frac{d}{dr} \left[r^4 e^{-2Zr/a_0} \right] = B \left[r^4 e^{-2Zr/a_0} (-2Z/a_0) + e^{-2Zr/a_0} (4r^3) \right] \\
&= Br^3 e^{-2Zr/a_0} [-2Z/a_0 + 4]
\end{aligned}$$

Maximum when: $-\frac{2Zr_{\max}}{a_0} + 4 = 0 \rightarrow r_{\max} = \frac{4a_0}{2Z}$

(b) $\langle r^2 \rangle$ (averaged squared distance from the nucleus)

Before we can use the RDF to compute averages we must calculate the normalization constant, B

$$\int_0^\infty P(r)dr = 1 = B \int_0^\infty r^4 e^{-Zr/a_0} dr = B \frac{4!}{\left(\frac{Z}{a_0}\right)^5} = B \cdot 24 \left(\frac{a_0}{Z}\right)^5$$

Therefore, $B = \frac{1}{24} \left(\frac{Z}{a_0}\right)^5$

$$\begin{aligned} \langle r^2 \rangle &= \int_0^\infty r^2 P(r)dr = \int_0^\infty r^2 \left[B r^4 e^{-Zr/a_0} \right] dr = B \int_0^\infty r^6 e^{-Zr/a_0} \\ &= B \cdot \frac{6!}{\left(\frac{Z}{a_0}\right)^7} = B \cdot 720 \cdot \left(\frac{a_0}{Z}\right)^7 = \left[\frac{1}{24} \left(\frac{Z}{a_0}\right)^5 \right] \cdot 720 \cdot \left(\frac{a_0}{Z}\right)^7 \\ &= 30 \left(\frac{a_0}{Z}\right)^2 \end{aligned}$$

4. $Y_{lm} = \sin^2 \theta e^{2i\phi}$

(a) $L^2 Y_{lm}(\theta, \phi)$

$$\begin{aligned} L^2 Y_{lm}(\theta, \phi) &= -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y_{lm}(\theta, \phi) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y_{lm}(\theta, \phi) \right\} \\ &= -\hbar^2 \left\{ \hat{A} Y_{lm}(\theta, \phi) + \hat{B} Y_{lm}(\theta, \phi) \right\} \end{aligned}$$

Let's work this in parts (A first, followed by B)

$$\begin{aligned} \hat{A} Y_{lm}(\theta, \phi) &= \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y_{lm}(\theta, \phi) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) [\sin^2 \theta e^{2i\phi}] \\ &= e^{2i\phi} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \sin^2 \theta}{\partial \theta} \right) = e^{2i\phi} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \cdot 2 \sin \theta \cos \theta) = 2e^{2i\phi} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin^2 \theta \cos \theta) \\ &= 2e^{2i\phi} \frac{1}{\sin \theta} [\sin^2 \theta (-\sin \theta) + \cos \theta (2 \sin \theta \cos \theta)] = 2e^{2i\phi} (-\sin^2 \theta + 2 \cos^2 \theta) \\ &= 2e^{2i\phi} (-\sin^2 \theta + 2[1 - \sin^2 \theta]) = 2e^{2i\phi} [2 - 3\sin^2 \theta] \end{aligned}$$

$$\begin{aligned}\hat{B}Y_{l,m}(\theta, \phi) &= \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} (\sin^2 \theta e^{2i\phi}) = \frac{\sin^2 \theta}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} (e^{2i\phi}) = (2i)^2 e^{2i\phi} = -4e^{2i\phi} \\ L^2 Y_{lm}(\theta, \phi) &= -\hbar^2 \left\{ \hat{A}Y_{lm}(\theta, \phi) + \hat{B}Y_{lm}(\theta, \phi) \right\} = -\hbar^2 \left\{ (2e^{2i\phi} [2 - 3\sin^2 \theta]) - 4e^{2i\phi} \right\} \\ &= -\hbar^2 \left\{ 4e^{2i\phi} - 6\sin^2 \theta e^{2i\phi} - 4e^{2i\phi} \right\} = +6\hbar^2 \sin^2 \theta e^{2i\phi} = 6\hbar^2 Y_{l,m}(\theta, \phi)\end{aligned}$$

Thus, the Eigenvalue is $6\hbar^2 = l(l+1)\hbar^2 \rightarrow l=2$

(b) $L_z Y_{l,m}(\theta, \phi)$

$$\begin{aligned}\hat{L}_z Y(\theta, \phi) &= \frac{\hbar}{i} \frac{\partial^2}{\partial \phi^2} [Y_{l,m}(\theta, \phi)] = \frac{\hbar}{i} \frac{\partial^2}{\partial \phi^2} [\sin^2 \theta e^{2i\phi}] = \frac{\hbar}{i} \sin^2 \theta (2ie^{2i\phi}) \\ &= 2\hbar \sin^2 \theta e^{2i\phi} = 2\hbar Y(\theta, \phi)\end{aligned}$$

Thus, the Eigenvalue is $2\hbar = m\hbar \rightarrow m=2$

(c) $\langle y^2 \rangle$ (set up integrals) $y = r \sin \theta \sin \phi$

$$\begin{aligned}\langle y^2 \rangle &= \iiint_{r,\theta,\phi} \psi^* y^2 \psi dV \\ &= \iiint_{r,\theta,\phi} \left(A r^2 e^{-Zr/3a_0} \sin^2 \theta e^{2i\phi} \right)^* (r \sin \theta \sin \phi)^2 \left(A r^2 e^{-Zr/3a_0} \sin^2 \theta e^{2i\phi} \right) (r^2 \sin \theta dr d\theta d\phi) \\ &= \iiint_{r,\theta,\phi} A^2 (r^8 e^{-2Zr/3a_0}) (\sin^7 \theta) (\sin^2 \phi) dr d\theta d\phi \\ &= A^2 \int_0^\infty r^8 e^{-2Zr/3a_0} dr \cdot \int_0^\pi \sin^7 \theta d\theta \cdot \int_0^{2\pi} \sin^2 \phi d\phi\end{aligned}$$

5. $\psi_{n22}(r, \theta, \phi) = R_{n2}(r) \cdot \sin^2 \theta \cdot e^{2i\phi} \quad \psi_{n2-2}(r, \theta, \phi) = R_{n2}(r) \cdot \sin^2 \theta \cdot e^{-2i\phi}$

$$\begin{aligned}\psi_1 &= \psi_{n22} + \psi_{n2-2} = R_{n2} \sin^2 \theta e^{2i\phi} + R_{n2} \sin^2 \theta e^{-2i\phi} \\ &= R_{nl} \sin^2 \theta \{ e^{2i\phi} + e^{-2i\phi} \} \\ &= R_{nl} \sin^2 \theta \{ (\cos(2\phi) + i \sin(2\phi)) + (\cos(2\phi) - i \sin(2\phi)) \} \\ &= 2R_{nl} \sin^2 \theta \cos(2\phi)\end{aligned}$$

Note: The real wavefunction could be normalized via division by $\sqrt{2}$

$$\begin{aligned}\psi_2 &= \psi_{n22} - \psi_{n2-2} = R_{n2} \sin^2 \theta e^{2i\phi} - R_{n2} \sin^2 \theta e^{-2i\phi} \\ &= R_{nl} \sin^2 \theta \{ e^{2i\phi} - e^{-2i\phi} \} \\ &= R_{nl} \sin^2 \theta \{ (\cos(2\phi) + i \sin(2\phi)) - (\cos(2\phi) - i \sin(2\phi)) \} \\ &= 2iR_{nl} \sin^2 \theta \sin(2\phi)\end{aligned}$$