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1. Atkins Prob. 8.14 (a)(ii) (12 pts total)

Find N such that $N^2 \int_{-\infty}^{\infty} \psi^* \psi \, d\tau = 1$

$$N^2 \int r^2 \sin^2\theta \cos^2\phi \, e^{-r/a_0} \, r^2 \sin\theta \, dr \, d\theta \, d\phi = 1$$

$$N^2 \int_{r=0}^{r=\infty} r^4 e^{-r/a_0} dr \int_{\theta=0}^{\theta=\pi} \sin^3\theta \, d\theta \int_{\phi=0}^{\phi=2\pi} \cos^2\phi \, d\phi = 1$$

2 pts

Evaluate each of the integrals separately:

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

(see inside front cover)

2 pts

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$$\int_0^{\pi} \sin^3\theta\, d\theta = \int_0^{\pi} (\sin^2\theta)(\sin\theta)\, d\theta = \int_0^{\pi} (1-\cos^2\theta)(\sin\theta)\, d\theta$$

$$= \int_0^{\pi} \sin\theta\, d\theta - \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta$$

Substitute: $u = \cos\theta$

$\Rightarrow du = -\sin\theta\, d\theta$

$$= \int_0^{\pi} \sin\theta\, d\theta + \int_1^{-1} u^2\, du \qquad \begin{bmatrix} \theta = 0 \Rightarrow u = \cos 0 = 1 \\ \theta = \pi \Rightarrow u = \cos\pi = -1 \end{bmatrix}$$

$$= -\cos\theta \Big]_0^{\pi} + \frac{1}{3}u^3\Big]_1^{-1}$$

$$= -(-1-1) + \frac{1}{3}(-1-1) = 2 - \frac{2}{3} = \boxed{\frac{4}{3}}$$

(Or you could look up the integral: $\int \sin^3\theta\, d\theta = -\frac{1}{3}(\cos\theta)(\sin^2\theta + 2)$ + constant)

4 pts

$$\int_0^{2\pi} \cos^2\phi\, d\phi = \int_0^{2\pi} (1-\sin^2\phi)\, d\phi = \int_0^{2\pi} d\phi - \int_0^{2\pi} \sin^2\phi\, d\phi$$

$$= \phi\Big]_0^{2\pi} - \left[\frac{1}{2}\phi - \frac{1}{4}\sin 2\phi\right]_0^{2\pi}$$

$$= 2\pi - \left[\pi - \frac{1}{4}(0-0)\right]$$

$$= \boxed{\pi}$$

3 pts

$$\therefore N^2(\cancel{24}^{\,8} a_0^5)\left(\frac{4}{\cancel{3}}\right)(\pi) = 1$$

$$N^2(32\pi a_0^5) = 1$$

$$N = \sqrt{\frac{1}{32\pi a_0^5}} = \frac{1}{4}\sqrt{\frac{1}{2\pi a_0^5}}$$

1 pt

2. Atkins Exercise 9.17b. (4 pts)

$$l = 2 \Rightarrow |\vec{L}| = \sqrt{l(l+1)}\,\hbar = \sqrt{2(2+1)}\,\hbar = \sqrt{6}\,\hbar$$

$$= \sqrt{6}\,(1.055 \times 10^{-34}\,\mathrm{J \cdot s})$$

$$= \boxed{2.584 \times 10^{-34}\,\mathrm{J \cdot s}}$$ 1 pt

$l = 2 \Rightarrow m_l = -2, -1, 0, +1, +2$ and $L_z = m_l \hbar$

so $L_z = \pm 2\hbar = \boxed{\pm 2.110 \times 10^{-34}\,\mathrm{J \cdot s}}$ 1 pt

or $L_z = \pm \hbar = \boxed{\pm 1.055 \times 10^{-34}\,\mathrm{J \cdot s}}$ 1 pt

or $\boxed{L_z = 0}$ 1 pt

−1 if unit or sig fig error

3. Atkins Prob 9.23 (16 pts total)

(a) $Y_{00} = \sqrt{\frac{1}{4\pi}}$

$$\hat{H}\psi = -\frac{\hbar^2}{2I}\Lambda^2\sqrt{\frac{1}{4\pi}}$$

$$= -\frac{\hbar^2}{2I}\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\sqrt{\frac{1}{4\pi}}$$

$= 0$ (since $\sqrt{\frac{1}{4\pi}}$ is a constant)

1 pt for some justification

$\therefore \boxed{E = 0}$ and $E = \frac{L^2}{2I} \Rightarrow \boxed{L = 0}$

1/2 pt — 1/2 pt

$\underbrace{\text{real \# } \Rightarrow Y_{00} \text{ is an eigenfunction of } \hat{H}}_{1\text{ pt}}$

(c) $Y_{3+3} = \sqrt{\frac{35}{64\pi}} \sin^3\theta\, e^{3i\phi}$ and $\hat{H}\psi = -\frac{\hbar^2}{2I} \Lambda^2 Y_{3+3}$

$$\frac{\partial Y_{3+3}}{\partial\theta} = \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}(3\sin^2\theta\cos\theta) \quad \text{1 pt}$$

$$\sin\theta\frac{\partial Y_{3+3}}{\partial\theta} = \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}(3\sin^3\theta\cos\theta) \quad \text{1 pt}$$

$$\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3+3}}{\partial\theta} = \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}\left[3\sin^3\theta(-\sin\theta) + \cos\theta(9\sin^2\theta\cos\theta)\right]$$

$$= \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}(9\sin^2\theta\cos^2\theta - 3\sin^4\theta) \quad \text{2 pts}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y_{3+3}}{\partial\theta} = \underline{\sqrt{\frac{35}{64\pi}}\, e^{3i\phi}(9\sin\theta\cos^2\theta - 3\sin^3\theta)} \quad \text{1 pt}$$

1 pt

$$\frac{\partial^2}{\partial\phi^2}Y_{3+3} = \sqrt{\frac{35}{64\pi}}\sin^3\theta\,(3i)^2 e^{3i\phi} = -9\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{3i\phi}$$

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y_{3+3}}{\partial\phi^2} = \underline{-9\sqrt{\frac{35}{64\pi}}\sin\theta\, e^{3i\phi}} \quad \text{1 pt}$$

$$\text{so } \Lambda^2 Y_{3+3} = \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}\left[-9\sin\theta + 9\sin\theta\cos^2\theta - 3\sin^3\theta\right] \quad \text{1 pt}$$

$$= \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}\left[-9\sin\theta + 9\sin\theta(1-\sin^2\theta) - 3\sin^3\theta\right] \quad \text{1 pt}$$

$$= \sqrt{\frac{35}{64\pi}}\, e^{3i\phi}\left[\cancel{-9\sin\theta} + \cancel{9\sin\theta} - 9\sin^3\theta - 3\sin^3\theta\right]$$

$$= -12\sqrt{\frac{35}{64\pi}}\, e^{3i\phi}\sin^3\theta \quad \text{1 pt}$$

$$\Lambda^2 Y_{3+3} = -12\, Y_{3+3}$$

$$\text{so } \underbrace{\hat{H}\psi = -\frac{\hbar^2}{\cancel{2}I}\left(-\cancel{12}^{\,6}\, Y_{3+3}\right)}_{1\text{ pt}} = \underbrace{\frac{6\hbar^2}{I}}\, Y_{3+3} = E\, Y_{3+3}$$

real # $\Rightarrow$ Y_{3+3} is an eigenfunction of $\hat{H}$ 1 pt

$$\text{and } \boxed{E = \frac{6\hbar^2}{I}} \quad \text{and } E = \frac{L^2}{2I} \Rightarrow L^2 = 2IE$$

1/2 pt

$$L^2 = 12\hbar^2$$

$$\Downarrow$$

$$\boxed{|\vec{L}| = 2\sqrt{3}\,\hbar}$$

1/2 pt

4. Atkins Prob. 9.24 (12 pts total)

$$Y_{3+3} = \sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{3i\phi}$$

$$\int \psi^* \psi\, d\tau = \int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\left(\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{-3i\phi}\right)\left(\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{3i\phi}\right)\sin\theta\, d\theta\, d\phi$$ 1 pt

$$= \frac{35}{64\pi}\int_{\theta=0}^{\theta=\pi}\sin^7\theta\, d\theta \int_{\phi=0}^{\phi=2\pi} d\phi$$ 1 pt

and $\sin^7\theta\, d\theta = \sin^6\theta \sin\theta\, d\theta = (\sin^2\theta)^3 \sin\theta\, d\theta$

$= (1-\cos^2\theta)^3 \sin\theta\, d\theta$ 1 pt

and let $u \equiv \cos\theta \Rightarrow du = -\sin\theta\, d\theta$ 1 pt

$\Rightarrow \sin^7\theta\, d\theta = (1-u^2)^3(-du)$; $\underline{\theta = 0 \Rightarrow u = 1 \text{ and } \theta = \pi \Rightarrow u = -1}$ 1 pt

so $\int \psi^*\psi\, d\tau = \frac{35}{\cancel{64}_{32}\cancel{\pi}}\underbrace{(2\cancel{\pi})}_{\text{integral over } \phi}\int_1^{-1}(-1)(1-u^2)^3 du$ 1 pt

$$= -\frac{35}{32}\int_1^{-1}(1-2u^2+u^4)(1-u^2)\, du$$

$$= -\frac{35}{32}\int_1^{-1}(1-2u^2+u^4-u^2+2u^4-u^6)\, du$$

$$= -\frac{35}{32}\int_1^{-1}(1-3u^2+3u^4-u^6)\, du$$ 2 pts

$$= -\frac{35}{32}\left[u - u^3 + \frac{3}{5}u^5 - \frac{1}{7}u^7\right]_1^{-1}$$ 1 pt

$$= -\frac{35}{32}\left[-1+1-\frac{3}{5}+\frac{1}{7}-1+1-\frac{3}{5}+\frac{1}{7}\right]$$ 2 pts for plugging into antiderivative

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$$= -\frac{35}{32}\left[-\frac{6}{5}+\frac{2}{7}\right] = -\frac{35}{32}\left[\frac{-42+10}{35}\right] = -\frac{35}{32}\left[\frac{-32}{35}\right]$$

$$\int \psi^* \psi \, d\tau = 1$$

$\therefore Y_{3,+3}$ is normalized 1pt

5. Atkins Exercise 10.8 b (5 pts total)

(a) 4d : $d \Rightarrow l = 2 \Rightarrow |\vec{L}| = \sqrt{2(2+1)}\,\hbar = \boxed{\sqrt{6}\,\hbar}$ 1pt

$\Downarrow$

$\boxed{\text{2 angular nodes}}$

1pt

$4-2-1 = \boxed{\text{1 radial node}}$

(b) 2p : $p \Rightarrow l = 1 \Rightarrow |\vec{L}| = \sqrt{1(1+1)}\,\hbar = \boxed{\sqrt{2}\,\hbar}$ 1pt

$\Downarrow$

$\boxed{\text{1 angular node}}$

1pt

$2-1-1 = \boxed{\text{0 radial nodes}}$

(c) 3p : $p \Rightarrow l = 1 \Rightarrow |\vec{L}| = \boxed{\sqrt{2}\,\hbar}$ (as in (b))

$\Downarrow$

$\boxed{\text{1 angular node}}$ (as in (b))

1pt

$3-1-1 = \boxed{\text{1 radial node}}$

NO PTS FOR FINAL ANSWERS

(16 pts total)

6. We need to evaluate $\langle r \rangle$ for 2s and 2p orbitals. Use only the radial part of the wavefunctions ($R_{n\ell}$) (remember that the spherical harmonics don't depend on r).

$$R_{20} = \frac{1}{\sqrt{8}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}\ ; \quad \underbrace{\rho = \frac{2Z}{na_0}r = \frac{Z}{a_0}r \ (n=2)}_{1\text{ pt}}$$

n ℓ

(2s orbital)

$$\langle r \rangle_{2s} = \int_{r=0}^{r=\infty} R_{20}^{*}\, r\, R_{20}\, r^2 dr$$

the position operator

$$= \int_0^\infty R_{20}^2\, r^3 dr$$

1 pt

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3 \int_0^\infty (2-\rho)^2 e^{-\rho} r^3 dr \quad 1\text{pt}$$

(now sub in for ρ:)

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

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3 \int_0^\infty \left(4-\frac{4Z}{a_0}r+\frac{Z^2}{a_0^2}r^2\right) e^{-Zr/a_0} r^3 dr \quad 1\text{pt}$$

$$= \frac{1}{8}\left(\frac{Z}{a_0}\right)^3 \left[4\int_0^\infty r^3 e^{-Zr/a_0} dr - \frac{4Z}{a_0}\int_0^\infty r^4 e^{-Zr/a_0} dr + \frac{Z^2}{a_0^2}\int_0^\infty r^5 e^{-Zr/a_0} dr\right]$$

2 pts

and $\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}}$ (Atkins inside front cover)

$$\text{so } \langle r\rangle_{2s} = \frac{1}{8}\left(\frac{Z}{a_0}\right)^3\left[4\cdot 3!\left(\frac{a_0}{Z}\right)^4 - \frac{4Z}{\cancel{a_0}}\cdot 4!\left(\frac{a_0}{Z}\right)^{\cancel{5}\,4} + \frac{Z^2}{\cancel{a_0^2}}5!\left(\frac{a_0}{Z}\right)^{\cancel{6}\,4}\right]$$

$$= \frac{1}{8}\left(\frac{Z}{\cancel{a_0}}\right)^{\cancel{3}}\left(\frac{a_0}{Z}\right)^{\cancel{4}}\left[24 - 96 + 120\right]$$

$$= \frac{1}{\cancel{8}}\left(\frac{a_0}{Z}\right)(\cancel{48}\,6)$$

2 pts for calculating integrals

$$= \boxed{\frac{6a_0}{Z}}$$

(right units!) 1 pt

$$R_{21} = \frac{1}{\sqrt{24}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2} \quad \text{and } \rho = \frac{Z}{a_0}r \text{ (as above)}$$

(2p orbital)

$$\langle r\rangle_{2p} = \int_0^\infty R_{21}^2 r^3\,dr = \frac{1}{24}\left(\frac{Z}{a_0}\right)^3\int_0^\infty \rho^2 e^{-\rho} r^3\,dr$$ 2 pts

$$= \frac{1}{24}\left(\frac{Z}{a_0}\right)^3\int_0^\infty \frac{Z^2}{a_0^2} r^2 e^{-Zr/a_0} r^3\,dr$$ 1 pt

$$= \frac{1}{24}\left(\frac{Z}{a_0}\right)^5\int_0^\infty r^5 e^{-Zr/a_0}\,dr = \frac{1}{24}\left(\frac{Z}{\cancel{a_0}}\right)^{\cancel{5}}5!\left(\frac{a_0}{Z}\right)^{\cancel{6}}$$ 1 pt

$$\boxed{\langle r\rangle_{2p} = \frac{5a_0}{Z}}$$ 1 pt

∴ $\boxed{\text{on average, a 2p } e^- \text{ in H is closer to the nucleus.}}$ 1 pt