ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS, SPRING 2006, H.W. WEEK 1

Chapter 13

8. (a) $\hat{L}^2 \psi_{532} = l(l+1)\hbar^2 \psi_{532}$

$\psi_{532} \Rightarrow n=5, \; l=3, \; m_l=2$

$= 3(3+1)\hbar^2 \psi_{532} = 12\hbar^2 \psi_{532}$

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

$|L| = \underline{\underline{\sqrt{12}\,\hbar}}$

(b) $\hat{L}_z \psi_{532} = m_l \hbar \psi_{532} = 2\hbar \psi_{532}$

$|L_z| = \underline{\underline{2\hbar}}$

(c) # of radial nodes $= n-l-1 = 5-3-1 = \underline{\underline{1}}$

# of angular nodes $= l = \underline{\underline{3}}$

(Don't worry about the coordinates)

(d)

$$E = \frac{-Z^2 e^4 \mu}{2(4\pi\varepsilon_0)^2 n^2 \hbar^2} = \frac{-Z^2 e^4 m_e}{2(4\pi\varepsilon_0)^2 n^2 \hbar^2}$$

$$= -13.6\,\text{eV}\left(\frac{Z^2}{n^2}\right)$$

for H atom $Z=1$

for ψ_{532} $n=5$

$$E = -13.6\,eV \left(\frac{1}{25}\right) \cdot \frac{(0.5\text{ Hartree})}{13.6\,eV}$$

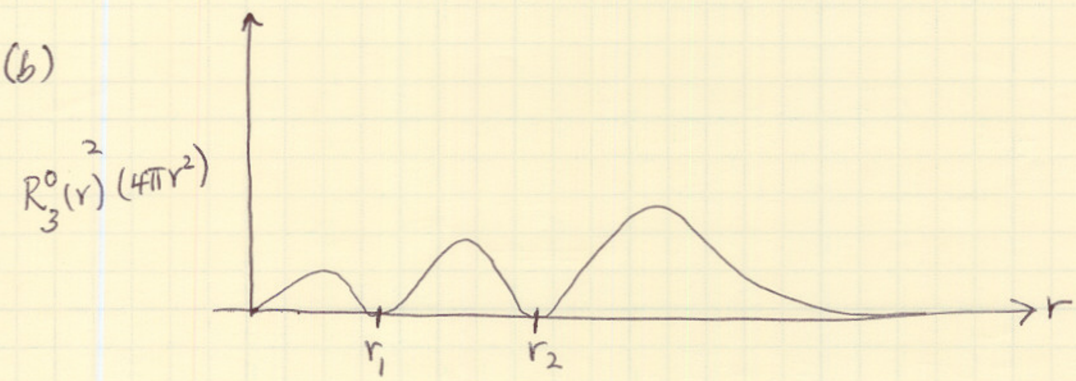
$$= \underline{\underline{-\,0.02\text{ Hartree}}}$$

(e) degeneracy $= n^2 = \underline{\underline{25}}$

(18) (a) $R_3^0(r)$ $\quad n = 3 \quad l = 0 \quad$ # of radial nodes $= n - l - 1$

$= 3 - 0 - 1 = \underline{\underline{2}}$

(b)



Nodes occur at r_1 and r_2 when $R_3^0(r)^2 = 0$

$$\Rightarrow R_3^0(r) = 0$$

$$R_3^0(r) = \frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2}\left[6 - 6\left(\frac{2Zr}{3a_0}\right) + \left(\frac{2Zr}{3a_0}\right)^2\right]e^{-Zr/3}$$

$R_3^0(r) = 0$ when $\quad 6 - 6\left(\frac{2Zr}{3a_0}\right) + \left(\frac{2Zr}{3a_0}\right)^2 = 0$

$$6 - \frac{4Zr}{a_0} + \frac{4Z^2r^2}{9a_0^2} = 0$$

$$\left(\frac{4Z^2}{9a_0^2}\right) r^2 - \left(\frac{4Z}{a_0}\right) r + 6 = 0$$

$$\therefore r = \frac{\left(\frac{4Z}{a_0}\right) \pm \sqrt{\left(\frac{4Z}{a_0}\right)^2 - 4\left(\frac{4Z^2}{9a_0^2}\right)(6)}}{\left(\frac{8Z^2}{9a_0^2}\right)}$$

for hydrogen $Z = 1$

$$r = \frac{\frac{4}{a_0} \pm \sqrt{\frac{16}{a_0^2} - \frac{32}{3a_0^2}}}{\left(\frac{8}{9a_0^2}\right)} = \frac{\frac{4}{a_0} \pm \frac{1}{a_0}\sqrt{16 - \frac{32}{3}}}{\frac{8}{9a_0^2}}$$

$$= \frac{4 \pm \frac{4}{\sqrt{3}}}{\frac{8}{9a_0}} = \frac{9a_0}{8} \cdot 4\left(1 \pm \frac{1}{\sqrt{3}}\right)$$

$r = 1.902\, a_0$ and $7.098\, a_0$

$\underline{\underline{r_1 = 1.902 \text{ Bohr}}}$ $\underline{\underline{r_2 = 7.098 \text{ Bohr}}}$ Can be expressed in Å also.

(22) (a) $E = -13.6\,\text{eV}\left(\dfrac{Z^2}{n^2}\right)$ for the 3d state $n = 3$ $Z = 1$

$$E = -13.6\,\text{eV}\left(\frac{1}{9}\right) \times \left(\frac{0.5\ \text{Hartree}}{13.6\,\text{eV}}\right) = \underline{\underline{0.0556\ \text{Hartree}}}$$

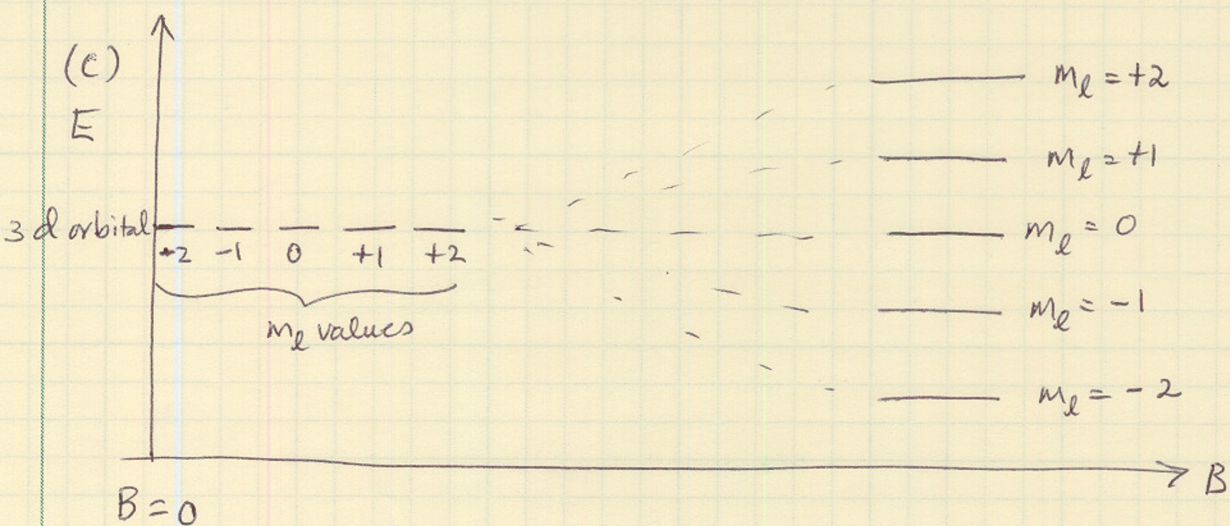
(b) For a 3d orbital $n = 3$ $l = 2$ $m_l = -2, -1, 0, 1, 2$

$$\hat{L}_z \psi_{3d} = m_l \hbar \psi_{3d}$$

$$= \left.\begin{array}{l} -2\hbar\,\psi_{3d} \\ -\hbar\,\psi_{3d} \\ 0 \\ \hbar\,\psi_{3d} \\ 2\hbar\,\psi_{3d} \end{array}\right\}$$

Possible values for L_z are $\underline{\underline{-2\hbar, -\hbar, 0, \hbar, 2\hbar}}$

(c)



The added energy term due to the external magnetic field B $\Big\}$ $= \mu_B \cdot B \cdot m_l$ where μ_B = Bohr magneton

$$\mu_B B = (9.274 \times 10^{-24}\ J T^{-1})(10^5 \text{ gauss})\left(\frac{1\,T}{10{,}000 \text{ gauss}}\right)$$

$$= 9.274 \times 10^{-23}\ J$$

$\therefore$ energy of the level will change as follows

m_l	energy change	
$+2$	$2(9.274 \times 10^{-23}\ J)$	$= 1.855 \times 10^{-22}\ J$
$+1$	$1(9.274 \times 10^{-23}\ J)$	$= 9.274 \times 10^{-23}\ J$
0	$0(9.274 \times 10^{-23}\ J)$	$= 0\ J$
-1	$-1(9.274 \times 10^{-23}\ J)$	$= -9.274 \times 10^{-23}\ J$
-2	$-2(9.274 \times 10^{-23}\ J)$	$= -1.855 \times 10^{-22}\ J$

Homework Sheet

(14) $$\hat{S}_z \alpha = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{2\times 2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}_{2\times 1} = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix}_{2\times 1} = \underline{\underline{\frac{1}{2}\alpha}}$$

$$\hat{S}_z \beta = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{2\times 2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}_{2\times 1} = \frac{1}{2}\begin{pmatrix} 0 \\ -1 \end{pmatrix}_{2\times 1} = -\frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \underline{\underline{-\frac{1}{2}\beta}}$$

a

(24) $\hat{L}^2 \psi = l(l+1)\hbar^2 \psi$

$\therefore |L^2| = l(l+1)\hbar^2$

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

ψ_{2p} $l = 1$ $m_l = -1, 0, +1$

$\hat{L}_z \psi_{2p} = m_l \hbar \psi_{2p} = -\hbar \psi_{2p}$

0

$\hbar \psi_{2p}$

$|L_z| = \underline{\underline{-\hbar, 0, \hbar}}$

ψ_{3d} $l = 2$ $m_l = -2, -1, 0, 1, 2$

$\hat{L}_z \psi_{3d} = m_l \hbar \psi_{3d} = -2\hbar \psi_{3d}$

$-\hbar \psi_{3d}$

0

$\hbar \psi_{3d}$

$2\hbar \psi_{3d}$

$|L_z| = \underline{\underline{-2\hbar, -\hbar, 0, \hbar, 2\hbar}}$

6

25 $\hat{L}^2 \psi_{3s} = l(l+1)\hbar^2 \psi_{3s}$ $\quad l=0$ for ψ_{3s}

$= 0$

$|\vec{L}| = \underline{0}$

$\hat{L}^2 \psi_{3p} = l(l+1)\hbar^2 \psi_{3p}$ $\quad l=1$ for ψ_{3p}

$= 2\hbar^2 \psi_{3p}$

$|L^2| = 2\hbar^2 \qquad |L| = \underline{\underline{\sqrt{2}\,\hbar}}$

$\hat{L}^2 \psi_{3d} = l(l+1)\hbar^2 \psi_{3d}$ $\quad l=2$ for ψ_{3d}

$= 6\hbar^2 \psi_{3d}$

$|L^2| = 6\hbar^2 \qquad |L| = \underline{\underline{\sqrt{6}\,\hbar}}$

Orbital	# of radial nodes = $n-l-1$	# of angular nodes = l
ψ_{3s}	$3-0-1 = 2$	0
ψ_{3p}	$3-1-1 = 1$	1
ψ_{3d}	$3-2-1 = 0$	2

C

(28) In the presence of a magnetic field

$$\hat{H} = \hat{H}_0 + \frac{eB}{2m_e}\hat{L}_z + \frac{g_e eB}{2m_e}\hat{S}_z$$

$$\hat{H}\psi_{1s} = E\psi_{1s}$$

$$\left[\hat{H}_0 + \frac{eB}{2m_e}\hat{L}_z + \frac{g_e eB}{2m_e}\hat{S}_z\right]\psi_{1s} = E\psi_{1s}$$

$$\hat{H}_0\psi_{1s} + \frac{eB}{2m_e}\hat{L}_z\psi_{1s} + \frac{g_e eB}{2m_e}\hat{S}_z\psi_{1s} = E\psi_{1s} \quad \text{—(1)}$$

$$\hat{H}_0\psi_{1s} = \frac{-Z^2e^4\mu}{2(4\pi\varepsilon_0)^2n^2\hbar^2}\psi_{1s} \qquad Z=1,\ n=1$$

$$= -13.6\,eV\left(\frac{Z^2}{n^2}\right)\psi_{1s} = -13.6\,eV(\psi_{1s}) \quad \text{—(2)}$$

$$\frac{eB}{2m_e}\hat{L}_z\psi_{1s} = \left(\frac{eB}{2m_e}\right)m_l\hbar\psi_{1s} \qquad m_l = 0 \text{ for } \psi_{1s}$$

$$= 0 \quad \text{—(3)}$$

$$\frac{g_e eB}{2m_e}\hat{S}_z\psi_{1s} = \left(\frac{g_e eB}{2m_e}\right)m_s\hbar\psi_{1s} \qquad m_s = \pm\frac{1}{2} \text{ for } \psi_{1s}$$

$$= \frac{g_e eB}{2m_e}\left(\pm\frac{1}{2}\hbar\right)\psi_{1s} \quad \text{—(4)}$$

$$\hat{H}\psi_{1s} = \left[-13.6\,eV + 0 + \frac{g_e eB}{2m_e}\left(\pm\frac{1}{2}\hbar\right)\right]\psi_{1s}$$

$$\frac{g_e eB}{2m_e}\hbar = g_e \underbrace{\left(\frac{e\hbar}{2m_e}\right)}_{\mu_B} B = g_e \mu_B B$$

$$= (2.002322)(9.274\times10^{-24}\,J\,T^{-1})(1\,T)$$

$$= 1.85695\times10^{-23}\,J \times \left(\frac{1\,eV}{1.602\times10^{-19}\,J}\right)$$

$$= 1.15915\times10^{-4}\,eV$$

$$\hat{H}\psi_{1s} = \left[-13.6\,eV + 1.15915\times10^{-4}\,eV\left(\pm\frac{1}{2}\right)\right]\psi_{1s}$$

$$= \left(-13.6\,eV \pm 5.7957\times10^{-5}\,eV\right)\psi_{1s}$$

∴ The two energies for ψ_{1s} under a 1T magnetic field are;

$$E_1 = \left(-13.6 + 5.7957\times10^{-5}\right)eV = -13.5999\,eV$$

$$E_2 = \left(-13.6 - 5.7957\times10^{-5}\right)eV = -13.6001\,eV$$

$$\therefore \Delta E = E_1 - E_2 = \left(-13.5999 + 13.6001\right)eV =$$

$$= \underline{\underline{1.5796\times10^{-4}\,eV}}$$

(e)

$$\Delta E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{\Delta E}$$

$$\lambda = \frac{(6.626 \times 10^{-34}\ Js)(2.99 \times 10^{8}\ ms^{-1})}{(1.5796 \times 10^{-4}\ eV)} \times \left(\frac{eV}{1.602 \times 10^{-19} J}\right)$$

$$= 7.82929 \times 10^{-3}\ m \times \frac{10^{3}\ mm}{m}$$

$$= \underline{\underline{7.82927\ mm}}$$

<u>Microwave region</u>

(30) $H \quad 1s^1 \qquad H^- = \underline{\underline{1s^2}}$

$Li \quad 1s^2 2s^1 \qquad Li^+ = \underline{\underline{1s^2}}$

$O \cdot 1s^2 2s^2 2p^4 \qquad O^{2-} = \underline{\underline{1s^2 2s^2 2p^6}}$

$F \quad 1s^2 2s^2 2p^5 \qquad F^- = \underline{\underline{1s^2 2s^2 2p^6}}$

$Na \quad 1s^2 2s^2 2p^6 3s^1 \qquad Na^+ = \underline{\underline{1s^2 2s^2 2p^6}}$

$Mg \quad 1s^2 2s^2 2p^6 3s^2 \qquad Mg^{2+} = \underline{\underline{1s^2 2s^2 2p^6}}$

(31)

1s	$2\bar{e}$
2s	$2\bar{e}$
2p	$6\bar{e}$
3s	$2\bar{e}$
3p	$6\bar{e}$
3d	$10\bar{e}$

(b)

effective ~~atomic~~ nuclear charge $= Z'$

$$E = -\frac{Z^2 e^4 \mu^2}{2(4\pi\varepsilon_0)^2 n^2 \hbar^2} = -13.6\,\text{eV}\left(\frac{Z'^2}{n^2}\right)$$

$$\therefore \text{I.P.} = 13.6\,\text{eV}\left(\frac{Z'^2}{n^2}\right) = 5.138\,\text{eV}$$

$$Z'^2 = \left(\frac{5.138\,\text{eV}}{13.6\,\text{eV}}\right)(9) = 3.400$$

$$Z' = \underline{\underline{1.8439}}$$

Similarly for $\underline{\underline{K}}$ $n = 4$ I.P. $= 4.341$ eV

$$Z'^2 = \left(\frac{4.341\,\text{eV}}{13.6\,\text{eV}}\right) 16 = 5.07529$$

$$Z' = \underline{\underline{2.2528}}$$

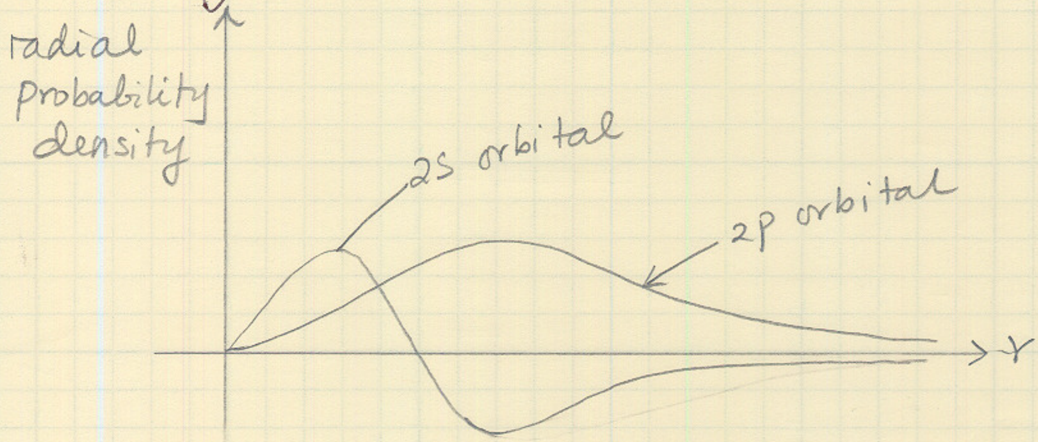
$\underline{\underline{\text{Rb}}}$ I.P. $= 4.166$ eV $n = 5$

$$Z'^2 = \left(\frac{4.166\,\text{eV}}{13.6\,\text{eV}}\right) 25 = 7.65809$$

$$Z' = \underline{\underline{2.7673}}$$

37 B $1s^2\ 2s^2\ 2p^1$ Be $1s^2\ 2s^2$

The valence electron in B is in the 2p orbital. The valence electron in Be is in the 2s orbital. The 2s orbital penetrates the nucleus more than the 2p orbital as seen in the following probability density diagram.



Therefore the 2s valence electron is more closely held by the nucleus compared with the 2p valence electron, making the 2s valence electron harder to remove.

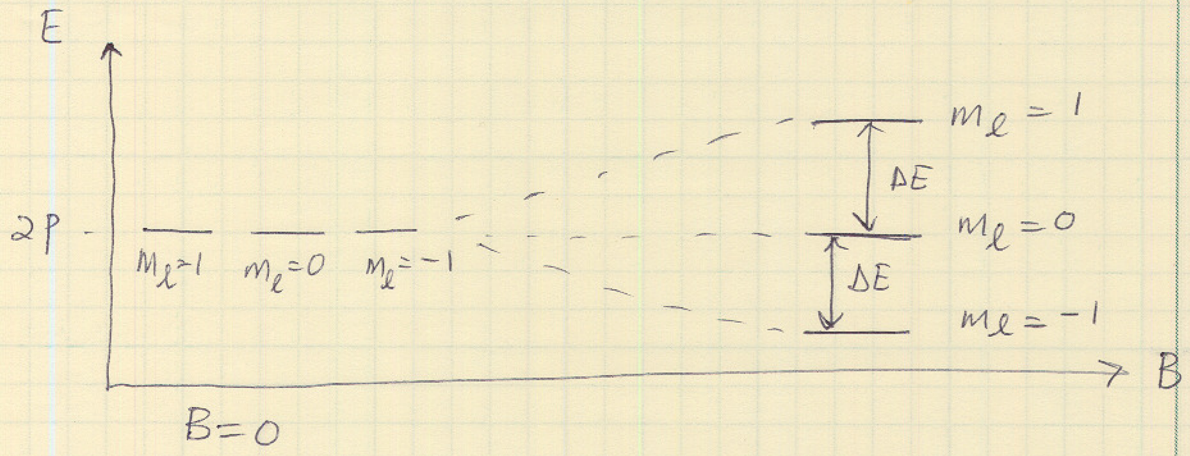
$\therefore$ I.E. of Be > I.E. of B

O $1s^2\ 2s^2\ 2p^4$ N $1s^2\ 2s^2 2p^3$

Both atoms have valence electrons in the 2p orbitals. There is higher electron-electron repulsion in oxygen (since it has four p electrons

$\therefore$ I.E. of O < I.E. of N.

(58)



splitting $= \Delta E \quad \hat{H}_B \psi_{2p_{-1}} = \dfrac{eB}{2m_e} \hat{L}_z \psi_{2p_{\pm 1}}$

$$= \frac{eB}{2m_e} m_\ell \hbar \, \psi_{2p_{\pm 1}}$$

$$= \left(\frac{e\hbar}{2m_e}\right) B m_\ell \psi_{2p} = \mu_B B m_\ell \psi_{2p_{\pm 1}}$$

$$\therefore \Delta E = \mu_B B m_\ell$$

$$= (9.274 \times 10^{-24}\ \mathrm{J\,T^{-1}})(10\ \mathrm{T})(\pm 1)$$

$$= 9.274 \times 10^{-24}\ \mathrm{J}$$ (lower or higher than when $B = 0$)

$$9.274 \times 10^{-24}\ \mathrm{J} \times \frac{\mathrm{eV}}{1.602 \times 10^{-19}\ \mathrm{J}} = \underline{\underline{5.789 \times 10^{-5}\ \mathrm{eV}}}$$

$$9.274 \times 10^{-24}\ \mathrm{J} \times \frac{\mathrm{kJ}}{10^3\ \mathrm{J}} \frac{(6.02 \times 10^{23}\ \mathrm{mol^{-1}})}{1\ \text{atom}} = \underline{\underline{5.583 \times 10^{-3}\ \mathrm{kJ\,mol^{-1}}}}$$

$$kT = (1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})(10^{-3}\ \mathrm{kJ/J}) = 4.115 \times 10^{-24}\ \mathrm{kJ}$$

$$= 4.115 \times 10^{-24}\ kJ \times 6.02 \times 10^{23}\ mol^{-1}$$

$$= \underline{\underline{2.477\ kJ\ mol^{-1}}}$$

$kT >$ splitting

$\therefore$ all three m_l levels will be occupied at room temperature.

(59) $$\hat{L}^2 \psi_{4s} = l(l+1)\hbar^2 \psi_{4s} = \underline{\underline{0}}\ \psi_{4s} \qquad l = 0 \text{ for } \psi_{4s}$$

$$L = \underline{\underline{0}}$$

$$\hat{L}^2 \psi_{4p} = l(l+1)\hbar^2 \psi_{4p} = 2\hbar^2 \psi_{4p}$$

$$|L^2| = 2\hbar^2$$

$$|L| = \underline{\underline{\sqrt{2}\,\hbar}}$$

$$\hat{L}^2 \psi_{4d} = 2(2+1)\hbar^2 \psi_{4d} = 6\hbar^2 \psi_{4d}$$

$$\underline{\underline{|L| = \sqrt{6}\,\hbar}}$$

$$\hat{L}^2 \psi_{4f} = 3(3+1)\hbar^2 \psi_{4f} = 12\hbar^2 \psi_{4f}$$

$$|L| = \underline{\underline{\sqrt{12}\,\hbar}}$$

radial nodes

ψ_{4s} $4-0-1 = 3$

ψ_{4p} $4-1-1 = 2$

ψ_{4d} $4-2-1 = 1$

ψ_{4f} $4-3-1 = 0$