## SUMMARY OF MATHEMATICS OF HYDROGEN ATOM SOLUTIONS

## CHEMISTRY 163A

1. $\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

2. (a)

$$\left.\begin{array}{l} \Phi_{|m|}(\varphi) = \dfrac{1}{\sqrt{2\pi}} e^{+i|m|\varphi} \\ \phantom{\Phi_{|m|}(\varphi) =} \dfrac{1}{\sqrt{2\pi}} e^{i-|m|\varphi} \end{array}\right\} \text{complex solutions}$$

or

(b)

$$\left.\begin{array}{l} \Phi_{|m|}(\varphi) = \dfrac{1}{\sqrt{\pi}} \cos|m|\varphi \\ \phantom{\Phi_{|m|}(\varphi)} = \dfrac{1}{\sqrt{\pi}} \sin|m|\varphi \\ \Phi_0(\varphi) = \dfrac{1}{\sqrt{2\pi}} \end{array}\right\} \text{real solutions}$$

(a) $|m|$ = 0, 1, 2, 3 for single valuedness at $\varphi_0$ and $\varphi_0 + 2\pi$: $\Phi(\varphi_0) = \Phi(\varphi_0 + 2\pi)$

(b) $|m|$ = number of nodes as you go around azimuth (for real solutions).

3. $$\Theta_{\ell|m|}(\theta) = B(\sin^2\theta)^{|m|/2} \sum_{k=0}^{k'} a_k (\cos\theta)^k$$

(a) Must terminate polynomial in $(\cos\theta)^k$ at $k = k'$ for $\Theta(\theta)$ to be finite at $\theta = 0, \pi$.

(b) have all $a_k$, $k$ = even, <u>or</u> $a_k$, $k$ = odd must be zero.

(c) From recursion and termination $k' = \ell - |m|$

(d) Since $k'$ is zero or *positive* integer $\ell$ must be integer with $\ell \geq |m|$

(e) Thus for given $\ell$, $m = 0, \pm 1, \pm 2 \ldots \pm\ \ell$ (these $m$ refer to $m$ in complex $e^{im\varphi}$ solutions, but the number of $\Phi$ solutions for a given $\ell$, $[2\ell + 1]$, is same for real and complex).

(f) Since order of polynomial in $(\cos\ \theta)^k$ is $k' = \ell - |m|$, there will be $\ell - |m|$ zeros (nodes) in $\Theta_{\ell|m|}$ (note, zeroes from $\sin^2\theta = 0$, for $|m| \neq 0$, coincide with the $xz$ nodal plane of $\Phi_{|m|} = \dfrac{1}{\sqrt{\pi}}\sin|m|\varphi$).

(g) Total **angular nodes** ($\Theta$ and $\Phi$) = $|m| + \ell - |m| = \ell$.

4. $$R_{n,\ell} = R_{E,\ell} = B\exp\left\{-\left[\frac{2(-E)4\pi\varepsilon_0}{a_0 e^2}\right]^{1/2} r\right\} r^{\ell}\sum_{q=0}^{q'} b_q r^q$$

$$E = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2} = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0\left(\frac{a_0}{Z}\right)}\frac{1}{n^2} = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 a_Z}\frac{1}{n^2}$$

$$a_0 = \frac{h^2\varepsilon_0}{\pi\mu e^2} \qquad a_Z = \frac{a_0}{Z} \qquad n^2\left(\frac{a_0}{Z}\right) = \left[\frac{Ze^2}{8\pi\varepsilon_0(-E)}\right]$$

substituting $\frac{n^2 a_0}{Z^2} = \frac{e^2}{8\pi\varepsilon_0(-E)}$ into (4)

$$R_{n\ell} = B\exp\left\{-\left[\frac{Z^2}{a_0^2 n^2}\right]^{1/2} r\right\} r^{\ell}\sum_{q=0}^{q'} b_q r^q$$

$$R_{n\ell} = B\, e^{-\left(\frac{Z}{a_0 n}\right)r}\, r^{\ell}\sum_{q=0}^{q'} b_q r^q$$

(a) Must terminate series in $r^q$ at $q'$ for $\lim R(r) \to 0$ as $r \to \infty$.

(b) $q' = n - \ell - 1$ for termination (from recursion relationship).

(c) $q'$ zero or positive integer $\quad n \geq \ell + 1$
$n$ is positive integer 1, 2, 3,…

(d) Thus $n \geq \ell + 1$ for given $n$

and $\ell$ can have the $n$ values 0, 1, 2, . . . $n - 1$.

(e) Since the order of the polynomial in $r^q$ is $q'$ there will be $q' = n - \ell - 1$ zeroes (radial nodes).

(f) **Total nodes** (radial + angular) = $n - \ell - 1 + \ell = \mathbf{n - 1}$.