Summary of Mathematics of Hydrogen Atom Solutions

Chemistry 163A

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

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

or

(b)
$$\left.\begin{array}{l} \Phi_{|m|}(\phi) = \frac{1}{\sqrt{\pi}}\cos|m|\phi \\ \qquad\quad = \frac{1}{\sqrt{\pi}}\sin|m|\phi \\ \Phi_0(\phi) = \frac{1}{\sqrt{2\pi}} \end{array}\right\} \begin{array}{l}\text{real} \\ \text{solutions}\end{array}$$

(a) $|m| = 0, 1, 2, 3$ for single valuedness at ϕ_0 and $\phi_0 + 2\pi$: $\Phi(\phi_0) = \Phi(\phi_0 + 2\pi)$

(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, or a_k, k = odd must be zero.

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

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

(e) Thus for given ℓ, $m = 0, \pm1, \pm2 \ldots \pm \ell$ (these m refer to m in complex $e^{im\phi}$ solutions, but the number of Φ solutions for a given ℓ, $[2\ell + 1]$, 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 $\Phi_{|m|} = \frac{1}{\sqrt{\pi}}\sin|m\phi|$).

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

$$E = -\frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{Z^2 e^2}{8\pi e_0 a_0}\frac{1}{n^2} = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0\left(\frac{a_0}{Z}\right)}\frac{1}{n^2} = -\frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0 a_Z}\frac{1}{n^2}$$

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

substituting $\dfrac{n^2 a_0}{Z^2} = \dfrac{e^2}{8\pi\varepsilon_0(-E)}$ 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 $\Rightarrow n \geq \ell + 1$
$\Rightarrow n$ is positive integer 1, 2, 3,…

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

and ℓ 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) = $n - \ell - 1 + \ell = \mathbf{n - 1}$.