The Radial Schrödinger Equation for Hydrogen-like Atoms **Chemistry BC3253x**

Separation of variables **$\Psi(r, \theta, \varphi) = R(r)\, Y_{\ell,m}(\theta,\varphi)$** leads to the Radial Schrödinger equation

$$\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left[\frac{2m_e}{\hbar^2}\left(E + \frac{ZA}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right]R(r) = 0 \tag{1}$$

where $A = e^2/4\pi\varepsilon_0$. We are also taking $\mu = m_e$.

As in the solution of the simple harmonic oscillator, dimensionless variables make the equation look a but simpler. Since the Bohr theory gives correct energies, the Bohr energy formula is the basis for the first equation below, which trades the old variable E for a new one, n. It is important to understand that <u>we are not assuming that n is an integer</u>; this will come as a conclusion later, when we apply proper boundary conditions. Then introduce reduced variables for E and r, using the Hartree and Bohr, respectively:

Let $E = -\frac{m_e A^2 Z^2}{2\hbar^2 n^2} = \frac{Z^2}{2n^2}E_h$ this replaces **E** with a new dimensionless variable **n**

and $r = x\left(\frac{n\hbar^2}{2m_e AZ}\right) = x\frac{n}{Z}a_0$ this replaces **r** with a new dimensionless variable **x**

Substituting, the Schrödinger equation becomes:

$$\frac{d^2R}{dx^2} + \frac{2}{x}\frac{dR}{dx} + \left[-\frac{1}{4} + \frac{n}{x} - \frac{\ell(\ell+1)}{x^2}\right]R(x) = 0 \tag{2}$$

As in the SHO solution, look first at the <u>asymptotic behavior</u> of this differential equation. When x gets very large, all terms with x in the denominator get very small.

The asymptotic differential equation is $\frac{d^2R}{dx^2} - \frac{R}{4} = 0$

The general solution to this is $R = C_1 \exp(-x/2) + C_2 \exp(+x/2)$

If the function is to be square-integrable, C_2 must be zero. Thus $R \to C_1 \exp(-x/2)$

We write the as yet unknown function R(x) in terms of a new unknown function g(x) as follows: **$R(x) = g(x)\, x^\ell \exp(-x/2)$.**

Why the x^ℓ factor? Since we don't know g(x), it is permissible to write any form we please. If we left out the x^ℓ term, then g(x) would be different. But the reason for putting in the x^ℓ is that the $\ell(\ell+1)$ factor in the equation is suggestive of taking a second derivative of x^ℓ. Substitute into equation (2) to get a new equation for g(x):

$$x\frac{d^2g}{dx^2} + [2(\ell+1) - x]\frac{dg}{dx} + [n - \ell - 1]g = 0 \tag{3}$$

Write a series solution: $g(x) = \sum_{k=0}^{\infty} a_k x^k$ and substitute into (3):

$$\sum_{j=2} j(j-1)a_j x^{j-1} + (2\ell+2)\sum_{m=1} m a_m x^{m-1} - \sum_{p=1} p a_p x^p + [n-\ell-1]\sum_{s=1} a_s x^s = 0\,. \tag{4}$$

In equation (4), different indices are used for each sum to emphasize that a summation index is a dummy variable.

Observe, for example, that $\sum_{j=2} j(j-1)a_j x^{j-1} = \sum_{k=0} k(k+1)a_k x^k$ where k = j–1.

Collect all terms with the same power of x:

$$\sum_{t=0} x^t \left\{a_{t+1}[t(t+1)+(2\ell+2)(t+1)] + a_t[-t+n-\ell-1]\right\} = 0 \qquad (5)$$

If this equation is to be true for any value of x, all coefficients must be zero. This leads to a recursion relation for the coefficients:

$$a_{t+1} = a_t \left\{\frac{t+1+\ell-n}{(t+1)(2\ell+2+t)}\right\}$$

Wavefunctions must be square-integrable, so R(x) must go to zero as $x \to \infty$. But a careful examination of this polynomial (looking at ratios of coefficients) shows that the function will diverge, even with the exp(–x/2) factor, if the power series is infinite. Therefore we must truncate the expansion at some value of t by setting the numerator to zero. Since t is an integer and ℓ is an integer, this forces n to be an integer; until now it was simply a scaled variable related to energy. Since $t \geq 0$, n must be greater that or equal to $\ell+1$. When we solved the angular equation, we found that $\ell \geq 0$, so $n \geq 1$. The quantum number n takes values 1, 2, 3, … This, then, gives the same equation for the energy levels of the H atom as were given by the Bohr theory.

Integral quantum number n is, of course, exactly what the Bohr theory took as a postulate. The important difference is that here it is a consequence of the mathematics: the boundary conditions of the problem force the quantization. Note that, while the energy depends on the quantum number n only, the radial wavefunctions depend on both n and ℓ.

$R_{n,\ell}(x) = g(x)\, x^{\ell} \exp(-x/2)$. What do these radial wavefunctions look like? g(x) is a polynomial whose coefficients are calculated using the recursion relation. We can arbitrarily set $a_0 = 1$, since the whole function will be normalized at the end. The recursion relation involves adjacent coefficients of the expansion, so no other assumptions are required. Again, the resulting polynomials g(x) were known. They are the **Associated Laguerre polynomials,** and (with different normalization) written $L_{n+1}^{2\ell+1}(x)$. A few examples of g(x) are tabulated below. Tables of $L_{n+1}^{2\ell+1}(x)$ may be found in mathematical handbooks.

n	ℓ	**g(x)**
1	0	1
2	0	$1 - x/2$
2	1	1
3	0	$1 - x + x^2/6$
3	1	$1 - x/4$
3	2	1