Hydrogen-like Wave Functions

Define

\[ \rho = \frac{2Z}{na_B} r; \quad a_B = \frac{\hbar^2}{4\pi^2 \mu e^2}, \quad \mu = \frac{m_e m_p}{m_e + m_p} \] (1.1)

The Hydrogen wave function separates into

\[ \psi_{n,\ell,m} (r, \theta, \phi) = R_{n,\ell} (r) \Theta_{\ell,m} (\theta) \Phi_m (\phi) \] (1.2)

The last term is

\[ \Phi_m (\phi) = \frac{1}{\sqrt{2\pi}} \exp( j m \phi) \] (1.3)

The middle term is

\[ \Theta_{\ell,m} (\theta) = \left\{ \frac{(2\ell + 1)(\ell - |m|)!}{2(\ell + |m|)!} \right\} \rho^{|m|} (\cos \theta) \] (1.4)

The P in (1.4) is the associated Legendre function. Press\(^2\) gives a short stable code for calculating these. He also gives a warning that "most of the recurrences involving m are unstable, and so dangerous for numerical work.\(^{1}\)

\[ R_{n,\ell} (r) = -\sqrt{\left[ \frac{(2Z)^3}{n a_B} \right] \frac{(n - \ell - 1)!}{2n (n + \ell)!^3} } \times \exp \left( -\frac{\rho}{2} \right) \rho^{\ell} L_{n+\ell}^{2\ell+1} (\rho) \] (1.5)

The associated Laguerre polynomial is

\[ L_{n+\ell}^{2\ell+1} (\rho) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{(n + \ell)!^2}{(n - \ell - 1 - k)!(2\ell + 1 + k)!k!} \rho^k \]

There appear to be no warnings about this function.

The 1s wave function is

\[ \psi_{1,0,0} (\vec{r}) = (Z / a_B)^{3/2} 2 \exp \left( -\frac{Zr}{a_B} \right) \frac{\sqrt{2}}{2 \sqrt{2\pi}} \] (1.6)

The 2s wave function is

\[ \psi_{2,0,0} (\vec{r}) = \left( \frac{Z / a_B}{2\sqrt{2}} \right) \left( 2 - \frac{Zr}{a_B} \right) \times \exp \left( -\frac{Zr}{2a_B} \right) \frac{\sqrt{2}}{2 \sqrt{2\pi}} \] (1.7) equation 1.7

The 3s wave function is

\[ \psi_{3,0,0} (\vec{r}) = \left( \frac{Z / a_B}{9\sqrt{3}} \right) \left( 6 - 6 \left( \frac{2Zr}{3a_B} \right) \left( \frac{2Zr}{3a_B} \right)^2 \right) \times \exp \left( -\frac{Zr}{3a_B} \right) \frac{\sqrt{2}}{2 \sqrt{2\pi}} \] (1.8)

Comment

The ground state H wave function in the limit as \( r \to \infty \) is

\[ \psi \to C \exp (-r) \]

The 2s Li wave function in the limit as \( r \to \infty \) is

\[ \psi \to C r \exp \left( -\frac{Z_{\text{eff}} r}{2} \right) \]

The 3s Na wave function in the limit as \( r \to \infty \) is

\[ \psi \to C r^2 \exp \left( -\frac{Z_{\text{eff}} r}{3} \right) \]

In each case the \( Z_{\text{eff}} \) is on the order of 1, owing to the fact that the inner shells are filled. Note that the higher order states are beginning to have a constant wave function in the asymptotic regions.

In the K shell region \( Z_{\text{eff}} = 11 \). In the L shell region \( Z_{\text{eff}} = 9 \). In the M shell region \( Z_{\text{eff}} = 1 \).