Physics 371 Lecture 30

Hydrogenic wavefunctions

$$u(\rho) = e^{-\rho/2} \rho^{\ell+1} \sum_{j=0}^{n-\ell-1} a_j \rho^j ,$$

where
$$\frac{a_{j+1}}{a_j} = \frac{j+\ell+1-n}{(j+1)(j+2\ell+2)} .$$

The polynomial
$$h(\rho) = \sum_{j=0}^{n-\ell-1} a_j \rho^j = -L_{n+\ell}^{2\ell+1}(\rho)$$

is known as an associated Laguerre polynomial.

The Laguerre polynomials are

defined by

$$L_q(\rho) = e^{\rho} \frac{d^q}{d\rho^q}\left(\rho^q e^{-\rho}\right),$$

and the associated Laguerre polynomials are then given by

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho).$$

A few of the polynomials are:

$L_0(\rho) = 1$

$L_1(\rho) = 1 - \rho$ $\quad L_1^1(\rho) = -1$

$L_2(\rho) = 2 - 4\rho + \rho^2$ $\quad L_2^1(\rho) = -4 + 2\rho$ $\quad L_2^2(\rho) = 2$

$L_3(\rho) = 6 - 18\rho + 9\rho^2 - \rho^3$ . . . .

The radial wavefunction is

$$\psi_{n\ell}(\rho) = \frac{u_{n\ell}(\rho)}{\rho} = -A e^{-\rho/2} \rho^{\ell} L_{n+\ell}^{2\ell+1}(\rho)$$

Normalization

$$\Psi_{n\ell m}(r,\theta,\phi) = \psi_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

$$1 = \int d^3r \, |\Psi(r,\theta,\phi)|^2$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, |Y_{\ell m}(\theta,\phi)|^2 \int_0^{\infty} r^2 |\psi_{n\ell}(r)|^2 dr$$

$$= \int_0^{\infty} r^2 |\psi_{n\ell}(r)|^2 dr = \left(\frac{1}{2\lambda}\right)^3 \int_0^{\infty} \rho^2 |\psi_{n\ell}(\rho)|^2 d\rho$$

$$= \frac{A^2}{(2\lambda)^3} \int_0^{\infty} \rho^2 e^{-\rho} \rho^{2\ell} \left[L_{n+\ell}^{2\ell+1}(\rho)\right]^2 d\rho$$

Now

$$\int_0^\infty e^{-\rho} \rho^{2\ell+2} \left[L_{n+\ell}^{2\ell+1}(\rho)\right]^2 d\rho = \frac{2n\left[(n+\ell)!\right]^3}{(n-\ell-1)!}.$$

Consequently, the normalized radial wavefunction is

$$\psi_{n\ell}(r) = -\left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}\right]^{1/2} \left(\frac{2Zr}{na_0}\right)^\ell e^{-\frac{Zr}{na_0}} L_{n+\ell}^{2\ell+1}\left(\frac{2Z}{na}\right.$$

where $\frac{2Zr}{na_0} = \rho$ and

$$\boxed{a_0 = \frac{\hbar^2}{\mu e^2} \cong \frac{\hbar^2}{m_e e^2} = 0.529\ \text{Å} \ \text{(Bohr radius)}}$$

The first few hydrogenic radial wavefunctions are

$$\psi_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\psi_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$\psi_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}$$

$$\psi_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{3/2}\left(1-\frac{2Zr}{3a_0}+\frac{2(Zr)^2}{27a_0^2}\right)e^{-Zr/3a_0}$$

$$\psi_{31}(r) = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{3/2}\frac{Zr}{a_0}\left(1-\frac{Zr}{6a_0}\right)e^{-Zr/3a_0}$$

$$\psi_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

etc.

The total hydrogenic wavefunctions can now be written as

$$\Psi_{n\ell m}(r,\theta,\phi,t) = \Psi_{n\ell m}(r,\theta,\phi)e^{\frac{-iE_n t}{\hbar}}$$

$$= \psi_{n\ell}(r)\,Y_{\ell m}(\theta,\phi)\,e^{\frac{-iE_n t}{\hbar}}$$

$n = 1, 2, 3, \ldots, \infty \qquad \ell = 0, 1, \ldots, n-1$

$m = -\ell, -\ell+1, \ldots, \ell$

Putting together all the factors, the hydrogenic wave-functions are:

$$\psi_{1s} \equiv \psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$\psi_{2s} \equiv \psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$\psi_{2p} = \psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}\, e^{-Zr/2a_0}\cos\theta$$

$$\psi_{2p} = \psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}\, e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi}$$

$$\psi_{3s} \equiv \psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+\frac{2Z^2r^2}{a_0^2}\right)e^{-\frac{Zr}{3a_0}}$$

$$\psi_{3p} = \psi_{310} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}\, e^{-\frac{Zr}{3a_0}}\cos\theta$$

$$\psi_{3p} = \psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0}\, e^{-\frac{Zr}{3a_0}}\sin\theta\, e^{\pm i\phi}$$

$$\psi_{3d} = \psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \left(3\cos^2\theta - 1\right)$$

$$\psi_{3d} = \psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin\theta\cos\theta \; e^{\pm i\phi}$$

$$\psi_{3d} = \psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2 r^2}{a_0^2} e^{-\frac{Zr}{3a_0}} \sin^2\theta \; e^{\pm 2i\phi}$$

etc.

Probability density

$$\rho_{n\ell m}(\vec{r})\, d^3r = |\psi_{n\ell m}|^2 d^3r = |\psi_{n\ell m}|^2 r^2 dr\, d\Omega$$

Integrating over solid angle,

$$\int_\Omega |\psi_{n\ell m}|^2 r^2 dr\, d\Omega = |\psi_{n\ell}(r)|^2 r^2 dr \int_\Omega |Y_{\ell m}|^2 d\Omega$$

$$= |\psi_{n\ell}(r)|^2 r^2 dr$$

- The quantity $r^2 |\psi_{n\ell}(r)|^2$ is the radial probability density, the probability to find the particle in a thin shell between r and r+dr.

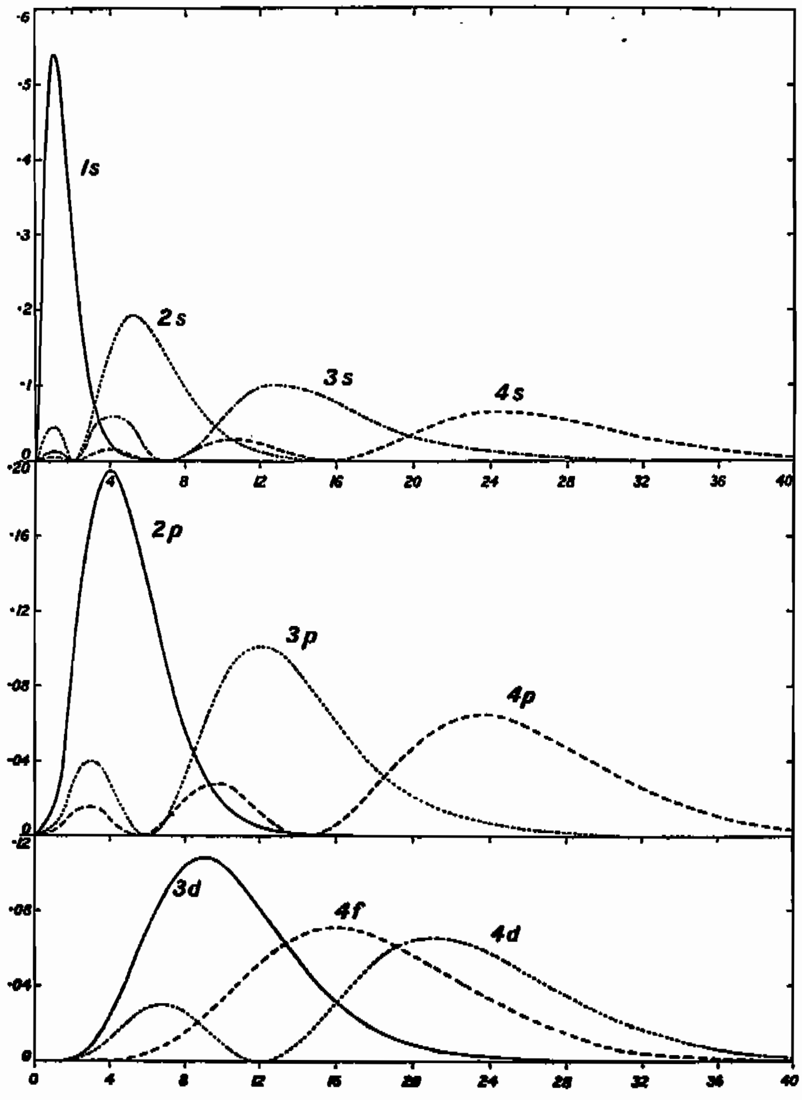

Figure 7-8 The radial probability distribution function $|rR_{n\ell}|^2$ for several values of the quantum numbers n, ℓ. (From E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1953. Used with permission.)