The Hydrogen Atom

$$H = \frac{\hat{P}_r^2}{2\mu} + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{r} \quad , \quad \frac{e^2}{\hbar c} = \alpha = \frac{1}{137}$$

$$\phi(\vec{r}) = R(r)\, Y_\ell^m(\theta,\phi)$$

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r}\right] R(r) = -E_b R(r)$$

$$E = -E_b \quad \text{where} \quad \underline{E_b > 0 \text{ - binding energy}}$$

$$R = \frac{u}{r}, \quad u(0) = 0$$

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} - \frac{2\mu}{\hbar^2}\frac{Ze^2}{r} + \frac{2\mu E_B}{\hbar^2}\right) u(r) = 0$$

$$E_B = \frac{\hbar^2 K^2}{2\mu}$$ - defines K, a typical inverse radial scale

remember $E = -E_B$

$$\rho = 2Kr$$ - this should be $\mathcal{O}(1)$

$$\lambda^2 = \left(\frac{Z}{Ka_0}\right)^2 = \frac{Z^2 \mathcal{R}}{E_B}$$

these constants appear naturally in any Coulomb hamiltonian

$$\mathcal{R} = \frac{\hbar^2}{2\mu a_0^2} \qquad a_0 = \frac{\hbar^2}{\mu e^2}$$

Rydberg constant — Bohr radius

Details

$$\frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u = 0$$

all of the 'arbitrary parameters now in one term

$$\xrightarrow[\rho\to\infty]{} \quad \frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0$$

$$u \xrightarrow[\rho\to\infty]{} e^{-\rho/2}$$

$$u = f(\rho)e^{-\rho/2}$$

$$\frac{du}{d\rho} = f'e^{-\rho/2} - \frac{1}{2}fe^{-\rho/2}$$

$$\frac{d^2u}{d\rho^2} = f''e^{-\rho/2} - f'e^{-\rho/2} + \frac{1}{4}fe^{-\rho/2}$$

$$f'' - f' + \cancel{\tfrac{1}{4}f} - \frac{\ell(\ell+1)}{\rho^2}f + \frac{\lambda}{\rho}f - \cancel{\tfrac{1}{4}f} = 0$$

$$\xrightarrow[\rho\to 0]{} \quad \frac{d^2u}{d\rho^2} - \frac{\ell(\ell+1)}{\rho^2}u \sim 0$$

$$u \xrightarrow[\rho\to 0]{} \rho^{\ell+1}$$

$$u = \rho^{l+1} e^{-\rho/2} F(\rho)$$

$$\left[\rho \frac{d^2}{d\rho^2} + (2l + 2 - \rho)\frac{d}{d\rho} - (l+1-\lambda)\right] F(\rho) = 0$$

Solve using $F(\rho) = \sum_{i=0}^{\infty} C_i \rho^i$

Recurrence relation:

$$C_{i+1} = \frac{(i+l+1) - \lambda}{(i+1)(i+2l+2)} C_i \equiv \Gamma_{il} C_i$$

The expansion will not converge unless it

terminates : $\Gamma_{i_{max} l} = 0$

$\rightarrow C_{i_{max}+1} = 0$

$$\boxed{i_{max} + l + 1 = \lambda}$$

principal quantum number:

$$n = i_{max} + \ell + 1$$

$$\lambda_n^2 = n^2 = \frac{Z^2 \mathcal{R}}{E_B}$$

$$\boxed{E_n = -E_{Bn} = \frac{Z^2 \mathcal{R}}{n^2}}$$

The energy is determined by the principle quantum number, n.

- infinite # of bound states

Laguerre Polynomials

$$u_{n\ell}(\rho) = e^{-\rho/2} \rho^{\ell+1} F_{n\ell}(\rho)$$

associated Laguerre Polynomials

$$F_{n\ell}(\rho) = A_{n\ell} \sum_{i=0}^{n-\ell-1} c_i \rho^i$$

$$C_{i+1} = \Gamma_{i\ell} C_i \, , \quad \rho \equiv 2 K_n r \, , \quad K_n = \frac{Z}{a_0 n}$$

Degeneracy

$$i_{max} \geq 0 \Rightarrow l \leq n-1$$

$$l_{max} = n-1$$

n fixes the energy, but for each n there are several degenerate states:

n	1	2	
l	0	0	1
spectroscopic notation	1S	2S	2P
m_l	0	0	-1, 0, +1
degeneracy	1	4	

$$\text{degeneracy} = n^2$$

Coulomb Eigenstates

- Bound State Wave Functions for Hydrogen

$$H_{\text{coulomb}}\,\phi_{n\ell m}(\vec{r}) = -E_B\,\phi_{n\ell m}(\vec{r})$$

$$E_B = \frac{Z^2}{n^2}\mathcal{R} = \frac{\mu (Ze^2)^2}{2\hbar^2 n^2}$$

1S $\quad \phi_{100} = \frac{2}{a_0^{3/2}} e^{-r/a_0}\, Y_0^0(\theta,\phi)$

2S $\quad \phi_{200} = \frac{2}{(2a_0)^{3/2}}\left(1-\frac{r}{2a_0}\right) e^{-r/2a_0}\, Y_0^0(\theta,\phi)$

2P $\quad \begin{pmatrix} \phi_{211} \\ \phi_{210} \\ \phi_{21-1} \end{pmatrix} = \frac{1}{\sqrt{3}(2a_0)^{3/2}}\frac{r}{a_0} e^{-r/2a_0} \begin{pmatrix} Y_1^1(\theta,\phi) \\ Y_1^0(\theta,\phi) \\ Y_1^{-1}(\theta,\phi) \end{pmatrix}$

3S $\quad \phi_{300} = \frac{2}{3(3a_0)^{3/2}}\left[3 - \frac{2r}{a_0} + 2\left(\frac{r}{3a_0}\right)^2\right] e^{-r/3a_0}\, Y_0^0(\theta,\phi)$

3P $\quad \begin{pmatrix} \phi_{311} \\ \phi_{310} \\ \phi_{31-1} \end{pmatrix} = \frac{4\sqrt{2}}{9(3a_0)^{3/2}}\frac{r}{a_0}\left(1-\frac{r}{6a_0}\right) e^{-r/3a_0} \begin{pmatrix} Y_1^1(\theta,\phi) \\ Y_1^0(\theta,\phi) \\ Y_1^{-1}(\theta,\phi) \end{pmatrix}$

3D $\quad \begin{pmatrix} \phi_{322} \\ \phi_{321} \\ \phi_{320} \\ \phi_{32-1} \\ \phi_{32-2} \end{pmatrix} = \frac{2\sqrt{2}}{27\sqrt{5}(3a_0)^{3/2}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \begin{pmatrix} Y_2^2(\theta,\phi) \\ Y_2^1(\theta,\phi) \\ Y_2^0(\theta,\phi) \\ Y_2^{-1}(\theta,\phi) \\ Y_2^{-2}(\theta,\phi) \end{pmatrix}$