Átomo de hidrogênio

Partícula num potencial central $V(r)$

$$H = \frac{p^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

momento angular $\vec{L} = \vec{r}\times\vec{p}$

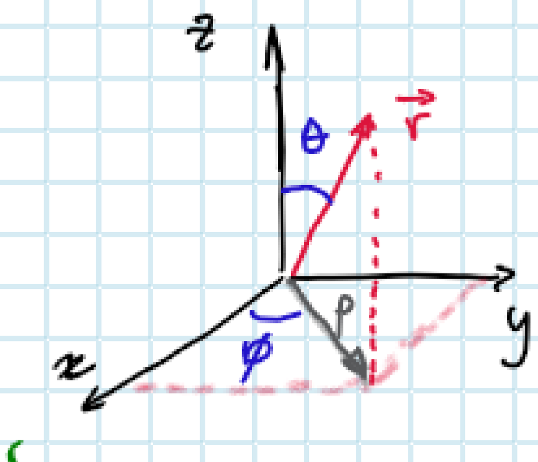
$$H = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\mathbb{L}^2\right) + V(r)$$

As três componentes de $\mathbb{L}$ comutam com $\mathbb{L}^2$ e, portanto, com H.

$$[H, L_x] = [H, L_y] = [H, L_z] = 0$$

$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\mathbb{L}^2$$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)}_{\frac{1}{r^2}\mathbb{L}^2}$$



$z = r\cos\theta$; $\rho = r\sin\theta$

$x = \rho\cos\phi = r\sin\theta\cos\phi$

$y = \rho\sin\phi = r\sin\theta\sin\phi$

O mínimo CSCO (conj. completo observ. que comutam) é $\{H, \mathbb{L}^2, L_z\}$

⇒ Portanto, devemos resolver as eq. de autovalores simultâneas:

$$\begin{aligned} H|\psi\rangle &= E|\psi\rangle \\ L^2|\psi\rangle &= l(l+1)\hbar^2|\psi\rangle \\ L_z|\psi\rangle &= m\hbar|\psi\rangle \end{aligned} \Rightarrow \begin{aligned} H\,\psi(r,\theta,\phi) &= E\,\psi(r,\theta,\phi) \\ L^2\,\psi(r,\theta,\phi) &= l(l+1)\hbar^2\,\psi(r,\theta,\phi) \\ L_z\,\psi(r,\theta,\phi) &= m\hbar\,\psi(r,\theta,\phi) \end{aligned}$$

Busca-se soluções separáveis, do tipo $\boxed{\psi(r,\theta,\phi) = R_{nl}(r)\,Y_l^m(\theta,\phi)}$

$$R(r) \to R_{nl}(r) = \frac{1}{r}u_{nl}(r)$$

$$\left[\frac{-\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2mr^2} + V(r)\right]R(r) = E\,R(r)$$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}u_{nl} + \left(V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u_{nl} = E\,u_{nl}$$

→ Eq. de Schrödinger 1D

$$V_{ef} = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

→ potencial efetivo (com barreira centrífuga)

$$\frac{1}{R.Y}\left[\frac{-\hbar^2}{2m}\frac{1}{r}Y_l^m(\theta,\phi)\frac{d^2}{dr^2}rR(r) + V.R.Y + R(r)\frac{\mathbb{L}^2}{2mr^2}Y_l^m(\theta,\phi)\right] = E.R.Y$$

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r)-E)\right] + \left[\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)\right] = 0$$

Coulomb: $V(r) = -\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}$

Eq. Radial: $\left\{\ \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r)-E) = l(l+1)\right.$

⇒ Soluções p/ potencial Coulomb: Polinômios de Laguerre multiplic. p/ exponencial

Eq. Angular: $\left\{\ \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -l(l+1)\right.$

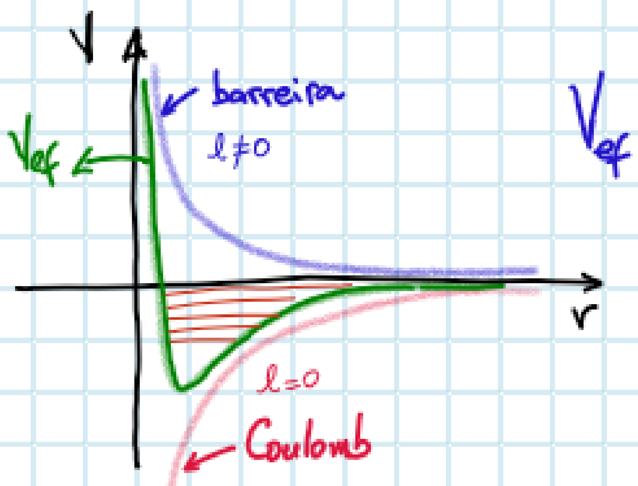
⇒ Soluções harmônicos esféricos $Y_l^m(\theta,\phi)$

$$-i\frac{\partial}{\partial\phi}Y_l^m(\theta,\phi) = m\,Y_l^m(\theta,\phi)$$

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_l^m(\theta,\phi) = l(l+1)\,Y_l^m(\theta,\phi)$$

$$L^2\,Y_l^m(\theta,\phi) = l(l+1)\hbar^2\,Y_l^m(\theta,\phi)$$

• Potencial efetivo



(p/ H: Z=1) # atômico ← p/ átomos hidrogenóides

$$V_{ef}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2} = -\frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{r} + \frac{\hbar^2}{2m}\cdot\frac{l(l+1)}{r^2}$$

• Solução da parte radial:

devido a grande diferença de massa entre o próton e elétron o problema pode ser bastante simplificado usando massa reduzida e C.M.

Na prática a posição relativa e massa reduzida são as do elétron (problema 1 partícula) num potencial de Coulomb... (efetivo)...

↳ *reduzindo o problema de 2 partículas interagentes p/ 1 partícula num potencial efetivo.

Definindo:

$a_0 \equiv \frac{\hbar^2}{\mu e^2} \cong 0{,}52\,Å$; → Raio de Bohr ; $\mu = \frac{m_e\cdot m_p}{m_e + m_p} \approx m_e\left(1 - \frac{m_e}{m_p}\right)$

$E_1 = \frac{\mu e^4}{2\hbar^2} \cong 13{,}6\ eV$ → Energia de ionização (Rydberg)

$\rho = \left(\frac{2Z}{n a_0}\right)r$ ~ raio "rescalado" p/ raio de Bohr (Z: # atômico)

Energia

$$\boxed{E_n = -\frac{\mu e^4}{2\hbar^2 n^2} = -\frac{E_1}{n^2} = -\frac{13{,}6\ eV}{n^2}}$$

Energia só depende de n ⇒ degenerescência

Solução radial:

$$R_{nl}(\rho) = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n((n+l)!)^3}}\ e^{-\rho/2}\,\rho^l\,L^{2l+1}_{n-l-1}(\rho)$$

Polinômio Associado de Laguerre

$$\int_0^\infty r^2|R(r)|^2\,dr = 1$$

condição de normalização

$$\int_0^{2\pi}\int_0^{\pi}(Y_{l'}^{m'})^*(Y_l^m)\sin\theta\,d\theta\,d\phi = \delta_{ll'}\delta_{mm'}$$

$l = 0, \dots, n-1$; $n = \{1, 2, 3 \dots\}$

$m = -l, -l+1, \dots, l$

conjunto de números quânticos

Solução Angular:

$$Y_l^m(\theta,\phi) = \varepsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\ e^{im\phi}\,P_l^m(\cos\theta)$$

$\varepsilon = (-1)^m$ p/ $m \geq 0$

$\varepsilon = 1$ p/ $m \leq 0$

Polinômios Associados de Legendre

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-l-1)!}{2n((n+l)!)^3}}\ e^{-r/na_0}\left(\frac{2r}{na_0}\right)L^{2n+1}_{n-l-1}\left(\frac{2r}{na_0}\right)\cdot Y_l^m(\theta,\phi)$$