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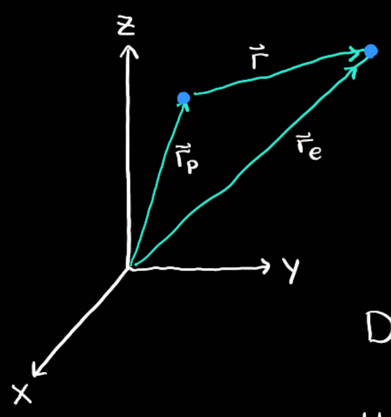
Átomo de Hidrógeno

Sea $\psi_{nlm}(\vec r)$ la función de onda el estado del "electrón". Teníamos el problema de eigenfunciones

$$H\psi(\vec r)=E\psi(\vec r)$$



$$\vec r=\vec r_p-\vec r_e$$

$$\vec R_{cm}=\frac{m_e\vec r_e+m_p\vec r_p}{m_e+m_p};\qquad M=m_e+m_p$$

$$M\vec R_{cm}=m_e\vec r_e+m_p\vec r_p$$

De forma "clásica",

$$H=\frac{P_e^2}{2m_e}+\frac{P_p^2}{2m_p}-\frac{e^2}{|\vec r_p-\vec r_e|}=\frac{m_e^2\dot{\vec r}_e^2}{2m_e}+\frac{m_p^2\dot{\vec r}_p^2}{2m_p}-\frac{e^2}{|\vec r_p-\vec r_e|}$$

$$=\frac{m_e\dot{\vec r}_e^2}{2}+\frac{m_p\dot{\vec r}_p^2}{2}-\frac{e^2}{|\vec r_p-\vec r_e|}$$

No obstante, como $\vec r_p=\vec r+\vec r_e\Rightarrow M\vec R_{CM}=m_e\vec r_e+m_p(\vec r+\vec r_e)$

$$M\vec R_{cm}=(m_e+m_p)\vec r_e+m_p\vec r$$

$\therefore\ \vec r_e=\frac{M\vec R_{cm}}{M}-\frac{m_p\vec r}{M}$ de lo cual

$$\dot{\vec r}_e=\dot{\vec R}_{cm}-\frac{m_p}{M}\dot{\vec r},\qquad \dot{\vec r}_p=\dot{\vec R}_{cm}+\frac{m_e}{M}\dot{\vec r}$$

El Hamiltoniano será entonces,

$$H=\frac{m_e}{2}\dot{\vec R}_{cm}-\cancel{\frac{m_em_p}{M}\dot{\vec R}_{cm}}\dot{\vec r}+\frac{m_em_p}{2M^2}\dot{\vec r}^2+\frac{m_p}{2}\dot{\vec R}_{cm}$$

$$+\cancel{\frac{m_pm_e}{M}\dot{\vec R}_{cm}}\dot{\vec r}+\frac{m_pm_e}{2M^2}\dot{\vec r}^2-\frac{e^2}{r}$$

$$\Rightarrow H=\frac{M}{2}\dot{\vec R}_{cm}^2+\frac{m_pm_e(m_e+m_p)}{2M^2}\dot{\vec r}^2-\frac{e^2}{r}.$$

Como la masa del electrón es prácticamente dos mil veces menor que la masa del protón podemos aproximar a M como $M=\frac{m_pm_e}{m_e+m_p}\sim m_e$.

De forma "cuántica" el Hamiltoniano se ve como

$$H=\frac{\vec p^2}{2M}-\frac{e^2}{r}$$

de donde $\hat H|\psi\rangle=E|\psi\rangle\Rightarrow\langle\vec r|\hat H|\psi\rangle=E\langle\vec r|\psi\rangle$

$$\Rightarrow\langle\vec r|\frac{\vec p^2}{2M}|\psi\rangle-\langle\vec r|\frac{e^2}{r}|\psi\rangle=E\langle\vec r|\psi\rangle$$

$$\Rightarrow-\frac{\hbar^2}{2M}\nabla^2\psi(\vec r)-\frac{e^2}{r}\psi(\vec r)=E\psi(\vec r)$$

$$\boxed{\nabla^2\psi(r,\theta,\varphi)+\frac{2Me^2}{\hbar^2r}\psi(r,\theta,\varphi)+\frac{2ME}{\hbar^2}\psi(r,\theta,\varphi)=0}$$

Cuya solución sabemos es de la forma $\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\varphi)$. Mas aún,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left(\frac{2ME}{\hbar^2}-\frac{2Me^2}{\hbar^2}\frac{1}{r}\right)R+\frac{\ell(\ell+1)}{r^2}R=0\qquad(1)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2}{\sin^2\theta}\Theta+\ell(\ell+1)\Theta=0$$

$$\frac{d^2\Phi}{d\varphi^2}+m^2\Phi=0;\qquad \Theta(\theta)\Phi(\varphi)=Y_\ell^m(\theta,\varphi),\qquad \begin{array}{l}m=-\ell,-\ell+1,\dots,0,\dots,\ell-1,\ell\\ \ell=0,1,\dots\end{array}$$

Pedimos además que $\int|\psi(r,\theta,\varphi)|^2d^3r=1$.

Sean $\alpha=\sqrt{-\frac{8ME}{\hbar^2}}$ y $\rho=\alpha r$, de lo cual $\frac{d\rho}{dr}=\alpha$ y entonces $\frac{d}{dr}=\frac{d\rho}{dr}\frac{d}{d\rho}=\alpha\frac{d}{d\rho}$. Mas aún, $\frac{d^2}{dr^2} = \alpha^2 \frac{d^2}{d\rho^2}$. Con esto se obtiene entonces $R(r) \to R\left(\frac{\rho}{\alpha}\right)$, así para (1) obtenemos

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(\frac{2ME}{\hbar^2} - \frac{2Me^2}{\hbar^2}\frac{1}{r}\right)R + \frac{\ell(\ell+1)}{r^2}R = 0$$

$$\Rightarrow \frac{1}{r^2}\left(r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right) + \left(\frac{2ME}{\hbar^2} - \frac{2Me^2}{\hbar^2}\frac{1}{r}\right)R + \frac{\ell(\ell+1)}{r^2}R = 0$$

$$\Rightarrow \frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left(\frac{2ME}{\hbar^2} - \frac{2Me^2}{\hbar^2}\frac{1}{r}\right)R + \frac{\ell(\ell+1)}{r^2}R = 0$$

$$\Rightarrow \frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(\frac{2ME}{\alpha^2\hbar^2} - \frac{2Me^2}{\alpha\hbar^2\rho}\right)R + \frac{\ell(\ell+1)}{\rho^2}R = 0$$

Pero $\frac{2ME}{\hbar^2}\left(\frac{1}{\alpha^2}\right) = \frac{2ME}{\hbar^2}\left(-\frac{\hbar^2}{8ME}\right) = -\frac{1}{4}$. Sea $\lambda = \frac{2Me^2}{\alpha\hbar^2}$, de modo tal que

$$\boxed{\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) + \left[\frac{\lambda}{\rho} - \frac{1}{4} + \frac{\ell(\ell+1)}{\rho}\right]R = 0} \qquad (2)$$

de donde $R(\rho) = \rho^\ell e^{-\rho/2}\chi(\rho)$. Sustituyendo $R(\rho)$ en (2) resulta que

$$\rho\frac{d^2\chi}{d\rho^2} + \frac{d\chi}{d\rho}(2\ell+2-\rho) + (\lambda-\ell-1)\chi = 0$$

Considere que la ecuación asociada de Laguerre es

$$\boxed{x L_m^{k\,''}(x) + (k+1-x)L_m^{k\,'}(x) + m' L_m^k(x) = 0} \qquad (3)$$

por lo cual, de (2) y (3)

$$m' = \lambda - \ell - 1 \qquad\qquad \lambda = m' + \ell + 1 \Rightarrow \lambda \in \mathbb{Z}$$

$$k+1 = 2\ell+2\,; \quad k = 2\ell+1 \qquad\qquad \chi(\rho) \equiv L_{\lambda-\ell-1}^{2\ell+1}(\rho)$$

Haciendo la asignación $\lambda \equiv n$, tenemos finalmente que

$$E = E_n = -\frac{e^4 M}{2\hbar^2 n^2}$$

y como fue visto en IFC, el radio de Bohr $a_0 = \frac{\hbar^2}{Me^2}$. Por otra parte,

$$\int |\psi(r,\theta,\varphi)|^2 d^3r = 1 \Rightarrow \int Y_\ell^m(\theta,\varphi)^2 R^2(r)\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = 1$$

$$\Rightarrow \int_0^\infty r^2 R^2(r)\,dr \int Y_\ell^m(\theta,\varphi)^2 \sin\theta\, d\theta\, d\varphi = 1$$

$$\Rightarrow \underbrace{\int_0^\infty r^2 R^2(r)\,dr = 1}_{\mathrm{I}}\,, \quad \underbrace{\int Y_\ell^m(\theta,\varphi)\sin\theta\, d\theta\, d\varphi = 1}_{\mathrm{II}}$$

considerando $\rho = \alpha r$, resulta en

$$\mathrm{I} = \frac{1}{\alpha^3}\int_0^\infty \rho^2 R_{n\ell}(\rho)R_{n\ell}^*(\rho)\,d\rho = \frac{1}{\alpha^3}\int_0^\infty \rho^{2\ell+2} e^{-\rho} L_{n-\ell-1}^{2\ell+1}(\rho) L_{n-\ell-1}^{2\ell+1}(\rho)\,d\rho$$