Masa finita del Núcleo: corrección a la fórmula de Bohr

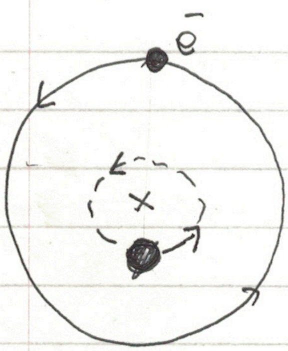
Escogiendo c. de coords. en el centro de masa

$$R = \frac{m_e\vec{r}_e + M\vec{r}_N}{m+M} = 0 \Rightarrow m_e r_e = M r_N$$

$$\Rightarrow r_N = (m_e/M)\, r_e \qquad (1)$$

hipótesis de De Broglie $\Leftrightarrow$ cuantización de $L = n\hbar$

$$m\omega_e r_e^2 + M\omega_N r_N^2 = n\hbar \qquad (2)$$



Coulomb $\Rightarrow \underbrace{\frac{Ze^2}{(r_e+r_N)^2}} = m_e\omega_e^2 r_e$

$$\frac{Ze^2}{r_e^2\left(1+\frac{m_e}{M}\right)^2} = m_e\omega_e^2 r_e \qquad (3)$$

$$(2) \rightarrow \quad m_e\omega_e r_e^2 + M\overset{\omega_e}{\overset{\parallel}{\omega_N}}\left(\frac{m_e}{M}\right)^2 r_e^2 = n\hbar$$

$$m_e\omega_e r_e^2\left(1+\left(\frac{m_e}{M}\right)\right) = n\hbar \qquad (2')$$

$$\frac{(2')^2}{(3)} \quad \frac{m^2\omega_e^2 r^4\left(1+\left(\frac{m}{M}\right)\right)^2}{m\omega_e^2 r^3} = \frac{n^2\hbar^2}{\frac{Ze^2}{\left(1+\frac{m}{M}\right)^2}}$$

$$\Rightarrow \frac{m^{-1} r^{-1}}{\cancel{\left(1+\frac{m}{M}\right)^2}} = \frac{Ze^2}{\cancel{\left(1+\frac{m}{M}\right)^2} n^2\hbar^2} \Rightarrow \boxed{r_n = \frac{n^2\hbar^2}{mZe^2} = \frac{a_0 n^2}{Z}} \qquad (4)$$

indep. de M (!)

$\Rightarrow$ radios son los mismos para todos los isótopos del Hidrógeno

$\underline{\text{Energía}}$: $E = \frac{1}{2} m \omega^2 r^2 + \frac{1}{2} M \omega^2 r_N^2 - \frac{Z e^2}{(r_n + r_e)}$

$$= \frac{1}{2} m \omega^2 r^2 + \frac{1}{2} M \omega^2 \left(\frac{m}{M}\right)^2 r^2 - \frac{Z e^2}{r\left(1 + \frac{m}{M}\right)}$$

$$= \frac{1}{2} m \omega^2 r^2 \left(1 + \frac{m}{M}\right) - \frac{Z e^2}{r\left(1 + \frac{m}{M}\right)}$$

pero $m \omega^2 r^2 \overset{(3)}{=} \dfrac{Z e^2}{r\left(1 + \frac{m}{M}\right)^2}$

$$\Rightarrow E = -\frac{Z e^2}{2r\left(1 + \frac{m}{M}\right)} = -\frac{Z e^2 m Z e^2}{2 n^2 \hbar^2 \left(1 + \frac{m}{M}\right)}$$

$$\boxed{E = -\frac{\mu Z^2 e^4}{2 n^2 \hbar^2}} \quad (8) \quad \text{where } \boxed{\mu \equiv \frac{m}{1 + \frac{m}{M}}}$$

masa reducida

cuando $M \to \infty$, $\mu \to m$.

$M = 1836\, m$ para el H $\Rightarrow \boxed{\mu = \frac{1836}{1837} m}$

ATOMO DE HIDROGENO

La soluc. del problema del átomo de H fué uno de los 1ros y mayores triunfos de la E. de S.

→ imposible de resolver exacto% para átomos con más de un electrón → desarrollo de técnicas numéricas y aprox. que permiten altos grados de precisión.

Atomo de H : 2 partículas → $\Psi(x_p, y_p, z_p, x_e, y_e, z_e, t)$

E. total : $\dfrac{P_p^2}{2m_p} + \dfrac{P_e^2}{2m_e} + V(r)$ (1)

o sea, $-\dfrac{\hbar^2}{2m_p}\nabla_p^2 - \dfrac{\hbar^2}{2m_e}\nabla_e^2 + V(r)$ (2)

donde $V(r) = -e^2/r$

$$\therefore \left(-\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r)\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (3)$$

C. de M.:

$$\left.\begin{aligned} X &= \frac{m_e x_e + m_p x_p}{m_e + m_p}, & x &= x_e - x_p \\ Y &= \frac{m_e y_e + m_p y_p}{m_e + m_p}, & y &= y_e - y_p \\ Z &= \frac{m_e z_e + m_p z_e}{m_e + m_p}, & z &= z_e - z_p \end{aligned}\right\} \qquad (4)$$

$$(4) \Rightarrow \quad \left.\begin{array}{l} M\cancel{X} = m_e x_e + m_p x_p \\ x = x_e - x_p \end{array}\right| \quad m_p \quad / m_e$$

$$\Rightarrow \quad \left.\begin{array}{l} M X = m_e x_e + m_p x_p \\ m_p x = m_p x_e - m_p x_p \end{array}\right| \Rightarrow \; M X + m_p x = (m_e + m_p) x_e$$

$$\Rightarrow \boxed{x_e = X + \frac{m_p}{M} x} \qquad (5)$$

luego, $\boxed{y_e = Y + \frac{m_p y}{M}}$, $\boxed{z_e = Z + \frac{m_p}{M} z}$

también, $\left.\begin{array}{l} M X = m_e x_e + m_p x_p \\ m_e x = m_e x_e - m_e x_p \end{array}\right| \quad M X - m_e x = M x_p$

$$\Rightarrow \boxed{x_p = X - \frac{m_e}{M} x} \text{ and } \boxed{y_p = Y - \frac{m_e}{M} y} \text{ and } \boxed{z_p = Z - \frac{m_e}{M} z} \qquad (6)$$

$$\Rightarrow \frac{1}{2} m_e (\dot{x}_e^2 + \dot{y}_e^2 + \dot{z}_e^2) + \frac{1}{2} m_p (\dot{x}_p^2 + \dot{y}_p^2 + \dot{z}_p^2) =$$

$$= \frac{1}{2} m_e \left\{ \dot{X}^2 + \left(\frac{m_p}{M}\right)^2 \dot{x}^2 + \frac{2 m_p}{M} \dot{x} \dot{X} + \dot{Y}^2 + \left(\frac{m_p}{M}\right) \dot{y}^2 + \frac{2 m_p}{M} \dot{Y} \dot{y} + \dot{Z}^2 + \left(\frac{m_p}{M}\right)^2 \dot{z}^2 + 2\left(\frac{m_p}{M}\right) \dot{Z} \dot{z} \right\}$$

$$+ \frac{1}{2} m_p \left\{ \dot{X}^2 + \left(\frac{m_e}{M}\right)^2 \dot{x}^2 - \frac{2 m_e}{M} \dot{x} \dot{X} + \dot{Y}^2 + \left(\frac{m_e}{M}\right) \dot{y}^2 - 2\left(\frac{m_e}{M}\right) \dot{y} \dot{Y} + \dot{Z}^2 + \left(\frac{m_e}{M}\right)^2 \dot{z}^2 - 2\left(\frac{m_e}{M}\right) \dot{z} \dot{Z} \right\}$$

$$= \frac{1}{2} (m_e + m_p) [\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2] + \frac{1}{2} \frac{m_e m_p}{(m_e + m_p)} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$= \frac{1}{2} M [\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2] + \frac{1}{2} \mu (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$P_x = M\dot{X} \; ; \quad P_y = M\dot{Y} \; ; \quad P_z = M\dot{Z}$$

$$E = \frac{P_x^2 + P_y^2 + P_z^2}{2M} + \frac{p_x^2 + p_y^2 + p_z^2}{2\mu} \quad (7)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2M}\nabla_{CM}^2 - \frac{\hbar^2}{2\mu}\nabla^2 + V(r) \right]\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (8)$$

$$\Psi(X,Y,Z,x,y,z,t) = u(x,y,z)\, U(X,Y,Z)\, e^{-i(E+E')t/\hbar} \quad (9)$$

$$\Rightarrow -\frac{\hbar^2}{2M}\nabla_{CM}^2 U = E' U \quad (10)$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \right] u = E\, u \quad (11)$$

(11) representa a 1 partícula efectiva bajo la influencia de un potencial con simetría esférica $\Rightarrow$ ya conocemos la dependencia angular, dada por $Y_{\ell m}(\theta,\phi)$

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

$$\frac{d^2}{dr^2}(rR) = -\frac{2m}{\hbar^2}\left[E - \underbrace{V(r)}_{\text{término Coulombiano}} - \underbrace{\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}}_{\text{potencial centrífugo}} \right](rR) \quad (12)$$

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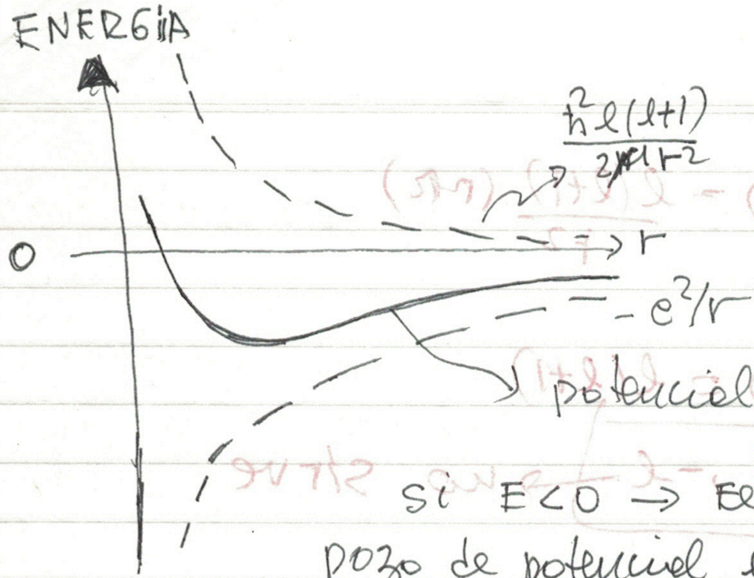


si $E<0 \Rightarrow$ el $\bar{e}$ está "atrapado" en el pozo de potencial efectivo. (clásico/. tenemos una órbita elíptica)

Solución [sin dem]:

$$\frac{d^2}{dr^2}(rR) = \frac{-2\mu}{\hbar^2}\left[E_n + \frac{Ze^2}{r} - \frac{\hbar^2 l(l+1)}{2\mu r^2}\right](rR) \qquad (1)$$

Def: $\alpha_n = \sqrt{-2\mu E_n/\hbar^2}$; $C = 2\mu Z e^2/\hbar^2$ (2)

$$\Rightarrow \frac{d^2}{dr^2}(rR) = \left[\alpha_n^2 - \frac{C}{r} + \frac{l(l+1)}{r^2}\right](rR) \qquad (3)$$

$r \gg 1$: $\frac{d^2}{dr^2}(rR) = \alpha_n^2 (rR) \Rightarrow \boxed{rR = e^{-\alpha_n r}}$ (4)

$\Rightarrow$ razonable suponer $rR(r) = \underbrace{g(r)}_{\text{serie en } r} e^{-\alpha_n r}$

$$\Rightarrow \frac{d^2 g}{dr^2} - 2\alpha_n \frac{dg}{dr} + \frac{Cg}{r} - \frac{l(l+1)}{r^2} g = 0 \qquad (5)$$

Pero $r \ll 1$, $\quad \frac{d^2}{dr^2}(rR) = \frac{l(l+1)}{r^2}(rR)$

$rR \propto r^s \Rightarrow s(s-1) = l(l+1)$

$\Rightarrow \boxed{s = l+1, -l} \rightarrow$ no sirve

$\therefore \boxed{rR \simeq r^{l+1}} \quad r \ll 1$

Se plantea una solución del tipo:

$$g(r) = r^s \sum_{q=0}^{\infty} b_q r^q$$ y se sustituye en (5),

imponiendo que $\lim_{r \to \infty} g(r) \to 0$

la $\exists$ de condiciones de borde para un $R(r)$ aceptable físicamente $\Rightarrow$

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2} \quad (6)$$ donde $n = 1, 2, 3, \ldots$

$l = 0, 1, 2, \ldots, n-1$

$\longrightarrow$ # cuántico radial.

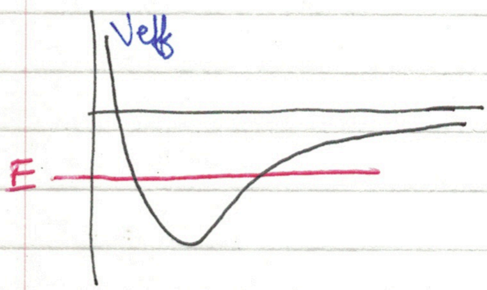
y $rR_{nl} \propto r^{l+1} e^{-\alpha_n r} \, Pol(r)$ (7)

<u>E_n NO depende de l</u> : NO enteramente cierto

$$\Psi(r,\theta,\phi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi) \tag{1}$$

donde $rR_{n\ell}(r)$ satisface una eq. tipo S 1-D.

$$\frac{d^2}{dr^2}(rR_{n\ell}) = -\frac{2\mu}{\hbar^2}\left[E - V_{eff}(r)\right](rR_{n\ell}) \tag{2}$$

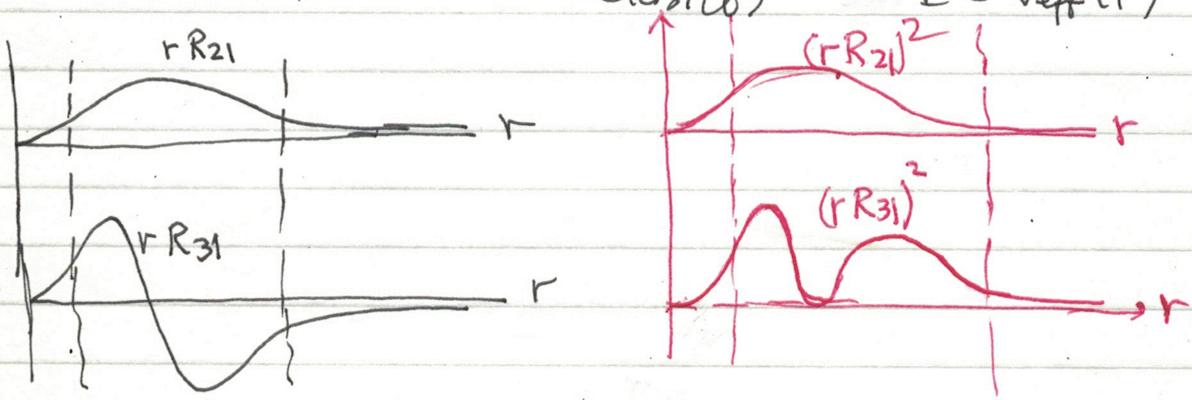


$\underline{E < V_{eff}} \Rightarrow (rR_{n\ell})'' = \alpha^2 (rR_{n\ell})$

$\Rightarrow$ crec. o decrecimiento exponencial

$E > V_{eff} \Rightarrow (rR_{n\ell})'' = -\alpha^2 (rR_{n\ell})$

$\Rightarrow$ oscilación entre los ptos de retorno clásicos $E = V_{eff}(r)$



$$P(r) = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |R_{n\ell}(r) Y_{\ell m}(\theta,\phi)|^2 r^2 \sin\theta\, d\theta\, d\phi = r^2 |R_{n\ell}(r)|^2 \tag{3}$$

Notar que $\lim_{r\to 0} [rR_{n\ell}(r)] = 0 \Rightarrow$ Es imposible "juntar" al e^- con el protón.

Notación (espectroscópico)

letra: s p d f | g h i ... (alfabético)

ℓ: 0 1 2 3 | 4 5 6

$\rho = \frac{Zr}{a_0'}$,

$a_0' = a_0\left(\frac{m_e + m_N}{m_N}\right)$ masa Núcleo

Z = carga núcleo

$$u_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0'}\right)^{3/2} e^{-\rho}$$

$$u_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}(2-\rho)\, e^{-\rho/2}$$

$$u_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}\rho\cos\theta\, e^{-\rho/2}$$

$$u_{2,1,\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}\rho\sin\theta\, e^{-\rho/2}\, e^{\pm i\phi}$$

$$u_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}(27-18\rho+2\rho^2)\, e^{-\rho/3}$$

$$u_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}(6-\rho)\rho\cos\theta\, e^{-\rho/3}$$

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

$$u_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}\rho^2(3\cos^2\theta-1)\, e^{-\rho/3}$$

$$u_{3,2,\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}\rho^2\sin\theta\cos\theta\, e^{-\rho/3}\, e^{\pm i\phi}$$

$$u_{3,2,\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0'}\right)^{3/2}\rho^2\sin^2\theta\, e^{-\rho/3}\, e^{\pm 2i\phi}$$

Ejercicio

Demuestre que, para este estado, la probabilidad de medir l=0 y l=1 es identicamente nula, mientras que la probabilidad de medir l=2 es 1.

$$\psi(x,y,z) = C(xy+yz+zx)e^{-\alpha r^2}$$

$x = r\sin\theta\cos\phi$; $y = r\sin\theta\sin\phi$; $z = r\cos\theta$

$$xy = r^2\sin^2\theta\sin\phi\cos\phi \qquad (1)$$

$$yz = r^2\sin\theta\cos\theta\sin\phi \qquad (2)$$

$$zx = r^2\sin\theta\cos\theta\cos\phi \qquad (3)$$

$Y_{00} = \sqrt{\frac{1}{4\pi}}$; $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$; $Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$

$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$; $Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi}$

$Y_{2,\pm2} = \sqrt{\left(\frac{15}{32\pi}\right)}\sin^2\theta e^{\pm 2i\phi}$

$(1) \Rightarrow \sin^2\theta\sin\phi\cos\phi = \frac{1}{2}\sin^2\theta\sin(2\phi)$

$$Y_{2,2} - Y_{2,-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\left(e^{2i\phi} - e^{-2i\phi}\right) = \sqrt{}\, 2i\sin^2\theta\sin(2\phi)$$

$$\boxed{\frac{(Y_{2,2} - Y_{2,-2})}{4i}\sqrt{\frac{32\pi}{15}} = \frac{1}{2}\sin^2\theta\sin(2\phi)} \qquad (4)$$

$$Y_{2,1} - Y_{2,-1} = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \left(e^{i\phi}\right) - \sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\, e^{-i\phi}$$

$$= -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \left(e^{i\phi} + e^{-i\phi}\right)$$

$$= -2\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\cos\phi$$

$$\Rightarrow \boxed{\sin\theta\cos\theta\cos\phi = -\frac{1}{2}\sqrt{\frac{8\pi}{15}} \left(Y_{21} - Y_{2-1}\right)} \qquad (5)$$

$$Y_{21} + Y_{2,-1} = -\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta \frac{\left(e^{i\phi} - e^{-i\phi}\right)}{2i} 2i$$

$$= -2i\sqrt{\frac{15}{8\pi}} \sin\theta\cos\theta\sin\phi$$

$$\boxed{\sin\theta\cos\theta\sin\phi = -\frac{1}{2i}\sqrt{\frac{8\pi}{15}} \left(Y_{21} + Y_{2,-1}\right)} \qquad (6)$$

$$xy + yz + zx = \left(\frac{8\pi}{15}\right)^{1/2} \left\{ \frac{(Y_{2,2} - Y_{2,-2})}{2i} - \frac{(Y_{2,1} - Y_{2,-1})}{2} + \right.$$

$$\left. - \frac{(Y_{21} + Y_{2,-1})}{2i} \right\}$$

Y_{00}: absent

$Y_{10}, Y_{1,\pm 1}$: absent

sólo $l=2$ está presente.

$\Rightarrow$ la prob. de hallar $l=2$ es 1.

$$L^2 = \hbar^2 l(l+1) = 6\hbar^2$$