03/08/23

Oscilador Harmônico Quântico

→ Sólidos, moléculas vibrando em um gás

→ Classicamente: $F(x) = -kx$, $F(x) = -\frac{dV}{dx}$ | $V(x) = -\int_0^x F(x')\,dx' = k\int_0^x x'\,dx' = \frac{1}{2}kx^2$

$$\therefore E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

↳ Ponto de retorno: $v = 0$

↳ $E = \frac{1}{2}kA^2 = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$

↳ conservação de energia

$$mv^2 = kA^2 - kx^2 \Rightarrow v = \sqrt{\frac{k}{m}}\,(A^2 - x^2)^{\frac{1}{2}}$$

cte de integração

↳ $\frac{dx}{dt} = \sqrt{\frac{k}{m}}\,(A^2 - x^2)^{\frac{1}{2}} \Rightarrow \int \frac{dx}{\sqrt{A^2 - x^2}} = \int \sqrt{\frac{k}{m}}\,dt + \delta$

↳ $\int \frac{dx}{A\sqrt{1 - \left(\frac{x}{A}\right)^2}} = \frac{1}{A}\int \frac{dx}{\sqrt{1 - \left(\frac{x}{A}\right)^2}} \overset{z \equiv \frac{x}{A}}{=} \frac{1}{A}\int \frac{A\,dz}{\sqrt{1 - z^2}} = \int \frac{dz}{\sqrt{1 - z^2}} = \arcsen(z)$

↳ $\arcsen\left(\frac{x}{A}\right) = \sqrt{\frac{k}{m}}\,t + \delta \Rightarrow \frac{x}{A} = \operatorname{sen}\left(\sqrt{\frac{k}{m}}\,t + \delta\right)$

$$x(t) = A\operatorname{sen}\left(\sqrt{\frac{k}{m}}\,t + \delta\right)$$

$$\therefore \boxed{x(t) = A\operatorname{sen}(\omega t + \delta)}, \quad \omega = \sqrt{\frac{k}{m}}$$

$\rightarrow$ Quanticamente: $\hat{H} = \dfrac{p^2}{2m} + V(x) \Rightarrow \underbrace{H\varphi = E\varphi}^{\text{indep. do tempo}}$

$\hookrightarrow \nu = \dfrac{\omega}{2\pi} = \dfrac{1}{2\pi}\sqrt{\dfrac{K}{m}} \Rightarrow \dfrac{K}{m} = 4\pi^2\nu^2 \Rightarrow K = 4m\pi^2\nu^2$

$\hookrightarrow \hat{p} = -i\hbar \dfrac{\partial}{\partial x}$

$$H = \frac{\left(-i\hbar \frac{\partial}{\partial x}\right)^2}{2m} + \frac{1}{2}Kx^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}Kx^2$$

$$\therefore H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + 2m\pi^2\nu^2x^2$$

$\hookrightarrow$ De $H\varphi = E\varphi$:

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + 2\pi^2 m\nu^2x^2\varphi = E\varphi \quad \Big\} \times \left(-\frac{2m}{\hbar^2}\right)$$

$$\frac{d^2\varphi}{dx^2} - \frac{4\pi^2m^2}{\hbar^2}\nu^2x^2\varphi = -\frac{2mE}{\hbar^2}\varphi$$

$$\frac{d^2\varphi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{4\pi^2m^2}{\hbar^2}\nu^2x^2\right)\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} + \left[\frac{2mE}{\hbar^2} - \left(\frac{2\pi m\nu}{\hbar}\right)^2x^2\right]\varphi = 0$$

$\hookrightarrow$ Sejam $\beta = \dfrac{2mE}{\hbar^2}$, $\alpha = \dfrac{2\pi m\nu}{\hbar}$: $\quad \dfrac{d^2\varphi}{dx^2} + (\beta - \alpha^2x^2)\varphi = 0 \quad (*)$

↳ Definimos $\eta = \sqrt{\alpha}\, x$ (1) $\Rightarrow \eta^2 = \alpha x^2$

↳ $\dfrac{d\varphi}{dx} = \dfrac{d\varphi}{d\eta} \cdot \dfrac{d\eta}{dx} = \sqrt{\alpha}\, \dfrac{d\varphi}{d\eta}$

↳ $\dfrac{d^2\varphi}{dx^2} = \dfrac{d}{d\eta}\left(\sqrt{\alpha}\, \dfrac{d\varphi}{d\eta}\right) \dfrac{d\eta}{dx} = \alpha \dfrac{d^2\varphi}{d\eta^2}$ (2)

↳ Substituindo (1) e (2) em (*):

$$\alpha \frac{d^2\varphi}{d\eta^2} + \left(\beta - \alpha^2 \frac{\eta^2}{\alpha}\right)\varphi = 0 \Rightarrow \frac{d^2\varphi}{d\eta^2} + \left(\frac{\beta}{\alpha} - \eta^2\right)\varphi = 0 \quad (3)$$

↳ Vamos nos ater à situação em que η é muito grande, uma vez que $\lim\limits_{\eta \to \pm\infty} \varphi(\eta) = 0$; ou seja, queremos soluções normalizáveis

↳ A equação (3) torna-se aproximadamente

$$\frac{d^2\varphi}{d\eta^2} - \eta^2\varphi = 0 \quad \left(\eta^2 \gg \frac{\beta}{\alpha}\right) \Rightarrow \frac{d^2\varphi}{d\eta^2} \approx \eta^2\varphi$$

↳ Chute: $\varphi(\eta) = Ae^{a\eta^2}$

↳ $\dfrac{d\varphi}{d\eta} = A \cdot 2a\eta e^{a\eta^2}$

↳ $\dfrac{d^2\varphi}{d\eta^2} = 2aA\left[e^{a\eta^2} + 2a\eta^2 e^{a\eta^2}\right]$

↳ $2a\cancel{A}e^{a\eta^2}\left[1+2a\eta^2\right] \approx \eta^2 \cancel{A} e^{a\eta^2}$

$$\left[2a+4a^2\eta^2\right] e^{a\eta^2} \approx \eta^2 e^{a\eta^2}$$

↳ $a>0$: $\varphi(\eta) = Ae^{a\eta^2} \to \infty$ quando $\eta \to \pm\infty \Rightarrow a<0$

↳ η grande: $4a^2\eta^2 e^{a\eta^2} \approx \eta^2 e^{a\eta^2}$

$$4a^2 = 1 \Rightarrow a = \pm\frac{1}{2} \Rightarrow a = -\frac{1}{2}$$

↳ a solução aproximada (assintótica) é: $\varphi(\eta) = Ae^{-\frac{1}{2}\eta^2}$

↳ Com a ideia para o regime assintótico podemos propor uma solução para a nossa equação original (3). Tentamos:

$$\varphi(\eta) = H(\eta)\, e^{-\frac{1}{2}\eta^2} \qquad (4)$$

↳ $\dfrac{d\varphi}{d\eta} = H'(\eta)\, e^{-\frac{1}{2}\eta^2} - \eta H(\eta)\, e^{-\frac{1}{2}\eta^2}$

↳ $\dfrac{d^2\varphi}{d\eta^2} = H''(\eta)\, e^{-\frac{1}{2}\eta^2} - \eta H'(\eta)\, e^{-\frac{1}{2}\eta^2} - H(\eta)\, e^{-\frac{1}{2}\eta^2} - \eta\left[H'(\eta)\, e^{-\frac{1}{2}\eta^2} - \eta H(\eta)\, e^{-\frac{1}{2}\eta^2}\right]$

$$= H''(\eta) - 2\eta H'(\eta)\, e^{-\frac{1}{2}\eta^2} + (\eta^2-1) H(\eta)\, e^{-\frac{1}{2}\eta^2} \qquad (5)$$

↳ (5) em (3) e fazendo $\gamma \equiv \beta/\alpha$:

$$\left[H''(\eta) - 2\eta H'(\eta) + (\eta^2-1)H(\eta)\right]e^{-\frac{1}{2}\eta^2} + (\gamma-\eta^2)H(\eta)e^{-\frac{1}{2}\eta^2} = 0$$
$$\left[H''(\eta) - 2\eta H'(\eta) + (\gamma-1)H(\eta)\right]e^{-\frac{1}{2}\eta^2} = 0$$

logo, $H''(\eta) - 2\eta H'(\eta) + (\gamma-1)H(\eta) = 0 \quad (6)$

↳ Vamos tentar uma solução do tipo série de potências:

$$H(\eta) = \sum_{j=0}^{\infty} a_j \eta^j \quad (7)$$
$$H'(\eta) = \sum_{j=1}^{\infty} j a_j \eta^{j-1} = \sum_{j=0}^{\infty} j a_j \eta^{j-1} \quad (8)$$
$$H''(\eta) = \sum_{j=2}^{\infty} j(j-1) a_j \eta^{j-2}$$

↳ Fazemos uma mudança de variáveis $i = j-2$

$$H''(\eta) = \sum_{i=0}^{\infty} (i+2)(i+1)a_{i+2}\eta^i = \sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}\eta^j \quad (9)$$

↳ Substituindo (7), (8) e (9) em (6):

$$\sum_{j=0}^{\infty}\left[(j+2)(j+1)a_{j+2} - 2ja_j + (\gamma-1)a_j\right]\eta^j = 0 \Rightarrow (j+2)(j+1)a_{j+2} + (\gamma-2j-1)a_j = 0$$

$$\therefore a_{j+2} = \frac{(2j+1-\gamma)}{(j+2)(j+1)}a_j, \quad j = 0, 1, 2, \dots \quad (10)$$

↳ $a_2 = \dfrac{(1-\gamma)}{2}a_0$

↳ $a_3 = \dfrac{(3-\gamma)}{6}a_1$

$a_4 = \dfrac{(5-\gamma)}{12}a_2 = \dfrac{(5-\gamma)(1-\gamma)}{24}a_0$

$a_5 = \dfrac{(7-\gamma)}{20}a_3 = \dfrac{(7-\gamma)(3-\gamma)}{120}a_1$

$\left.\begin{matrix} a_0 \\ a_1 \end{matrix}\right\}$ arbitrários (EDO 2ª ordem)

$$\hookrightarrow a_1\eta + a_3\eta^3 + a_5\eta^5 + \cdots$$

↳ assim: $H(\eta) = H_{par}(\eta) + H_{ímpar}(\eta)$

$$\hookrightarrow a_0 + a_2\eta^2 + a_4\eta^4 + \cdots$$

↳ suponha j grande. Da eq. (10),

↳ $a_{j+2} = \dfrac{j\left(2+\frac{1}{j}-\frac{\tilde{\varepsilon}}{j}\right)}{j\left(1+\frac{1}{j}\right)j\left(1+\frac{2}{j}\right)} a_j \approx \dfrac{2j}{j^2} a_j = \dfrac{2}{j} a_j$

↳ $a_j \approx \dfrac{2}{j-2} a_{j-2}$

$$a_{j+2} = \frac{2}{j} \cdot \frac{2}{j-2} \cdot a_{j-2} \cdots = \frac{1}{\frac{j}{2}} \cdot \frac{1}{\frac{j}{2}-1} \cdot \frac{1}{\frac{j}{2}-2} \cdots c \approx \frac{c}{\left(\frac{j}{2}\right)!}$$

$$\Rightarrow H(\eta) = \sum_{j=0}^{\infty} a_j \eta^j \approx \sum_{j=0}^{\infty} \frac{c}{\left(\frac{j}{2}\right)!}\eta^j$$

↳ Fazendo $i = j/2$: $H(\eta) = c\displaystyle\sum_{i=0}^{\infty} \frac{1}{i!}\eta^{2i} = c\sum_{i=0}^{\infty}\frac{(\eta^2)^i}{i!} = ce^{\eta^2}$

↳ Mas a nossa solução é do tipo $\psi(\eta) = H(\eta)e^{-\frac{1}{2}\eta^2} \sim ce^{\frac{1}{2}\eta^2} \to \infty$ quando $\eta \to \pm\infty$

$\therefore$ $H(\eta)$ não pode ter infinitos termos

14/08/23

$$\rightarrow -\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + \frac{1}{2}kx^2\varphi = E\varphi$$

$$\frac{d^2\varphi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{\cancel{2}mk}{\cancel{2}\hbar^2}x^2\right)\varphi = 0$$

$$\frac{d^2\varphi}{dx^2} + \left(\beta - \alpha^2 x^2\right)\varphi = 0,$$

$\hookrightarrow \beta = \frac{2mE}{\hbar^2}$

$k = m\omega^2 = 4\pi^2\nu^2 m$

$\hookrightarrow \alpha^2 = \frac{mk}{\hbar^2} = \frac{4m^2\pi^2\nu^2}{\hbar^2} = \left(\frac{2m\pi\nu}{\hbar}\right)^2 \Rightarrow \alpha = \frac{2\pi m\nu}{\hbar}$

→ Fazendo $\eta = \sqrt{\alpha}\,x$: $\quad \frac{d^2\varphi}{d\eta^2} + \left(\frac{\beta}{\alpha} - \eta^2\right)\varphi = 0 \quad (1)$

→ Solução assintótica: $\varphi(\eta) \sim e^{-\frac{1}{2}\eta^2} \quad (\eta \to \pm\infty)$

→ Tentativa: $\varphi(\eta) = H(\eta)e^{-\frac{1}{2}\eta^2} \quad (2)$

→ (2) em (1): $H''(\eta) - 2\eta H'(\eta) - (1-\gamma)H(\eta) = 0 \quad (3)$ → Eq. Hermite

$\hookrightarrow$ onde $\gamma = \beta/\alpha$

→ solução tentativa: $H(\eta) = \sum_{j=0}^{\infty} a_j \eta^j \quad (4)$

→ substituindo (4) em (3): $a_{j+2} = \dfrac{(2j+1-\gamma)}{(j+1)(j+2)} a_j$, $H(\eta) = H_{par}(\eta) + H_{impar}(\eta)$

↳ $H_{par}(\eta) = a_0 + a_2\eta^2 + a_4\eta^4 + \cdots$, $a_n \to a_0$

↳ $H_{impar}(\eta) = a_1\eta + a_3\eta^3 + \cdots$, $a_n \to a_1$

→ cálculo assintótico: $H(\eta) \sim e^{\eta^2} \Rightarrow \varphi(\eta) \sim H(\eta)e^{-\frac{1}{2}\eta^2} \sim e^{\frac{1}{2}\eta^2} \to \infty$ quando $\eta \to \pm\infty$

* Conclusão: $H(\eta)$ deve ser uma série truncada: deve existir $j = n$ (máximo) tal que $a_{j+2} = a_{j+4} = a_{j+6} = \cdots = 0$

$$\Rightarrow 2n+1-\gamma = 0 \Rightarrow \gamma = 2n+1$$

→ $\gamma = \dfrac{\beta}{\alpha} = \dfrac{\frac{2mE}{\hbar^2}}{\frac{2\pi m\nu}{\hbar}} = \dfrac{\frac{2mE}{\hbar^2}}{\frac{m\omega}{\hbar}} = \dfrac{2E}{\hbar\omega}$

$\gamma = 2n+1$

$E = \dfrac{\hbar\omega}{2}(2n+1)$

$E = \hbar\omega\left(n+\frac{1}{2}\right) = h\nu\left(n+\frac{1}{2}\right)$ (5), $n = 0, 1, 2, \ldots$

↳ energias quantizadas

→ $a_0 \neq 0 \Rightarrow a_2, a_4, \ldots, a_n$ (n par)
$a_1 = 0$
$\Big\}$ $H(\eta) = H_{par}(\eta)$

→ $a_1 \neq 0 \Rightarrow a_3, a_5, \ldots, a_n$ (n ímpar)
$a_0 = 0$
$\Big\}$ $H(\eta) = H_{impar}(\eta)$

$$\therefore \boxed{\varphi_n(\eta) = H_n(\eta)e^{-\frac{1}{2}\eta^2}}$$

→ Escolhas para a_0 e a_1 de forma que $H_n(\eta)$ sejam os conhecidos polinômios de Hermite da literatura:

$$\boxed{a_0 = (-1)^{\frac{n}{2}} \frac{n!}{\left(\frac{n}{2}\right)!}} \qquad \boxed{a_1 = (-1)^{\frac{n-1}{2}} \cdot 2 \frac{n!}{\left(\frac{n-1}{2}\right)!}}$$

→ Testando:

* $n = 0$: $a_0 = (-1)^{\frac{0}{2}} \frac{0!}{\left(\frac{0}{2}\right)!} \Rightarrow a_0 = 1$ | $a_1 = a_3 = \ldots = 0$

$$H_0(\eta) = a_0 = 1$$

* $n = 1$: $a_1 = (-1)^{\frac{1-1}{2}} \cdot 2 \cdot \frac{1!}{\left(\frac{1-1}{2}\right)!} \Rightarrow a_1 = 2$

$$H_1(\eta) = a_1 \eta = 2\eta$$

* $n = 2$: $a_0 = (-1)^{\frac{2}{2}} \cdot \frac{2!}{\left(\frac{2}{2}\right)!} \Rightarrow a_0 = -2$

$$a_{j+2} = \frac{2j+1-(2n+1)}{(j+1)(j+2)} a_j = \frac{2(j-n)}{(j+1)(j+2)} a_j \Rightarrow a_2 = \frac{2(0-2)}{(0+1)(0+2)} \overset{-2}{a_0} \Rightarrow a_2 = 4$$

$$H_2(\eta) = a_0 + a_2 \eta^2 = -2 + 4\eta^2$$

$\vdots$

$$H_3(\eta) = 8\eta^3 - 12\eta$$

$\vdots$

$$H_4(\eta) = 16\eta^4 - 48\eta^2 + 12$$

→ Autoestados do oscilador: $\varphi_n(\eta) = H_n(\eta)e^{-\frac{1}{2}\eta^2}$ (6)

→ Normalização: $\int_{-\infty}^{+\infty} \varphi_n^*(x)\,\varphi_m(x)\,dx = ?$

→ Considere a seguinte função:

$$f(t,z) = e^{2tz-t^2}$$

$$= \sum_{n=0}^{\infty} \frac{(2tz-t^2)^n}{n!}$$

$$= 1 + \frac{(2tz-t^2)}{1!} + \frac{(2tz-t^2)^2}{2!} + \frac{(2tz-t^2)^3}{3!}$$

$$= 1 + 2tz - t^2 + \frac{4t^2z^2 + t^4 - 4t^3z}{2} + \frac{8t^3z^3 - 12t^4z^2 + 6t^5z - t^6}{6} + \dots$$

$$= 1 + \frac{2z}{1!}t + \frac{(4z^2-2)}{2!}t^2 + \dots$$

$$= H_0(z) + H_1(z)t + \frac{H_2(z)}{2!}t^2 + \frac{H_3(z)}{3!}t^3 + \dots$$

$$= \sum_{n=0}^{\infty} \frac{H_n(z)t^n}{n!}$$

$$\rightarrow e^{(2tz-t^2)}e^{(2sz-s^2)} = \sum_{n=0}^{\infty} \frac{H_n(z)t^n}{n!} \cdot \sum_{m=0}^{\infty} \frac{H_m(z)s^m}{m!}$$

$$e^{(2tz-t^2)}e^{(2sz-s^2)} = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{H_n(z)H_m(z)}{n!\,m!}t^n s^m \quad (7)$$

→ Multiplicando (7) por e^{-z^2} e integrando de $-\infty$ a $+\infty$:

$$\int_{-\infty}^{+\infty} e^{2tz+2sz-t^2-s^2-z^2}\,dz = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{t^n s^m}{n!\,m!} \int_{-\infty}^{+\infty} H_n(z)\,H_m(z)\,e^{-z^2}\,dz = (*)$$

↳ $(a_1+a_2+a_3)^2 = a_1^2 + a_2^2 + a_3^2 + 2a_1a_2 + 2a_2a_3 + 2a_1a_3$

↳ $(z-t-s)^2 = z^2+t^2+s^2 - 2tz - 2zs + 2ts$

→ lado esquerdo de $(*)$:
$$\begin{aligned}(*) &= \int_{-\infty}^{+\infty} e^{-(z-t-s)^2+2ts}\,dz \\ &= e^{2ts}\int_{-\infty}^{+\infty} e^{-(z-t-s)^2}\,dz \\ &= \sqrt{\pi}\,e^{2ts} \\ &= \sqrt{\pi}\sum_{n=0}^{\infty}\frac{(2ts)^n}{n!} \\ &= \sqrt{\pi}\sum_{n=0}^{\infty}\left(\frac{2^n}{n!}s^n\right)t^n\end{aligned}$$

→ lado direito de $(*)$:
$$(*) = \sum_{n=0}^{\infty}\left(\sum_{m=0}^{\infty}\frac{s^m}{n!\,m!}\int_{-\infty}^{+\infty} H_n(z)\,H_m(z)\,e^{-z^2}\,dz\right)t^n$$

→ Comparando as duas expressões:

$$\sum_{m=0}^{\infty}\frac{s^m}{m!}\int_{-\infty}^{+\infty} H_n(z)\,H_m(z)\,e^{-z^2}\,dz = \sqrt{\pi}\,2^n s^n$$

→ Concluímos que $\int_{-\infty}^{+\infty} H_n(z)\,H_m(z)\,e^{-z^2}\,dz = 0 \quad \forall\, m\neq n$ e

$$\frac{1}{n!}\int_{-\infty}^{+\infty} H_n^2(z)\,e^{-z^2}\,dz = \sqrt{\pi}\,2^n$$

$$\therefore \boxed{\int_{-\infty}^{+\infty} H_n(z)\,H_m(z)\,e^{-z^2}\,dz = \begin{cases} 0, & n\neq m \\ \sqrt{\pi}\,2^n n!, & n=m\end{cases}}$$

* Resumindo:

$$\rightarrow -\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + \frac{1}{2}Kx^2\varphi = E\varphi \quad \Big| \quad \eta = \sqrt{\alpha}\,x, \quad \alpha = \frac{2\pi m\nu}{\hbar}$$

$$\rightarrow \frac{d^2\varphi}{d\eta^2} + \left(\frac{\beta}{\alpha} - \eta^2\right)\varphi = 0 \quad \Big| \quad \beta = \sqrt{\frac{2mE}{\hbar}}$$

$$\rightarrow E_n = \left(n + \frac{1}{2}\right)h\nu = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

$$\rightarrow \varphi_n(\eta) = H_n(\eta)\,e^{-\frac{1}{2}\eta^2}$$

* obs.: $\varphi_n(\eta) \rightarrow \varphi_n(x) \Rightarrow \varphi_n(x)\,dx = \varphi_n(\eta)\,d\eta \Rightarrow \varphi_n(x) = \varphi_n(\eta)\,d\eta/dx$

$$\varphi_n(x) = \sqrt{\alpha}\,\varphi_n(\eta)$$

$$\rightarrow \varphi_n(x) = \sqrt{\alpha}\,N_n H_n(\sqrt{\alpha}\,x)\,e^{-\frac{\alpha}{2}x^2}$$

* Normalização:

$$\int_{-\infty}^{+\infty}\varphi_n^*(x)\varphi_n(x)\,dx = N_n^2\,\alpha\int_{-\infty}^{+\infty}H_n^2(\sqrt{\alpha}\,x)\,e^{-\alpha x^2}\,dx$$

$$= N_n^2\,\alpha\int_{-\infty}^{+\infty}H_n^2(z)\,e^{-z^2}\frac{1}{\sqrt{\alpha}}\,dz, \quad z \equiv \sqrt{\alpha}\,x$$

$$= N_n^2\sqrt{\alpha}\int_{-\infty}^{+\infty}H_n^2(z)\,e^{-z^2}\,dz$$

$$= N_n^2\sqrt{\pi\alpha}\,2^n n! = 1$$

$$\therefore N_n = \frac{1}{(\alpha\pi)^{\frac{1}{4}}\sqrt{2^n n!}}$$

$$\boxed{\therefore \varphi_n(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\frac{1}{\sqrt{2^n n!}}H_n(\sqrt{\alpha}\,x)\,e^{-\frac{\alpha}{2}x^2}}$$

16/08/23

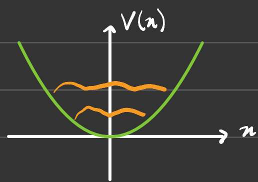
→ Da aula anterior: $\varphi_n(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n(\sqrt{\alpha}\, x)\, e^{-\frac{\alpha}{2}x^2}$

↳ $\alpha = \frac{m\omega}{\hbar}$

↳ $H_n(\eta)$: Polinômios de Hermite de ordem n

→ As autoenergias são $E_n = \left(n+\frac{1}{2}\right)\hbar\omega = \left(n+\frac{1}{2}\right)h\nu$, $n = 0, 1, 2, \dots$

↳ Obs.: $\boxed{E_0 = \frac{h\nu}{2}}$



* Evolução temporal do oscilador:

→ $\psi(x,t) = \sum_{n=0}^{\infty} c_n \varphi_n(x)\, e^{-i\frac{E_n}{\hbar}t}$

→ $\psi(x,0) = \sum_{n=0}^{\infty} c_n \varphi_n(x)$

→ $\int_{-\infty}^{+\infty} \varphi_m^*(x)\,\psi(x,0)\,dx = \sum_{n=0}^{\infty} c_n \underbrace{\int_{-\infty}^{+\infty} \varphi_n^*(x)\,\varphi_n(x)\,dx}_{\delta_{n,m}} = \sum_{n=0}^{\infty} c_n \delta_{n,m} = c_m$

$\Rightarrow c_m = \langle \varphi_m | \psi(x,0)\rangle = \int_{-\infty}^{+\infty} \varphi_m^*(x)\,\psi(x,0)\,dx$

→ $\langle \psi(x,t)|\psi(x,t)\rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\,\psi(x,t)\,dx$

$= \sum_{n=0}^{\infty} |c_n|^2 \int_{-\infty}^{+\infty} \varphi_n^*(x)\,\varphi_n(x)\,dx + \sum_{n\neq m} c_n^* c_m\, e^{i\frac{(E_n-E_m)}{\hbar}t} \int_{-\infty}^{+\infty} \varphi_n^*(x)\,\varphi_m(x)\,dx$

$= \sum_{n=0}^{\infty} |c_n|^2$

* Energia:

→ $\langle H\rangle = \langle \psi|\hat{H}|\psi\rangle = \sum_{n=0}^{\infty} p_n E_n$, $\quad H\varphi_n = E_n\varphi_n$, $\quad p_n = |c_n|^2$

$*$ Exercício: $\psi(x,0) = c_0\varphi_0(x) + c_1\varphi_1(x)$, onde $\varphi_n(x)$ são os autoestados normalizados do oscilador harmônico quântico. Sabendo que $\langle H\rangle = \hbar\omega$,

1) Determine $\psi(x,t)$

2) $\langle x\rangle = ?$

1) $\psi(x,0) = \sum_{n=0}^{\infty} c_n\varphi_n(x) = c_0\varphi_0(x) + c_1\varphi_1(x) \Rightarrow c_n = 0 \quad \forall n \geq 2$

$$\rightarrow \begin{cases} |c_0|^2 + |c_1|^2 = 1 \\ |c_0|^2 E_0 + |c_1|^2 E_1 = \hbar\omega \end{cases}$$

$\rightarrow$ Se $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$, $E_0 = \frac{1}{2}\hbar\omega$ e $E_1 = \frac{3}{2}\hbar\omega$

$$\rightarrow \begin{cases} p_0 + p_1 = 1 \\ \frac{1}{2}\hbar\omega\, p_0 + \frac{3}{2}\hbar\omega\, p_1 = \hbar\omega \end{cases} \Rightarrow \begin{matrix} p_0 + p_1 = 1 \\ p_0 + 3p_1 = 2 \end{matrix} \Rightarrow 2p_1 = 1 \Rightarrow \quad p_0 = p_1 = \frac{1}{2}, \quad c_0 = c_1 = \frac{1}{\sqrt{2}}$$

$$\rightarrow \psi(x,t) = \sum_{n=0}^{\infty} c_n\varphi_n(x)\, e^{-i\frac{E_n}{\hbar}t} = c_0\varphi_0(x)\, e^{-i\frac{E_0}{\hbar}t} + c_1\varphi_1(x)\, e^{-i\frac{E_1}{\hbar}t}$$

$$\rightarrow \varphi_n(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{H_n(\sqrt{\alpha}\,x)}{\sqrt{2^n\, n!}}\, e^{-\frac{1}{2}\alpha x^2}, \quad \alpha = \frac{m\omega}{\hbar}$$

$$\hookrightarrow \varphi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \underbrace{H_0(\sqrt{\alpha}\,x)}_{H_0 = 1}\, e^{-\frac{1}{2}\alpha x^2} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2}$$

$$\hookrightarrow \varphi_1(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{\overbrace{H_1(\sqrt{\alpha}\,x)}^{H_1 = 2\sqrt{\alpha}\,x}}{\sqrt{2}}\, e^{-\frac{1}{2}\alpha x^2} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{2\sqrt{\alpha}\,x}{\sqrt{2}}\, e^{-\frac{1}{2}\alpha x^2} = \sqrt{2\alpha}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} x\, e^{-\frac{1}{2}\alpha x^2}$$

$$\Rightarrow \psi(x,t) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha x^2} e^{-i\frac{E_0}{\hbar}t} + \frac{1}{\sqrt{2}}\sqrt{2\alpha}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{1}{2}\alpha x^2} e^{-i\frac{E_1}{\hbar}t}$$

$$= \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left[e^{-\frac{1}{2}\alpha x^2 - \frac{i\omega}{2}t} + \sqrt{2\alpha}\, x e^{-\frac{1}{2}\alpha x^2 - i\frac{3}{2}\omega t}\right]$$

$$\therefore \boxed{\psi(x,t) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-i\frac{\omega}{2}t}\left[e^{-\frac{\alpha}{2}x^2} + \sqrt{2\alpha}\, x e^{-\frac{\alpha}{2}x^2 - i\omega t}\right]}$$

2) $\langle x\rangle = \int_{-\infty}^{+\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx = \langle\psi|x|\psi\rangle$

$$= \frac{1}{2}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} e^{i\frac{\omega}{2}t}\left[e^{-\frac{\alpha}{2}x^2} + \sqrt{2\alpha}\, x\, e^{-\frac{\alpha}{2}x^2 + i\omega t}\right] x\, e^{-i\frac{\omega}{2}t}\left[e^{-\frac{\alpha}{2}x^2} + \sqrt{2\alpha}\, x e^{-\frac{\alpha}{2}x^2 - i\omega t}\right] dx$$

$$= \frac{1}{2}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\left[\int_{-\infty}^{+\infty} \cancel{x e^{-\alpha x^2}}^{\,0} dx + \sqrt{2\alpha}\, e^{-i\omega t}\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx + \right.$$

$$\left. + \sqrt{2\alpha}\, e^{i\omega t}\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx + 2\alpha \int_{-\infty}^{+\infty} \cancel{x^3 e^{-\alpha x^2}}^{\,0} dx\right]$$

$$\Rightarrow \langle x\rangle = \frac{1}{2}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \sqrt{2\alpha}\, \underbrace{\left(e^{-i\omega t} + e^{i\omega t}\right)}_{2\cos(\omega t)} \underbrace{\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx}_{(*)}$$

$$\rightarrow \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\rightarrow (*) = -\frac{d}{d\alpha}\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx$$

$$(*) = -\frac{d}{d\alpha}\left(\sqrt{\frac{\pi}{\alpha}}\right) = -\frac{d}{d\alpha}\left(\sqrt{\pi}\,\alpha^{-\frac{1}{2}}\right) = \frac{1}{2}\sqrt{\pi}\,\alpha^{-\frac{3}{2}} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\,\frac{1}{\alpha}$$

$\rightarrow$ substituindo: $\langle x\rangle = \frac{1}{2}\cancel{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}}\sqrt{2\alpha}\cdot 2\cos(\omega t)\cdot \frac{1}{2}\cancel{\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}}\frac{1}{\alpha} = \frac{1}{\sqrt{2\alpha}}$

$$\alpha = \frac{m\omega}{\hbar} \Rightarrow \boxed{\langle x\rangle = \sqrt{\frac{\hbar}{2m\omega}}\cos(\omega t)}$$

Princípio da Correspondência para o oscilador harmônico

→ Para $n >> 1$, esperamos recuperar o resultado clássico.

→ $\rho_Q(x) = |\varphi_n(x)|^2 = \varphi_n^*(x)\,\varphi_n(x)$ = probabilidade de que a partícula no n-ésimo estado esteja entre x e $x + dx$

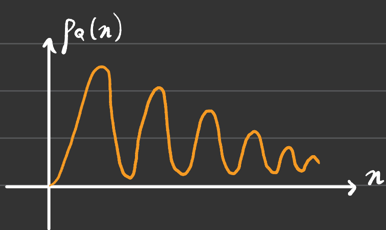
→ vamos tomar $n = 12$ como grande:

$$H_{12}(x) = 665280 - 7983360\,x^2 + 13305600\,x^4 - 7096320\,x^6 + \\ + 1520640\,x^8 - 135168\,x^{10} + 4096\,x^{12}$$

→ sem perda de generalidade, tomamos $\alpha = \frac{m\omega}{\hbar} = 1$

↳ $$\varphi_n(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}}\, H_n(\sqrt{\alpha}\,x)\, e^{-\frac{1}{2}\alpha x^2} = \frac{1}{\pi^{\frac{1}{4}}} \frac{1}{\sqrt{2^n n!}}\, H_n(x)\, e^{-\frac{1}{2}x^2}$$

→ $$\rho_Q(x) = \frac{1}{\sqrt{\pi}\, 2^{12}\, 12!}\, H_{12}^2(x)\, e^{-x^2} = \frac{1}{\sqrt{\pi}\, 2^{12}\, 12!} \left[665280 + \dots + 4096\,x^{12}\right] e^{-x^2}$$



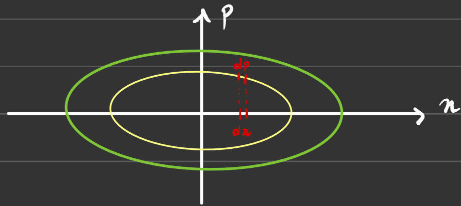
→ Classicamente: $\frac{1}{2}mv^2 + \frac{1}{2}kx^2 = E$

Ponto de retorno: $v = 0,\ x = \pm A$

$\Big\}\ E = \frac{1}{2}kA^2$

$$\rightarrow \cancel{\tfrac{1}{2}} m v^2 + \cancel{\tfrac{1}{2}} k x^2 = \cancel{\tfrac{1}{2}} k A^2$$

$$\rightarrow v = \frac{dx}{dt} \Rightarrow m\left(\frac{dx}{dt}\right)^2 = k\left(A^2 - x^2\right) \Rightarrow \frac{dx}{dt} = \sqrt{\frac{k}{m}}\sqrt{A^2 - x^2}$$



$$\rightarrow \frac{p^2}{2m} + \frac{1}{2} k x^2 = E \Rightarrow \frac{p^2}{\left(\sqrt{2mE}\right)^2} + \frac{x^2}{\left(\sqrt{\frac{2E}{k}}\right)^2} = 1$$

$\rightarrow \dfrac{dt}{T} = \rho_c(x)\,dx \rightarrow$ densidade de probabilidade da partícula

$T \rightarrow$ período de oscilação

$$\rightarrow \frac{1}{\sqrt{\frac{k}{m}}\sqrt{A^2 - x^2}}\,dx = dt \Rightarrow \frac{dt}{T} = \frac{1}{T\sqrt{\frac{k}{m}}\sqrt{A^2 - x^2}}\,dx$$

$$\rightarrow T = 2\pi\sqrt{\frac{m}{k}} \Rightarrow \frac{dt}{T} = \underbrace{\frac{1}{2\pi\sqrt{A^2 - x^2}}}_{\rho_c(x)}\,dx$$

$\rightarrow$ Está normalizado? $(*) = \displaystyle\int_{-A}^{A} \rho_c(x)\,dx = \frac{1}{2\pi}\int_{-A}^{A} \frac{dx}{\sqrt{A^2 - x^2}} = \frac{1}{2\pi A}\int_{-A}^{A} \frac{dx}{\sqrt{1 - \frac{x^2}{A^2}}}$

$$z = \frac{x}{A} \Rightarrow (*) = \frac{1}{2\pi A}\int_{-1}^{1} \frac{A\,dz}{\sqrt{1 - z^2}} = \frac{1}{2\pi}\operatorname{arcsen}(z)\Big|_{-1}^{1} = \frac{1}{2\pi}\left(\frac{\pi}{2} - \left(-\frac{\pi}{2}\right)\right) = 2$$

$$\therefore \boxed{\rho_c(x) = \frac{1}{\pi}\,\frac{1}{\sqrt{A^2 - x^2}}}$$

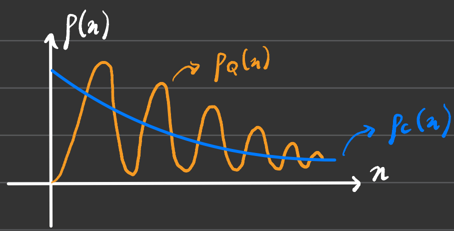
$\rightarrow \frac{1}{2} k A^2 = E \Rightarrow A^2 = \frac{2E}{k}$

$\rightarrow E_{12} = \left(12 + \frac{1}{2}\right)\hbar\omega = \frac{25}{2}\hbar\omega$

$A^2 = \frac{2}{k} \cdot \frac{25}{2}\hbar\omega = \frac{25\hbar\omega}{k}$

$\rightarrow \alpha = \frac{m\omega}{\hbar} = 1, \quad \omega = \sqrt{\frac{k}{m}} \Rightarrow A^2 = 25\frac{\hbar\omega}{m\omega^2} = 25\frac{\hbar}{m\omega} = 25$

$$\therefore \boxed{\rho_c = \frac{1}{\pi}\frac{1}{\sqrt{25 - x^2}}}$$

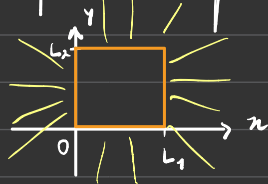


18/08/23

Eq. Schrödinger em mais dimensões

→ Vamos considerar uma partícula em um poço de potencial infinito em 2D:

$$V(x,y) = \begin{cases} 0, & 0 < x < L_1 \text{ e } 0 < y < L_2 \\ \infty, & \text{senão} \end{cases}$$



vale para retângulo ($L_1 \neq L_2$) ou quadrado ($L_1 = L_2$)

→ Momento: $\vec{p} = (p_x, p_y) = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right) = -i\hbar\vec{\nabla}$

$$p^2 = \vec{p}\cdot\vec{p} = -\hbar^2\left(\frac{\partial^2}{\partial x^2}, \frac{\partial^2}{\partial y^2}\right) = -\hbar^2\nabla^2$$

→ Hamiltoniano: $H = \frac{p^2}{2m} + V(x,y) = -\frac{\hbar^2}{2m}\nabla^2 + V$

→ Eq. Schrödinger independente do tempo:

$$H\psi = E\psi \Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) + V\psi(x,y) = E\psi(x,y)$$

→ Tentamos uma solução da forma $\psi(x,y) = X(x)\,Y(y)$ (1)

→ Para o poço: $-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) = E\psi(x,y)$ (2)

$\rightarrow$ (1) em (2): $-\frac{\hbar^2}{2m}\left[YX'' + XY''\right] = EXY \quad * \left(-\frac{2m}{\hbar^2}\frac{1}{XY}\right)$ $\rightarrow -k^2 \rightarrow k = \sqrt{\frac{2mE}{\hbar^2}}$

$$\frac{X''}{X} + \frac{Y''}{Y} = -\frac{2mE}{\hbar^2} \Rightarrow \underbrace{\frac{X''}{X}}_{\text{só depende de } X} = -\frac{2mE}{\hbar^2} - \underbrace{\frac{Y''}{Y}}_{\text{só depende de } Y} = \text{cte}$$

$\rightarrow$ Escolhemos a constante no formato $\text{cte} = -k_x^2$:

$$\frac{X''}{X} = -k_x^2 \Rightarrow X'' + k_x X = 0 \Rightarrow X(x) = A\,\text{sen}(k_x x) + B\cos(k_x x) \quad (3)$$

$\rightarrow$ Em y: $-k^2 - \frac{Y''}{Y} = -k_x^2 \Rightarrow \frac{Y''}{Y} + \overbrace{k^2 - k_x^2}^{\equiv k_y^2} = 0$

$$Y'' + k_y^2 Y = 0 \Rightarrow Y(y) = C\,\text{sen}(k_y y) + D\cos(k_y y) \quad (4)$$

$\rightarrow$ assim, $\varphi(x,y) = \left[A\,\text{sen}(k_x x) + B\cos(k_x x)\right]\left[C\,\text{sen}(k_y y) + D\cos(k_y y)\right]$

$\rightarrow$ Condições de contorno: $\varphi(0,y) = \varphi(x, L_2) = \varphi(L_1, y) = \varphi(x, 0) = 0$

$\hookrightarrow \varphi(x,0) = 0 \Rightarrow \left[A\,\text{sen}(k_x x) + B\cos(k_x x)\right]D = 0 \Rightarrow D = 0$

$\hookrightarrow \varphi(0,y) = 0 \Rightarrow B\left[C\,\text{sen}(k_y y) + D\cos(k_y y)\right] = 0 \Rightarrow B = 0$

$\Rightarrow \varphi(x,y) = A\,\text{sen}(k_x x)\, C\,\text{sen}(k_y y)$

$\hookrightarrow \varphi(x, L_2) = AC \, sen(k_x x) \, sen(k_y L_2) = 0 \Rightarrow K_y L_2 = n_y \pi, \quad n_y = 1, 2, 3, \ldots$

$$\boxed{K_y = \frac{n_y \pi}{L_2}}$$

$\hookrightarrow \varphi(L_1, y) = AC \, sen(k_x L_1) \, sen(k_y y) = 0 \Rightarrow K_x L_1 = n_x \pi, \quad n_x = 1, 2, 3, \ldots$

$$\boxed{K_x = \frac{n_x \pi}{L_1}}$$

$$\therefore \varphi(x,y) = AC \, sen\left(\frac{n_x \pi}{L_1} x\right) sen\left(\frac{n_y \pi}{L_2} y\right)$$

$\rightarrow K^2 = K_x^2 + K_y^2 \Rightarrow \frac{2mE}{\hbar^2} = \left(\frac{n_x \pi}{L_1}\right)^2 + \left(\frac{n_y \pi}{L_2}\right)^2 = \pi^2 \left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2}\right)$

$$\therefore \boxed{E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2}\right)}$$

$\rightarrow$ Normalização: $\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \varphi^*(x,y) \, \varphi(x,y) \, dx \, dy = 1$

$$|AC|^2 \int_0^{L_1} \int_0^{L_2} sen^2\left(\frac{n_x \pi}{L_1} x\right) sen^2\left(\frac{n_y \pi}{L_2} y\right) dy \, dx = 1$$

$$|AC|^2 \underbrace{\int_0^{L_1} sen^2\left(\frac{n_x \pi}{L_1} x\right) dx}_{L_1/2} \underbrace{\int_0^{L_2} sen^2\left(\frac{n_y \pi}{L_2} y\right) dy}_{L_2/2} = 1$$

$$|AC|^2 \cdot \frac{L_1 L_2}{4} = 1 \Rightarrow |AC| = \sqrt{\frac{4}{L_1 L_2}} = \sqrt{\frac{2}{L_1}} \sqrt{\frac{2}{L_2}}$$

$$\therefore \boxed{\varphi_{n_x, n_y} = \sqrt{\frac{2}{L_1}} \sqrt{\frac{2}{L_2}} \, sen\left(\frac{n_x \pi}{L_1} x\right) sen\left(\frac{n_y \pi}{L_2} y\right)}$$

$$\rightarrow \psi(x,y,t) = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} C_{n_x,n_y} \varphi_{n_x,n_y}(x,y)\, e^{-i\frac{E_{n_x,n_y}}{\hbar}t}$$

$$\boxed{\psi(x,y,t) = \sqrt{\frac{2}{L_1}}\sqrt{\frac{2}{L_2}} \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} C_{n_x,n_y}\, \mathrm{sen}\left(\frac{n_x \pi}{L_1} x\right) \mathrm{sen}\left(\frac{n_y \pi}{L_2} y\right) e^{-\frac{i\pi^2\hbar}{2m}\left(\frac{n_x^2}{L_1^2}+\frac{n_y^2}{L_2^2}\right)t}}$$

* 3D: $\psi(\vec{r},t) = \psi(x,y,z,t) = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} C_{n_x,n_y,n_z}\, \mathrm{sen}\left(\frac{n_x \pi}{L_1} x\right) \mathrm{sen}\left(\frac{n_y \pi}{L_2} y\right) \mathrm{sen}\left(\frac{n_z \pi}{L_3} z\right) *$

$$* \; e^{-\frac{i\pi^2\hbar}{2m}\left(\frac{n_x^2}{L_1^2}+\frac{n_y^2}{L_2^2}+\frac{n_z^2}{L_3^2}\right)t}$$

* Obs: $L_1 = L_2 \Rightarrow E_{n_x,n_y} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2+n_y^2)$

↳ Estado fundamental: $n_x = n_y = 1 \Rightarrow E_{1,1} = \frac{\hbar^2\pi^2}{2mL^2}(1^2+1^2) = \frac{\hbar^2\pi^2}{mL^2}$

↳ $n_x = 1,\ n_y = 2 \Rightarrow E_{1,2} = \frac{5}{2}\frac{\hbar^2\pi^2}{mL^2}$

↳ $n_x = 2,\ n_y = 1 \Rightarrow E_{2,1} = \frac{5}{2}\frac{\hbar^2\pi^2}{mL^2}$

$\varphi_{1,2}(x,y)$ e $\varphi_{2,1}(x,y)$ são estados degenerados (possuem a mesma autoenergia)

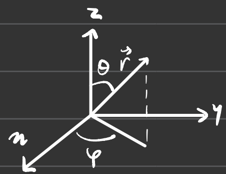
$$\rightarrow \sqrt{\frac{2}{L_1}}\sqrt{\frac{2}{L_2}} \int_0^{L_1}\int_0^{L_2} \mathrm{sen}\left(\frac{n_x \pi}{L_1} x\right) \mathrm{sen}\left(\frac{n_x' \pi}{L_1} x\right) \mathrm{sen}\left(\frac{n_y \pi}{L_2} y\right) \mathrm{sen}\left(\frac{n_y' \pi}{L_2} y\right) dy\, dx = \delta_{n_x,n_x'}\delta_{n_y,n_y'}$$

Eq. Schrödinger para potenciais centrais $V = V(r)$

→ Inicialmente: $-\frac{\hbar^2}{2m}\nabla^2\psi + V(x,y,z)\psi = E\psi$

→ Se o potencial é central: $V = V(r) = V\left(\sqrt{x^2+y^2+z^2}\right)$

→ Mudança de variáveis: $\begin{cases} x = r\,\text{sen}\,\theta\cos\varphi \\ y = r\,\text{sen}\,\theta\,\text{sen}\,\varphi \\ z = r\cos\theta \end{cases}$



→ $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\,\text{sen}\,\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\,\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\,\text{sen}^2\theta}\frac{\partial}{\partial\varphi^2}$

→ $-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\,\text{sen}\,\theta}\frac{\partial}{\partial\theta}\left(\text{sen}\,\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\,\text{sen}^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right] + V(r)\psi = E\psi$

→ Tentamos $\psi(r,\theta,\varphi) = R(r)\,\Omega(\theta)\,\Phi(\varphi)$

→ $-\frac{\hbar^2}{2m}\left[\frac{\Omega(\theta)\Phi(\varphi)}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R(r)\Phi(\varphi)}{r^2\,\text{sen}\,\theta}\frac{d}{d\theta}\left(\text{sen}\,\theta\frac{d\Omega}{d\theta}\right) + \frac{R(r)\,\Omega(\theta)}{r^2\,\text{sen}^2\theta}\frac{d^2\Phi}{d\varphi^2}\right] + V(r)R\Omega\Phi = ER\Omega\Phi$

$\downarrow * \left(-\frac{2mr^2}{\hbar^2\psi}\right)$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\text{sen}\,\theta\,\Omega}\frac{d}{d\theta}\left(\text{sen}\,\theta\frac{d\Omega}{d\theta}\right) + \frac{1}{\text{sen}^2\theta\,\Phi}\frac{d^2\Phi}{d\varphi^2} - \frac{2mr^2V}{\hbar^2} = -\frac{2mE\,r^2}{\hbar^2}$$

$$\Rightarrow \underbrace{\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left[E - V(r)\right]}_{r \to \text{parte radial}} = \underbrace{-\frac{1}{\text{sen}\,\theta\,\Omega}\frac{d}{d\theta}\left(\text{sen}\,\theta\frac{d\Omega}{d\theta}\right) - \frac{1}{\text{sen}^2\theta\,\Phi}\frac{d^2\Phi}{d\varphi^2}}_{\theta,\varphi \to \text{parte angular}}$$

→ Os lados esquerdo e direito são uma constante: escolhemos $\ell(\ell+1)$

→ Parte radial: $\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left[E - V(r)\right] = \ell(\ell+1)$

→ Parte angular: $-\frac{1}{\operatorname{sen}\theta\,\Omega}\frac{d}{d\theta}\left(\operatorname{sen}\theta\frac{d\Omega}{d\theta}\right) - \frac{1}{\operatorname{sen}^2\theta\,\Phi}\frac{d^2\Phi}{d\varphi^2} = \ell(\ell+1)$ $\Big) * \operatorname{sen}^2\theta$

$$-\frac{\operatorname{sen}\theta}{\Omega}\frac{d}{d\theta}\left(\operatorname{sen}\theta\frac{d\Omega}{d\theta}\right) - \frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = \ell(\ell+1)\operatorname{sen}^2\theta$$

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = \frac{\operatorname{sen}\theta}{\Omega}\frac{d}{d\theta}\left(\operatorname{sen}\theta\frac{d\Omega}{d\theta}\right) + \ell(\ell+1)\operatorname{sen}^2\theta$$

→ Equação em φ: $-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = \text{cte} = m^2$

→ $\frac{d^2\Phi}{d\varphi^2} + m^2\Phi = 0 \Rightarrow \Phi(\varphi) = Ae^{im\varphi}$, $m<0$ ou $m>0$

→ $\Phi(0) = \Phi(2\pi) \Rightarrow A = Ae^{i2\pi m} \Rightarrow e^{i2\pi m} = 1 \Rightarrow m \in \mathbb{Z}$

$A = \frac{1}{\sqrt{2\pi}} \longrightarrow \therefore \boxed{\Phi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im\varphi}}$, $m \in \mathbb{Z}$ → nº quântico magnético

eq. Legendre associada

→ A equação em θ fica: $\frac{\operatorname{sen}\theta}{\Omega}\frac{d}{d\theta}\left(\operatorname{sen}\theta\frac{d\Omega}{d\theta}\right) + \ell(\ell+1)\operatorname{sen}^2\theta = m^2$

nº quântico azimutal

$\ell \in \mathbb{Z}$

→ Depois de um bom investimento: $\boxed{\Omega(\theta) = A P_\ell^m(\cos\theta)}$ } funções associadas de Legendre

↳ $P_\ell^m(x) = (1-x^2)^{\frac{|m|}{2}}\frac{d^{|m|}}{dx^{|m|}}P_\ell(x)$, $\boxed{P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell}$

$\boxed{m = 0, \pm1, \pm2, \ldots, \pm\ell}$

Fórmula de Rodrigues: polinômios da Física Matemática

21/08/23

→ solução da parte angular: $Y_\ell^m(\theta,\varphi) = A_{\ell,m}\, P_\ell^m(\cos\theta)\, e^{im\varphi}$

Harmônicos esféricos

* Função de onda: $\psi(r,\theta,\varphi) = R(r)\, Y_\ell^m(\theta,\varphi)$

↳ Normalização: $\int \psi^*(r,\theta,\varphi)\,\psi(r,\theta,\varphi)\, d^3\vec{r} = 1$

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi R^*(r) R(r) \left[Y_\ell^m(\theta,\varphi)\right]^* Y_\ell^m(\theta,\varphi)\, r^2 \operatorname{sen}\theta\, dr\, d\theta\, d\varphi = 1$$

$$\underbrace{\int_0^\infty |R(r)|^2 dr}_{1}\ \underbrace{\int_0^{2\pi}\int_0^\pi |Y_\ell^m(\theta,\varphi)|^2 \operatorname{sen}\theta\, d\theta\, d\varphi}_{1} = 1$$

$$\therefore \boxed{Y_\ell^m(\theta,\varphi) = \xi_m \sqrt{\frac{(2\ell+1)(\ell-|m|)}{4\pi\ (\ell+|m|)!}}\ e^{im\varphi}\, P_\ell^m(\cos\theta)}, \quad \xi_m = \begin{cases} (-1)^m, & m \geq 0 \\ 1, & m < 0 \end{cases}$$

$$\int_0^{2\pi}\int_0^\pi Y_\ell^{m\,*}(\theta,\varphi)\, Y_{\ell'}^{m'}(\theta,\varphi) \operatorname{sen}\theta\, d\theta\, d\varphi = \delta_{\ell,\ell'}\,\delta_{m,m'}$$

* Voltando à parte radial: $\frac{d}{dr}\left[r^2 \frac{dR}{dr}\right] - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right] R = \ell(\ell+1) R$

→ Considere: $R(r) = \frac{u(r)}{r} \rightarrow \frac{dR}{dr} = -\frac{1}{r^2} u(r) + \frac{1}{r}\frac{du}{dr}$

$$\frac{d}{dr}\left[r^2\left(-\frac{1}{r^2}u(r) + \frac{1}{r}\frac{du}{dr}\right)\right] - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\frac{u}{r} = \ell(\ell+1)\frac{u}{r}$$

$$-\frac{du}{dr} + \frac{d}{dr}\left[r\frac{du}{dr}\right] - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\frac{u}{r} = \ell(\ell+1)\frac{u}{r}$$

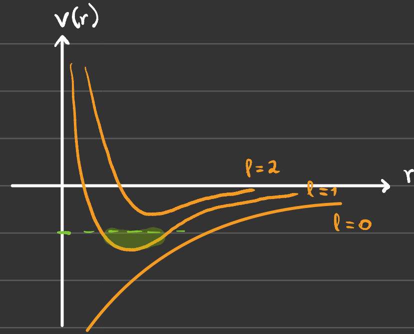
$$-\cancel{\frac{du}{dr}} + \cancel{\frac{du}{dr}} + r\frac{d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\frac{u}{r} = \ell(\ell+1)\frac{u}{r}$$

↓

$$\rightarrow \frac{d^2u}{dr^2} - \frac{2m}{\hbar^2}\left[V-E\right]u = \frac{l(l+1)}{r^2}u \quad * \left(-\frac{\hbar^2}{2m}\right)$$

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

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V(r) + \frac{\hbar^2}{2mr^2}\,l(l+1)\right]}_{V_{eff}(r)}u(r) = Eu$$



Átomo de hidrogênio

→ Para o átomo de hidrogênio: $V(r) = -\dfrac{e^2}{4\pi\varepsilon_0 r}$

→ $$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2}{2mr^2}\,l(l+1)\right]u = Eu \quad (*)$$

→ Definimos:
$$\begin{cases} K = \sqrt{-\dfrac{2mE}{\hbar^2}} \Rightarrow K^2 = -\dfrac{2mE}{\hbar^2} \Rightarrow E = -\dfrac{\hbar^2}{2m}K^2 \\ \rho = Kr \Rightarrow \dfrac{du}{dr} = \dfrac{du}{d\rho}\dfrac{d\rho}{dr} = K\dfrac{du}{d\rho} \Rightarrow \dfrac{d^2u}{dr^2} = \dfrac{d}{dr}\left[K\dfrac{du}{d\rho}\right]\dfrac{d\rho}{dr} = K^2\dfrac{d^2u}{d\rho^2} \end{cases}$$

→ Dividindo (*) por E:
$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} + \left[-1 - \frac{e^2}{4\pi\varepsilon_0 rE} + \frac{\hbar^2}{2mr^2}\frac{l(l+1)}{E}\right]u = 0$$

$$\frac{1}{K^2}\frac{d^2u}{dr^2} + \left[-1 - \frac{e^2}{4\pi\varepsilon_0\left(-\frac{\hbar^2}{2m}K\right)Kr} + \frac{\hbar^2}{2mr^2}\frac{l(l+1)}{\left(-\frac{\hbar^2}{2m}K^2\right)}\right]u = 0$$

↳ $\equiv \rho_0 = \dfrac{me^2}{2\pi\varepsilon_0\hbar^2K}$

$$\frac{d^2u}{d\rho^2} + \left[-1 + \frac{\rho_0}{\rho} - \frac{l(l+1)}{\rho^2}\right]u = 0 \quad (1)$$

→ Solução assintótica: $\rho \to \infty$

↳ $\dfrac{d^2u}{d\rho^2} \approx u \Rightarrow u = e^{\alpha\rho}$

↳ $\alpha^2 e^{\alpha\rho} - e^{\alpha\rho} = 0 \Rightarrow \alpha = \pm 1$

↳ $u(\rho) = \cancel{A}e^{\rho} + Be^{-\rho} \Rightarrow u(\rho) \sim e^{-\rho}$

→ Solução assintótica: $\rho \to 0$

↳ $\frac{d^2u}{d\rho^2} \sim \frac{\ell(\ell+1)}{\rho^2} u$

↳ Verifique por substituição direta que $u(\rho) = C\rho^{\ell+1} + \cancel{D\rho^{-\ell}}$

$u(\rho) \sim \rho^{\ell+1}$

→ Vamos supor $u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$ (2)

onde $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$ (3)

→ Substituindo (2) em (1)

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + \left[\rho_0 - 2(\ell+1)\right] v = 0 \quad (4)$$

→ Substituindo (3) em (4): $c_{j+1} = \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)} c_j$

↳ Para j grande: $c_{j+1} = \frac{2j\left(1+\cancel{\frac{\ell+1}{j}}^{\sim 0}\right)-\rho_0}{(j+1)j\left(1+\cancel{\frac{2\ell+2}{j}}^{\sim 0}\right)} c_j \sim \frac{2j}{(j+1)j} c_j = \frac{2}{j+1} c_j \approx \frac{2}{j} c_j$

$$c_{j+1} = \frac{2}{j}\frac{2}{j-1} \cdots = \frac{2^j}{j!} c_0$$

$$v(\rho) \sim \sum_{j=0}^{\infty} \frac{2^j}{j!} c_0 \rho^j \sim c_0 \sum_{j=0}^{\infty} \frac{(2\rho)^j}{j!} = c_0 e^{2\rho}$$

↳ Voltando em (2): $u(\rho) \sim \rho^{\ell+1} e^{-\rho} c_0 e^{2\rho} = c_0 \rho^{\ell+1} e^{\rho} \xrightarrow[\rho\to\infty]{} \infty$ X

→ Logo, o polinômio deve ser truncado: $2(\underbrace{j_{max}+\ell+1}_{\equiv n \to \text{ nº quântico principal}}) - \rho_0 = 0$

$$2n - \rho_0 = 0$$

* Parte radial: $u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$ $\begin{cases} v(\rho) = \sum_{j=0}^{j_{max}} c_j \rho^j \\ c_j = \dfrac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)} \end{cases}$

$$\to 2n = \rho_0 = \frac{me^2}{2\pi\varepsilon_0 \hbar^2 k}$$

$$\to k = \frac{me^2}{4\pi\varepsilon_0 \hbar^2}\frac{1}{n} \Rightarrow k^2 = \frac{m^2 e^4}{(4\pi\varepsilon_0)^2\hbar^4}\frac{1}{n^2}$$

$$-\frac{2mE}{\hbar^2} = \frac{m^2e^4}{(4\pi\varepsilon_0)^2\hbar^4}\frac{1}{n^2}$$

$$\therefore \boxed{E_n = \frac{-me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2}}$$

→ independe de m e ℓ

⇒ degenerado

* $\begin{cases} m = 0, \pm 1, \pm 2, \dots, \pm \ell & \to \text{magnético} \\ \ell = 0, 1, 2, \dots n-1 & \to \text{secundário / azimutal} \\ n = 1, 2, 3, \dots & \to \text{principal} \end{cases}$

23/08/23

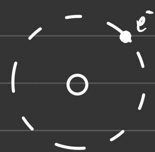
$\rightarrow \psi(r, \theta, \varphi) = R(r)\, Y_\ell^m(\theta, \varphi)$

$\rightarrow R(r) = \frac{u(r)}{r}$ $\Big|$ $u(r) = \rho^{\ell+1} e^{-\rho} v(\rho)$ $\Big|$ $\rho = kr$ $\Big|$ $\rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2 k} = 2n$

$k = \sqrt{-\frac{2mE}{\hbar^2}}$ $\Big|$ $v(\rho) = \sum_{j=0}^{j_{max}} c_j v$ $\Big|$ $c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)}\, c_j$

$\rightarrow$ As condições de contorno impõem $\begin{cases} n = 1, 2, 3, \dots \\ \ell = 0, 1, 2, \dots, n-1 \\ m = 0, \pm 1, \pm 2, \dots, \pm \ell \end{cases}$

$\rightarrow$ Originalmente: $-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi = E\psi$



$$\frac{me^2}{2\pi\varepsilon_0\hbar^2 k} = 2n \Rightarrow k = \frac{me^2}{4\pi\varepsilon_0\hbar^2 n}$$

$$-\frac{2mE}{\hbar^2} = \frac{m^2e^4}{(4\pi\varepsilon_0)^2\hbar^4 n^2}$$

$$\therefore \boxed{E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = \frac{E_1}{n^2}}$$

→ Lembrando da órbita do átomo de Bohr:

$$\rightarrow L = mvr = n\hbar \Rightarrow v = \frac{n\hbar}{mr}$$

$$\rightarrow \frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$\frac{m}{r}\frac{n^2\hbar^2}{m^2r^2} = \frac{e^2}{4\pi\varepsilon_0 r^2} \Rightarrow r_n = \frac{4\pi\varepsilon_0\hbar^2}{me^2}n^2$$

$$\rightarrow r_1 = a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \qquad k = \frac{me^2}{4\pi\varepsilon_0\hbar^2 n} = \frac{1}{a_0 n}$$

$$\rightarrow \rho = kr \Rightarrow \boxed{\rho = \frac{r}{a_0 n}} \Rightarrow \boxed{R_{nl}(r) = \frac{1}{r}\left(\frac{r}{a_0 n}\right)^{l+1} e^{-\frac{r}{a_0 n}}\, v\left(\frac{r}{a_0 n}\right)}$$

Polinômios associados de Laguerre

* Estado fundamental: $n = 1,\ l = 0,\ m = 0$

$$\rightarrow \psi = \psi_{n,l,m} = (r,\theta,\varphi) = R_{nl}(r)\, Y_l^m(\theta,\varphi)$$

$$\rightarrow u(r) = \left(\frac{r}{a_0}\right)^{0+1} e^{-\frac{r}{a_0}} c_0 = c_0 \frac{r}{a_0} e^{-\frac{r}{a_0}}$$

↳ $j_{max} = n - l - 1 = 1 - 0 - 1 = 0 \Rightarrow$ só existe c_0

$$\rightarrow R = R_{nl}(r) \Rightarrow R_{10}(r) = \frac{u(r)}{r} = \frac{c_0}{a_0} e^{-\frac{r}{a_0}}$$

→ Normalização: $\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} |\psi_{n,l,m}(r,\theta,\varphi)|^2 r^2 \,\text{sen}\,\theta \, dr\, d\theta\, d\varphi = 1$

$$= \int_0^{\infty} |R_{nl}(r)|^2 r^2 dr \int_0^{\pi}\int_0^{2\pi} |Y_l^m(\theta,\varphi)|^2 \,\text{sen}\,\theta\, d\theta\, d\varphi$$

↳ $Y_0^0(\theta,\varphi) = \dfrac{1}{\sqrt{4\pi}} \Rightarrow \displaystyle\int_0^{\pi}\int_0^{2\pi} \frac{1}{4\pi} \,\text{sen}\,\theta\, d\theta\, d\varphi = \frac{1}{4\pi} \overbrace{\int_0^{\pi}\int_0^{2\pi} \text{sen}\,\theta\, d\theta\, d\varphi}^{4\pi} = 1$

→ $\psi_{1,0,0} = R_{1,0}(r)\, Y_0^0(\theta,\varphi) = \dfrac{C_0}{\sqrt{4\pi}\, a_0} e^{-\frac{r}{a_0}}$

→ $\displaystyle\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} |\psi_{1,0,0}(r,\theta,\varphi)|^2 r^2 \,\text{sen}\,\theta\, dr\, d\theta\, d\varphi = 1$

$$\frac{C_0^2}{4\pi a_0^2}\left(\int_0^{\infty} r^2 e^{-\frac{2r}{a_0}} dr\right)\left(\int_0^{2\pi}\int_0^{\pi} \text{sen}\,\theta\, d\theta\, d\varphi\right) = 1$$

$$\frac{C_0^2}{a_0^2} \underbrace{\int_0^{\infty} r^2 e^{-\frac{2r}{a_0}}}_{\frac{a_0^3}{4}} = \frac{C_0^2}{a_0^2} \cdot \frac{a_0^3}{4} = 1 \Rightarrow C_0 = \frac{2}{\sqrt{a_0}}$$

$$\int_0^{\infty} x^2 e^{-\alpha x} dx = \frac{d^2}{d\alpha^2}\int_0^{\infty} e^{-\alpha x} dx$$

$$= \frac{d^2}{d\alpha^2} \frac{e^{-\alpha x}}{-\alpha}\Big|_0^{\infty} = \frac{d^2}{d\alpha^2}\left(\frac{1}{\alpha}\right)$$

$$= \frac{d}{d\alpha}\left(-\frac{1}{\alpha^2}\right) = \frac{2}{\alpha^3}$$

$$\int_0^{\infty} r^2 e^{-\frac{2r}{a_0}} dr = \frac{2}{\left(\frac{2}{a_0}\right)^3} = \frac{a_0^3}{4}$$

$$\boxed{\therefore \psi_{1,0,0}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}\, a_0^{\frac{3}{2}}} e^{-\frac{r}{a_0}}}$$

→ Densidade de probabilidade: $p(r,\theta,\varphi)\, dr\, d\theta\, d\varphi = |\psi_{1,0,0}|^2 r^2 \,\text{sen}\,\theta\, dr\, d\theta\, d\varphi$

→ Só a parte radial: $p(r)\, dr = \left(\displaystyle\int_0^{\pi}\int_0^{2\pi} \text{sen}\,\theta\, d\theta\, d\varphi\right) \frac{1}{a_0^3 \pi} e^{-\frac{2r}{a_0}} r^2 dr = \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2 dr$

$$\boxed{p(r) = \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}}}$$

→ Raio de máxima probabilidade: $\frac{dp}{dr} = 0$

$$\frac{4}{a_0^3}\left[2re^{-\frac{2r}{a_0}} + r^2\left(-\frac{2}{a_0}\right)e^{-\frac{2r}{a_0}}\right] = 0 \Rightarrow \frac{4}{a_0^3}\,2re^{-\frac{2r}{a_0}}\left[1 - \frac{r}{a_0}\right] = 0 \Rightarrow \boxed{r = a_0}$$

→ Raio de Bohr é o mais provável

→ Raio médio: $\langle r\rangle = \frac{1}{a_0^3}\int_0^\infty r^3 e^{-\frac{2r}{a_0}}\,dr$

$$z \equiv \frac{2r}{a_0} \Rightarrow dr = \frac{a_0}{2}dz \Rightarrow r = \frac{a_0}{2}z$$

$$\langle r\rangle = \frac{4}{a_0^3}\int_0^\infty \frac{a_0^3}{8} z^3 e^{-z}\frac{a_0}{2}dz = \frac{a_0^4}{4a_0^3}\int_0^\infty z^3 e^{-z}dz = \frac{a_0}{4}\Gamma(4) \Rightarrow \boxed{\langle r\rangle = \frac{3}{2}a_0}$$

→ Raio médio / esperado é maior do que o raio de Bohr

→ Elétron além do átomo de Bohr: $P_r(r>a) = \int_a^\infty \rho(r)\,dr$

$$P_r(r>a) = \frac{4}{a_0^3}\int_a^\infty r^2 e^{-\frac{2r}{a_0}}dr = \frac{4}{a_0^3}\left[-\frac{r^2 e^{-\frac{2r}{a_0}}}{\frac{2}{a_0}}\Bigg|_a^\infty + \int_a^\infty 2r\frac{a_0}{2}e^{-\frac{2r}{a_0}}dr\right]$$

$$= \frac{4}{a_0^3}\left[a^2\cdot\frac{a_0}{2}e^{-\frac{2a}{a_0}} + a_0\int_a^\infty re^{-\frac{2r}{a_0}}dr\right]$$

$$= \frac{4}{a_0^3}\left\{a_0\frac{a^2}{2}e^{-\frac{2a}{a_0}} + a_0\left[-\frac{a_0}{2}re^{-\frac{2r}{a_0}}\Bigg|_a^\infty + \frac{a_0}{2}\int_a^\infty e^{-\frac{2r}{a_0}}dr\right]\right\}$$

$$P_r(r>a) = \frac{4}{a_0^3}\left[\frac{a^2}{2}a_0e^{-\frac{2a}{a_0}} + \frac{aa_0^2}{2}e^{-\frac{2a}{a_0}} + \frac{a_0^3}{4}e^{-\frac{2a}{a_0}}\right]$$

↳ $a = a_0$: $P_r(r>a_0) = \frac{4}{\cancel{a_0^3}}\left[\frac{\cancel{a_0^3}}{2}e^{-2} + \frac{\cancel{a_0^3}}{2}e^{-2} + \frac{\cancel{a_0^3}}{4}e^{-2}\right] \Rightarrow \boxed{P_r(r>a_0) = 5e^{-2} \approx 0{,}68}$

* $n=2,\ \ell=0,\ \ell=1$:

* $\ell=0$:

$\rightarrow j_{max} = n-\ell-1 = 2-0-1 = 1 \rightarrow j=0,1$

$\rightarrow c_0,\ c_{j+1} = \dfrac{2(j+\ell+1)-2n}{(j+1)(j+2\ell+2)}\, c_j \Rightarrow c_1 = \dfrac{2(0+0+1)-2\cdot 2}{(0+1)(0+2)}\, c_0 = -\dfrac{2}{2} c_0 \Rightarrow c_1 = -c_0$

$\rightarrow v(\rho) = c_0 + c_1\rho = c_0(1-\rho)$

$\rightarrow R(r) = \dfrac{u(r)}{r}\ \Big|\ u(r) = \rho^{\ell+1} e^{-\rho}\, v(\rho)\ \Big|\ \rho = \dfrac{r}{na_0} = \dfrac{r}{2a_0}$

$\rightarrow R_{2,1}(r) = \dfrac{\left(\frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}\, c_0\left(1-\frac{r}{2a_0}\right)}{r} = \dfrac{c_0}{2a_0}\, e^{-\frac{r}{2a_0}}\left(1-\dfrac{r}{2a_0}\right)$

$\rightarrow \ell=0 \Rightarrow m=0 \Rightarrow Y_0^0(\theta,\varphi) = \dfrac{1}{\sqrt{4\pi}}$

$\Rightarrow \psi_{2,0,0}(r,\theta,\varphi) = \dfrac{c_0}{4a_0\sqrt{\pi}}\, e^{-\frac{r}{2a_0}}\left(1-\dfrac{r}{2a_0}\right)$

* $\ell = 1$:

$\rightarrow j_{max} = 2-1-1 = 0 \Rightarrow v(\rho) = c_0$

$\rightarrow R_{2,1}(r) = \dfrac{\left(\frac{r}{2a_0}\right)^2 e^{-\frac{r}{2a_0}} c_0}{r} = c_0 \dfrac{r}{4a_0^2} e^{-\frac{r}{2a_0}}$

$$\rightarrow \ell = 1 \Rightarrow \begin{cases} m = -1 \rightarrow Y_1^{-1} = C_- \,\text{sen}\,\theta\, e^{-i\varphi} \\ m = 0 \rightarrow Y_1^{0} = C_0 \cos\theta \\ m = 1 \rightarrow Y_1^{+1} = C_+ \,\text{sen}\,\theta\, e^{i\varphi} \end{cases}$$

$$\psi_{2,1,-1}(r,\theta,\varphi) = \frac{c_0}{4a_0^2}\, r e^{-\frac{r}{2a_0}} \,\text{sen}\,\theta\, e^{-i\varphi}$$

$$\Rightarrow \psi_{2,1,0}(r,\theta,\varphi) = \frac{c_0}{4a_0^2}\, r e^{-\frac{r}{2a_0}} \cos\theta$$

$$\psi_{2,1,1}(r,\theta,\varphi) = \frac{c_0}{4a_0^2}\, r e^{-\frac{r}{2a_0}} \,\text{sen}\,\theta\, e^{i\varphi}$$

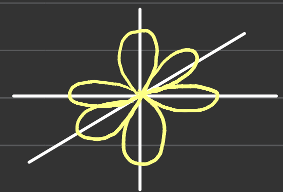
$\rightarrow$ Normalizando: $\iiint |\psi|^2 r^2 \,\text{sen}\,\theta\, dr\, d\theta\, d\varphi = 1$

$$\boxed{\psi_{2,1,0}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}} \frac{1}{a_0^{\frac{3}{2}}} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \cos\theta}$$

$$\boxed{\psi_{2,1,\pm 1}(r,\theta,\varphi) = \frac{1}{8\sqrt{\pi}} \frac{1}{a_0^{\frac{3}{2}}} \left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \,\text{sen}\,\theta\, e^{\pm i\varphi}}$$

coeficientes iguais

$$\psi_{2,1} = \frac{1}{\sqrt{3}}\psi_{2,1,0} + \frac{1}{\sqrt{3}}\psi_{2,1,1} + \frac{1}{\sqrt{3}}\psi_{2,1,-1}$$



$$|\psi|^2 = \frac{1}{3}\left[|\psi_{210}|^2 + |\psi_{21-1}|^2 + |\psi_{211}|^2\right]$$
$$= \frac{1}{3}\left[\frac{1}{32\pi}\frac{1}{a_0^3}\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} \cos^2\theta + 2\cdot\frac{1}{64\pi}\frac{1}{a_0^3}\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}} \,\text{sen}^2\theta\right]$$

$$|\psi|^2 = \frac{1}{96\pi}\frac{1}{a_0^3}\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{a_0}}$$

$\hookrightarrow$ simetria esférica

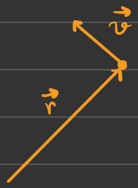
* Genericamente: $\psi_{n,\ell,m}(r,\theta,\varphi) = \underbrace{R_{n\ell}(r)}_{\text{depende do potencial}}\underbrace{Y_\ell^m(\theta,\varphi)}_{A_\ell^m P_\ell^m(\cos\theta) e^{im\varphi}}$

$\hookrightarrow A_\ell^m P_\ell^m(\cos\theta) e^{im\varphi}$

$\hookrightarrow$ depende do potencial

25/08/23

Momento angular



$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \overbrace{(y p_z - z p_y)}^{L_x}\hat{i} + \overbrace{(z p_x - x p_y)}^{L_y}\hat{j} + \overbrace{(x p_y - y p_x)}^{L_z}\hat{k}$$

$\rightarrow p_x = -i\hbar \dfrac{\partial}{\partial x}, \quad p_y = -i\hbar \dfrac{\partial}{\partial y}, \quad p_z = -i\hbar \dfrac{\partial}{\partial z}$

$\rightarrow L_x = -i\hbar \left(y \dfrac{\partial}{\partial z} - z \dfrac{\partial}{\partial y} \right) \;\Big|\; L_y = -i\hbar \left(z \dfrac{\partial}{\partial x} - x \dfrac{\partial}{\partial z} \right) \;\Big|\; L_z = -i\hbar \left(x \dfrac{\partial}{\partial y} - y \dfrac{\partial}{\partial x} \right) \Big|$

$\rightarrow$ Em coordenadas esféricas:

$\hookrightarrow L_x = -i\hbar \left\{ -\operatorname{sen}\varphi \dfrac{\partial}{\partial \theta} - \cos\varphi \cot\theta \dfrac{\partial}{\partial \varphi} \right\}$

$\hookrightarrow L_y = -i\hbar \left\{ \cos\varphi \dfrac{\partial}{\partial \theta} - \operatorname{sen}\varphi \cot\theta \dfrac{\partial}{\partial \varphi} \right\}$

$\hookrightarrow L_z = -i\hbar \dfrac{\partial}{\partial \varphi}$

$$\rightarrow L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2 \left[\frac{1}{\operatorname{sen}\theta} \frac{\partial}{\partial \theta} \left(\operatorname{sen}\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\operatorname{sen}^2\theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

$$\rightarrow \psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \underbrace{Y_l^m(r, \theta, \varphi)}_{C_n^m \Omega_l^m(\theta) e^{im\varphi}}$$

$$\rightarrow sen\,\theta \frac{d}{d\theta}\left(sen\,\theta \frac{d\Omega}{d\theta}\right) + \left[\ell(\ell+1)\, sen^2\theta - m^2\right]\Omega = 0$$

$$\times -\frac{1}{sen^2\theta}$$

$$-\frac{1}{sen\,\theta}\frac{d}{d\theta}\left(sen\,\theta \frac{d\Omega}{d\theta}\right) + \left[-\ell(\ell+1) + \frac{m^2}{sen^2\theta}\right]\Omega = 0$$

$$-\frac{1}{sen\,\theta}\frac{d}{d\theta}\left(sen\,\theta \frac{d\Omega}{d\theta}\right) + \frac{m^2}{sen^2\theta}\Omega = \ell(\ell+1)\Omega$$

$$\times e^{im\varphi}$$

$$-\frac{1}{sen\,\theta}\frac{d}{d\theta}\left(sen\,\theta \frac{d}{d\theta}\right)\Omega e^{im\varphi} + \frac{m^2}{sen^2\theta}\Omega e^{im\varphi} = \ell(\ell+1)\Omega e^{im\varphi}$$

$$-\frac{1}{sen\,\theta}\frac{d}{d\theta}\left(sen\,\theta \frac{d}{d\theta}\right)\Omega e^{im\varphi} - \frac{1}{sen^2\theta}\frac{\partial^2}{\partial\varphi^2}\left(\Omega e^{im\varphi}\right) = \ell(\ell+1)\Omega e^{im\varphi}$$

$$Y_\ell^m = \Omega e^{im\varphi}$$

$$\left[-\frac{1}{sen\,\theta}\frac{\partial}{\partial\theta}\left(sen\,\theta \frac{\partial}{\partial\theta}\right) - \frac{1}{sen^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] Y_\ell^m(\theta,\varphi) = \ell(\ell+1)\, Y_\ell^m(\theta,\varphi)$$

$$\times \hbar^2$$

$$L^2 Y_\ell^m(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_\ell^m(\theta,\varphi)$$ → Y_ℓ^m é autofunção de L^2

$$L^2 Y_\ell^m(\theta,\varphi) R_{n\ell}(r) = \hbar^2 \ell(\ell+1)\, Y_\ell^m(\theta,\varphi) R_{n\ell}(r)$$

$$\therefore \boxed{L^2 \psi_{n\ell m} = \hbar^2 \ell(\ell+1)\psi_{n\ell m}}$$

$$\rightarrow H\psi_{n\ell m}(r,\theta,\varphi) = E_n \psi_{n\ell m}(r,\theta,\varphi) \Rightarrow [H, L^2] = 0$$

$$\rightarrow L_z = -i\hbar\frac{\partial}{\partial\varphi}, \quad \frac{\partial}{\partial\varphi} = i m e^{im\varphi} \Rightarrow L_z e^{im\varphi} = \hbar m e^{im\varphi}$$

$$L_z \Omega(\theta) e^{im\varphi} = \hbar m \Omega(\theta) e^{im\varphi}$$

$$L_z Y_\ell^m(\theta,\varphi) = m\hbar\, Y_\ell^m(\theta,\varphi)$$

$$L_z R_{n\ell}(r) Y_\ell^m(\theta,\varphi) = m\hbar\, R_{n\ell}(r) Y_\ell^m(\theta,\varphi)$$

$$\therefore \boxed{L_z \psi_{n\ell m} = m\hbar\,\psi_{n\ell m}}$$

$$\rightarrow [L_z, L^2] = [L_z, H] = [L^2, H] = 0$$

$$\rightarrow \psi(\vec{r},t) = \sum_{n,m,\ell} C_{nm\ell}\, \psi_{n\ell m}(r,\theta,\varphi)\, e^{-i\frac{E_n}{\hbar}t}$$

$$\rightarrow H\psi_{n\ell m} = E_n \psi_{n\ell m} \quad \rightarrow \quad E_n = \frac{E_1}{n^2} \rightarrow$$ *energia do estado fundamental*

$$\rightarrow \langle H \rangle = \langle \psi | H | \psi \rangle = \int d^3\vec{r}\, \psi^*(\vec{r},t)\, H \psi(\vec{r},t)$$

$$= \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} r^2 \operatorname{sen}\theta \left[\sum_{n\ell m} C_{n\ell m}\psi_{n\ell m}\, e^{-i\frac{E_n}{\hbar}t}\right]^* H \left[\sum_{n'\ell'm'} C_{n'\ell'm'}\psi_{n'\ell'm'}\, e^{-i\frac{E_{n'}}{\hbar}t}\right] dr\, d\theta\, d\varphi$$

$$= \sum_{\substack{n,\ell,m \\ n',\ell',m'}} C^*_{n\ell m}\, C_{n'\ell'm'}\, E_{n'}\, e^{i\frac{(E_n - E_{n'})}{\hbar}t} \underbrace{\iiint \psi^*_{n\ell m}\, \psi_{n'\ell'm'}\, r^2 \operatorname{sen}\theta\, dr\, d\theta\, d\varphi}_{\delta_{n,n'}\,\delta_{\ell,\ell'}\,\delta_{m,m'}}$$

$$\therefore \boxed{\langle H \rangle = \sum_{n,\ell,m} |C_{n\ell m}|^2 E_n}$$