Models exactament resolubles

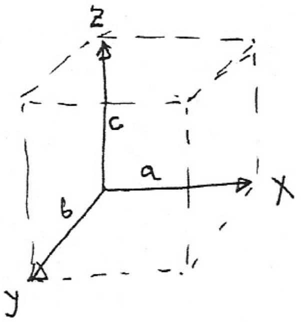
Moviment translacional

- Si $\hat{H}(x,y) = \hat{h}(x) + \hat{g}(y)$ i $\begin{cases} \hat{h}(x)\,\phi_i(x) = \lambda_i\,\phi_i(x) & i = 1,2\ldots \\ \hat{g}(y)\,\chi_j(y) = \mu_j\,\chi_j(y) & j = 1,2\ldots \end{cases}$

$$\Rightarrow \begin{cases} \Psi_k(x,y) = \Phi_i(x)\cdot\chi_j(y) \\ \Lambda_k = \lambda_i + \mu_j \end{cases}$$

- Caixa tridimensional $\quad \hat{H}(x,y,z) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$

però $\quad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \alpha^2} \quad \begin{cases} \Phi_p(\alpha) = \left(\frac{2}{L_\alpha}\right)^{1/2} \sin\frac{p\pi\alpha}{L_\alpha} \\ E_p = \frac{h^2 p^2}{8m L_\alpha^2} \end{cases}$



$$\Psi(x,y,z) = \left(\frac{2}{a}\right)^{1/2}\left(\frac{2}{b}\right)^{1/2}\left(\frac{2}{c}\right)^{1/2} \sin\frac{p\pi x}{a}\,\sin\frac{q\pi y}{b}\,\sin\frac{s\pi z}{c}$$

$$\begin{cases} \mathbb{Z}, \quad \boxed{\Psi_{pqs}(xyz) = \left(\frac{2}{V}\right)^{1/2} \sin\frac{p\pi x}{a}\,\sin\frac{q\pi y}{b}\,\sin\frac{s\pi z}{c}} \\ \mathbb{Z}, \quad \boxed{E_{pqs} = \frac{h^2}{8m}\left[\left(\frac{p}{a}\right)^2 + \left(\frac{q}{b}\right)^2 + \left(\frac{s}{c}\right)^2\right]} \end{cases}$$

caixa cúbica $\longrightarrow$ degeneració $\quad E(p=1, q=2, s=1) = E(p=2, q=1, s=1)$ etc.

Moviment vibracional

1. hamiltonià : $\quad E = \frac{p^2}{2m} + \frac{1}{2}kx^2 \quad$; k, m relacionats amb ω: $\omega = \sqrt{\frac{k}{m}}$

$$\rightarrow \boxed{\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2} \quad \xrightarrow[\hat{H}/\hbar\omega]{\text{adimensional}} \quad \frac{\hat{H}}{\hbar\omega} = -\frac{\hbar}{2m\omega}\frac{d^2}{dx^2} + \frac{1}{2}\frac{k}{\hbar\omega}x^2$$

canvi de variable $\quad x = \beta\xi \rightarrow dx = \beta\, d\xi \rightarrow d/dx = 1/\beta \; d/d\xi$

$$\boxed{\hat{H}/\hbar\omega = -\frac{\hbar^2}{2m\omega}\frac{1}{\beta^2}\frac{d^2}{d\xi^2} + \frac{1}{2}\frac{k}{\hbar\omega}\beta^2\xi^2} \quad \xrightarrow[\text{per fer igual 1}]{\text{tria } \beta} \quad \boxed{\frac{\hat{H}}{\hbar\omega} = -\frac{1}{2}\frac{d^2}{d\xi^2} + \frac{1}{2}\xi^2}$$

2. Creadors, aniquiladors

Suma x diferència = diferència de quadrats

$$\boxed{b^+ = \frac{1}{\sqrt{2}}\left(\xi - \frac{d}{d\xi}\right)} \quad ; \quad \boxed{b = \frac{1}{\sqrt{2}}\left(\xi + \frac{d}{d\xi}\right)} \Rightarrow \boxed{[b, b^+] = 1}$$

$$\hat{H} = \hbar\omega\left(-\frac{1}{2}\frac{d^2}{d\xi^2} + \frac{1}{2}\xi^2\right) = \hbar\omega\left(b^+b + \frac{1}{2}\right) \Rightarrow \boxed{\hat{H}' = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2} = b^+b}$$

si $H' \to$ autovalor E_0' $\Rightarrow$ $\hat{H}$ autovalor $E_0 = (E_0' + \frac{1}{2})\hbar\omega$.

3. Ressolució equació valors propis

Estat fonamental: $H'\psi_0 = E_0'\psi_0 \iff b^+b\,\psi_0 = E'\psi_0$

aniquile $\xrightarrow{\;b\;}$

$$b\,b^+ b\,\psi_0 \overset{[b,b^+]=1}{=\!=} (b\,b^+ + 1)\underbrace{b\psi_0}_{\chi} = E_0'\underbrace{b\psi_0}_{\chi} \Rightarrow b\,b^+\chi = (E_0' - 1)\chi$$

¡¡¡ !!!

$\Rightarrow \boxed{b\psi_0 = 0} \to E_0' = 0 \Rightarrow E_0 = \frac{1}{2}\hbar\omega$

$\quad \to \psi_0 = N e^{-\xi^2/2}$

Estats excitats: $H'\psi_0 = E'\psi_0 \iff b^+b\,\psi_0 = E_0\psi_0$

cree $\xrightarrow{\;b^+\;}$

$$b^+\,b^+ b\,\psi_0 \overset{[b,b^+]=1}{=} b^+(b\,b^+ - 1)\psi_0 = (b^+b - 1)\underbrace{(b^+\psi_0)}_{\psi_1} = E_0'\underbrace{(b^+\psi_0)}_{\psi_1}$$

$\to b^+b\,\psi_1 = (E_0' + 1)\psi_1$

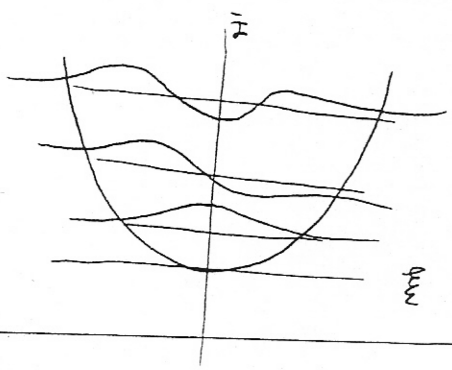
$\quad \to E_1' = E_0' + 1 \Rightarrow E_1 = (1 + \frac{1}{2})\hbar\omega$

$\quad \to \psi_1 = b^+\psi_0 \iff \psi_1 = N\, 2\xi\, e^{-\xi^2/2}$

$$\boxed{\begin{aligned} &\to E_n = (n + \tfrac{1}{2})\hbar\omega \\ &\to \psi_n = (b^+)^n \psi_0 \end{aligned}}$$

$\psi_n = N\, H_n(\xi)\, e^{-\xi^2/2}$

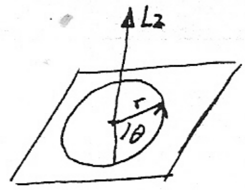
↑ Polinomis hermite



- Probabilitat clàssica vs. quàntica
- Efecte túnel

Moviment rotacional

1. Anell : clàssica



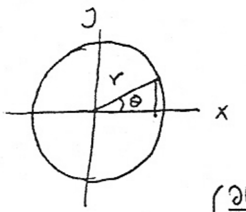
$$E = \frac{L_z^2}{2I} \quad ; \quad \vec{L} = \vec{r} \wedge \vec{p} = \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$L_z = x p_y - y p_x$$

quàntica $\quad \hat{\mathcal{H}} = \frac{1}{2I} \hat{L}_z^2 \quad ; \quad \hat{L}_z = x \hat{p}_y - y \hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

- Si $\hat{L}_z \phi = \lambda \phi \Rightarrow \hat{\mathcal{H}} \phi = \frac{1}{2I} \hat{L}_z \hat{L}_z \phi = \frac{\lambda^2}{2I} \phi \Rightarrow$ ataquem $\hat{L}_z$ que és més simple.

- Simetria polar $\longrightarrow$ canvi a coordenades polars



$$\left.\begin{array}{l} tg\,\theta = \frac{y}{x} \\ \theta = arctg \frac{y}{x} \end{array}\right\} \quad \begin{array}{l} \frac{\partial}{\partial x} = \left(\frac{\partial \theta}{\partial x}\right)_y \cdot \frac{\partial}{\partial \theta} \\ \frac{\partial}{\partial y} = \left(\frac{\partial \theta}{\partial y}\right)_x \frac{\partial}{\partial \theta} \end{array}$$

$$\left(\frac{\partial \theta}{\partial x}\right)_y = -\frac{y}{\underbrace{x^2+y^2}_{r^2}} \quad ; \quad \left(\frac{\partial \theta}{\partial y}\right)_x = \frac{x}{x^2+y^2}$$

$$\boxed{\hat{L}_z = -i\hbar \frac{d}{d\theta}}$$

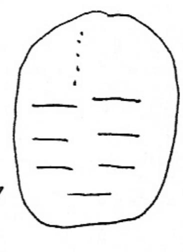
r = constant

- Equació valors propis :

$$\left.\begin{array}{l} \hat{L}_z \psi(\theta) = -i\hbar \, d\psi/d\theta \\ \parallel \\ \lambda \psi(\theta) \equiv m\hbar \, \psi(\theta) \end{array}\right\} \quad \frac{d\psi}{\psi} = im \, d\theta$$

$$\boxed{\begin{array}{ll} \psi_m = e^{im\theta} & m = 0 \pm 1 \pm 2 \dots \\ \lambda_m = m\hbar & \end{array}} \xrightarrow{\hat{\mathcal{H}}} \boxed{\hat{E} = \frac{\hbar^2 m^2}{2I}}$$

CONDICIONS CONTORN



2. Moment Angular $\hat{L}^2, \hat{L}_x, \hat{L}_y, \hat{L}_z$

- Commutacions: $[L_x, L_y] = i\hbar L_z \; ; \; [L_y, L_z] = i\hbar L_x \; ; \; [L_z, L_x] = i\hbar L_y$

$[L^2, L_\alpha] = 0$ PODEM CONEIXER MÒDUL I UNA COMPONENT

- Coordenades esfèriques i eq. autovalors : $\hat{L}^2 \Psi(\theta\varphi) = \lambda \Psi(\theta\varphi)$

separació de variables : $\Psi(\theta\varphi) \equiv Y_{\ell m}(\theta\varphi) = \Theta_{\ell|m|}(\theta) \, \Phi_m(\phi)$

$$\lambda = \ell(\ell+1)\hbar^2 \quad ; \quad \ell = 0, 1, 2 \dots$$
$$m = -\ell, \dots\dots, \ell$$

▶ Ressolució algebraica : $\hat{L}_+$, $\hat{L}_-$

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad ; \quad \hat{L}_- = \hat{L}_x - i\hat{L}_y$$

- Commutacions : $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\,\hat{L}_\pm \quad ; \quad [\hat{L}^2, L_\pm] = 0$
- Les funcions $(L_\pm\psi)$ enfront $\hat{L}^2$, $\hat{L}_z$. Hipòtesi: $\begin{cases}\hat{L}^2\psi = \alpha\psi \\ \hat{L}_z\psi = \beta\psi\end{cases}$

$$\left.\begin{aligned}\hat{L}^2(L_\pm\psi) &= \alpha\,(L_\pm\psi) \\ \hat{L}_z(L_\pm\psi) &= (\beta\pm\hbar)\,(L_\pm\psi)\end{aligned}\right\}\quad \begin{aligned}&\hat{L}_\pm \text{ no canvia } \alpha \\ &\hat{L}_\pm \text{ canvia } \beta : \pm\hbar\end{aligned}$$

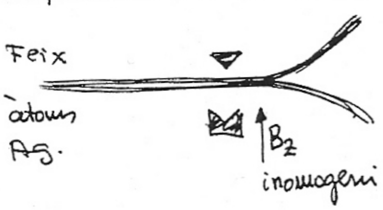
$\Downarrow$

- Càlcul autovalors $\quad \boxed{\hat{L}_+\psi_{Max} = 0} \quad \boxed{\hat{L}_-\psi_{MIN} = 0}$

$$\left.\begin{aligned}\hat{L}_-\underline{\hat{L}_+\psi_M} &= 0 \\ \hat{L}_+\hat{L}_-\psi_m &= 0\end{aligned}\right\}\quad \left.\begin{aligned}\hat{L}_-\hat{L}_+ &= \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z \\ \hat{L}_+\hat{L}_- &= \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z\end{aligned}\right\}\quad \begin{aligned}&\alpha = l(l+1)\hbar^2 \ ; \ l = 0, \tfrac{1}{2}, 1 \ldots \\ &\beta = m\hbar \ ; \ m = -l, \ldots, l\end{aligned}$$

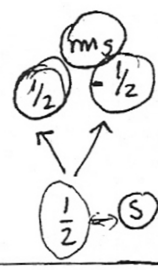
NOMBRES FRACCIONARIS !!!

▶ Espim. Experiment Stern-Gerlach

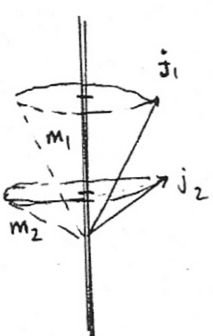


- Moment magnètic associat amb moment angular fraccionari

POSTULAT 5 : L'ESPIN



▶ Suma de moments angulars ...



$\boxed{|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle\,|j_2 m_2\rangle} \longrightarrow$ base 1

SUMA : $\vec{J}$: $J_x = j_{1x} + j_{2x}$; $J_y = j_{1y} + j_{2y}$ etc.

- COMMUTACIONS $0 = [\hat{J}^2, \hat{j}_1] = [\hat{J}^2, \hat{j}_2] = [\hat{J}_z, \hat{j}_1] = [\hat{J}_z, \hat{j}_2]$

però e.g. $[\hat{J}^2, j_{1z}] \neq 0 \quad \boxed{|J M j_1 j_2\rangle} \to$ base 2

exemple : $j_1 = 1 \otimes j_2 = 2$

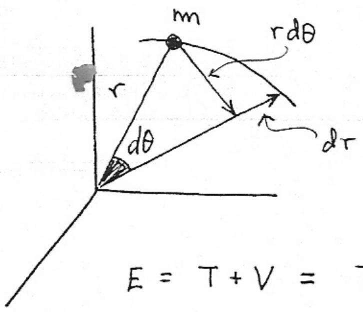
$m_1 \backslash m_2$	2	1	0	−1	−2
1	3	2	1	0	−1
0	2	1	0	−1	−2
−1	1	0	−1	−2	−3

J=1 J=2 J=3

$\boxed{\text{REGLA : } J = (j_1+j_2),\ (j_1+j_2-1),\ \ldots,\ |j_1-j_2|}$

▶ Acoblament spin-òrbita

Àtom hidrogen (camp central)



clàssica $\quad \vec{dr} = dr\,\vec{u_r} + r\,d\theta\,\vec{u_\theta}$; $\quad \dot{\vec{r}} = \dot{r}\,\vec{u_r} + r\dot{\theta}\,\vec{u_\theta}$

$$2T = m\dot{\vec{r}}^{\,2} = m\dot{r}^2 + mr^2\dot{\theta}^2 = m\dot{r}^2 + I\dot{\theta}^2$$

$$\boxed{2T = m\dot{r}^2 + \frac{L^2}{I} = 2T(r) + \frac{L^2}{I}}$$

$$E = T + V = T(r) + V(r) + \frac{L^2(\theta\phi)}{2I} = Q(r) + \frac{L^2(\theta\phi)}{2I}$$

quàntica $\quad \hat{\mathcal{H}}(r\theta\varphi) = \frac{\hat{L}^2}{2I} + \hat{Q}(r)$; $\quad \hat{\mathcal{H}}\, R(r)\, Y(\theta\varphi) = E\, R(r)\, Y(\theta\varphi)$

¿separem variables?

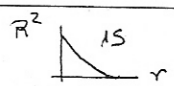
$$\frac{1}{RY}\,\frac{1}{2I}\,\hat{L}^2(\theta\varphi)\,R(r)\,Y(\theta\phi) + \frac{1}{RY}\,\hat{Q}(r)\,R(r)\,Y(\theta\phi) = \frac{1}{\cancel{RY}}\,E\,\cancel{RY}$$

$$\longrightarrow \boxed{\frac{\hat{L}^2\,Y(\theta\varphi)}{Y(\theta\varphi)} = 2EI - \frac{2I}{R}\,\hat{Q}(r)\,R(r) = \lambda \qquad \lambda = l(l+1)\hbar^2}$$

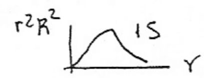
$$\left\{\begin{array}{l} L^2\,Y(\theta\phi) = l(l+1)\hbar^2\,Y(\theta\phi) \Longrightarrow Y_{lm}(\theta\varphi) \\ \left\{\begin{array}{l} \hat{Q}(r)\,R(r) = \left(E - \frac{l(l+1)\hbar^2}{2I}\right)R(r) \\ R(\infty) = 0 \end{array}\right\} \quad R_{n,l}(r) \end{array}\right\} \quad \boxed{\Psi_{nlm}(r\theta\varphi) = R_{nl}(r)\,Y_{lm}(\theta\phi)}$$

E_n Bohr $\longleftrightarrow$ $\boxed{E_n = -\frac{e^2}{2a_0}\,\frac{1}{n^2}}$

REPRESENTACIONS GRÀFIQUES



- Probabilitat radial $\iint_{\theta\phi} R^2 Y^2\, r^2 \sin\theta\, dr\, d\theta\, d\varphi = cte \quad r^2 R^2(r)$



etc

- Probabilitats angulars : funcions
  - reals $\{P_x \; P_y\}$ no pròpies de $\hat{L}_z$
  - complexes $\{P_{+1}, P_{-1}\}$ pròpies de $\hat{L}_z$
- Diagrames de contorn
- Formules dels nodes radials/angulars $\left\{\begin{array}{l} rad = n - l - 1 \\ ang = l \end{array}\right\}$ tot $= n-1$

ESPINORBITALS

$\hat{\mathcal{H}}(r\theta\varphi)$ però $\Psi(r, \theta, \varphi, \sigma)$ ← espin $\quad \longrightarrow \quad \Psi = \underbrace{\overbrace{\phi(r\theta\varphi)}^{\text{orbital}}\,\eta(\sigma)}_{\text{espinorbital}}$

$$\eta(\sigma) \left\langle \begin{array}{lll} \alpha(\sigma) & \uparrow & s = 1/2 \quad m_s = 1/2 \\ \beta(\sigma) & \downarrow & s = 1/2 \quad m_s = -1/2 \end{array} \right.$$