F 689 – Mecânica Quântica I

2º Semestre de 2022

31/10/2022

Aula 19

Aula passada

Descrição quântica do momento angular de spin ½: espaço $\mathcal{E}$ de dimensão 2.

$$\text{Base de } \mathcal{E} \Rightarrow \{|+\rangle, |-\rangle\} \qquad \langle+|+\rangle = \langle-|-\rangle = 1, \; \langle+|-\rangle = 0$$

Fechamento: $|+\rangle\langle+| + |-\rangle\langle-| = \mathbb{1}$

Observável associado a $L_z \rightarrow S_z$

$$\boxed{\begin{aligned} S_z|+\rangle &= \frac{\hbar}{2}|+\rangle \\ S_z|-\rangle &= -\frac{\hbar}{2}|-\rangle \end{aligned}}$$

Outras componentes (representação matricial **na base acima**):

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \; S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \; S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Matrizes de Pauli:

$$\boxed{\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \; \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \; \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

Aula passada

Componente genérica do spin numa direção arbitrária **u**:

$$\mathbf{S}\cdot\hat{\mathbf{u}} \equiv S_u = S_x \sin\theta\cos\phi + S_y \sin\theta\sin\phi + S_z\cos\theta$$

Representação matricial de S_u:

$$S_u = \frac{\hbar}{2}\begin{pmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{pmatrix}$$

Qualquer projeção de **S** tem os mesmos auto-valores:

$$\mathrm{Auto-valores\ de}\ S_x, S_y, S_z, S_u \rightarrow \pm\frac{\hbar}{2}$$

Aula passada

Na $\mathrm{Base\ de}\ \mathcal{E} \Rightarrow \{|+\rangle, |-\rangle\}$, os auto-vetores das componentes de $\mathbf{S}$ são:

Para S_x e S_y: $$|\pm\rangle_x = \frac{1}{\sqrt{2}}\left[|+\rangle \pm |-\rangle\right]$$

$$|\pm\rangle_y = \frac{1}{\sqrt{2}}\left[|+\rangle \pm i\,|-\rangle\right]$$

Para S_u (convenção de fase diferente da do livro):

$$|+\rangle_u = \cos\frac{\theta}{2}\,|+\rangle + e^{i\phi}\sin\frac{\theta}{2}\,|-\rangle$$

$$|-\rangle_u = -\sin\frac{\theta}{2}\,|+\rangle + e^{i\phi}\cos\frac{\theta}{2}\,|-\rangle$$

Para S_u (convenção do livro):

$$|+\rangle_u = e^{-i\phi/2}\cos\frac{\theta}{2}\,|+\rangle + e^{i\phi/2}\sin\frac{\theta}{2}\,|-\rangle$$

$$|-\rangle_u = -e^{-i\phi/2}\sin\frac{\theta}{2}\,|+\rangle + e^{i\phi/2}\cos\frac{\theta}{2}\,|-\rangle$$

Aula passada

O estado mais geral possível pode ser preparado por um Stern-Gerlach:

$$|\psi\rangle = \alpha\,|+\rangle + \beta\,|-\rangle = |+\rangle_u = e^{-i\phi/2}\cos\frac{\theta}{2}\,|+\rangle + e^{i\phi/2}\sin\frac{\theta}{2}\,|-\rangle$$

desde que se escolha $\mathbf{u}$ tal que: $\tan\frac{\theta}{2} = \frac{|\beta|}{|\alpha|}$

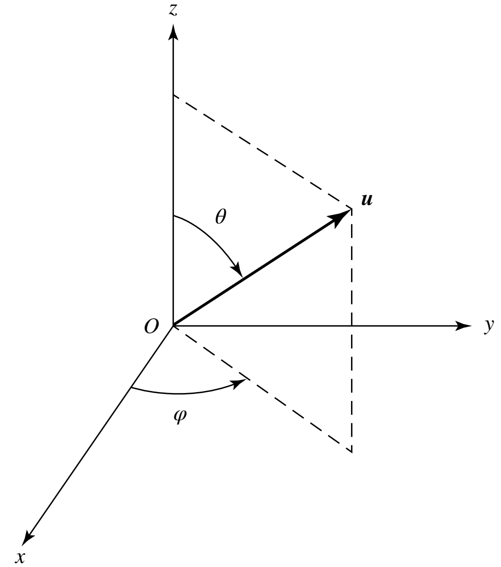
$$\phi = \arg(\beta) - \arg(\alpha)$$

Valores esperados nesse estado genérico são:

$$\langle S_x\rangle = {}_u\langle +|\,S_x\,|+\rangle_u = \frac{\hbar}{2}\sin\theta\cos\phi$$

$$\langle S_y\rangle = {}_u\langle +|\,S_y\,|+\rangle_u = \frac{\hbar}{2}\sin\theta\sin\phi$$

$$\langle S_z\rangle = {}_u\langle +|\,S_z\,|+\rangle_u = \frac{\hbar}{2}\cos\theta$$



que correspondem a um vetor clássico: $\langle \mathbf{S}\rangle = \frac{\hbar}{2}\hat{\mathbf{u}}$

Aula passada

Evolução temporal sob um campo magnético externo:

$$H = -\mathbf{M}\cdot\mathbf{B} = -\gamma\mathbf{L}\cdot\mathbf{B} = -\gamma B_0 S_z \equiv \omega_0 S_z$$

$$\boxed{\begin{aligned} H\left|+\right\rangle &= \frac{\hbar\omega_0}{2}\left|+\right\rangle \\ H\left|-\right\rangle &= -\frac{\hbar\omega_0}{2}\left|-\right\rangle \end{aligned}}$$

Evolução temporal de um estado genérico:

$$\left|\psi(0)\right\rangle = e^{-i\phi/2}\cos\frac{\theta}{2}\left|+\right\rangle + e^{i\phi/2}\sin\frac{\theta}{2}\left|-\right\rangle$$

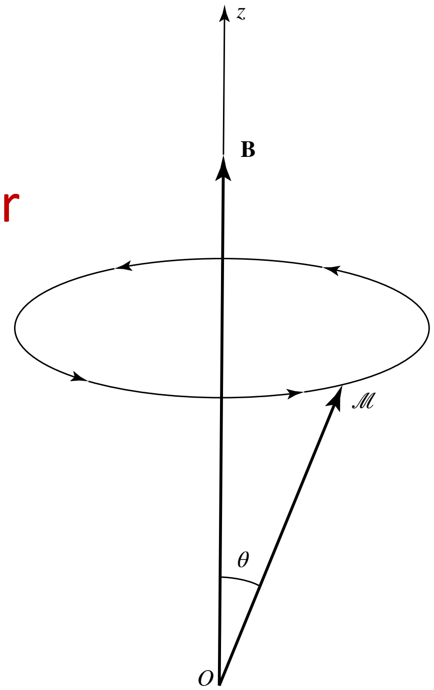
$$\Rightarrow \left|\psi(t)\right\rangle = e^{-i(\phi+\omega_0 t)/2}\cos\frac{\theta}{2}\left|+\right\rangle + e^{i(\phi+\omega_0 t)/2}\sin\frac{\theta}{2}\left|-\right\rangle$$

Evolução temporal dos valores esperados: precessão de Larmor

$$\left\langle S_x\right\rangle(t) = \left\langle\psi(t)\right| S_x \left|\psi(t)\right\rangle = \frac{\hbar}{2}\sin\theta\cos(\phi+\omega_0 t)$$

$$\left\langle S_y\right\rangle(t) = \left\langle\psi(t)\right| S_y \left|\psi(t)\right\rangle = \frac{\hbar}{2}\sin\theta\sin(\phi+\omega_0 t)$$

$$\left\langle S_z\right\rangle(t) = \left\langle\psi(t)\right| S_z \left|\psi(t)\right\rangle = \frac{\hbar}{2}\cos\theta$$

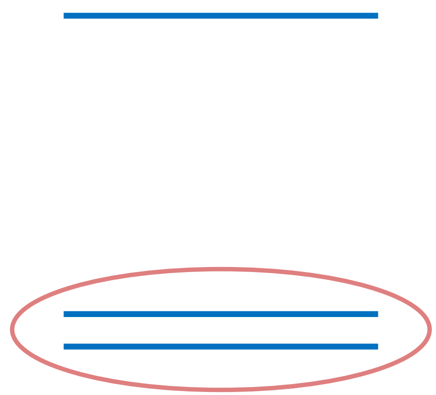


Aula passada

$H_0|\varphi_1\rangle = E_1|\varphi_1\rangle$

$H_0|\varphi_2\rangle = E_2|\varphi_2\rangle$

Sistema de dois níveis:



$$H = H_0 + W$$

$$= \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{pmatrix}$$

$$= \begin{pmatrix} E_1 + W_{11} & W_{12} \\ W_{21} & E_2 + W_{22} \end{pmatrix}$$

$\widetilde{E}_1$ $\quad$ $\widetilde{E}_2$

$$H = \begin{pmatrix} \widetilde{E}_1 & W_{12} \\ W_{21} & \widetilde{E}_2 \end{pmatrix} = \begin{pmatrix} \frac{\widetilde{E}_1 + \widetilde{E}_2}{2} & 0 \\ 0 & \frac{\widetilde{E}_1 + \widetilde{E}_2}{2} \end{pmatrix} + \begin{pmatrix} \frac{\widetilde{E}_1 - \widetilde{E}_2}{2} & W_{12} \\ W_{21} & -\frac{\widetilde{E}_1 - \widetilde{E}_2}{2} \end{pmatrix}$$

$$= \begin{pmatrix} E_m & 0 \\ 0 & E_m \end{pmatrix} + \begin{pmatrix} \Delta & W_{12} \\ W_{21} & -\Delta \end{pmatrix} = E_m \mathbb{1} + \begin{pmatrix} \Delta & W_{12} \\ W_{21} & -\Delta \end{pmatrix}$$

onde: $\quad E_m = \dfrac{\widetilde{E}_1 + \widetilde{E}_2}{2}$

$$\Delta = \frac{\widetilde{E}_1 - \widetilde{E}_2}{2}$$

$W_{21}^* = W_{12}$

Auto-valores e auto-vetores

$$\boxed{H = \begin{pmatrix} \widetilde{E}_1 & W_{12} \\ W_{21} & \widetilde{E}_2 \end{pmatrix} = E_m \mathbb{1} + \begin{pmatrix} \Delta & W_{12} \\ W_{21} & -\Delta \end{pmatrix}}$$

COMPLEMENTO B_{IV}

Auto-valores:

$$E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{12}|^2}$$

$$E_m = \frac{\widetilde{E}_1 + \widetilde{E}_2}{2}$$

$$\Delta = \frac{\widetilde{E}_1 - \widetilde{E}_2}{2}$$

$\langle \varphi_2 | \psi_+ \rangle = e^{i\phi} \sin \frac{\theta}{2}$

$\langle \varphi_2 | \psi_- \rangle = e^{i\phi} \cos \frac{\theta}{2}$

Auto-vetores:

$$|\psi_+\rangle = \cos\frac{\theta}{2}|\varphi_1\rangle + e^{i\phi}\sin\frac{\theta}{2}|\varphi_2\rangle$$

$\langle \psi_+ | \varphi_1 \rangle = \cos \frac{\theta}{2}$

$$|\psi_-\rangle = -\sin\frac{\theta}{2}|\varphi_1\rangle + e^{i\phi}\cos\frac{\theta}{2}|\varphi_2\rangle$$

$\langle \psi_- | \varphi_1 \rangle = -\sin \frac{\theta}{2}$

$$\tan\theta = \frac{|W_{12}|}{\Delta}, \ \theta \in [0, \pi)$$

$$e^{i\phi} = \frac{W_{21}}{|W_{21}|} \Rightarrow \phi = \arg(W_{21}) = -\arg(W_{12}) \in [0, 2\pi)$$

Analogia com spin ½ num campo magnético numa direção genérica

$$H = -\mathbf{M}\cdot\mathbf{B} = -\gamma\mathbf{S}\cdot\mathbf{B} = -\gamma\left(B_xS_x + B_yS_y + B_zS_z\right)$$

$$H = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}$$

Compare com: $\begin{pmatrix} \Delta & W_{12} \\ W_{21} & -\Delta \end{pmatrix}$

$$\Delta = -\frac{\gamma\hbar}{2}B_z$$

$$W_{12} = -\frac{\gamma\hbar}{2}\left(B_x - iB_y\right)$$

$$E_{\pm} = E_m \pm \sqrt{\Delta^2 + |W_{21}|^2}$$

SE E_m É O PONTO DE REFERÊNCIA DE ENERGIA

$(E_m = 0)$

$$\Rightarrow E_{\pm} = \pm \sqrt{\Delta^2 + |W_{21}|^2}$$

SE $W_{21} = 0$ $\Rightarrow$ $E_{\pm} = \pm \Delta = \pm \left(\frac{\tilde{E}_1 - \tilde{E}_2}{2}\right)$

SE EU RECUPERO O E_m:

$$E_{\pm} \longrightarrow E_m \pm \left(\frac{\tilde{E}_1 - \tilde{E}_2}{2}\right) = \frac{\tilde{E}_1 + \tilde{E}_2}{2} \pm \left(\frac{\tilde{E}_1 - \tilde{E}_2}{2}\right)$$

$$\longrightarrow \begin{cases} \tilde{E}_1 \longrightarrow |\varphi_1\rangle \\ \\ \tilde{E}_2 \longrightarrow |\varphi_2\rangle \end{cases}$$

Repulsão de níveis

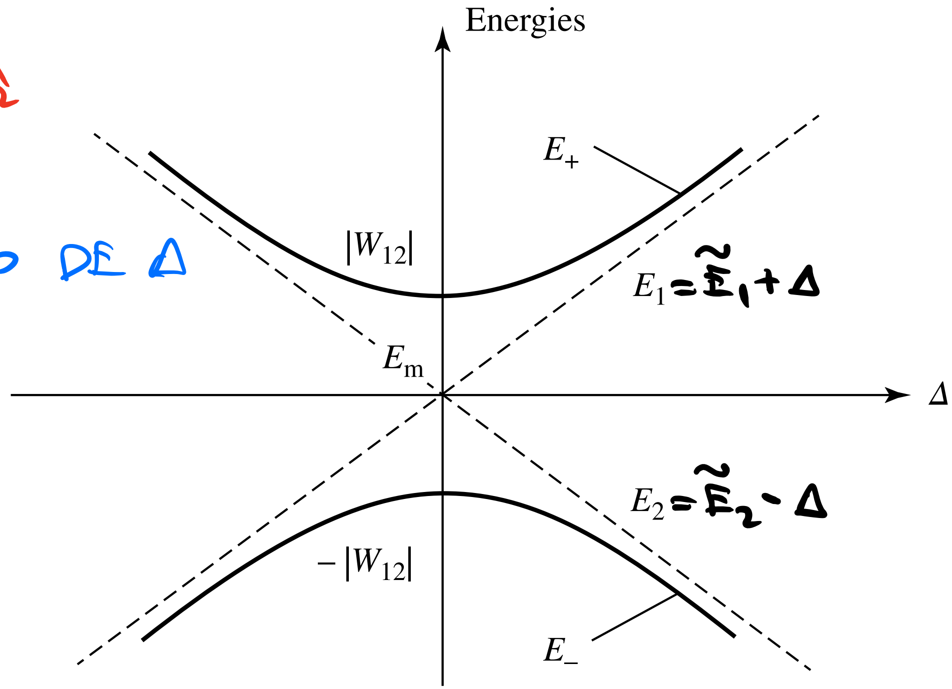
CASO GERAL:

$E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{21}|^2} \Rightarrow \pm\sqrt{\Delta^2 + |W_{21}|^2}$

2 HIPÉRBOLES COMO FUNÇÃO DE Δ

LIGAR O W_{21} LEVA

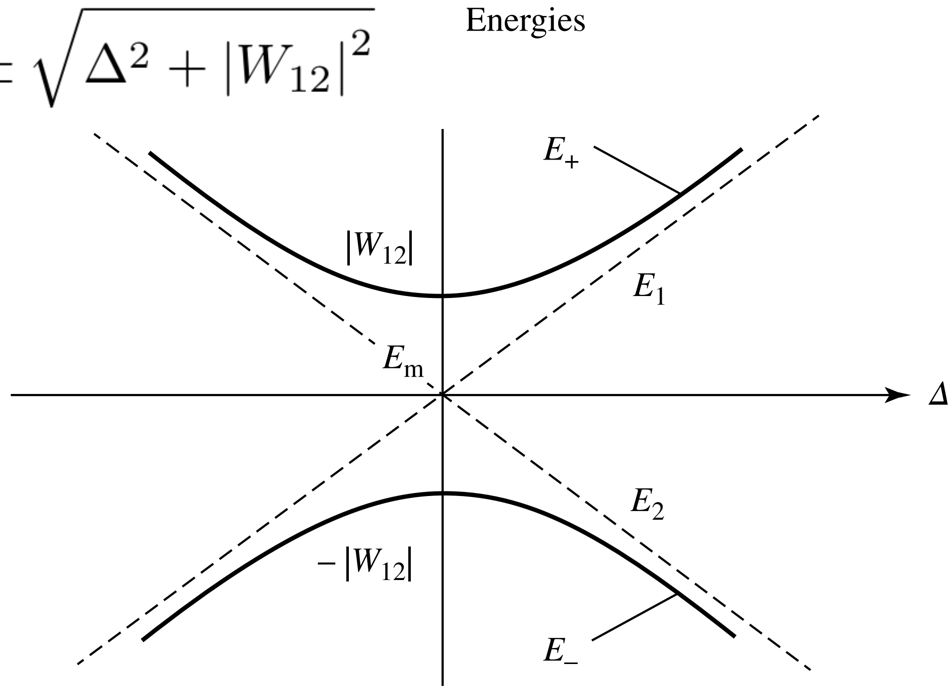
À "REPULSÃO DO NÍVEIS"



Acoplamento forte

$|W_{12}| >> \Delta$

$$E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{12}|^2}$$



$E_\pm \simeq E_m \pm |W_{12}|$

$\theta \simeq \frac{\pi}{2}$

$|\psi_+\rangle \simeq \frac{1}{\sqrt{2}}\left[|\varphi_1\rangle + e^{i\phi}|\varphi_2\rangle\right]$

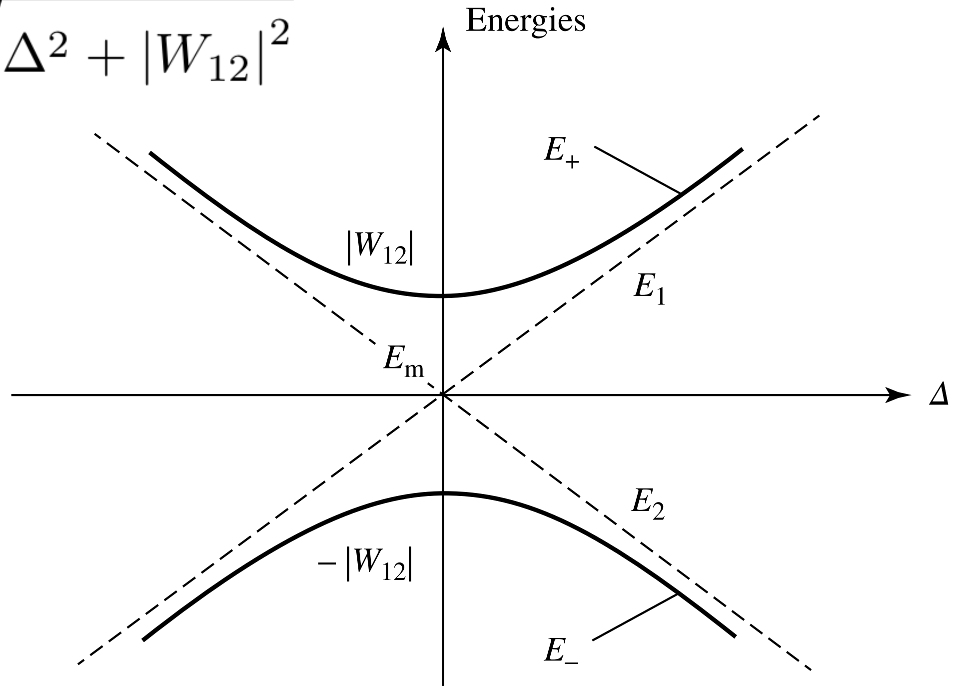
$|\psi_-\rangle \simeq \frac{1}{\sqrt{2}}\left[-|\varphi_1\rangle + e^{i\phi}|\varphi_2\rangle\right]$

SUPERPOSIÇÃO LINEAR DE $|\varphi_1\rangle$ E $|\varphi_2\rangle$ COM COEFICIENTES DE MESMO MÓDULO.

Acoplamento fraco

$|W_{21}| \ll \Delta$

$$E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{12}|^2}$$



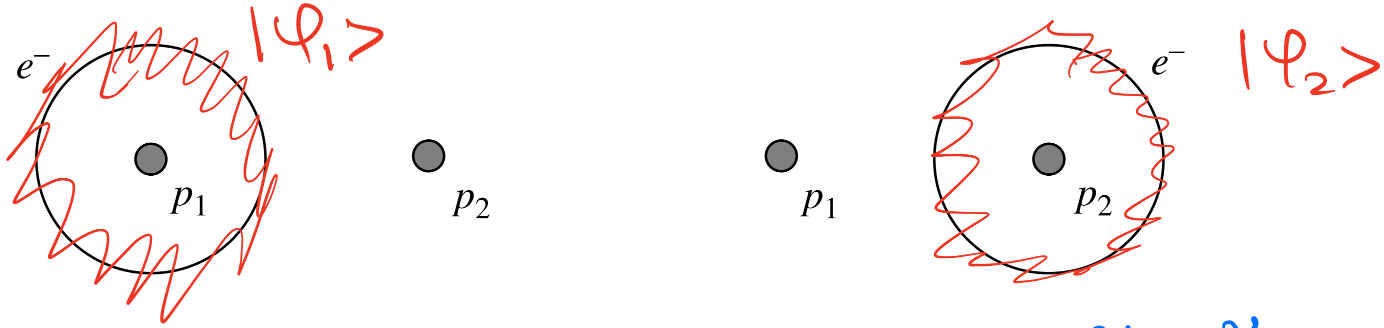
$$E_\pm = E_m \pm |\Delta| \pm \frac{|W_{12}|^2}{|\Delta|}$$

$$|\psi_+\rangle = |\varphi_1\rangle + \frac{W_{21}}{2\Delta}|\varphi_2\rangle$$

$$|\psi_-\rangle = \cancel{e^{i\phi}}\left[|\varphi_2\rangle - \frac{W_{12}}{2\Delta}|\varphi_1\rangle\right]$$

Exemplos físicos importantes

A molécula ionizada de H_2^+:



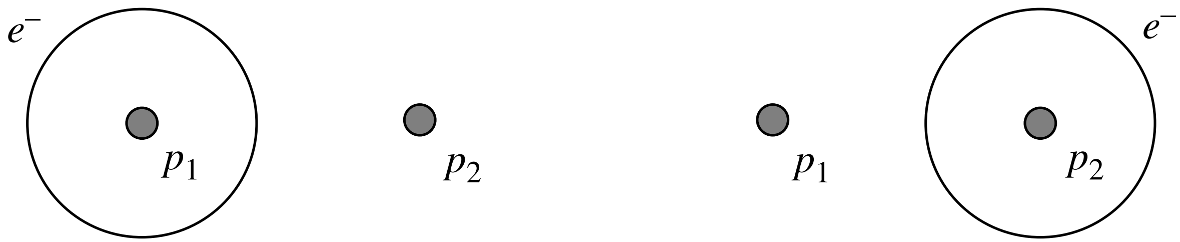
$$H = \begin{pmatrix} \tilde{E}_1 & W_{12} \\ W_{21} & \tilde{E}_2 \end{pmatrix}$$

POR SIMETRIA: $\tilde{E}_1 = \tilde{E}_2 \Rightarrow \Delta = 0$

$$E_\pm = E_m \pm |W_{21}| = \tilde{E}_1 \pm |W_{21}|$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}\left[-|\varphi_1\rangle + e^{i\phi}|\varphi_2\rangle\right]$$

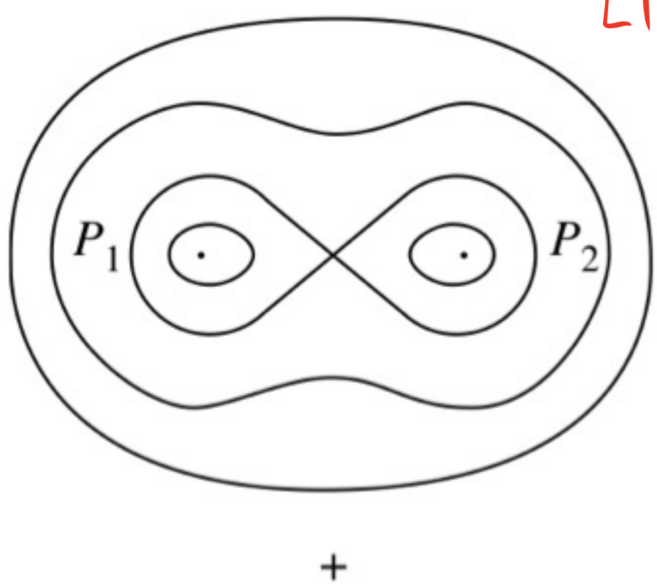
Função de onda da molécula de H_2+ com menor energia: ligação química



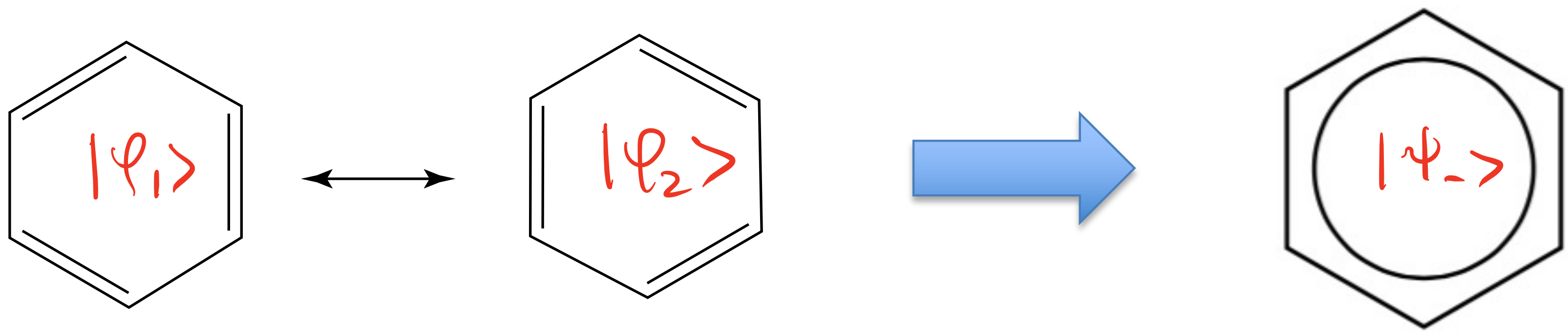
$$|\psi_-\rangle = \frac{1}{\sqrt{2}}\left[-|\varphi_1\rangle + e^{i\phi}|\varphi_2\rangle\right]$$

LIGAÇÃO COVALENTE

ESTADO LIGANTE



A molécula de benzeno

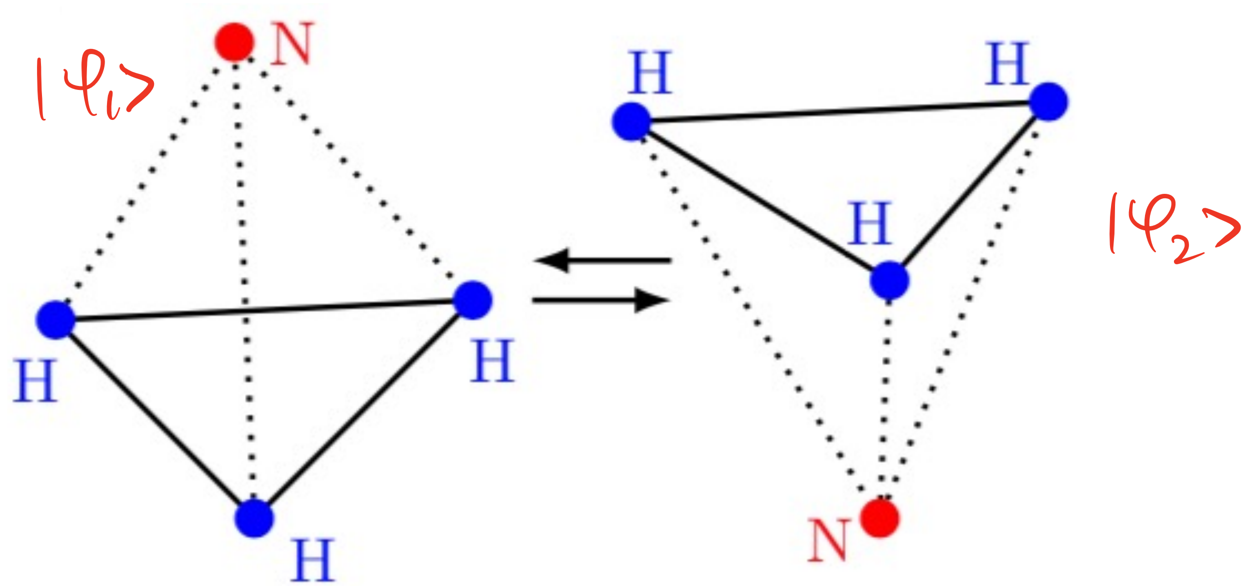


$$H = \begin{pmatrix} \tilde{E} & W_{12} \\ W_{12} & \tilde{E} \end{pmatrix}$$

$\tilde{E}_1 = \tilde{E}_2 = \tilde{E}$ (POR SIMETRIA)

$$|\psi_-\rangle = \frac{1}{\sqrt{2}}\left[-|\varphi_1\rangle + e^{i\phi}|\varphi_2\rangle\right]$$

A molécula de amônia NH_3



$$H = \begin{pmatrix} \tilde{E} & W_{12} \\ W_{12} & \tilde{E} \end{pmatrix}$$

$\tilde{E}_1 = \tilde{E}_2 = \tilde{E}$ (POR SIMETRIA)

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} \left[-|\varphi_1\rangle + e^{i\phi} |\varphi_2\rangle \right]$$

Dinâmica

O QUE ACONTECE SE O SISTEMA É PREPARADO NUM AUTO-ESTADO DE H_0 : $|\varphi_1\rangle = |\psi(0)\rangle$

SE O ESTADO INICIAL É GENÉRICO:

$$|\psi(0)\rangle = C_+(0)\,|\psi_+\rangle + C_-(0)\,|\psi_-\rangle$$

$$C_\pm(0) = \langle\psi_\pm|\psi(0)\rangle = \langle\psi_\pm|\varphi_1\rangle$$

$$|\psi(t)\rangle = C_+(0)\,e^{-iE_+t/\hbar}\,|\psi_+\rangle + C_-(0)\,e^{-iE_-t/\hbar}\,|\psi_-\rangle$$

$$\langle\psi_+|\varphi_1\rangle = \cos\frac{\theta}{2} = C_+(0)$$

$$\langle\psi_-|\varphi_1\rangle = -\sin\frac{\theta}{2} = C_-(0)$$

$$|\psi(t)\rangle = \cos\frac{\theta}{2}\,e^{-iE_+t/\hbar}\,|\psi_+\rangle - \sin\frac{\theta}{2}\,e^{-iE_-t/\hbar}\,|\psi_-\rangle$$

PROBABILIDADE DE ENCONTRAR O SISTEMA EM $|\varphi_2\rangle$

$$P(|\varphi_2\rangle) = \left|\langle\varphi_2|\psi(t)\rangle\right|^2$$

$$= \left| \cos\frac{\theta}{2}\, e^{-iE_+t/\hbar}\langle\varphi_2|\psi_+\rangle - \sin\frac{\theta}{2}\, e^{-iE_-t/\hbar}\langle\varphi_2|\psi_-\rangle \right|^2$$

$$= \left| s\,c\; e^{-iE_+t/\hbar} e^{i\phi} - s\,c\; e^{-iE_-t/\hbar} e^{i\phi} \right|^2$$

$$\langle\varphi_2|\psi_+\rangle = e^{i\phi}\sin\frac{\theta}{2}$$

$$\langle\varphi_2|\psi_-\rangle = e^{i\phi}\cos\frac{\theta}{2}$$

$$= \sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2}\left| e^{-iE_+t/\hbar} - e^{-iE_-t/\hbar} \right|^2$$

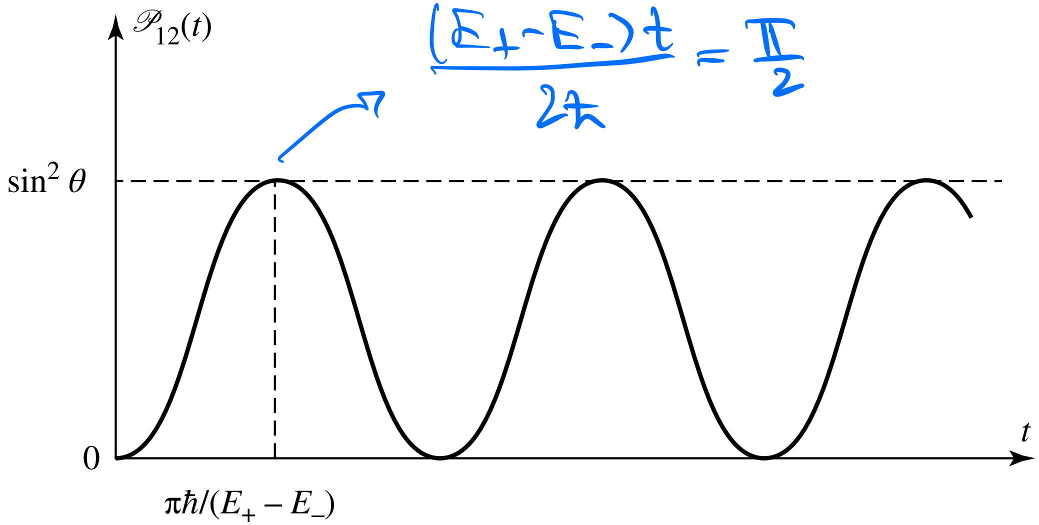
$$\sin\theta = 2\cos\frac{\theta}{2}\sin\frac{\theta}{2}$$

$$= \frac{1}{4}\sin^2\theta \times \left[1 + 1 - 2\,\underbrace{\mathrm{Re}\left[e^{iE_+t/\hbar} e^{-iE_-t/\hbar} \right]}_{\cos\left(\frac{E_+-E_-}{\hbar}t\right)} \right]$$

$$= \frac{1}{2}\sin^2\theta\left[1 - \cos\left(\frac{E_+-E_-}{\hbar}t\right) \right] = \sin^2\theta\,\sin^2\left[\frac{(E_+-E_-)t}{2\hbar}\right]$$

"FÓRMULA DE RABI"

Oscilações de Rabi



$$\frac{(E_+ - E_-)t}{2\hbar} = \frac{\pi}{2}$$

$$P_{12}(t) = \sin^2\theta \, \sin^2\left[\frac{(E_+ - E_-)t}{2\hbar}\right]$$

O CASO MAIS COMUM (VER EXEMPLOS ANTERIORES)

$$\Delta = 0 \Rightarrow \theta = \frac{\pi}{2} \Rightarrow E_+ - E_- = 2|W_{21}|$$

$$P_{12}(t) = \sin^2\left[\frac{|W_{21}|t}{\hbar}\right]$$

$$T = \frac{2\pi\hbar}{|W_{12}|} = \frac{h}{|W_{12}|}$$