THEORIE DES PERTURBATIONS

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \qquad \lambda \ll 1 \qquad [\hat{H}_0, \lambda\hat{V}] \neq 0$$

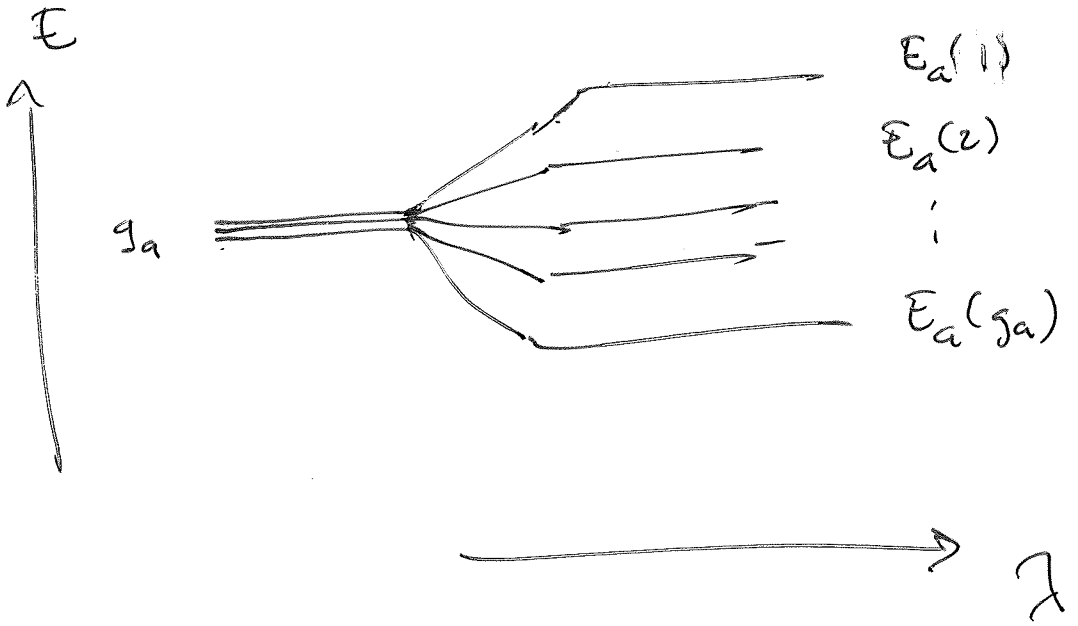
$\hat{H}_0$: resoluble

$$\hat{H}_0 |\varepsilon_a^{(0)}\rangle = \varepsilon_a^{(0)} |\varepsilon_a^{(0)}\rangle$$

cas dégénéré :

$$\hat{H}_0 |\varepsilon_a^{(0)}; p\rangle = \varepsilon_a^{(0)} |\varepsilon_a^{(0)}; p\rangle \qquad p = 1, \to g_a$$

g_a dégénérescence de $\varepsilon_a^{(0)}$



$$\varepsilon_a(q) = \varepsilon_a^{(0)} + \lambda \overbrace{\epsilon_a^{(1)}(q)}^{\epsilon_1} + \lambda^2 \overbrace{\epsilon_a^{(2)}(q)}^{\epsilon_2} + \cdots$$

$$\hat{H} |\psi_a; q\rangle = \varepsilon_a(q) |\psi_a; q\rangle$$

$$|\psi_a; q\rangle = \sum_{p=1}^{g_a} \alpha_p^{(q)} |\varepsilon_a^{(0)}; p\rangle + \lambda \overbrace{|\phi_a^{(1)}(q)\rangle}^{|\phi_1\rangle} + \lambda^2 \underbrace{|\phi_a^{(2)}(q)\rangle}_{|\phi_2\rangle} + \cdots$$

$$\hat{H} |\psi_a; q\rangle = \varepsilon_a(q) |\psi_a; q\rangle$$

$$(\hat{H}_0 - \varepsilon_a^{(0)}) |\phi_1\rangle + (\hat{V} - \epsilon_1) \sum_{p=1}^{g_a} \alpha_p^{(q)} |\varepsilon_a^{(0)}; p\rangle = 0$$

$p, q, p' = 1, \dots \to g_a$

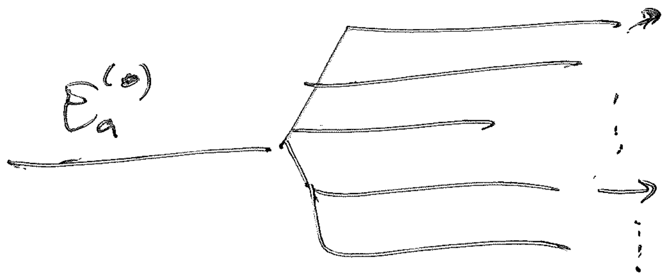
$$\langle \varepsilon_a^{(0)}; p' | \Big(\qquad \Big) = 0$$

$$\sum_{p=1}^{g_a} \underbrace{\langle \varepsilon_a^{(0)}; p' | \hat{V} | \varepsilon_a^{(0)}; p\rangle}_{V_{p'p}} \alpha_p^{(q)} - \epsilon_a^{(1)}(q)\, \alpha_{p'}^{(q)} = 0 \implies \sum_p V_{p'p}\, \alpha_p^{(q)} = \epsilon_a^{(1)}(q)\, \alpha_{p'}^{(q)}$$

$V\vec{\alpha}^{(q)} = \epsilon^{(q)}\vec{\alpha}^{(q)}$ pour calculer $\epsilon_a^{(1)}(q)$ construire la matrice de $\hat{V}$ sur la base des états propres dégénérés de H_0

$$\langle E_a^{(0)}; p' | \hat{V} | E_a^{(0)}; p\rangle = V_{p'p}$$

si $\epsilon_a^{(1)}(q)$ sont tous différents

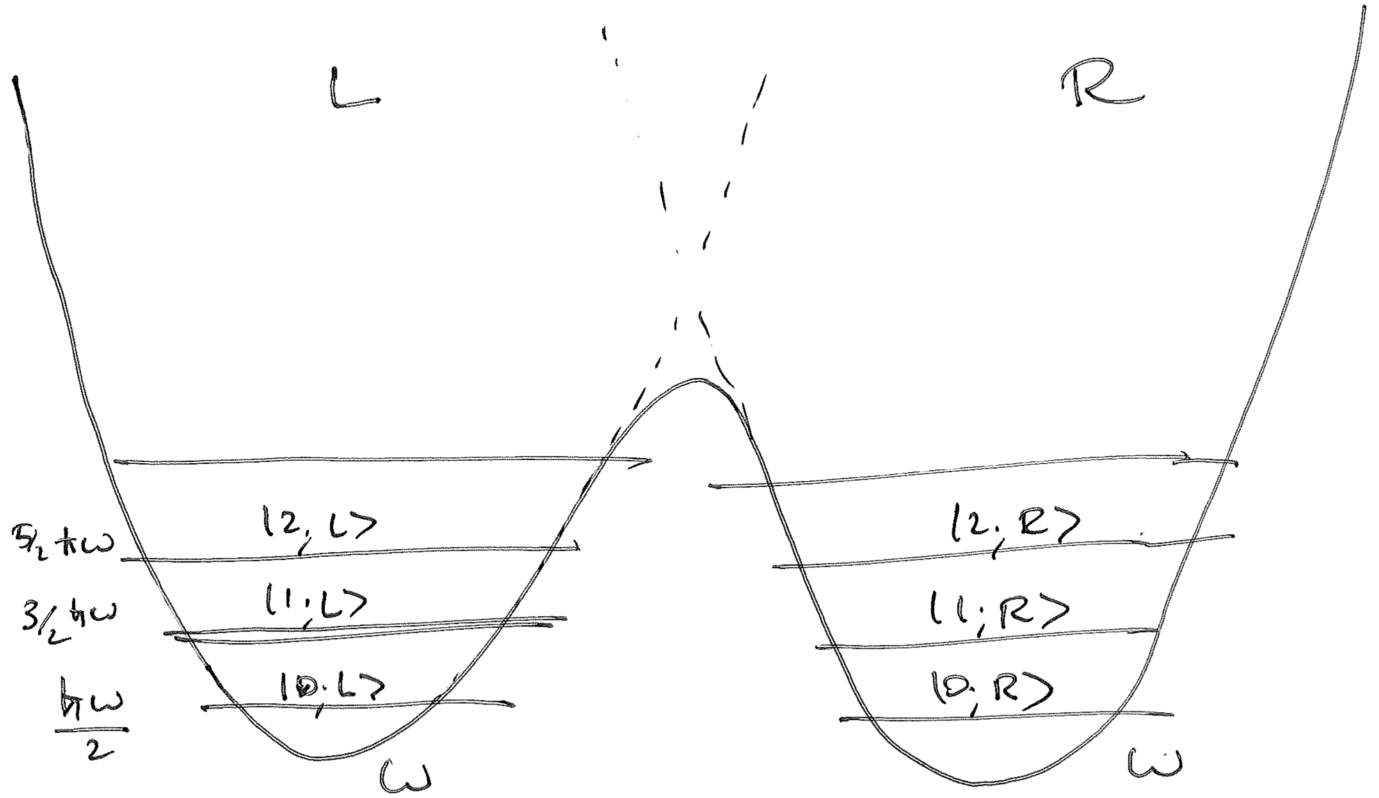


$\to E_a^{(0)} + \lambda\,\epsilon_a^{(1)}(1) + \dots$

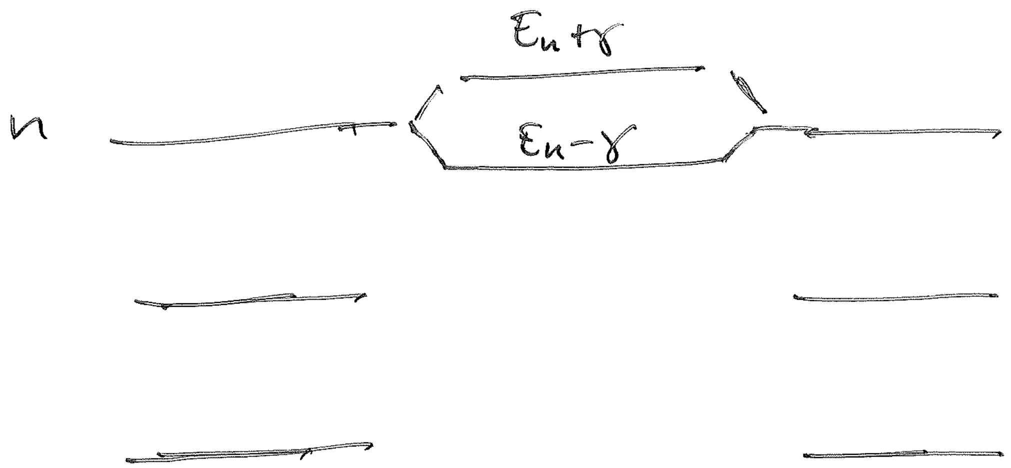
$\to E_a^{(0)} + \lambda\,\epsilon_a^{(1)}(p) + \dots$

$\Rightarrow$ clivage ("splitting")

$$|\psi_a; 1\rangle = \sum_{p=1}^{g_a} \alpha_p^{(1)} |E_a^{(0)}; p\rangle + \lambda(\dots)$$



clivage par effet tunnel ("tunnel splitting")



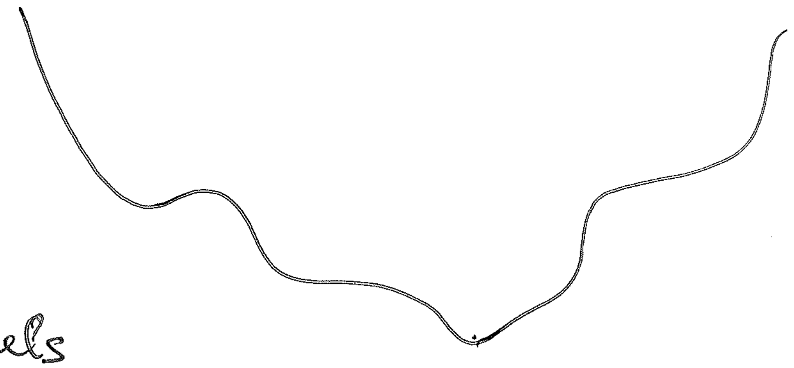
$E_n = \hbar\omega\left(n+\frac{1}{2}\right)$ $\quad |n;L\rangle, |n;R\rangle$ vecteurs propres imperturbés

$$V = \begin{array}{c} \\ \langle n;L| \\ \langle n;R| \end{array} \begin{array}{cc} |n;L\rangle & |n;R\rangle \\ \multicolumn{2}{c}{\left(\begin{array}{cc} \beta^{(n)} & -\gamma^{(n)} \\ -\gamma^{(n)*} & \beta^{(n)} \end{array}\right)} \end{array} \longrightarrow \epsilon_n^{(1)} = \pm|\gamma^{(n)}| \to \frac{|n;L\rangle \mp |n;R\rangle}{\sqrt{2}}$$

$\beta^{(n)} \pm \gamma^{(n)}$

MÉTHODE DES VARIATIONS

$\hat{\mathcal{H}}$ $\qquad |\psi(\vec{a})\rangle \qquad \vec{a} = (a_1, a_2, \dots, a_N)$



exemple $\quad \vec{a} = (a_1, a_2)$

$$\psi(x, \vec{a}) = N\, e^{-\frac{(x-a_1)^2}{2a_2^2}}$$

"Ansatz" variationnel

principes variationnels

1) état fondamental $\qquad \hat{\mathcal{H}} \to E_0$ énergie de l'état fondamental

$|\psi\rangle$ vecteur quelconque en $\mathcal{H}$ $\qquad \| \psi \|^2 = 1$

$$\langle \psi | \hat{\mathcal{H}} | \psi \rangle \geq E_0$$

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle \qquad \hat{\mathcal{H}} |\phi_n\rangle = E_n |\phi_n\rangle \qquad E_n \geq E_0$$

$$\langle \psi | \hat{\mathcal{H}} | \psi \rangle = \sum_{nn'} c_n^* c_{n'} \underbrace{\langle \phi_n | \hat{\mathcal{H}} | \phi_{n'} \rangle}_{\delta_{nn'} E_n} = \sum_n |c_n|^2 E_n \geq \underbrace{\sum_n |c_n|^2}_{1} E_0 = E_0$$

$|\psi(\vec{a})\rangle$

$$\min_{\vec{a}} \underbrace{\frac{\langle \psi(\vec{a}) | \hat{\mathcal{H}} | \psi(\vec{a}) \rangle}{\langle \psi(\vec{a}) | \psi(\vec{a}) \rangle}}_{E(\vec{a})} = \underline{\underline{E(\vec{a}_0)}} \Rightarrow \vec{a}_0$$

$|\psi(\vec{a}_0)\rangle$ meilleure approximation de $|\phi_0\rangle$ à l'intérieur de la classe d'état $|\psi(\vec{a})\rangle$

2) états propres $|\psi\rangle \in H$, $\hat{\mathcal{H}}$

$$\mathcal{E}_\psi = \frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle}$$

$\boxed{\mathcal{E}_\psi \text{ est stationnaire par rapport à tout changement de } |\psi\rangle \iff |\psi\rangle \text{ est état propre de } \hat{\mathcal{H}}.}$

$$|\psi\rangle \to |\psi\rangle + |\delta\psi\rangle \qquad \cancel{\|\psi\|^2 = 1}$$

$$\mathcal{E}_{\psi+\delta\psi} = \frac{(\langle\psi| + \langle\delta\psi|)\hat{\mathcal{H}}(|\psi\rangle + |\delta\psi\rangle)}{(\langle\psi| + \langle\delta\psi|)(|\psi\rangle + |\delta\psi\rangle)} = \frac{1}{\langle\psi|\psi\rangle}\frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle + \langle\delta\psi|\hat{\mathcal{H}}|\psi\rangle + \langle\psi|\hat{\mathcal{H}}|\delta\psi\rangle + o(\delta\psi^2)}{\left[1 + \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + o(\delta\psi^2)\right]}$$

$$= \frac{1}{\langle\psi|\psi\rangle}\left(1 - \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + o(\delta\psi^2)\right)\left(\overbrace{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}^{\mathcal{E}_\psi\,\hat{\mathbb{1}}} + \langle\delta\psi|\hat{\mathcal{H}}|\psi\rangle + \langle\psi|\hat{\mathcal{H}}|\delta\psi\rangle + o(\delta\psi^2)\right)$$

$$= \left[\overbrace{\frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle}}^{\mathcal{E}_\psi} + \underbrace{\frac{\langle\delta\psi|(\hat{\mathcal{H}} - \mathcal{E}_\psi)|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|(\hat{\mathcal{H}} - \mathcal{E}_\psi)|\delta\psi\rangle}{\langle\psi|\psi\rangle}} + o(\delta\psi^2)\right]$$

$$\Rightarrow \langle\delta\psi|(\hat{\mathcal{H}} - \mathcal{E}_\psi)|\psi\rangle = 0 \qquad \forall\, |\delta\psi\rangle$$

$$\hat{\mathcal{H}}|\psi\rangle = \mathcal{E}_\psi|\psi\rangle \qquad |\psi\rangle \text{ état propre de } \hat{\mathcal{H}}$$

$(\hat{H} - E_\psi)|\psi\rangle = 0$ $\quad E_\psi$ stationnaire

$\vec{a}_e$

$|\psi(\vec{a})\rangle$ $\quad$ extrema de $E(\vec{a}) = \dfrac{\langle\psi(\vec{a})|\hat{H}|\psi(\vec{a})\rangle}{\langle\psi(\vec{a})|\psi(\vec{a})\rangle}$ $\quad \vec{\nabla}_{\vec{a}} E(\vec{a})\Big|_{\vec{a}_e} = 0$

MOMENT ANGULAIRE ou CINÉTIQUE en MQ

MQ

$$\vec{L} = \vec{r} \times \vec{p} = (y p_z - z p_y,\ -x p_z + z p_x,\ x p_y - y p_x)$$

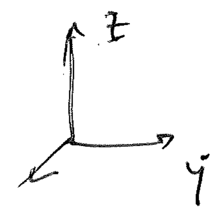
$$[\hat{x}, \hat{p}_y] = 0$$

$$\to \quad \hat{\vec{L}} = (\hat{y}\hat{p}_z - \hat{z}\hat{p}_y,\ \text{---}\ )$$

$$\boxed{[\hat{x}, \hat{p}_x] = i\hbar}$$

$$[\hat{x}, \hat{p}_y] = [\hat{z}, \hat{p}_z]$$

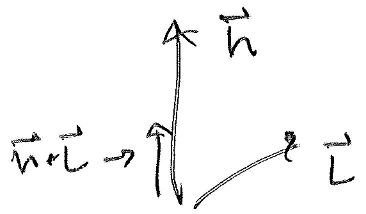
$$[\hat{L}^x, \hat{L}^y] = \dots = i\hbar \hat{L}^z \neq 0$$



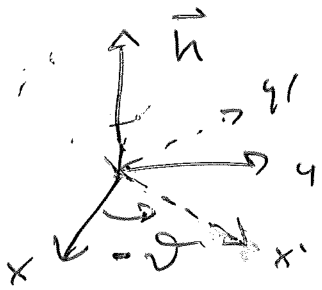
$$\epsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \text{si } (\alpha\beta\gamma) \text{ ~~est~~ une permutation paire de } (xyz) : (xyz), (yzx), (zxy) \\ -1 & \text{si " " " " impaire " "} \\ 0 & \text{autrement} \end{cases}$$

$$\boxed{[\hat{L}^\alpha, \hat{L}^\beta] = i\hbar \sum_\gamma \epsilon_{\alpha\beta\gamma} \hat{L}^\gamma}$$

$\vec{n}\cdot\vec{L}$ est conservé $\iff$ invariance par rotation autour de l'axe $\vec{n}$



$$\hat{R}_{\vec{n}}(\vartheta)\,|\psi\rangle = |\psi'\rangle$$



$$\vec{v} \to \vec{v}' = R_{\vec{n}}(\vartheta)\,\vec{v}$$
$$\downarrow$$
$$3\times 3$$

$\hat{\vec{V}}$ ex. $\hat{\vec{L}}$, $\hat{\vec{r}}$, $\hat{\vec{p}}$ etc...

$$\langle \hat{\vec{V}} \rangle_\psi \to \langle \vec{V} \rangle_{\psi'} = \langle \psi | \hat{R}^{+}_{\vec{n}}(\vartheta)\, \hat{\vec{V}}\, \hat{R}_{\vec{n}}(\vartheta) |\psi\rangle = R_{\vec{n}}(\vartheta)\, \langle \hat{\vec{V}} \rangle_\psi$$

unitaire

$$[\hat{\mathcal{H}}, \hat{R}_{\vec{n}}(\vartheta)] = 0$$ si le système est invariant par rotation autour $\vec{n}$

$$[\hat{\mathcal{H}}, \hat{\vec{L}}\cdot\vec{n}] = 0 \qquad \hat{R}_{\vec{n}}(\vartheta) = e^{\frac{i}{\hbar} f(\vartheta)(\hat{\vec{L}}\cdot\vec{n})} \qquad [\hbar] = [L]$$

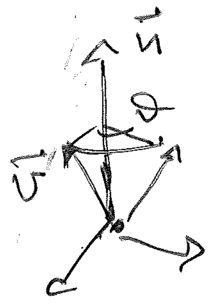
$$\hat{R}_{\vec{n}}(\vartheta_1)\,\hat{R}_{\vec{n}}(\vartheta_2) = \hat{R}_{\vec{n}}(\vartheta_1+\vartheta_2) \qquad f(\vartheta) = \alpha\vartheta \qquad \hat{U} = e^{i\phi\hat{A}}$$

$$\alpha = -1$$

$$\hat{R}_{\vec{n}}(\vartheta) = e^{-\frac{i}{\hbar}\vartheta(\hat{\vec{L}}\cdot\vec{n})} \simeq \left(\mathbb{1} - \frac{i}{\hbar}\vartheta(\hat{\vec{L}}\cdot\vec{n}) + \dots\right)$$

$\downarrow$

$\hat{\vec{L}}\cdot\vec{n}$ est générateur des rotations



$$\vec{v}' = (1-\cos\vartheta)(\vec{n}\cdot\vec{v})\,\vec{n} + \cos\vartheta\,\vec{v} + \sin\vartheta\,(\vec{n}\times\vec{v})$$

$$\underset{\vartheta\to 0}{\simeq} \vec{v} + \vartheta(\vec{n}\times\vec{v}) + \mathcal{O}(\vartheta^2)$$

$$= \left[\mathbb{1} + \vartheta\begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix} + \dots\right]\vec{v}$$

$$= \left[\mathbb{1} - (i\vartheta\,\vec{n}\cdot\vec{T})\right]\vec{v} + \dots$$

$$T_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} \qquad T_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \qquad T_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\vec{v}' = R_{\vec{n}}(\vartheta)\,\vec{v} = \exp(-i\vartheta\,\vec{n}\cdot\vec{T})\,\vec{v}$$

$$\langle\hat{\vec{V}}\rangle_{\psi'} \overset{\vartheta\to 0}{=} \langle\psi|\left(\mathbb{1} + \frac{i}{\hbar}\vartheta(\hat{\vec{L}}\cdot\vec{n})\right)\hat{\vec{V}}\left(\mathbb{1} - \frac{i}{\hbar}\vartheta(\hat{\vec{L}}\cdot\vec{n})\right)|\psi\rangle$$

$$= \langle\hat{\vec{V}}\rangle_\psi + \frac{i}{\hbar}\vartheta\langle[\hat{\vec{L}}\cdot\vec{n}, \hat{\vec{V}}]\rangle_\psi + \mathcal{O}(\vartheta^2)$$

$$= \left[\mathbb{1} - i\vartheta(\vec{n}\cdot\vec{T})\right]\langle\hat{\vec{V}}\rangle_\psi = \langle\hat{\vec{V}}\rangle_\psi - i\vartheta\,\langle\psi|(\vec{n}\cdot\vec{T})\hat{\vec{V}}|\psi\rangle \leftarrow$$

$$\boxed{[\hat{\vec{L}}\cdot\vec{n}, \hat{\vec{V}}] = -\hbar\,(\vec{n}\cdot\vec{T})\,\hat{\vec{V}}}$$

$\vec{V} = \vec{L} \qquad \vec{n} = \vec{e}_x$

$$[\hat{L}^x, \hat{L}^y] = \hbar\,(\vec{T}_x \hat{L})_y = i\hbar\,\hat{L}^z$$