Operadores hermitianos

- $\int_a^b \psi^*(x)\,\varphi(x)\,dx = (\psi, \varphi)$ → notação p/ o produto escalar de duas funções no intervalo (a, b)

- $\int \psi^*(x)\left[\frac{d}{dx}\varphi(x)\right]dx = \left(\psi, \frac{d}{dx}\varphi\right)$

- valores médios:

$$\begin{cases} \langle x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\,x\,\psi(x)\,dx = (\psi, x\psi) \\ \langle p_x\rangle = \int_{-\infty}^{\infty}\psi^*(x)\left[-i\hbar\frac{\partial\psi(x)}{\partial x}\right]dx = \left(\psi, -i\hbar\frac{\partial}{\partial x}\psi\right) = (\psi, p_x\psi) \\ \langle E\rangle = (\psi, H\psi) \end{cases}$$

- operador adjunto

$$\Big(\psi, \underbrace{\frac{d}{dx}}_{\text{operador linear}}\varphi\Big) = \int_{-\infty}^{\infty}\psi^*\frac{d\varphi}{dx}\,dx = \cancelto{0}{\psi^*\varphi\Big|_{-\infty}^{\infty}} - \int\varphi\frac{d\psi^*}{dx}\,dx = \int\left(-\frac{d\psi^*}{dx}\right)\varphi\,dx$$

$$= \Big(\underbrace{-\frac{d\psi}{dx}}_{\text{operador adjunto de }\frac{d}{dx}}, \varphi\Big) \Longrightarrow \boxed{\left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}} \quad \text{(operador adjunto)}.$$

- Para q.q. operador linear A, existe o operador adjunto tal que:

$$(\psi, A\varphi) = (A^{+}\psi, \varphi) \implies \boxed{(A^{+})^{+} = A}$$

- Se $A^{+} = A$, operador é dito hermitiano (auto adjunto)

- $$(\psi, A\underbrace{B\varphi}_{\chi}) = ((AB)^{+}\psi, \varphi)$$

$$\| $$

$$(A^{+}\psi, \chi) = (A^{+}\psi, B\varphi) = (B^{+}(A^{+}\psi), \varphi) = ((B^{+}A^{+})\psi, \varphi) \implies \boxed{(AB)^{+} = B^{+}A^{+}}$$

- $$(\psi, A\psi) = (A\psi, \psi)^{*} = (A^{+}\psi, \psi)$$

se $A^{+} = A$ (hermitiano) $\implies (A\psi, \psi) = (A\psi, \psi)^{*} = (\psi, A\psi)$ (real) $\implies$ valor médio real

- $$(\psi, x\psi) = \int \psi^{*} (x\varphi)\, dx = \int (x\psi^{*})\, \varphi\, dx = (x\psi, \varphi) \implies \boxed{x^{+} = x} \text{ (hermitiano)} \implies \langle x \rangle \text{ real}$$

$$- \ (\psi, p_x \varphi) = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial \varphi}{\partial x}\right) dx = -i\hbar \left\{ \cancel{\psi^* \varphi \Big|_{-\infty}^{\infty}}^{\,0} - \int_{-\infty}^{\infty} \varphi \frac{\partial \psi^*}{\partial x} dx \right. = \int_{-\infty}^{\infty} \left(i\hbar \frac{\partial \psi^*}{\partial x}\right) \varphi \, dx$$

$$= \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \psi}{\partial x}\right)^* \varphi \, dx = \int_{-\infty}^{\infty} (p_x \psi)^* \varphi \, dx = (p_x \psi, \varphi) \Longrightarrow \boxed{p_x^{\dagger} = p_x} \text{ (hermitiano)}$$

$$- \ (\psi, p_x^2 \psi) = (p_x^{\dagger} \psi, p_x \psi) = (p_x \psi, p_x \psi) = (p_x^{\dagger} p_x \psi, \psi) = (p_x^2 \psi, \psi) \geq 0 \Longrightarrow p_x^{2\dagger} = p_x^2 \text{ (hermitiano)}$$

$$\Downarrow$$

$$\boxed{H^{\dagger} = H} \text{ (hermitiano)}$$

autovalor

$$- \ A \varphi_n = a_n \varphi_n \Longrightarrow \begin{cases} (\varphi_n, A\varphi_n) = (A\varphi_n, \varphi_n) \text{ (hermitiano)} \\ (\varphi_n, a_n \varphi_n) = (a_n \varphi_n, \varphi_n) \\ a_n (\varphi_n, \varphi_n) = a_n^* (\varphi_n, \varphi_n) \Longrightarrow a_n^* = a_n \text{ (autovalores reais)} \end{cases}$$

operador hermitiano

autofunção

$$(\varphi_\ell, A\varphi_n) - (A\varphi_\ell, \varphi_n) = (a_n - a_\ell)(\varphi_\ell, \varphi_n) = 0 \Longrightarrow (\varphi_\ell, \varphi_n) = 0 \ (\ell \neq n) \text{ (autofunções ortogonais)}$$

Equações de Ehrenfest

$$\frac{d\langle A\rangle}{dt} = \frac{d}{dt}(\psi, A\psi) = \frac{d}{dt}\int \psi^*(A\psi)\,dx$$

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \implies \begin{cases} \dfrac{\partial\psi}{\partial t} = -\dfrac{i}{\hbar}H\psi \\[2ex] \dfrac{\partial\psi^*}{\partial t} = \dfrac{i}{\hbar}H\psi^* \end{cases}$$

$$= \int \frac{\partial\psi^*}{\partial t}(A\psi)\,dx + \int \psi^*\left(\frac{\partial A}{\partial t}\right)\psi\,dx + \int \psi^* A\frac{\partial\psi}{\partial t}\,dx$$

$$= \frac{i}{\hbar}\int (H\psi^*)(A\psi)\,dx - \frac{i}{\hbar}\int \psi^* A(H\psi)\,dx + \left\langle\frac{\partial A}{\partial t}\right\rangle$$

$\Downarrow$ hermitico

$$= \frac{i}{\hbar}\int \psi^* H A\psi\,dx - \frac{i}{\hbar}\int \psi^* A H\psi\,dx + \left\langle\frac{\partial A}{\partial t}\right\rangle$$

$$= \frac{i}{\hbar}\int \psi^*\underbrace{(HA - AH)}_{[H,A]}\psi\,dx + \left\langle\frac{\partial A}{\partial t}\right\rangle$$

$$\boxed{\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle[H,A]\rangle + \left\langle\frac{\partial A}{\partial t}\right\rangle}$$

$$\frac{d\langle x\rangle}{dt} = \frac{i}{\hbar}\left\langle [H, x] \right\rangle$$

$$H = \frac{p_x^2}{2m} + V(x) \Rightarrow$$

$$[H, x] = \frac{1}{2m}[p_x^2, x]$$

$$= \frac{1}{2m}[p_x p_x, x] = \frac{1}{2m}\Big(p_x p_x x - x p_x p_x + - p_x x p_x + p_x x p_x \Big)$$

$$= \frac{1}{2m}\Big\{ p_x \underbrace{(p_x x - x p_x)}_{[p_x, x]} + \underbrace{(p_x x - x p_x)}_{[p_x, x]} p_x \Big\}$$

$$[H, x] = \frac{1}{m}\underbrace{[p_x, x]}_{-i\hbar} p_x = -\frac{i\hbar}{m} p_x$$

$$\boxed{\frac{d\langle x\rangle}{dt} = \frac{\langle p_x\rangle}{m}}$$

$$\frac{d\langle p_x\rangle}{dt} = \frac{i}{\hbar}\left\langle [H, p_x] \right\rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

$$[H, p_x] = [V(x), p_x]$$

$$V(x)(p_x \psi) = V(x)\left(-i\hbar \frac{\partial}{\partial x}\psi\right) = -i\hbar V(x)\frac{\partial \psi}{\partial x}$$

$$p_x(V(x)\psi) = -i\hbar\frac{\partial}{\partial x}(V\psi) = -i\hbar\left(\frac{\partial V}{\partial x}\right)\psi - i\hbar V\frac{\partial \psi}{\partial x}$$

$$V(x)\, p_x\psi - p_x V(x)\psi = i\hbar\left(\frac{\partial V}{\partial x}\right)\psi$$

$$[H, p_x] = [V(x), p_x] = i\hbar\frac{\partial V}{\partial x}$$

$$\boxed{\frac{d\langle p_x\rangle}{dt} = \left\langle -\frac{\partial V}{\partial x}\right\rangle}$$

$$\Downarrow$$

$$\boxed{m\frac{d^2\langle x\rangle}{dt^2} = \left\langle -\frac{\partial V}{\partial x}\right\rangle}$$

③

$$m \frac{d^2\langle x\rangle}{dt^2} = \left\langle -\frac{\partial V}{\partial x}\right\rangle = \langle F(x)\rangle \neq F(\langle x\rangle) \qquad F(x) = -\frac{\partial V}{\partial x}$$

$\neq$ 2ª lei

<u>Casos excepcionais</u>: partícula livre e oscilador

$$F(x) = F(0) + F'(0)\,x + F''(0)\frac{x^2}{2} + F'''(0)\frac{x^3}{3!} + \cdots$$

$$\langle F(x)\rangle = F(0) + F'(0)\langle x\rangle + F''(0)\frac{\langle x^2\rangle}{2} + F'''(0)\frac{\langle x^3\rangle}{3!} + \cdots$$

$$= \left(-\frac{\partial V}{\partial x}\right)_0 - \left(\frac{\partial^2 V}{\partial x^2}\right)_0\langle x\rangle + \cancel{\frac{\partial^3 V}{\partial x^3}} \cdots$$

part. livre: $V(x) = \text{cte} \Rightarrow \frac{\partial V}{\partial x} = 0,\ \frac{\partial^2 V}{\partial x^2} = 0, \ldots \Longrightarrow \frac{d^2\langle x\rangle}{dt^2} = 0 \Rightarrow \boxed{\frac{d\langle x\rangle}{dt} = \text{cte} \Rightarrow \langle p_x\rangle = \text{cte}}$

osc. harmônico: $V(x) = \frac{1}{2}kx^2 \Rightarrow \left(\frac{\partial V}{\partial x}\right)_0 = 0,\ \left(\frac{\partial^2 V}{\partial x^2}\right)_0 = k,\ \left(\frac{\partial^3 V}{\partial x^3}\right)_0 = 0, \ldots$

$\Downarrow$

$$\langle F(x)\rangle = -k\langle x\rangle = F\langle x\rangle$$

$$\boxed{m\frac{d^2\langle x\rangle}{dt^2} = -k\langle x\rangle}$$