Operador Hermiteano

$$\hat{A}\,\psi = a\ \psi$$

autovalor é um número real

$$\psi^*\hat{A}\,\psi = a\,\psi^*\psi$$

$$\int \psi^*\hat{A}\,\psi\,d\tau = a\int \psi^*\psi\,d\tau$$

$$\int \psi^*\hat{A}\,\psi\,d\tau = a$$

$$\hat{A}^*\psi^* = a\,\psi^*$$

$$\psi\hat{A}^*\psi^* = a\,\psi\psi^*$$

$$\int \psi\hat{A}^*\psi^*\,d\tau = a$$

Operador Hermiteano: $\int \psi^*\hat{A}\,\psi d\tau = \int \psi\hat{A}^*\psi^*\,d\tau$

Se o operador é Hermiteano, então suas autofunções são ortogonais

$$\hat{A}\,\psi_n = a_n \psi_n \qquad \int \psi_m^* \hat{A}\,\psi_n d\tau = a_n \int \psi_m^* \psi_n d\tau$$

$$\hat{A}^* \psi_m^* = a_m \psi_m^* \qquad \int \psi_n \hat{A}^* \psi_m^* d\tau = a_m \int \psi_n \psi_m^* d\tau$$

$$\int \psi_m^* \hat{A}\,\psi_n d\tau - \int \psi_n \hat{A}^* \psi_m^* d\tau = (a_n - a_m) \int \psi_m^* \psi_n d\tau$$

zero, porque é hermiteano

$$(a_n - a_m) \int \psi_m^* \psi_n d\tau = 0$$

Se o operador é Hermiteano, então suas autofunções são ortogonais

$$(a_n - a_m) \int \psi_m^* \psi_n d\tau = 0$$

Se $n = m \rightarrow (a_n - a_m) = 0$

Se $n \neq m \rightarrow \int \psi_m^* \psi_n d\tau = 0$

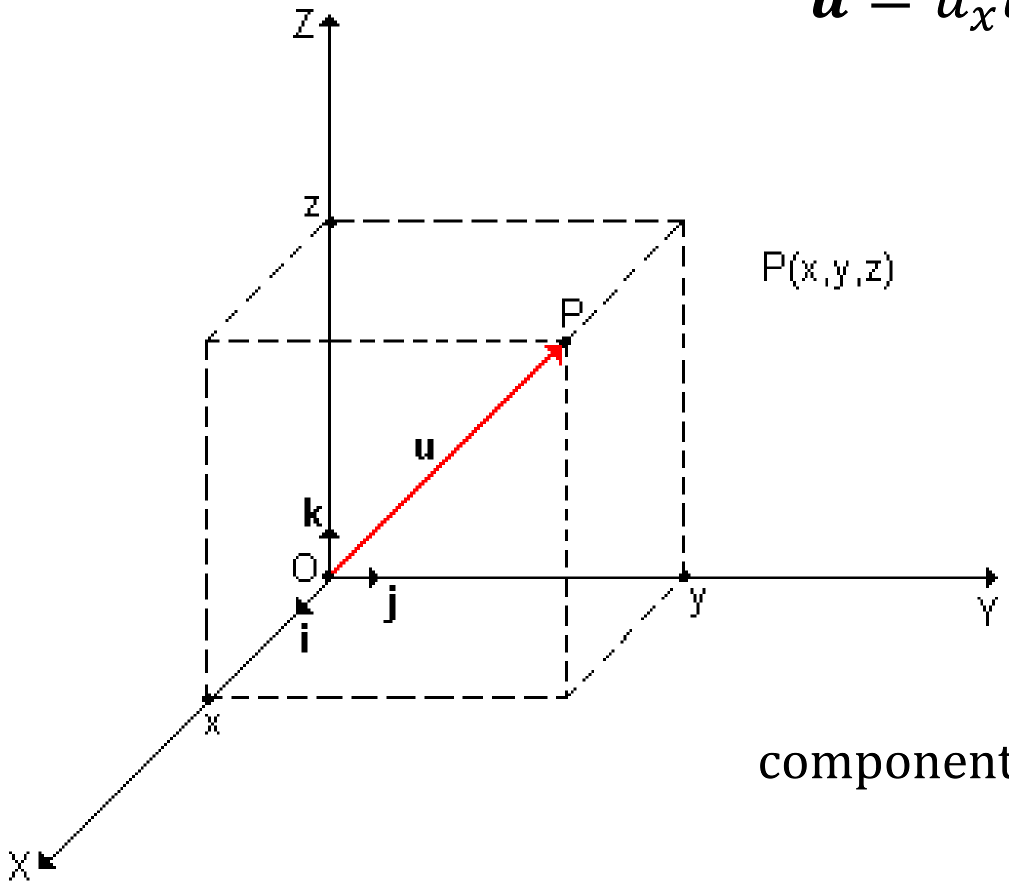
Ortogonalidade das autofunções de operadores Hermiteanos:

$$\int \psi_m^* \psi_n d\tau = \delta_{mn}$$

$$\delta_{mn} = \begin{cases} 1 \text{ se } m = n \\ 0 \text{ se } m \neq n \end{cases}$$

↑ delta de Kroenecker

$$\vec{\boldsymbol{u}} = u_x\hat{\boldsymbol{\imath}} + u_y\hat{\boldsymbol{\jmath}} + u_z\widehat{\boldsymbol{k}}$$



vetores unitários ortogonais

$$\hat{\boldsymbol{\imath}}.\hat{\boldsymbol{\jmath}} = 0 \qquad \hat{\boldsymbol{\imath}}.\widehat{\boldsymbol{k}} = 0 \qquad \hat{\boldsymbol{\jmath}}.\widehat{\boldsymbol{k}} = 0$$

normalizados

$$\hat{\boldsymbol{\imath}}.\hat{\boldsymbol{\imath}} = 1 \qquad \hat{\boldsymbol{\jmath}}.\hat{\boldsymbol{\jmath}} = 1 \qquad \widehat{\boldsymbol{k}}.\widehat{\boldsymbol{k}} = 1$$

componentes u_x, u_y e u_z obtidos pela projeção de $\vec{\boldsymbol{u}}$ em $\hat{\boldsymbol{\imath}}, \hat{\boldsymbol{\jmath}}$ e $\widehat{\boldsymbol{k}}$

$$\widehat{\boldsymbol{u}}.\hat{\boldsymbol{\imath}} = u_{\boldsymbol{x}} \qquad \widehat{\boldsymbol{u}}.\hat{\boldsymbol{\jmath}} = u_{\boldsymbol{y}} \qquad \widehat{\boldsymbol{u}}.\widehat{\boldsymbol{k}} = u_{\boldsymbol{z}}$$

Expansão de uma função de onda em um conjunto completo ortonormal

$$\int \psi_i^* \psi_j d\tau = \delta_{ij} \qquad \delta_{ij} = \begin{cases} 1 \text{ se } i = j \\ 0 \text{ se } i \neq j \end{cases}$$

combinação linear de todas as autofunções ψ_i

$$\psi_j^* \sum_{i=1}^{\infty} c_i \psi_i = \phi(x)\ \psi_j^*$$

$$\sum_{i=1}^{\infty} c_i \int \psi_j^* \psi_i d\tau = \int \psi_j^* \phi(x) d\tau$$

δ_{ij}

$$\phi(x) = \sum_{j=1}^{\infty} c_j \psi_j \text{, onde } c_j = \int \psi_j^* \phi(x) d\tau$$

Por exemplo, sobreposição de dois estados:

$$\Psi = c_1\psi_1 + c_2\psi_2$$

$$\hat{A}\psi_1 = a_1\psi_1 \qquad \hat{A}\psi_2 = a_2\psi_2$$

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau \; = \int (c_1\psi_1 + c_2\psi_2)^* \hat{A}(c_1\psi_1 + c_2\psi_2) d\tau$$

$$= \int c_1^* c_1 \psi_1^* \hat{A} \psi_1 d\tau + \int c_1^* c_2 \psi_1^* \hat{A} \psi_2 d\tau + \int c_2^* c_1 \psi_2^* \hat{A} \psi_1 d\tau + \int c_2^* c_2 \psi_2^* \hat{A} \psi_2 d\tau$$

$$= c_1^* c_1 a_1 \underbrace{\int \psi_1^* \psi_1 d\tau}_{1} + c_1^* c_2 a_2 \underbrace{\int \psi_1^* \psi_2 d\tau}_{0} + c_2^* c_1 a_1 \underbrace{\int \psi_2^* \psi_1 d\tau}_{0} + c_2^* c_2 a_2 \underbrace{\int \psi_2^* \psi_2 d\tau}_{1}$$

$$\boxed{\langle a \rangle = |c_1|^2 a_1 + |c_2|^2 a_2}$$

Comutador de dois operadores

Note que, em geral, $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$

Quando $\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$, os operadores comutam.

$$\left[\hat{A}\hat{B} - \hat{B}\hat{A}\right] f(x) = 0 \qquad \text{notação: } \left[\hat{A}, \hat{B}\right] \equiv \left[\hat{A}\hat{B} - \hat{B}\hat{A}\right]$$

Por exemplo,

$$[\hat{x}\hat{p}_x - \hat{p}_x\hat{x}]\,\psi(x) = \left[x\left(-i\hbar\frac{d}{dx}\right) - \left(-i\hbar\frac{d}{dx}\right)x\right]\psi(x)$$

$$= -i\hbar x\frac{d\psi}{dx} - \left(-i\hbar\psi\frac{dx}{dx} - i\hbar x\frac{d\psi}{dx}\right)$$

$$= i\hbar\psi$$

$\hat{x}$ e $\hat{p}_x$ não comutam

4–6. The Physical Quantities Corresponding to Operators That Commute Can Be Measured Simultaneously to Any Precision

Thus, we see that there is an intimate connection between commuting operators and the Uncertainty Principle. If two operators $\hat{A}$ and $\hat{B}$ commute, then a and b can be measured simultaneously to any precision. If two operators $\hat{A}$ and $\hat{B}$ do not commute, then a and b cannot be measured simultaneously to arbitrary precision.

D. McQuarrie, J. D. Simon, *Physical Chemistry*, Univ. Sc. Books, 1997.