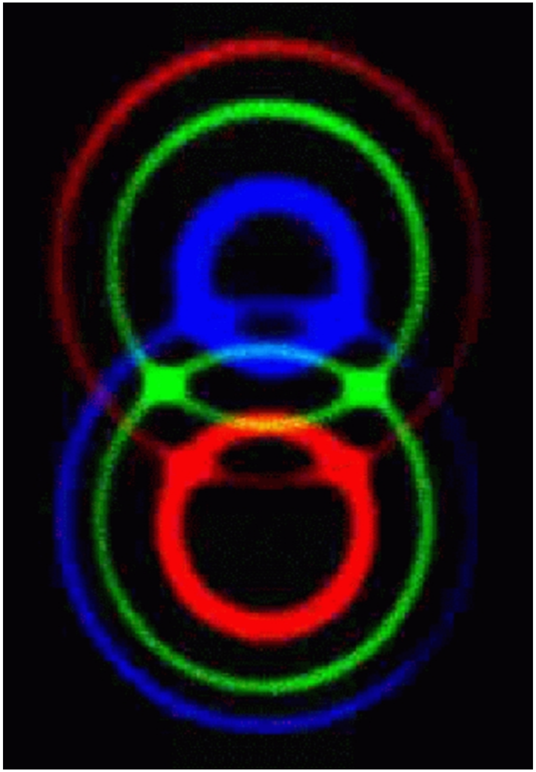
# Introduction to Quantum Chemistry





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# I.A. Discrete spectrum: Defininition of probability



- Discrete spectrum $\Rightarrow$ Finite number of possible measurement results

  Ex. Coin toss: Espectrum = 1,2

  Ex. Dice toss: Espectrum = 1,2,3,4,5,6

- Probability $P_N \Rightarrow$ Frequency of every result

$$P_N = \frac{\text{Number of measurements providing } N \text{ as result}}{\text{Number of possible measurements}}$$

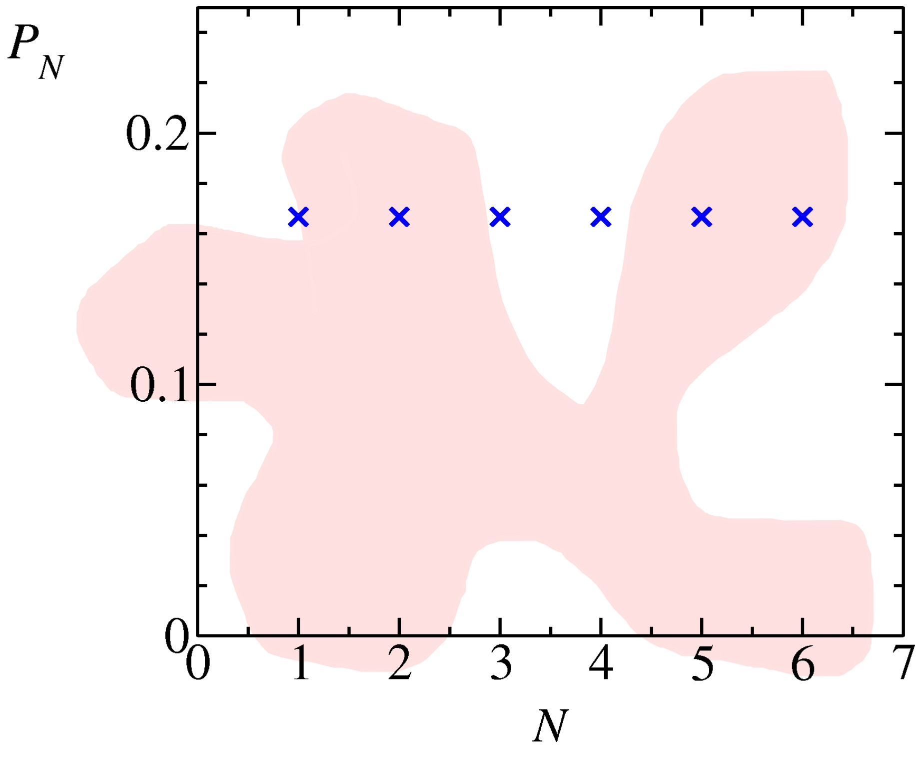
- Normalization $\Rightarrow \sum_i P_i = 1$

  Ex. Coin toss: $P_1 = \frac{1}{2} = P_2$

  Ex. Dice toss: $P_1 = \frac{1}{6} = P_2 = P_3 = P_4 = P_5 = P_6$

# I.A. Discrete spectrum: Graphical representation

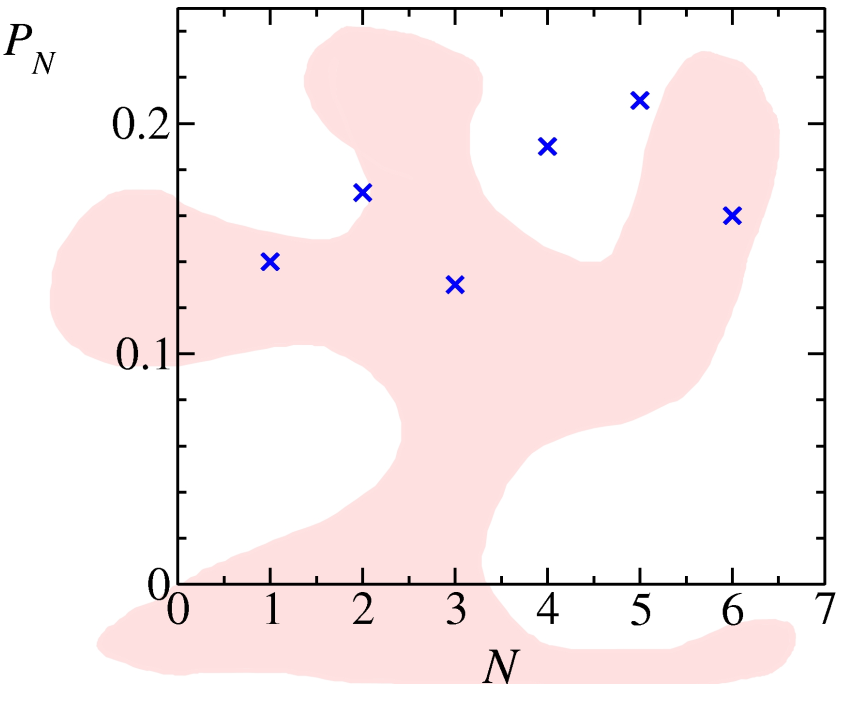
Ex. Dice toss: $P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = \frac{1}{6}$



# I.A. Discrete spectrum: Graphical representation

Ex. Real dice toss:

$$P_1 = 0.14, P_2 = 0.17, P_3 = 0.13, P_4 = 0.19, P_5 = 0.21, P_6 = 0.16$$



# I.A. Discrete spectrum: Mean value of a measurement

- Mean value of a measurement $\langle f \rangle$

$$
\begin{aligned}
\text{N measurements} &\Rightarrow \; f_5, f_3, f_1, f_1, f_3, \ldots \\
\text{Mean value} &= \frac{1}{N}(f_5 + f_3 + f_1 + f_1 + f_3 + \ldots) \\
&= \frac{1}{N}(f_1 N_1 + f_2 N_2 + \ldots) \\
&= f 1 \frac{N_1}{N} + f_2 \frac{N_2}{N} + \ldots
\end{aligned}
$$

$$\langle f \rangle = \sum_i f_i P_i$$

# I.A. Discrete spectrum: Mean value of a measurement

Ex. Dice toss:

$$\langle N \rangle = 1 \cdot \frac{1}{6} + 2 \cdot \frac{1}{6} + 3 \cdot \frac{1}{6} + 4 \cdot \frac{1}{6} + 5 \cdot \frac{1}{6} + 6 \cdot \frac{1}{6} = \frac{21}{6} = 3.5$$

$$\langle \sqrt{N} \rangle = \sqrt{1} \cdot \frac{1}{6} + \sqrt{2} \cdot \frac{1}{6} + \sqrt{3} \cdot \frac{1}{6} + \sqrt{4} \cdot \frac{1}{6} + \sqrt{5} \cdot \frac{1}{6} + \sqrt{6} \cdot \frac{1}{6}$$

$$= 1.8$$

$$\sqrt{\langle N \rangle} \neq \langle \sqrt{N} \rangle$$

$$\sqrt{3.5} \neq 1.8$$

# I.A. Discrete spectrum: Mean squared deviation

- Mean squared deviation $\Delta f \Rightarrow$ Measures the mean deviation of the values from their mean value

Measurements: $f_1,\ f_2,\ f_3,\ldots$

Mean value of the deviations = $\langle f - \langle f \rangle \rangle = \langle f \rangle - \langle f \rangle = 0$

$$(\Delta f)^2 = \langle (f - \langle f \rangle)^2 \rangle = \langle f^2 - 2f\langle f \rangle + \langle f \rangle^2 \rangle$$

$$= \langle f^2 \rangle - 2\langle f \rangle\langle f \rangle + \langle f \rangle^2$$

$$\Delta f = \sqrt{\langle f^2 \rangle - \langle f \rangle^2}$$

# I.B. Continuous spectrum: Probability density



- Continuous spectrum $\Rightarrow$ Infinite number of possible results of the measurements $\tau \in (a, b)$. It makes no sense to ask about the probability of a particular outcome.

- Probability density $\rho_\tau \Rightarrow$ It describes how the probability is distributed among the possible results of the measurement

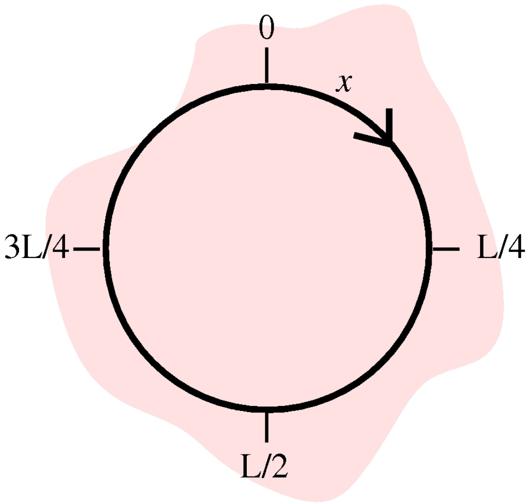
$$\rho_\tau = \frac{dP}{d\tau}$$

$$P(\tau \in (\tau_1, \tau_2)) = \int_{\tau_1}^{\tau_2} \rho_\tau \, d\tau$$

- Normalization $\Rightarrow \int_{\forall\tau} \rho_\tau \, d\tau = 1$

# I.B. Continuous spectrum: Probability density

Ex. Ring toss $\Rightarrow \quad \rho_x = \frac{dP}{dx}$




$$P(x \in [x_1, x_2]) = \int_{x_1}^{x_2} \rho_x \, dx$$

Normalization $\Rightarrow \int_0^L \rho_x \, dx = 1$

$$\rho_x = \text{cte.} \Rightarrow \rho_x \int_0^L dx = 1 \Rightarrow \rho_x = \frac{1}{L}$$

$$P(x \in [0, L/2]) = \int_0^{L/2} \rho_x \, dx = \frac{1}{L} \int_0^{L/2} dx$$

$$= \frac{1}{2}$$

# I.B. Continuous spectrum: Mean value of measurement



- Mean value of a measurement $\langle f \rangle$

$$\langle f \rangle = \int_{\forall \tau} f_\tau \rho_\tau \, d\tau$$

Ex. Ring toss

$$\langle x \rangle = \int_0^L x \rho_x \, dx = \frac{1}{L} \int_0^L x \, dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \int_0^L x^2 \rho_x \, dx = \frac{1}{L} \int_0^L x^2 \, dx = \frac{L^2}{3}$$

# I.B. Continuous spectrum: Mean squared deviation

- Mean squared deviation $\Delta f$

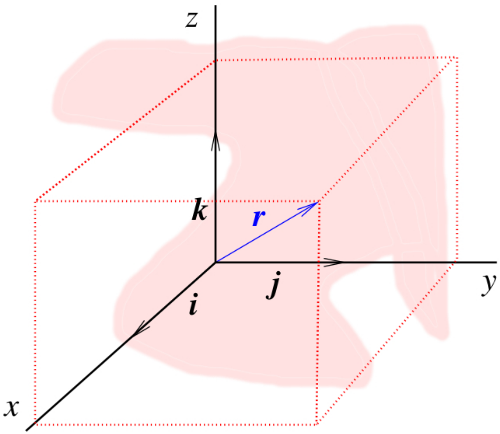
$$\Delta f = \sqrt{\langle f^2 \rangle - \langle f \rangle^2}$$

Ex. Ring toss

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{L}{\sqrt{12}}$$

# II.A. Vectorial space

- Vector ⇒ Member of a vectorial space




base $(\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k})$

- Normalized
  $|\boldsymbol{i}|^2 = \boldsymbol{i} \cdot \boldsymbol{i} = 1$ (*idem* $\boldsymbol{j}, \boldsymbol{k}$)
- Orthogonal/Perpendicular
  $\boldsymbol{i} \cdot \boldsymbol{j} = \boldsymbol{i} \cdot \boldsymbol{k} = \ldots = 0$
- Generator system
  $\boldsymbol{r} = a\boldsymbol{i} + b\boldsymbol{j} + c\boldsymbol{k}$

$$\boldsymbol{r} \cdot \boldsymbol{i} = a\, \underbrace{\boldsymbol{i} \cdot \boldsymbol{i}}_{1} + b\, \underbrace{\boldsymbol{j} \cdot \boldsymbol{i}}_{0} + c\, \underbrace{\boldsymbol{k} \cdot \boldsymbol{i}}_{0} = a$$

$$\boldsymbol{r} \cdot \boldsymbol{j} = a\, \underbrace{\boldsymbol{i} \cdot \boldsymbol{j}}_{0} + b\, \underbrace{\boldsymbol{j} \cdot \boldsymbol{j}}_{1} + c\, \underbrace{\boldsymbol{k} \cdot \boldsymbol{j}}_{0} = b$$

$$\boldsymbol{r} \cdot \boldsymbol{k} = a\, \underbrace{\boldsymbol{i} \cdot \boldsymbol{k}}_{0} + b\, \underbrace{\boldsymbol{j} \cdot \boldsymbol{k}}_{0} + c\, \underbrace{\boldsymbol{k} \cdot \boldsymbol{k}}_{1} = c$$

$$\boldsymbol{r} = (\boldsymbol{r} \cdot \boldsymbol{i})\boldsymbol{i} + (\boldsymbol{r} \cdot \boldsymbol{j})\boldsymbol{j} + (\boldsymbol{r} \cdot \boldsymbol{k})\boldsymbol{k}$$

# II.A. Vectorial space

- Vector $\Rightarrow$ $f(x)$ $\Rightarrow$ Hilbert's space

Dot product $\Rightarrow$ $\langle f|g\rangle = \int_{\forall x} f^*(x) g(x) dx$

David Hilbert

base $(\{\phi_i(x)\}_{i=1}^N)$

- Normalized
  $\langle \phi_i|\phi_i\rangle = 1, \;\; i = 1,\ldots,N$
- Orthogonal/Perpendicular
  $\langle \phi_i|\phi_j\rangle = 0, \;\; i \neq j = 1,\ldots,N$
- Generator system
  $f(x) = \sum_{i=1}^N a_i \phi_i(x)$

$$\langle \phi_j|f\rangle = \sum_{i=1}^N a_i \langle \phi_j|\phi_i\rangle = a_j \quad (\langle \phi_j|\phi_i\rangle \to \delta_{ij}) \Bigg\} \; f(x) = \sum_{i=1}^N \langle \phi_i|f\rangle \, \phi_i(x)$$

# II.B. Concept of state: Classic state

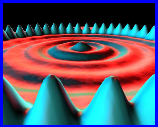


- Classical Mechanics $\Rightarrow$ The state of the system is characterized by the positions and moments of all the particles in the system $(\vec{r}, \vec{p})$

$$\vec{p} = m\frac{d\vec{r}}{dt}$$

If these magnitudes are known at a given time $(\vec{r}(0), \vec{p}(0))$ they can be known at any later $(\vec{r}(t), \vec{p}(t))$ or earlier time $(\vec{r}(-t), \vec{p}(-t))$ using the second Newton's law

$$\overrightarrow{F} = m\frac{d^2\vec{r}}{dt^2}$$



# II.B. Concept of state: Quantum state



- Quantum Mechanics $\Rightarrow$ Postulate 1. The state of the system is characterized by a function depending on the coordinates of the particles in the system and time $\psi(\vec{r},t)$ referred to as state function.

  The squared modulus of the state function $|\psi(\vec{r},t)|^2$ is the probability density of the system

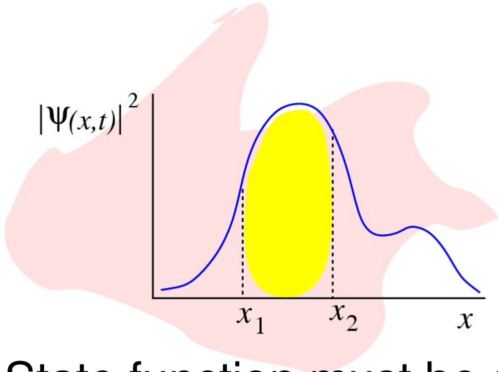
$$dP(\vec{r} \in [\vec{r}, \vec{r} + d\vec{r}]) = |\psi(\vec{r},t)|^2 d\vec{r}$$

Modulus of a complex number

$$a = a_r + i a_i \Rightarrow |a|^2 = a \cdot a^* = (a_r + i a_i)(a_r - i a_i) = a_r^2 + a_i^2$$

# II.C. State function

- Probabilistic interpretation




$$P(x \in [x_1, x_2]) = \int_{x_1}^{x_2} |\psi(x,t)|^2 dx$$

- State function must be *well behaved*:

  a) Normalizable $\Rightarrow$ $\int_{\forall \vec{r}} |\psi(\vec{r},t)|^2 d\vec{r} = 1$

  b) Single valued $\Rightarrow$ Probability density has only one value in any space point

  c) Continuous $\Rightarrow$ No jumps

# II.D. Operators



- Postulate 2. Every measurable physical quantity is described by a lineal and hermitian operator obtained from the clasic expression of the magnitude using the correspondence principle
  - $x \rightarrow \hat{x}$
  - $p_x \rightarrow \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$

# II.D. Operators



- Operator

$$\hat{A} = \frac{d}{dx} \qquad f(x) = e^{-2x} \qquad \hat{B} = x^2$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\hat{A}f = \frac{d}{dx}e^{-2x} = -2e^{-2x} \qquad \hat{B}f = x^2 e^{-2x}$$

- Lineal $\begin{cases} \hat{A}(f(x)+g(x)) = \hat{A}f(x)+\hat{A}g(x) \\ \hat{A}(c\,f(x)) = c\hat{A}f(x) \end{cases}$

- Hermitian $\Rightarrow \langle f|\hat{A}g\rangle = \langle \hat{A}f|g\rangle$

$$\langle f|\hat{A}g\rangle = \int_{\forall x} f^* \hat{A} g dx$$

$$\langle \hat{A}f|g\rangle = \int_{\forall x} (\hat{A}f)^* g dx = \left[\int_{\forall x} (\hat{A}f) g^* dx\right]^* = \left[\int_{\forall x} g^* (\hat{A}f) dx\right]^* = \langle g|\hat{A}f\rangle^*$$

# II.D. Operators



## Ex. Kinetic energy operator

$$T = \frac{p^2}{2m} \rightarrow \hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

## Ex. Potential energy operator

$$V(x) \rightarrow \hat{V} = V(x)$$

## Ex. Hamiltonian operator

$$E = \frac{p^2}{2m} + V(x) \rightarrow \hat{H} = \hat{T} + \hat{V}(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$$

# II.D. Operators: Result of a measurement



- Postulado 3. The only possible result of the measurement of a physical quantity $A$ is one of the eigenvalues of the correspon-ding eigenvalue equation

$$\hat{A}\varphi_i = a_i\varphi_i \qquad i = 1, 2, \ldots$$

The numbers $a_1, a_2, \ldots$ are known as eigenvalues of the $\hat{A}$ ope-rator and the functions $\varphi_i$ are their corresponding eigenfun-ctions. The eigenfunctions define a basis set in the Hilbert's spa-ce.

$$\psi = \sum_i \langle\varphi_i|\psi\rangle\,\varphi_i$$

# II.D. Operators: Result of a measurement

- When the system is described by the state function $\psi$, the measurement of the $A$ magnitude will provide the result $a_i$ with a probability equal to $P_{a_i} = |\langle\varphi_i|\psi\rangle|^2$.

$$\psi = \sum_i \langle\varphi_i|\psi\rangle\,\varphi_i \Rightarrow P_{a_i} = |\langle\varphi_i|\psi\rangle|^2$$

# II.D. Operators: Result of a measurement



- Consequence 1 $\Rightarrow \hat{A}\varphi_i = a_i \varphi_i$ y $\psi = \varphi_i$

$$P_{a_i} = |\langle \varphi_i | \psi \rangle|^2 = 1$$

- Consecuence 2 $\Rightarrow$ the mean value of a measurement of the $A$ magnitude is

$$\langle \hat{A} \rangle = \sum_i P_{a_i} a_i = \sum_i |\langle \varphi_i | \psi \rangle|^2 a_i = \langle \psi | \hat{A} | \psi \rangle$$

$\Rightarrow$ Mean squared deviation$\Delta A = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$

# II.D. Operators



- Consequence 3 $\Rightarrow f \equiv g, \hat{A} f = a\, f$

$$\langle f | \hat{A} f \rangle = \left[ \langle f | \hat{A} f \rangle \right]^*$$
$$\langle f | a\, f \rangle = \left[ \langle f | a\, f \rangle \right]^*$$
$$a \langle f | f \rangle = a^* \left[ \langle f | f \rangle \right]^* \Rightarrow a = a^* \Rightarrow a \text{ real}$$

- Consequence 4 $\Rightarrow \hat{A} f = a\, f,\ \hat{A} g = b\, g,\ a \neq b$

$$\langle f | \hat{A} g \rangle = \left[ \langle g | \hat{A} f \rangle \right]^*$$
$$b \langle f | g \rangle = a \langle g | f \rangle^*$$
$$\downarrow \quad \langle g | f \rangle^* = \left[ \int_{\forall x} g^* f dx \right]^* = \int_{\forall x} f^* g dx = \langle f | g \rangle$$
$$(b - a) \langle f | g \rangle = 0 \Rightarrow f, g \text{ orthogonals}$$

# II.D. Operators: Commutators

- The commutator between two operators is defined by

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Ex. $\hat{A} = \frac{d}{dx}$ y $\hat{B} = x^2$

$$[\hat{A},\hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f = \frac{d}{dx}\left(x^2 f\right) - x^2\frac{df}{dx}$$

$$= 2xf + x^2\frac{df}{dx} - -x^2\frac{df}{dx} = 2xf$$

$$[\hat{A},\hat{B}] = 2x$$

# II.D. Operators: Simultaneous measurement

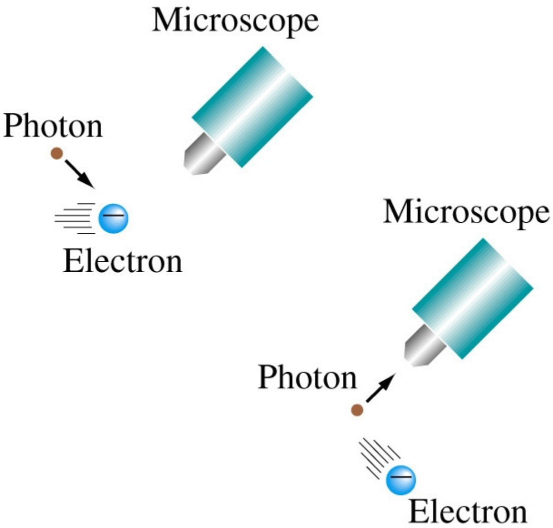
- **Consequence.** If the hermitian operators $\hat{A}$ and $\hat{B}$ commute, then there is a common set of eigenfunctions.

$$
\begin{aligned}
[\hat{A}, \hat{B}] = 0 \;&\Rightarrow\; \hat{A}\hat{B}f = \hat{B}\hat{A}f \\
\hat{A}f_i &= a_i f_i \\
&\downarrow \\
\hat{B}\hat{A}f_i &= \hat{B}(a_i f_i) \\
\hat{A}(\hat{B}f_i) &= a_i(\hat{B}f_i) \\
&\downarrow \;\; \hat{B}f_i \text{ is eigenfunction of } \hat{A} \text{ with eigenvalue } a_i \\
\hat{B}f_i &= k f_i
\end{aligned}
$$


# II.E. Uncertainty principle



- Heisenberg's uncertainty principle




$$\Delta A \Delta B \geq \frac{1}{2} \langle [\hat{A}, \hat{B}] \rangle$$

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

$$\Delta x \Delta p \geqslant \frac{\hbar}{2}$$