Chapter 4

Q. M. → **Particle Superposition of Momentum Eigenstates**

Partially localized → **Wave Packet** → $\Delta x \Delta p \geq \hbar/2$

Photon – Electron

Photon wave packet description of light same as wave packet description of electron.

Electron and Photon can act like waves – diffract or act like particles – hit target.

Wave – Particle duality of both light and matter.

Commutators and the Correspondence Principle

Formal Connection

Q.M. ↔ Classical Mechanics

Correspondence between

Classical Poisson bracket of

functions $f(x, p)$ and $g(x, p)$

And

Q.M. Commutator of

operators $\underline{f}$ and $\underline{g}$.

Commutator of Linear Operators

$$\left[\underline{A}, \underline{B}\right] = \underline{A}\,\underline{B} - \underline{B}\,\underline{A}$$

(This implies operating on an arbitrary ket.)

If *A* and *B* numbers = 0

Operators don't necessarily commute.

$$\underline{A}\,\underline{B}\left|C\right\rangle = \underline{A}\left[\underline{B}\left|C\right\rangle\right]$$
$$= \underline{A}\left|Q\right\rangle$$
$$= \left|Z\right\rangle$$

$$\underline{B}\,\underline{A}\left|C\right\rangle = \underline{B}\left[\underline{A}\left|C\right\rangle\right]$$
$$= \underline{B}\left|S\right\rangle$$
$$= \left|T\right\rangle$$

In General

$$\left|Z\right\rangle \neq \left|T\right\rangle$$

$\underline{A}$ and $\underline{B}$ do not commute.

Classical Poisson Bracket

$$\{f,g\} = \frac{\partial f}{\partial x}\frac{\partial g}{\partial p} - \frac{\partial g}{\partial x}\frac{\partial f}{\partial p}$$

$$f = f(x,p)$$
$$g = g(x,p)$$

These are functions representing classical dynamical variables ⟶ not operators.

Consider position and momentum, classical.

x and p

Poisson Bracket

$$\{x,p\} = \frac{\partial x}{\partial x}\frac{\partial p}{\partial p} - \frac{\partial x}{\partial p}\frac{\partial p}{\partial x}$$

zero

$$\{x,p\} = 1$$

Dirac's Quantum Condition

"The quantum-mechanical operators $\underline{f}$ and $\underline{g}$, which in quantum theory replace the classically defined functions f and g, must always be such that the commutator of $\underline{f}$ and $\underline{g}$ corresponds to the Poisson bracket of f and g according to

$$i\hbar\{f,g\} \rightarrow [\underline{f},\underline{g}]."$$

Dirac

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$$i\hbar\left\{f(x,p),\; g(x,p)\right\} \Rightarrow \left[\underline{f},\underline{g}\right]$$

(commutator operates on a ket)

Poisson bracket of classical functions

Commutator of quantum operators

Q.M. commutator of $\underline{x}$ and $\underline{p}$.

$$\left[\underline{x},\underline{p}\right] = i\hbar\left\{x,\; p\right\}$$

commutator **Poisson bracket**

Therefore,

$$\left[\underline{x},\underline{p}\right] = i\hbar \qquad \left\{x,\; p\right\} = 1$$

Remember, the relation implies operating on an arbitrary ket.

This means that if you select operators for x and p such that they obey this relation, they are acceptable operators.

The particular choice → a representation of Q.M.

Schrödinger Representation

$$p \rightarrow \underline{P} = -i\hbar\frac{\partial}{\partial x}$$

momentum operator, –*iħ* times derivative with respect to *x*

$$x \rightarrow \underline{x} = x$$

position operator, simply *x*

Operate commutator on arbitrary ket $|s\rangle$.

$$[\underline{x},\underline{P}]|S\rangle =$$

$$(\underline{x}\,\underline{P} - \underline{P}\,\underline{x})|S\rangle =$$

$$x\left(-i\hbar\frac{\partial}{\partial x}\right)|S\rangle + i\hbar\frac{\partial}{\partial x}\;x|S\rangle$$

Using the product rule

$$= i\hbar\left(-\cancel{x\frac{\partial}{\partial x}}|S\rangle + |S\rangle + \cancel{x\frac{\partial}{\partial x}}|S\rangle\right)$$

$$= i\hbar|S\rangle$$

Therefore,

$$[\underline{x},\underline{P}]|S\rangle = i\hbar|S\rangle$$

and

$$[\underline{x},\underline{P}] = i\hbar$$

because the two sides have the same result when operating on an arbitrary ket.

Another set of operators – Momentum Representation

$$x \rightarrow \underline{x} = i\hbar \frac{\partial}{\partial p}$$

position operator, $i\hbar$ times derivative with respect to p

$$p \rightarrow \underline{p}$$

momentum operator, simply p

A different set of operators, a different representation.

In Momentum Representation, solve position eigenvalue problem for the free particle.

Get $\left| x \right\rangle$, states of definite position.

They are waves in p space. All values of momentum.

Commutators and Simultaneous Eigenvectors

$$\underline{A}\left|S\right\rangle = \alpha\left|S\right\rangle \qquad \underline{B}\left|S\right\rangle = \beta\left|S\right\rangle$$

$\left|S\right\rangle$ are simultaneous Eigenvectors of operators $\underline{A}$ and $\underline{B}$ with egenvalues α and β.

Eigenvalues of linear operators → observables.

$\underline{A}$ and $\underline{B}$ are different operators that represent different observables, e. g., energy and angular momentum.

If $\left|S\right\rangle$ are simultaneous eigenvectors of two or more linear operators representing observables, then these observables can be simultaneously measured.

$$\underline{A}|S\rangle = \alpha|S\rangle \qquad \underline{B}|S\rangle = \beta|S\rangle$$

$$\underline{B}\,\underline{A}|S\rangle = \underline{B}\,\alpha|S\rangle \qquad \underline{A}\,\underline{B}|S\rangle = \underline{A}\,\beta|S\rangle$$

$$= \alpha\,\underline{B}|S\rangle \qquad = \beta\,\underline{A}|S\rangle$$

$$= \alpha\,\beta|S\rangle \qquad = \beta\,\alpha|S\rangle$$

Therefore, $\underline{A}\,\underline{B}|S\rangle = \underline{B}\,\underline{A}|S\rangle$

Rearranging $\left(\underline{A}\,\underline{B} - \underline{B}\,\underline{A}\right)|S\rangle = 0$

$\left(\underline{A}\,\underline{B} - \underline{B}\,\underline{A}\right)$ is the commutator of $\underline{A}$ and $\underline{B}$, and since in general $|S\rangle \neq 0$,

$$\left[\underline{A}, \underline{B}\right] = 0$$

The operators $\underline{A}$ and $\underline{B}$ commute.

Operators having simultaneous eigenvectors commute.

The eigenvectors of commuting operators can always be constructed in such a way that they are simultaneous eigenvectors.

There are always enough Commuting Operators (observables) to completely define a system.

Example: ⟶ **Energy operator, $\underline{H}$, may give degenerate states.**

H atom 2s and 2p states have same energy.

$\underline{J}^2 \Rightarrow$ **square of angular momentum operator**

$j \Rightarrow 1$ **for p orbital**
$j \Rightarrow 0$ **for s orbital**

But p_x, p_y, p_z

$\underline{J}_z \Rightarrow$ **angular momentum projection operator**

$\underline{H}, \underline{J}^2, \underline{J}_z$ **all commute.**

Commutator Rules

$$\left[\underline{A},\underline{B}\right]=-\left[\underline{B},\underline{A}\right]$$

$$\left[\underline{A},\underline{B}\underline{C}\right]=\left[\underline{A},\underline{B}\right]\underline{C}+\underline{B}\left[\underline{A},\underline{C}\right]$$

$$\left[\underline{A}\underline{B},\underline{C}\right]=\left[\underline{A},\underline{C}\right]\underline{B}+\underline{A}\left[\underline{B},\underline{C}\right]$$

$$\left[\underline{A},\left[\underline{B},\underline{C}\right]\right]+\left[\underline{B},\left[\underline{C},\underline{A}\right]\right]+\left[\underline{C},\left[\underline{A},\underline{B}\right]\right]=0$$

$$\left[\underline{A},\underline{B}+\underline{C}\right]=\left[\underline{A},\underline{B}\right]+\left[\underline{A},\underline{C}\right]$$

Expectation Value and Averages

$$\underline{A}\left|a\right\rangle = \alpha\left|a\right\rangle \longleftarrow$$ normalized

eigenvector eigenvalue

If make measurement of observable *A* on state $\left|a\right\rangle$ will observe α.

What if measure observable *A* on state not an eigenvector of operator $\underline{A}$.

$$\underline{A}\left|b\right\rangle \Rightarrow ?$$

normalized

Expand $\left|b\right\rangle$ in complete set of eigenkets $\left|a\right\rangle \Rightarrow$ Superposition principle.

Eigenkets – complete set. One for each state. Spans state space.

$$|b\rangle = c_1|a_1\rangle + c_2|a_2\rangle + c_3|a_3\rangle + \cdots$$

(If continuous range ⟶ integral)

$$|b\rangle = \sum_i c_i|a_i\rangle$$

Consider only two states (normalized and orthogonal).

$$|b\rangle = c_1|a_1\rangle + c_2|a_2\rangle$$

$$\underline{A}|b\rangle = \underline{A}\left(c_1|a_1\rangle + c_2|a_2\rangle\right)$$

$$= c_1\underline{A}|a_1\rangle + c_2\underline{A}|a_2\rangle$$

$$= \alpha_1 c_1|a_1\rangle + \alpha_2 c_2|a_2\rangle$$

Left multiply by $\langle b|$.

$$\langle b|\underline{A}|b\rangle = \left(c_1^*\langle a_1| + c_2^*\langle a_2|\right)\left(\alpha_1 c_1|a_1\rangle + \alpha_2 c_2|a_2\rangle\right)$$

$$= \alpha_1 c_1^* c_1 + \alpha_2 c_2^* c_2$$

$$= \alpha_1|c_1|^2 + \alpha_2|c_2|^2$$

The absolute square of the coefficient c_i, $|c_i|^2$, in the expansion of $|b\rangle$ in terms of the eigenvectors $|a_i\rangle$ of the operator (observable) $\underline{A}$ is the probability that a measurement of $\underline{A}$ on the state $|b\rangle$ will yield the eigenvalue α_i.

If there are more than two states in the expansion

$$|b\rangle = \sum_i c_i |a_i\rangle$$

$$\langle b|\underline{A}|b\rangle = \sum_i \alpha_i |c_i|^2$$

eigenvalue **probability of eigenvalue**

Definition: The average is the value of a particular outcome times its probability, summed over all possible outcomes.

Then

$$\langle b|\underline{A}|b\rangle = \sum_i |c_i|^2 \alpha_i$$

is the average value of the observable when many measurements are made.

Assume: One measurement on a large number of identically prepared non-interacting systems is the same as the average of many repeated measurements on one such system prepared each time in an identical manner.

$\langle b|\underline{A}|b\rangle \Rightarrow$ **Expectation value of the operator $\underline{A}$.**

In terms of particular wavefunctions

$$\langle b|\underline{A}|b\rangle = \int_{-\infty}^{\infty} \psi_b^* \underline{A} \psi_b \, d\tau$$

The Uncertainty Principle - derivation

Have shown - $\left[\underline{x}, \underline{P}\right] \neq 0$

and that $\Delta x \, \Delta p \approx \hbar$

Want to prove:

Given $\underline{A}$ *and* $\underline{B}$, **Hermitian with**

$\left[\underline{A}, \underline{B}\right] = i\,\underline{C}$ $\underline{C}$ **another Hermitian operator (could be number – special case of operator, identity operator).**

Then

$$\Delta A \Delta B \geq \frac{1}{2}\left|\left\langle \underline{C} \right\rangle\right|$$

with $\left\langle \underline{C} \right\rangle = \left\langle S \middle| \underline{C} \middle| S \right\rangle$

short hand for expectation value

$\left\langle S \right|$ **and** $\left| S \right\rangle$ **arbitrary but normalized.**

Consider operator

$$\underline{D} = \underline{A} + \alpha \underline{B} + i\,\beta \underline{B}$$

arbitrary real numbers

$$\underline{D}\left|S\right\rangle = \left|Q\right\rangle$$

$$\left\langle Q \middle| Q \right\rangle = \left\langle S \middle| \overline{\underline{D}}\,\underline{D} \middle| S \right\rangle \geq 0$$

Since $\left\langle Q \middle| Q \right\rangle$ is the scalar product of vector with itself.

$$\left\langle Q \middle| Q \right\rangle = \left\langle S \middle| \overline{\underline{D}}\,\underline{D} \middle| S \right\rangle = \left\langle \underline{A}^2 \right\rangle + \left(\alpha^2 + \beta^2\right)\left\langle \underline{B}^2 \right\rangle + \alpha \left\langle \underline{C}' \right\rangle - \beta \left\langle \underline{C} \right\rangle \geq 0$$

(derive this in home work)

$$\underline{C}' = \underline{A}\,\underline{B} + \underline{B}\,\underline{A}$$

is the anticommutator of $\underline{A}$ and $\underline{B}$.

$$\underline{A}\,\underline{B} + \underline{B}\,\underline{A} = \left[\underline{A}, \underline{B}\right]_+$$

anticommutator

$$\left\langle \underline{A}^2 \right\rangle = \left\langle S \middle| \underline{A}^2 \middle| S \right\rangle = \left\langle S \middle| \underline{A}\,\underline{A} \middle| S \right\rangle$$

$$\langle Q|Q\rangle = \langle S|\overline{\underline{D}}\,\underline{D}|S\rangle = \langle \underline{A}^2\rangle + (\alpha^2+\beta^2)\langle \underline{B}^2\rangle + \alpha\langle \underline{C}\,'\rangle - \beta\langle \underline{C}\rangle \ge 0$$

$\underline{B}|S\rangle \neq 0$ for arbitrary ket $|S\rangle$.

Can rearrange to give

$$\langle \underline{A}^2\rangle + \langle \underline{B}^2\rangle\left(\alpha + \frac{1}{2}\frac{\langle \underline{C}\,'\rangle}{\langle \underline{B}^2\rangle}\right)^2 + \langle \underline{B}^2\rangle\left(\beta - \frac{1}{2}\frac{\langle \underline{C}\rangle}{\langle \underline{B}^2\rangle}\right)^2 - \frac{1}{4}\frac{\langle \underline{C}\,'\rangle^2}{\langle \underline{B}^2\rangle} - \frac{1}{4}\frac{\langle \underline{C}\rangle^2}{\langle \underline{B}^2\rangle} \ge 0$$

Holds for any value of α and β.

Pick α and β so terms in parentheses are zero.

Multiplied through by $\langle \underline{B}^2\rangle$ and transposed.

Then $\langle \underline{A}^2\rangle\langle \underline{B}^2\rangle \ge \frac{1}{4}\left(\langle \underline{C}\rangle^2 + \langle \underline{C}\,'\rangle^2\right) \ge \frac{1}{4}\langle \underline{C}\rangle^2$

Positive numbers because square of real numbers.

The sum of two positive numbers is ≥ one of them.

Thus,

$$\langle \underline{A}^2\rangle\langle \underline{B}^2\rangle \ge \frac{1}{4}\langle \underline{C}\rangle^2$$

$$\langle \underline{A}^2 \rangle \langle \underline{B}^2 \rangle \geq \frac{1}{4} \langle \underline{C} \rangle^2 \qquad [\underline{A}, \underline{B}] = i\,\underline{C} \qquad \Delta A\, \Delta B \geq \frac{1}{2} \left| \langle \underline{C} \rangle \right|$$

Define

$$(\Delta A)^2 = \langle \underline{A}^2 \rangle - \langle \underline{A} \rangle^2$$

$$(\Delta B)^2 = \langle \underline{B}^2 \rangle - \langle \underline{B} \rangle^2$$

Second moment of distribution
- for Gaussian →
standard deviation squared.

For special case

$$\langle \underline{A} \rangle = \langle \underline{B} \rangle = 0$$

Average value of the observables are zero.

$$\Delta A\, \Delta B \geq \frac{1}{2} \left| \langle \underline{C} \rangle \right|$$

$$\left(\langle \underline{C} \rangle^2 \right)^{\frac{1}{2}} = \left| \langle \underline{C} \rangle \right|$$

square root of the
square of a number

Have proven that for $\left[\underline{A},\underline{B}\right]=i\,\underline{C}$

$$\Delta\underline{A}\,\Delta\underline{B}\geq\frac{1}{2}\left|\left\langle\underline{C}\right\rangle\right|$$

$$\left\langle\underline{A}\right\rangle=\left\langle\underline{B}\right\rangle=0$$

Average value of the observables are zero.

Example

$$\left[\underline{x},\underline{P}\right]=i\,\hbar$$

Number, special case of an operator.
Number is implicitly multiplied by the identity operator.

$$\left\langle\underline{x}\right\rangle=\left\langle\underline{P}\right\rangle=0$$

Therefore

$$\Delta x\,\Delta p\geq\hbar/2.$$

Uncertainty comes from superposition principle.

The more general case is discussed in the book.