Review of Quantum Mechanics

Classical Mechanics

Classical mechanics is based on

on the assumption that any physically interesting variables connected with a system/particle, such as its position, velocity or its energy can be measured with arbitrary precisions and without mutual interference for any other such measurement.

LAWs of classical mechanics can be expressed in various mathematical forms.

1, Newtonian Mechanics

2, Hamiltonian Mechanics

⇒ Quantum Mechanics is based on the realization that the measuring process may affect the physical system.

⇒ It is therefore impossible to measure simultaneously certain pair of variables

with precision.

⇒ Quantum mechanics can be expressed by.

1, Wave Mechanics

2, Dirac's Notion.

Wave Mechanics

A quantum system, such as atoms, molecules, ion etc, are given by its wave function $\psi(\vec{r},t)$

⇒ Itself $\psi(\vec{r},t)$ has no physical meaning but it allows to calculate the expectation values of all observables of interest.

Observables.

⇒ Measurable quantities are called observable and are represented by Hermition operators $\hat{O}$

Expectation values:

$$\langle \hat{O} \rangle = \int \psi^*(r,t)\, \hat{O}\, \psi(r,t)\, d\vec{r}$$

Probability

⇒ As the system exist, its probality of being somewhere has to equal 1.

$$\int \psi^*(\bar{r},t)\,\psi(\bar{r},t)\,d^3\bar{r} = 1$$

$$\int \psi_n^*(r,t)\,\psi_m(r,t)\,d^3\bar{r} = \delta_{nm} \begin{cases} 1 \text{ for } n=m \\ 0 \text{ for } n\neq m \end{cases}$$

The time development of system

Schrodinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) = H\psi(r,t)$$

⇒ H → Hamiltonian of the system.
→ Energy of the system.

→ For unperturbed system for instance an atom not interacting with light (EM-field) is the sum of its potential and kinetic energies

$$H = \frac{p^2}{2m} + V(\bar{r})$$

Stationar States

States for which space and time dependence are separated.

$$\psi_n(\bar{r}, t) = U_n(\bar{r})\, A(t) = U_n(\bar{r})\, e^{-i\omega_n t}$$

Time independent equation.

$$H U_n(\bar{r}) = E_n U_n(\bar{r}) = \hbar\omega_n U_n(r)$$

(will prove it.)

$U_n(\bar{r})$ — called eigen function of H
E_n — called eigen value.

⇒ The eigen functions of Hermitian operators belonging to different eigen values are orthogonal

⇒ Eigen functions having same eigen values are normal.

$$\int U_n^*(\bar{r})\, U_m(\bar{r})\, d\bar{r} = \delta_{nm}$$

and Complete.

$$\sum_n U_n^*(r)\, U_m(r) = 1$$

⇒ The completeness relation means that any function can be written as a linear combination of the $U_n(\bar{r})$

The wave function

$$\psi(\bar{r},t) = \sum_n \psi_n(\bar{r},t) = \sum_n C_n(t) U(\bar{r}) e^{-i\omega_n t}$$

$C_n(t)$ — expansion co-efficients.

$C_n(t)$ — Constant for problems related to free part of Hamiltonian.

$C_n(t)$ — change with time for interaction Hamiltonian.

Putting value of $\psi(\bar{r},t)$ in normalization condition.

$$\psi_n(\bar{r},t) = \sum_n C_n(t) U_n(\bar{r}) e^{-i\omega_n t}$$

$$\psi_m^*(\bar{r},t) = \sum_m C_m^*(t) U_m^*(r) e^{+i\omega_m t}$$

$$\int \psi_m^*(\bar{r},t)\, \psi_n(\bar{r},t)\, d\bar{r} = \sum_{n,m} \int C_n(t)\, C_m^*(t)$$

$$U_n(\bar{r})\, U_m^*(\bar{r})\, e^{-i(\omega_n - \omega_m)t}\, d\bar{r}$$

Using

$$\int u_m^*(\bar{r})\, u_n(\bar{r})\, d\bar{r} = \delta_{nm}$$

$$\int \psi_m^*(\bar{r},t)\, \psi_n(\bar{r},t)\, d\bar{r} = \sum_{n,m} C_n(t)\, C_m^*(t)\, \delta_{nm}$$

$$e^{-i(\omega_n - \omega_m)t}$$

$$= \sum_n |C_n|^2 = 1$$

$\Rightarrow$ gives the probability of finding the system in staten.

Expectation Value

$$\langle \hat{O} \rangle = \int \sum_{n,m} C_n(t)\, C_m^*(t)\, u_m^*(r)\, \hat{O}\, u_n(r) \times e^{-i(\omega_n - \omega_m)t}\, d\bar{r}$$

$$= \sum_{n,m} C_n(t)\, C_m^*(t)\, O_{nm}\, e^{-i\omega_{nm}}$$

where $\omega_n - \omega_m = \omega_{nm}$

and

$$O_{nm} = \int U_m^*(\bar{r})\, \hat{O}\, U_n(r)\, d\bar{r}$$

↑ Matrix element of operator.

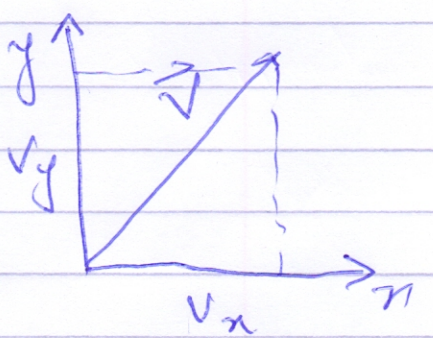
DIRAC NOTATION

⇒ The wave function of wave mechanics corresponds to the stat vector in Dirac's formulation of quantum Mech-anics.

⇒ The relation between state vector and wave function is analogous to using vectors instead of co-ordinates.

A vector $\vec{V}$ is 2-D space can be expanded as.

$$\vec{V} = V_x \hat{x} + V_y \hat{y}$$



$\hat{x}$ - compt of vector V is

$$\vec{V} \cdot \hat{x} = V_x$$

$$\vec{V} \cdot \hat{y} = V_y$$

} By taking dot product.

In Dirac's notation

$$|V\rangle = V_x|x\rangle + V_y|y\rangle$$

Taking inner product with

$$\langle x|V\rangle = V_x$$

& $\langle y|V\rangle = V_y$.

putting in above eqn we get.

$$|V\rangle = |x\rangle\langle x|V\rangle + |y\rangle\langle y|V\rangle$$

$$= [|x\rangle\langle x| + |y\rangle\langle y|]|V\rangle$$

The identity diadic (outer product of two vectors)

$$|x\rangle\langle x| + |y\rangle\langle y| = I$$

For n-dimensional space

$$|V\rangle = \sum_n |n\rangle\langle n|V\rangle$$

$$\Rightarrow \sum_n |n\rangle\langle n| = I$$

$\{|n\rangle\} \rightarrow$ complete set of vectors

$\rightarrow$ a basis.

The inner products $\langle n|v\rangle$ are the expansion co-efficients of the vector V in this basis.

Expansion co-effs are in general Complex.

$$\langle k|v\rangle = \langle v|k\rangle^*$$

For continous basis $\{|r\rangle\}$

$$I = \int d\bar{r}\, |r\rangle\langle r|$$

$\Rightarrow$ The wave vector

$$|\psi(\bar{r},t)\rangle = \int d\bar{r}\, |r\rangle\langle r|\psi(\bar{r},t)\rangle$$

where $\psi(\bar{r}) = \langle r|\psi\rangle$ are the wave functions of wave mechanics.

$\Rightarrow$ Hermitian

$$\langle\psi(\bar{r},t)|\hat{O}|\psi(\bar{r},t)\rangle = \left[\langle\psi(t)|O^\dagger|\psi(t)\rangle\right]^*$$

$$= \langle\psi(t)|\hat{O}|\psi\rangle^*$$

$$\hat{O} = O^\dagger$$

⇒ The set of eigen vectors of a hermitian operator is complete.

⇒ Any arbitrary vector $|\psi(t)\rangle$ can be expressed as a sum of orthogonal eigen vectors.

$$|\psi(t)\rangle = \sum_{n=0}^{\infty} C_n |X_n\rangle e^{-i\omega n t}$$

Eigen vectors are orthogonal

$$\langle X_n | X_m \rangle = \delta_{nm} \qquad \delta_{nm} = \begin{matrix} 0 & n \neq m \\ 1 & n = m \end{matrix}$$

Completeness relation

$$\sum |X_n\rangle\langle X_n| = I$$

$$|\psi(r)\rangle = \int dr\, |\vec{r}\rangle\langle \vec{r}|\psi\rangle$$

$$\Rightarrow \int d\vec{r}\, |\vec{r}\rangle\langle\vec{r}| = I$$

State vector obeys the Schrodinger's equation.

$$i\hbar|\dot{\psi}\rangle = H|\psi\rangle$$

$$|\psi\rangle = \sum_n C_n e^{-i\omega_n t}|n\rangle$$

Expectation value can be written as.

$$\langle\psi|\hat{O}|\psi\rangle = \sum_{n,m} C_n^* C_m e^{-i(\omega_m - \omega_n)t}\hat{O}_{mn}$$

$$\hat{O}_{mn} = \langle m|\hat{O}|n\rangle = \hat{O}_{nm}$$

Matrix element of operator $\hat{O}$.

Two-level System

Wave function for two-level system is

$$\psi(\bar{r},t) = C_a u_a(\bar{r}) e^{i\omega_a t} + C_b u_b(\bar{r}) e^{-i\omega_b t}$$

State-vector.

$$|\psi(\bar{r},t)\rangle = C_a e^{i\omega_a t}|a\rangle + C_b e^{-i\omega_b t}|b\rangle$$

Schrodinger, Heisenberg and Interaction Pictures:

Schrodinger Picture:

→ The interaction of radition with matter involves a hamiltonian.

$$H = H_0 + V$$

H_0 —— unperturbed energy

V —— Interaction energy

The corresponding Schrodinger eqn

$$|\dot{\psi}(\bar{r},t)\rangle = \frac{-i}{\hbar} H |\psi(\bar{r},t)\rangle$$

$$\Rightarrow |\dot{\psi}(\bar{r},t)\rangle = \frac{-i}{\hbar}(H_0 + V)|\psi(\bar{r},t)\rangle$$

Integrating

$$\Rightarrow |\psi(\bar{r},t)\rangle = e^{-iHt/\hbar}|\psi(\bar{r},0)\rangle$$

The expectation of an operator $\hat{O}$

$\dot{x} = -iAx$

$\frac{dx}{x} = -iA\,dt$

$\int_0^t \ln(x) = \int_0^t -iA\,t$

$x(t) = e^{-iAt}x(0)$

$$\langle \hat{O} \rangle = \langle \psi(t) | \hat{O}(0) | \psi(t) \rangle$$

Operator $\hat{O}$ is independent of time, but $|\psi(t)\rangle$ is a function of time.

$\Rightarrow$ Schrodinger picture way of writing the expectation value of an operator.

Heisenberg Picture.

$\rightarrow$ Total time dependence goes into operator $\rightarrow$ State vector is independent of time.

Expectation value of $\hat{O}(0)$ in Sch. pic

$$\Rightarrow \langle \hat{O} \rangle = \langle \psi(t) | \hat{O}(0) | \psi(t) \rangle$$

Can be written as

$$\langle \hat{O}(t) \rangle = \langle \psi(t) | e^{-iHt/\hbar} e^{+iHt/\hbar} \hat{O} e^{-iHt/\hbar} e^{+iHt/\hbar} | \psi(t) \rangle$$

where $H = H_0 + V$ — Total hamiltonian

As $|\psi(t)\rangle = e^{-iHt/\hbar} |\psi(0)\rangle$

$$\Rightarrow e^{iHt/\hbar} |\psi(t)\rangle = |\psi(0)\rangle$$

As

$$e^{iHt/\hbar}\,|\psi(t)\rangle = |\psi(0)\rangle$$

Taking Complex conjugate of

$$|\psi(t)\rangle = e^{-iHt/\hbar}\,|\psi(0)\rangle$$

$$\langle\psi(t)| = \langle\psi(0)|\,e^{iHt/\hbar}$$

$$\langle\psi(t)|\,e^{-iHt/\hbar} = \langle\psi(0)|\,e^{iHt/\hbar}\,e^{-iHt/\hbar}$$

$$\Rightarrow \langle\hat{O}(t)\rangle = \langle\psi(0)|\,e^{iHt/\hbar}\,\hat{O}(0)\,e^{-iHt/\hbar}\,|\psi(0)\rangle$$

Define

$$\hat{O}(t) = e^{iHt/\hbar}\,\hat{O}(0)\,e^{-iHt/\hbar}$$

Then

$$\langle O(t)\rangle = \langle\psi(0)|\,\hat{O}(t)\,|\psi(0)\rangle$$

$\Rightarrow$ Total time dependence is with operator. State vector is time independent

Heisenberg Picture method to calculate expectation value.

Why called Heisenberg Picture?

$$\hat{O}(t) = e^{+iHt/\hbar}\, O(0)\, e^{-iHt/\hbar}$$

$$\dot{\hat{O}}(t) = \frac{i}{\hbar} H\hat{O} + \frac{-i}{\hbar}\hat{O}H$$

$$= \frac{i}{\hbar}[H, \hat{O}]$$

is Heisenberg equation of motion.

Interaction Picture

$$\langle \hat{O}(t) \rangle = \langle \psi(0) | e^{iHt/\hbar} O(0) e^{-iHt/\hbar} | \psi(0) \rangle$$

As $H = H_0 + V$

$\Rightarrow$ If the time dependence created by the interaction energy is only assigned to the state vector and rest of time dependence goes to the operator, the the expectation value is written as.

$$\langle \hat{O}(t) \rangle = \langle \psi(0) e^{iVt/\hbar} | e^{iH_0 t/\hbar} \hat{O}(0) e^{-iH_0 t/\hbar} | e^{-iVt/\hbar} \psi(0) \rangle$$

$$\Rightarrow \langle \hat{O}(t) \rangle = \langle \psi_I(t) | \hat{O}_I(t) | \psi_I(t) \rangle$$

$\Rightarrow$ The Interaction picture state vector

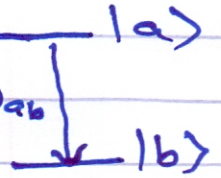
$$|\psi_I(t)\rangle = e^{-iVt/\hbar} |\psi(0)\rangle$$

Pauli Spin Matrix:

→ Another way to write two-level atom is matrix notation

$$|a\rangle \longleftrightarrow u_a \longleftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$|b\rangle \longleftrightarrow u_b \longleftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

} Column matrix



$$\psi(\vec{r},t) = \begin{bmatrix} C_a e^{-i\omega_a t} \\ C_b e^{-i\omega_b t} \end{bmatrix} = \begin{bmatrix} C_a(t) \\ C_b(t) \end{bmatrix}$$

⇒ Two-level atom is analogus to spin up & down states

The spin-flip operators:

$$\sigma_+ = \frac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\sigma_- = \frac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Pauli-Spin matrices

$$\sigma_- |a\rangle = \sigma_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = |b\rangle$$

$\Rightarrow \sigma_-$ flips the system from uppa- level to a lower-level

while σ_+

$$\sigma_+ |b\rangle = \sigma_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |a\rangle$$

flips the system from lower - level to the upper- level.

Dipole operator for two-level atom

The expectation value of any operator is given by.

$$\langle \psi | \hat{O} | \psi \rangle = C_a C_a^* \hat{O}_{aa} + C_b C_b^* \hat{O}_{bb} + \{ C_a C_b^* \hat{O}_{ab} \times e^{-i\omega_{ab} t} + c.c \}$$

The expectation value of er is

$$\langle \psi | er | \psi \rangle = eC_a C_a^* \langle a | r | a \rangle + eC_b C_b^* \langle b | r | b \rangle + e \{ C_a C_b^* e^{-i(\omega_a - \omega_b)t} \langle b | r | a \rangle + c.c \}$$

As the diagonal matrix element of "er" between eigen states of the Hamiltonian generally vanishes:

$$er_{aa} = \langle a|er|a\rangle = e\int u_a^*(r)\,\hat{r}\,u_a(\bar{r})\,d\bar{r} = 0$$

$$er_{bb} = \langle b|er|b\rangle = e\int u_b^*(r)\,r\,u_b(r)\,d\bar{r} = 0$$

$$er_{ab} = \langle a|er|b\rangle = e\int u_a^*(r)\,r\,u_b(r)\,d\bar{r} \neq 0$$

$$\Rightarrow \langle er\rangle = e\,C_a C_b^*\, e^{-i(\omega_a-\omega_b)t} r_{ba} + c.c$$

$$= e\begin{pmatrix} 0 & r_{ab} \\ r_{ba} & 0 \end{pmatrix}$$