Quantum Mechanics II
EP 423

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Typical Contents of QM I

- Review of Quantum Ideas of PH 107 (Left to Students)
- Elements of wave mechanics
- Simple applications of the Schrodinger equation
- Spin ½ systems and Stern Gerlach Experiments
- Linear Vector spaces, Operators, concept of state vector
- Postulates of QM; Eigenfunctions and eigenvalues
- Simple Harmonic Oscillator

Typical Contents of QM I…

- Application of Schrodinger eqn. to Central potentials
- Hydrogen Atom
- Angular Momentum and Spin
- Additional of Angular momentum (If time permits)
- Clebsch-Gordan coefficients (If time permits)

Typical Contents of QM II

- Approximation methods
- Variational Principle, WKB Method
- Time dependent and independent perturbation theory (Huge topic, many applications throughout physics)
- Symmetries, Identical Particles
- Scattering (Potential scattering, Phase Shift analysis, General formalism of scattering)

Reference Books (Undergraduate Level)

- Introduction to Quantum Mechanics by David Griffiths, Pearson (2nd Indian Edition)
- Principles of Quantum Mechanics by R. Shankar (Indian Edition available)
- Lectures on Quantum Mechanics by Ashok Das, by Hindustan Book Agency
- Introductory Quantum Mechanics by Richard Liboff (Pearson,4th Indian Edition)
- A Modern Approach to Quantum Mechanics by John S Townsend (Viva Books, Indian Edition available)
- Quantum Mechanics: Concepts & Applications by Nouredine Zettili (John Wiley, Indian Edition Available)

Reference Books (Graduate Level)

- Modern Quantum Mechanics by JJ. Sakurai (Addison Wesley)
- Quantum Mechanics by Eugen Merzbacher (John Wiley, Indian Edition)
- Quantum Mechanics by Bransden & Joachain (Pearson Indian Edition)
- Quantum Mechanics by Franz Schwabl (Springer, NO Indian Edition)

Classics

- Principles of Quantum Mechanics by P.A.M. Dirac (Oxford University Press, Low Prized Indian Edition available)
- Quantum Mechanics (Non-Relativistic theory) by Landau & Lifshitz
- Quantum Mechanics in two volumes by Albert Messiah
- Quantum Mechanics by L. Schiff (Tata McGraw Hill, Indian Edition available)
- The Feynman Lectures on Physics Vol III (Quantum Mechanics)

Huge number of Online Resources

For this course, I would recommend

- CDEEP Lectures on QM II by Prof. Uma Sankar
- CDEEP Lectures on QM II by Prof. Ramadevi
- NPTEL course on QM I topics by Prof. Ramadevi
- NPTEL course on QM I+II topics by Prof. V. Balakrishnan and Prof. Lakshmi Bala (IIT Madras)

NPTEL lectures are on YouTube

I would refer you to the above lectures videos on specific topics, as we go along

These videos are edited and polished and are good for learning and viewing at your own pace later

Postulates of Quantum Mechanics

1.) In QM the state of a system at a fixed time is described by an infinite dimensional vector $|\psi(t)\rangle$, which belongs to a Hilbert space

Typically states are labelled by operators whose eigenstates they are:

Ex. A particle with a fixed position is denoted by $|\mathbf{x}\rangle$

A particle with a fixed momentum is denoted by $|\mathbf{p}\rangle$

A particle with a fixed energy is denoted by $|E\rangle$

A spin $\frac{1}{2}$ particle with $S_z = \pm\frac{1}{2}$ is labelled as $\left|\frac{1}{2};\pm\frac{1}{2}\right\rangle$

State vectors are either normalized to unity (for discrete states) or Dirac delta functions (for continuous states):

$$\langle\psi|\psi\rangle = 1 \text{ or } \langle\mathbf{x}'|\mathbf{x}\rangle = \delta^{(3)}(\mathbf{x}-\mathbf{x}')$$

2.) Observables in classical mechanics like **x**, **p**, Angular momentum **L**, Energy H etc. are replaced by the Hermitian operators in Quantum mechanics

So, in the coordinate representation, **x** an **p** are replaced by the operators

$$\mathbf{x} \rightarrow \boldsymbol{X} = \mathbf{x}$$

$$\mathbf{p} \rightarrow \boldsymbol{P} = -i\hbar\boldsymbol{\nabla} = -\mathrm{i}\hbar\left(\partial_x, \partial_y, \partial_z\right)$$

with the non-trivial commutation relation $\left[X_i, P_j\right] = i\hbar\delta_{ij}\mathbf{1}$

Further, say, in one dimension, the matrix elements of X and P are

$$\langle x'|X|x\rangle = x\,\delta(x - x')$$

$$\langle x|P|x'\rangle = -i\hbar\frac{d}{dx}\,\delta(x - x')$$

Any Quantum operator $\boldsymbol{\Omega(X, P)}$ corresponding to the classical observable $\boldsymbol{\omega(\mathbf{x}, \mathbf{p})}$ is obtained by replacing $\mathbf{x}$ with $\boldsymbol{X}$ and $\mathbf{p}$ with $\boldsymbol{P}$:

$$\boldsymbol{\omega(\mathbf{x}, \mathbf{p}) \longrightarrow \Omega(X, P)}$$

Hence,

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} \rightarrow -i\hbar\, \mathbf{x} \times \boldsymbol{\nabla}$$

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) \rightarrow -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{x})$$

Since in classical mechanics $xp = px$, there is an ambiguity in the ordering of operators when going to QM. In this case, we symmetrize the product

$$xp \longrightarrow \frac{1}{2}(XP + PX)$$

3.) If a system is in a state $|\psi(t)\rangle$, then a measurement corresponding to the observable Ω yields one of the eigenvalues ω_i of Ω, with a probability

$$P(\omega_i) = \frac{|\langle\omega_i|\psi\rangle|^2}{\langle\psi|\psi\rangle}\ , \qquad \sum_i P(\omega_i) = 1$$

As a result of the measurement the system changes to the eigenstate $|\omega_i\rangle$ of the operator Ω

The Born Rule:

If a system is the state $|\psi\rangle$, the probability of being found in another state $|\phi\rangle$ is given by $|\langle\phi|\psi\rangle|^2$

(assuming $\langle\psi|\psi\rangle = \langle\phi|\phi\rangle = 1$)

In particular, if a particle is in a general state $|\psi(t)\rangle$, the probability amplitude of it being found at some position $\mathbf{x}$ is

$$\langle \mathbf{x}|\psi(t)\rangle = \psi(\mathbf{x}, t)$$

which is the familiar wavefunction you encountered when starting your study of QM in PH 107

Similarly, the wavefunction of a particle in a state with definite momentum $\mathbf{p}$, is

$$\langle \mathbf{x}|\mathbf{p}\rangle \propto e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}}$$

Hence the probability (or rather probability density) of finding a particle with fixed momentum $\mathbf{p}$ is $|\langle \mathbf{x}|\mathbf{p}\rangle|^2 = |\exp i/\hbar(\,\mathbf{p}\cdot\mathbf{x})|^2 = 1$

The particle has equal probability of being found at all points, i.e., it is completely delocalized!

4.) **Dynamics**: The state vectors $|\psi(t)\rangle$ evolve with time according to the Schrodinger eqn.

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

where $H = H(\boldsymbol{X}, \boldsymbol{P})$ is the Hamiltonian operator (there may be other terms in the Hamiltonian, which do not depend on X and P like spin terms)

It is important to understand that the above eqn. is a ket eqn., i.e., an equation that determines how the state vector evolves.

It is independent of any particular representation (position, momentum, energy etc.)

The Hamiltonian has to be determined for the system under study and the corresponding Schrodinger eqn. solved

In the special case that the Hamiltonian of the system is independent of time, the time evolution operator which takes the state vector at an initial time t_0 to a final time $t(> t_0)$ is

$$|\psi(t)\rangle = \exp\left(-\frac{i}{\hbar}Ht\right)|\psi(t_0)\rangle$$

For the usual case of a non-relativistic particle moving under the influence of a potential, the Hamiltonian operator is taken over from the classical form

$$H = \frac{\boldsymbol{P}^2}{2m} + V(\boldsymbol{X})$$

So the abstract Schrodinger eqn. in ket form is

$$\left(\frac{\boldsymbol{P}^2}{2m} + V(\boldsymbol{X})\right)|\psi(t)\rangle = i\hbar\frac{d}{dt}\,|\psi(t)\rangle$$

In the x-representation it is a good exercise to show that the above gives the familiar time dependent Schrodinger eqn. for the wavefunction $\psi(\mathbf{x}) \equiv \langle \mathbf{x}|\psi\rangle$:

$$\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\mathbf{x})\right)\psi(\mathbf{x},t) = i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x},t)$$

For the case of charged particles interacting with an external electromagnetic field described by the 4-vector potential $A^{\mu}(x) = (\phi, \mathbf{A})$ (a very important case!) , where ϕ is the electrostatic scalar potential and $\mathbf{A}$ the magnetic vector potential, the appropriate Hamiltonian is

$$H = \frac{1}{2m}(\boldsymbol{P} - q\mathbf{A})^2 + q\phi = \frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\mathbf{A})^2 + q\phi$$

For a spin ½ particle with a magnetic moment $\boldsymbol{\mu}$ interacting with an external magnetic field **B,** the interaction Hamiltonian is $H_B = -\boldsymbol{\mu} \cdot \mathbf{B}$

Here the magnetic momentum operator for a spin ½ particle is $\boldsymbol{\mu} = g\frac{q}{2m}\mathbf{S}$ and $\mathbf{S} = \frac{1}{2}\hbar\boldsymbol{\sigma}$ is the spin operator and $g = 2$ is the g factor of the electron and $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ are the three 2×2 Pauli matrics

Similarly the interaction Hamiltonian for an electric dipole in an external electric field is $H_E = -\mathbf{p} \cdot \mathbf{E}$. Two particles with magnetic moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ can also have an interaction energy of the form $H = -\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2$

More complicated Hamiltonians occur in condensed matter systems, atomic, molecular and nuclear physics

So, in principle, the main task in quantum mechanics is to determine the form of the Hamiltonian for a quantum system and then compute the eigenvalues and eigenstates, i.e., "solve the theory"

Unfortunately, it is only possible to do that for very few simple systems. For most realistic systems some sort of approximation methods have to be used

Note:

The probabilistic nature of QM (postulate 3) implies that two states $|\psi\rangle$ and $\alpha|\psi\rangle$ give the same probability for a particular measurement, for all possible complex values of α (this set is a ray of states)

A physical state, even after normalizing $\langle\psi|\psi\rangle = 1$ (or Dirac delta function), still allows for a ray of the form $e^{i\theta}|\psi\rangle$

Also, very important for the rest of the course, are math concepts like properties of linear vector spaces, orthonormality of basis functions, completeness, Dirac delta functions and Fourier transforms etc.

All these will be extensively used in the topics to be covered later…

It will be assumed that you are familiar with important concepts like expanding an arbitrary ket into orthonormal basis vectors:

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle$$

with $\langle\phi_m|\phi_n\rangle = \delta_{mn}$ and expansion coefficients c_n

And the completeness property

$$\sum_n |\phi_n\rangle\langle\phi_n| = \mathbf{1}$$

The corresponding relations for <u>continuous</u> basis eigenkets like position (which are infinite dimensional) are

$$|\psi\rangle = \int d^3\mathbf{x}\ \langle\mathbf{x}|\psi\rangle\ |\mathbf{x}\rangle = \int d^3\mathbf{x}\ \psi(\mathbf{x})|\mathbf{x}\rangle$$

Where the <u>continuous</u> "expansion coefficients" is the wavefunction $\psi(\mathbf{x})$

For a superb discussion of what the completeness relation means physically, see Feynman's discussion and analysis of the Stern-Gerlach experiment, Vol 3.

The completeness relation for continuous basis eigenkets like position take the form

$$\int d^3\mathbf{x}\,|\mathbf{x}\rangle\,\langle\mathbf{x}| = \mathbf{1}$$

Similar relations hold for momentum basis, with the difference that factors of 2π occur in the momentum integrals (taking $\langle\mathbf{x}|\mathbf{p}\rangle = e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}}$)

$$|\psi\rangle = \int \frac{d^3\mathbf{p}}{(2\pi\hbar)^3}\langle\mathbf{p}|\psi\rangle\,|\mathbf{p}\rangle$$

With

$$\int \frac{d^3\mathbf{p}}{(2\pi\hbar)^3}\,|\mathbf{p}\rangle\,\langle\mathbf{p}| = \mathbf{1}$$

To become familiar with using these concepts, recall some simple sample calculations using the above techniques

Consider the normalization condition $\langle\psi|\psi\rangle = 1$

Inserting the identity operator in the form $\int d^3\mathbf{x}\,|\mathbf{x}\rangle\,\langle\mathbf{x}| = \mathbf{1}$ we get

$$\int d^3\mathbf{x}\,\langle\psi|\mathbf{x}\rangle\langle\mathbf{x}|\psi\rangle = 1$$

Since $\langle\mathbf{x}|\psi\rangle = \psi(\mathbf{x})$ and $\langle\psi|\mathbf{x}\rangle = \langle\mathbf{x}|\psi\rangle^* = \psi^*(\mathbf{x})$, we get

$$\int d^3\mathbf{x}\;|\psi(\mathbf{x})|^2 = 1$$

Which is the familiar normalization conditions for coordinate space wavefunctions

Consider now the inner product $\langle \mathbf{p}'|\mathbf{p}\rangle$ for momentum states

Inserting the identity operator in the coordinate basis in the above inner product we get

$$\langle \mathbf{p}'|\mathbf{p}\rangle = \int d^3\mathbf{x}\ \langle \mathbf{p}'|\mathbf{x}\rangle\langle \mathbf{x}|\mathbf{p}\rangle$$

$$= \int d^3\mathbf{x} \exp\left(\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}')\cdot\mathbf{x}\right)$$

$$= (2\pi\hbar)^3\ \delta^3(\mathbf{p}-\mathbf{p}')$$

So a factor $(2\pi\hbar)^3$ occurs in the normalization of momentum eigenstates, since we have taken $\langle \mathbf{x}|\mathbf{p}\rangle = \exp\left(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}\right)$

The normalization for the positions eigenstates can be checked as

$$\langle \mathbf{x}' | \mathbf{x} \rangle = \int \frac{d^3\mathbf{p}}{(2\pi\hbar)^3} \langle \mathbf{x}' | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{x} \rangle$$

$$= \int \frac{d^3\mathbf{p}}{(2\pi\hbar)^3} \exp\left(\frac{i}{\hbar}(\mathbf{x}' - \mathbf{x}) \cdot \mathbf{p}\right)$$

$$= \delta^3(\mathbf{x} - \mathbf{x}')$$

The convention for including factors of 2π (or $2\pi\hbar$) in the momentum integrals is used in relativistic quantum mechanics and field theory (where one also usually sets $\hbar = 1$ in "natural units")

On the other hand, if we take the normalization of plane wave states to be $1/\sqrt{(2\pi\hbar)^3}$ (instead of 1 as in previous slides) so that

$$\langle \mathbf{x}|\mathbf{p}\rangle = \psi_{\mathbf{p}}(\mathbf{x}) = \frac{1}{\sqrt{(2\pi\hbar)^3}} \exp\left(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{x}\right),$$

then we can take the position and momentum completeness relations to be

$$\int d^3\mathbf{x}\,|\mathbf{x}\rangle\langle\mathbf{x}| = \int d^3\mathbf{p}\,|\mathbf{p}\rangle\langle\mathbf{p}| = \mathbf{1}$$

with the normalization conditions being

$$\langle \mathbf{p}'|\mathbf{p}\rangle = \delta^3(\mathbf{p}-\mathbf{p}')$$
$$\langle \mathbf{x}'|\mathbf{x}\rangle = \delta^3(\mathbf{x}-\mathbf{x}')$$

With no factor of $(2\pi\hbar)^3$ in the normalization of momentum eigenstates

It is important not to mix the two conventions when solving a problem!

Exercise: 1) Using the above methods, prove that the matrix elements of the momentum operator in the coordinate basis is (see Sakurai's book section 1.7)

$$\langle x|P|x'\rangle = -i\hbar \frac{d}{dx}\,\delta(x-x')$$

Of course, in the x-basis the position operator X is already (trivially) diagonal

$$\langle x'|X|x\rangle = x\,\delta(x-x') = x'\delta(x-x')$$

2) Starting from the abstract ket form of the Schrodinger eqn. derive the Schrodinger eqn. in the coordinate basis.

3) The matrix elements of the time evolution operator in the coordinate basis $\langle x' \left|\exp\left(-\frac{i}{\hbar}Ht\right)\right| x\rangle$ is called the propagator. Calculate the propagator for a free non-relativistic particle (say in one dimension for simplicity)