Lecture 8a: Postulates of Quantum Mechanics

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Three Questions for Classical Physics

1. How does one specify the state of the system at a given time?
2. Can we predict what its state will be at later time?
3. What can we say about the physical quantities that we obtain by making measurements on the system?

If we have particle of mass m moving under the influence of a conservative force field, we know the answer.

1. You need to give the position and momentum of the particle at the given time. **A point in phase space**
2. Newton's laws tell us how the system evolves with time on integration.

$$
\begin{aligned}
d\mathbf{x}/dt &= \mathbf{p}/m \\
d\mathbf{p}/dt &= -\nabla V(\mathbf{x})
\end{aligned}
$$

3. Physical quantities are typically functions of $(\mathbf{x}, \mathbf{p})$.

Mécanique analytique *(1788-89) is a two volume French treatise on analytical mechanics, written by* **Joseph-Louis Lagrange***, and published 101 years following Isaac Newton's Philosophiæ Naturalis Principia Mathematica. It consolidated into one unified and harmonious system, ... the historical transition from geometrical methods, as presented in Newton's Principia, to the methods of mathematical analysis. The treatise expounds a great labor-saving and thought-saving general analytical method by which every mechanical question may be stated in a single differential equation. – From Wikipedia*

This differential equation (actually a system of equations) generalize Newton's laws to a more general setting and are called the Euler-Lagrange (E-L) equations of motion.

Maxwell's equations also fit the general framework of Lagrange!

Two developments

Analogous to Archimedes' claim that he could move the earth if he had a long enough lever and a place to stand on, it appeared that if one could solve the E-L equations for any system, we could answer everything about it. This is not entirely true.

- Chaos or exponential sensitivity to initial conditions: Recall that if you are given an initial condition (i.e., a point in 'phase space'), solving the E-L equations gives you the trajectory of the system in time. However, due to uncertainties in measurement, one can only specify the intial condition to some degree of accuracy. There exist systems where two points very close to each other at some initial time will have trajectories that separate exponentially fast.
- Quantum Mechanics: Quantum Mechanics puts fundamental, not experimental, bounds on what can be measured. We can't, for instance, specify points in 'phase space'. We study some of the ideas behind this next.

How does the quantum world work?

Three Questions for Quantum Physics

1. How does one specify the state of the system at a given time?
2. Can we predict what its state will be at later time?
3. What can we say about the physical quantities that we obtain by making measurements on the system?

We will answer these questions in the form of three postulates, each of which addresses one of them.

The Postulates of Quantum Mechanics

1. The state of a quantum system

Postulate 1 (The State of a Quantum System)

The state of a quantum system is a vector (the state vector) in a complex inner product space (Hilbert space, more generally) which we will denote by $\mathcal{H}$.

- When the dimension of the inner product spaces becomes infinite, issues such as convergence become important.
- Hilbert spaces are inner product spaces with additional conditions that are relevant for the infinite dimensional spaces.
- How does one figure out the relevant Hilbert space for a system? We will illustrate some of the ideas through examples.
- Two state vectors, $|v\rangle$ and $|w\rangle$ represent the same state if they are related by

$$|v\rangle = \lambda\, |w\rangle \quad \text{for some non-zero} \quad \lambda \in \mathbb{C}\ .$$

  One uses this to normalize the vector to have unit norm. This leaves it unfixed up to an overall phase.

Example 1: Qubit

We begin with the spin-half system that we encountered in our study of the Stern-Gerlach experiment.

- Let SS denote the 'classical' State Space. This is the two outcomes of a SGz experiment or a coin flip. We might label the set in various ways: $SS = (\uparrow, \downarrow)$ or (H, T) or $(0, 1)$.
- We shall use the last representation and call it the bit space.
- The Hilbert space is $\mathcal{H} = \mathbb{C}[SS] = Span(|0\rangle, |1\rangle) = \mathbb{C}^2$ and is called the quantum bit (or qubit) space.
- A state vector $|\psi\rangle$ is then of the form

$$|\psi\rangle = a\,|0\rangle + b\,|1\rangle \ , \quad a, b \in \mathbb{C} \ .$$

- A normalized state vector is then (φ is an arbitrary phase)

$$|\widehat{\psi}\rangle = e^{i\varphi}\,\frac{(a\,|0\rangle + b\,|1\rangle)}{\sqrt{|a|^2 + |b|^2}} \ .$$

Example 2: Multiple Qubits

- Consider a system of n spin-half particles or n bits. The classical state space is of order 2^n and is represented by an n-bit number in binary form:

$$SS_n = \Big(b_1 b_2 \ldots b_n \;\Big|\; b_i \in (0,1) i = 1, \ldots, n \Big) \; .$$

- The Hilbert space is given by the

$$\mathcal{H}_n = Span\Big(|b_1 b_2 \ldots b_n\rangle \;\Big|\; b_i \in (0,1) i = 1, \ldots, n \Big) \; .$$

- For two qubits, $\mathcal{H}_2 = Span(|00\rangle, |01\rangle, |10\rangle, |11\rangle)$ and a normalized state vector is given by

$$|\widehat{\psi}\rangle = e^{i\varphi} \; \frac{(a \; |00\rangle + b \; |01\rangle + c \; |10\rangle + d \; |11\rangle)}{\sqrt{|a|^2 + |b|^2 + |c|^2 + |d|^2}} \; .$$

Example 3: Spin j Hilbert Space

- The S_z component of the spin angular momentum of a spin $j \in \frac{1}{2}\mathbb{Z}_{\geq 0}$ can take $(2j+1)$ values $m\hbar$ with $m \in SS$

$$SS = (-j, -j+1, \ldots, j-1, j) \ .$$

- A Stern-Gerlach experiment would thus have $(2j+1)$ possible outcomes.
- The Hilbert space is $(2j+1)$ dimensional and is given by

$$\mathbb{C}[SS] = Span(|-j\rangle, |-j+1\rangle, \ldots, |j-1\rangle, |j\rangle) \ .$$

- The z-component of the orbital angular momentum $\mathbf{L}_z$ is similar but only integer values of spin ℓ are possible. The values $\ell = 0, 1, 2, 3$ are called s, p, d, f in Quantum Chemistry. Thus for $\ell = 1$, $m_\ell = -1, 0, 1$.

Example 4: Young double slit with electrons

This example is meant to be pedagogical and we will only discuss a caricature of the full double-slit experiment. We will focus on the screen where the electrons are observed.

- We assume the screen is the x-axis and thus the classical space of states of electrons is the set of points on the x-axis.

  $$SS = \left(x \,\middle|\, -\infty < x < \infty \right) = \mathbb{R}.$$

  The order of the set is infinite.
- The vector space $\mathbb{C}[\mathbb{R}]$ which is given by

  $$\mathbb{C}[\mathbb{R}] = Span\left(|x\rangle \,\middle|\, -\infty < x < \infty \right)$$

  is too large and other issues appear.
- Naively, we would write a state vector as

  $$|\psi\rangle = \sum_x \psi(x)\ |x\rangle \stackrel{?}{=} \int dx\, \psi(x)\ |x\rangle\ .$$

  Should $\psi(x)$ be Riemann/Lebesgue integrable? (Let's ignore this issue for now.)

$$|\psi\rangle = \int dx\, \psi(x)\, |x\rangle \ .$$

- Call $\psi(x)$ the wavefunction of the state $|\psi\rangle$.
- Define the Hilbert space to the subspace of wavefunctions $\psi(x)$ with finite norm i.e.,

$$\big|\big||\psi\rangle\big|\big|^2 = \int_{-\infty}^{\infty} dx\, \psi(x)^* \psi(x) < \infty \ .$$

- This space is denoted by $L^2[\mathbb{R}]$ and is called the space of square-integrable wavefunctions.
- In analogy with the Young double slit with light, the absolute square of the normalized wavefunction, $|\widehat{\psi}(x)|^2 dx$, is the probability of the electron being found at $(x, x + dx)$.
- In the double slit experiment, one has $\psi(x) = \widehat{\psi}_1(x) + \widehat{\psi}_2(x)$, where the subscript indicates the slit through which the electron may have passed. Superposition makes sense in a LVS

Example 5: A one-dimensional particle

- Classically, the state space is the phase space $(x, p_x) \in \mathbb{R}^2$.
- The first guess $\mathbb{C}[\mathbb{R}^2]$ turns out to be incorrect. In the quantum mechanical world, the Heisenberg Uncertainty Principle operates. So the correct space is either the position space or momentum space, but not both.
- The Hilbert space for the quantum one-dimensional particle is $\mathcal{H} = L^2[\mathbb{R}] \subset \mathbb{C}[\mathbb{R}]$.
- Again $|\widehat{\psi}(x)|^2$ is interpreted as the probability density of finding the particle at location x.
- Similarly, for a particle moving in space, the Hilbert space is $L^2[\mathbb{R}^3]$, the space of square-integrable functions on $\mathbb{R}^3$.

$$\big|\big||\psi\rangle\big|\big|^2 = \int_{-\infty}^{\infty} d^3x \, \psi(\mathbf{x})^* \psi(\mathbf{x}) < \infty \ .$$

The Postulates of Quantum Mechanics

2. Time Evolution of a quantum state

Postulate 2 (Time Evolution in Quantum Mechanics)

Given a system in the state, $|\psi(t_0)\rangle \in \mathcal{H}$, at time t_0, the state at time $t > t_0$ is given by a unitary operator $U(t, t_0)$ i.e.,

$$|\psi(t)\rangle = U(t, t_0)\ |\psi(t_0)\rangle \in \mathcal{H}\ .$$

The unitary operator satisfies
(i) $U(t_0, t_0) = I$,
(ii) For $t \geq t_1 \geq t_0$, one has $U(t, t_0) = U(t, t_1)U(t_1, t_0)$.

- For infinitesimal ϵ, we can write

$$U(t+\epsilon, t) = 1 - \frac{i}{\hbar} H(t)\ \epsilon + O(\epsilon^2)\ ,$$

  where $H(t_0)$ is a hermitian operator if $U(t+\epsilon, t)$ is unitary.
- We can rewrite the time-evolution as a differential equation called the Schrödinger equation

$$i\hbar \tfrac{\partial}{\partial t}|\psi(t)\rangle = H(t)\ |\psi(t)\rangle\ .$$

  $H(t)$ is called the Hamiltonian (operator) for the system.

Time-evolution

- It is easy to verify that the Hamiltonian, $H(t)$, has the same physical dimension as energy.
- When $H(t)$ is independent of time, one can show that

$$U(t, t_0) = \exp\left(\frac{-iH\,(t-t_0)}{\hbar}\right) \ ,$$

  where $e^A := \sum_{m=0}^{\infty} \frac{A^m}{m!}$ for any linear operator A.
- When $|\psi(t)\rangle$ is an eigenvector of H with real eigenvalue E, then one obtains the equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = E\ |\psi(t)\rangle \ ,$$

  which has a simple solution

$$|\psi(t)\rangle = \overbrace{e^{-iE(t-t_0)/\hbar}}^{\text{a phase}}\ |\psi(t_0)\rangle \ .$$

  This only changes the phase and hence the system remains in the same state. Such states are called stationary states.

An example of time-evolution

Consider the spin-half system in the presence of a constant magnetic field along the z-direction. The Hamiltonian is

$$H = -g\mu_B \mathbf{S} \cdot \mathbf{B} = -g\mu_B B \; S_z =: -\omega \, S_z$$

The stationary states are $|S_z, \pm\rangle$ with eigenvalues $E = \mp\frac{\hbar\omega}{2}$.

$$\text{If } |\psi(0)\rangle = |S_z, \pm\rangle \;, \quad \text{then} \quad |\psi(t)\rangle = e^{\pm i\omega t/2} \, |S_z, \pm\rangle \;.$$

However if $|\psi(0)\rangle = a\,|S_z, +\rangle + b\,|S_z, -\rangle$, then

$$\begin{aligned} |\psi(t)\rangle &= e^{i\omega t/2}\, a\,|S_z, +\rangle + e^{-i\omega t/2}\, b\,|S_z, -\rangle \\ &= e^{i\omega t/2}\Big(a\,|S_z, +\rangle + e^{-i\omega t}\, b\,|S_z, -\rangle\Big) \end{aligned}$$

The overall phase outside is not important but the relative phase shown in red is relevant. **Exercise:** Let $a = b = 1/\sqrt{2}$. What are the states at times $\omega t = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$?

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The overall phase outside is not important but the relative phase shown in red is relevant. **Exercise:** Let $a = b = 1/\sqrt{2}$. What are the states at times $\omega t = 0, \frac{\pi}{2}, \pi, \frac{3\pi}{2}$?

Ans: $|S_x,+\rangle, |S_y,-\rangle, |S_x,-\rangle, |S_y,+\rangle$

General time evolution

- Let H be the Hamiltonian for a quantum system with a n-dimensional Hilbert space, $\mathcal{H}$.
- Since H is hermitian, its eigenvalues are real. Further, let $|\phi_i\rangle$ be an ON basis of eigenvectors of H with eigenvalue $E_i = \hbar\omega_i$, These are the stationary states for the quantum evolution.
- An arbitary initial state $|\psi(0)\rangle$ can be expanded in this ON basis as:

$$|\psi(0)\rangle = \sum_{i=1}^{n} a_i \, |\phi_i\rangle \ ,$$

  where $a_i := \langle\phi_i|\psi(0)\rangle$.
- The state at time t is then given by

$$|\psi(t)\rangle = \sum_{i=1}^{n} a_i \, e^{-i\omega_i t} \ |\phi_i\rangle \ .$$

Examples from Chemistry: The simple harmonic oscillator:

- $\mathcal{H} = L^2[\mathbb{R}]$. The Hamiltonian is given by the hermitian operator:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \ .$$

acting on the space of square-integrable functions of $x \in \mathbb{R}$.

- The eigenvalues of the Hamiltonian are $E_n = (n + \frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$ ad inf.
- Each eigenvalue appears once and let $|n\rangle$ denote the corresponding eigenvector. Thus, any state can be written as

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)|x\rangle = \sum_{n=0}^{\infty} a_n\ |n\rangle \ .$$

with $|n\rangle = \int dx\, \phi_n(x)\, |x\rangle$ and $\psi(x) = \sum_n a_n\, \phi_n(x)$.

- One has $\phi_n(x) \propto H_n(x/x_0)\, e^{-x^2/(2x_0^2)}$, where $x_0 = \sqrt{\hbar/m\omega}$. $H_n(x)$ is the Hermite polynomial of degree n.

Examples from Chemistry: The Hydrogen atom

- $\mathcal{H} = L^2[\mathbb{R}^3]$. The Hamiltonian is the hermitian operator:

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{r} \ ,$$

- The eigenvalues of the Hamiltonian are $E = -m_e e^4/(2\hbar^2 n^2)$, $n = 1, 2, 3, \ldots$ ad inf.
- The subspace of $\mathcal{H}$ with energy E_n has dimension $2n^2$.
- States in this subspace are distinguished by eigenvalues (aka quantum numbers) of other operators such as orbital and spin angular momentum. For fixed n, one has

$$|n, \ell, m_\ell, m_s\rangle \quad ,$$

with $\ell = 0, 1, \ldots, n-1$, $m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell$ and $m_s = \pm\frac{1}{2}$ being the S_z eigenvalue of the electron.
- The stationary eigenfunctions are ($a = \hbar^2/(m_e e^2)$)

$$\phi_{n,\ell,m_\ell,m_s=\pm 1/2}(\mathbf{x}) \propto R_{n,\ell}(\tfrac{r}{a})\, e^{-r/(na)}\, Y_\ell^m(\theta,\varphi)\ |S_z, \pm\rangle$$

Recap of this lecture

Three Questions for Quantum Physics

1. How does one specify the state of the system at a given time?
2. Can we predict what its state will be at later time?
3. What can we say about the physical quantities that we obtain by making measurements on the system?

Answers to 1. and 2.

1. The state of the system is a vector in a Hilbert space up to overall normalization i.e., $|\widehat{\psi}\rangle \in \mathcal{H}$.
2. The time-evolution is given by the Schrödinger equation.

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)\;|\psi(t)\rangle\;.$$

   Integrated this implies that $|\psi(t)\rangle = U(t,0)|\psi(0)\rangle$, where $U(t,0)$ is a unitary operator and hence norm preserving.