Quantum Mechanics I

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1 Classical Mechanics

In order to later compare quantum mechanics, let us first introduce some classical mechanics.

In classical mechanics, we study classical objects/particles which has a mass $m \in \mathbb{R}$ and a state. In particular, the state of the particle is represented by its position, commonly $r \in \mathbb{R}^3$, and its velocity $v = \dot{r} \in \mathbb{R}^3$. More conveniently, we can also represent the velocity in terms of its momentum $p = mv$.

We recall Newton's second law which describes how the state of a particle changes in time in the presence of external forces. That is,

$$\dot{p} = F(r),$$

where F is the external force depending on r.

As the state of a particle is represented by its position and momentum, visually the state of a particle can be represented by a phase-space with a trajectory corresponding to $(r(t), p(t))$.

An another formulation of classical mechanics is Hamilton's formulation. While Hamilton's formulation is very powerful, it does not apply to every classical system. In particular, Hamilton's formulation requires the system to be conservative.

Definition 1.1 (Conservative)**.** A classical system is said to be conservative if

$$F(r) = -\nabla V(r),$$

where V is the potential given the position.

Definition 1.2 (Hamiltonian Function)**.** The Hamiltonian function H is defined as

$$H(p, q) = \frac{p^2}{2m} + V(q),$$

where $p^2/2m$ is the kinetic energy and V the potential.

Thus, with the definition of conservative in mind, we see that for a one dimensional system with position given by $q \in \mathbb{R}$, we have

$$\dot{p} = F(q) = -\frac{\partial V}{\partial q} \text{ and } \dot{q} = \frac{p}{m}.$$

Writing in terms of the Hamiltonian function, we obtain,

$$\dot{p} = -\frac{\partial H}{\partial q} \text{ and } \dot{q} = \frac{\partial H}{\partial p}.$$

These two equations are known as Hamilton's canonical equations and describe the motion of a particle in a conservative system. The theory itself is more general in which we simply require p, q to be canonically conjugate variables.

Example 1.1 (Free Particle)**.** Consider a free particle with $V(q) = 0$ (thus, $H = p^2/2m$), we have the canonical equations $\dot{p} = 0$ and $\dot{q} = p/m$, and thus, $p(t) = p(0)$ and $q(t) = q(0) + \frac{p}{m}t$.

Example 1.2 (Harmonic Oscillator)**.** A harmonic oscillator is described by $V(q) \propto q^2$. By similar calculation we find $\ddot{q} = -\frac{2k}{m}q$ for some k such that $V = kq^2$.

As for a particle in classical mechanics, the state is given by its position and momentum, any measurable quantity A is given as a function $A(p, q)$ such that

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial p}\dot{p} + \frac{\partial A}{\partial q}\dot{q} + \frac{\partial A}{\partial t}.$$

Substituting the Hamiltonian equations, we have

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -\frac{\partial A}{\partial p}\frac{\partial H}{\partial q} + \frac{\partial A}{\partial q}\frac{\partial H}{\partial p} + \frac{\partial A}{\partial t} = \frac{\partial A}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial A}{\partial p}\frac{\partial H}{\partial q} + \frac{\partial A}{\partial t}.$$

As the first term of this equation is very common, we denote it as $\{H, A\}$ such that

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \{H, A\} + \frac{\partial A}{\partial t}.$$

Similarly, for general variables F, G,

$$\{F, G\} := \sum_{n=1}^{N} \frac{\partial F}{\partial p_n}\frac{\partial G}{\partial q_n} - \frac{\partial F}{\partial q_n}\frac{\partial G}{\partial q_n},$$

and is known as the Poisson bracket of F and G.

Definition 1.3 (Poisson Bracket)**.** A Poisson bracket is simply any bracket of functions satisfying

- $\{A, A\} = 0$;
- $\{c_1 A + c_2 B, C\} = c_1\{A, C\} + c_2\{B, C\}$;
- $\{A, B\} = -\{B, A\}$.
- $\{c, A\} = 0$ for any constant c;
- $\{AB, C\} = A\{B, C\} + \{A, C\}B$ (Leibniz rule);
- $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$ (Jacobi identity).

As an exercise, one may check that the Poisson bracket defined above is indeed a Poisson bracket.

Proposition 1.1. $\{p, q\} = 1$ and in higher dimensions. $\{p_i, q_j\} = \delta_{ij}$.

Definition 1.4 (Canonical Conjugate Variables)**.** $P(p, q), Q(p, q)$ are called canonical conjugate variables if $\{P, Q\} = 1$. Similarly, for higher dimensions, P, Q are canonical conjugates if $\{P_i, Q_j\} = \delta_{ij}$.

Proposition 1.2. For any pair of canonical conjugate variables P, Q, we have

$$\dot{P}_j = -\frac{\partial H}{\partial Q_j} = \{H, P_j\} \text{ and } \dot{Q}_j = \frac{\partial H}{\partial P_j} = \{H, Q_j\}.$$

2 Schödinger Dynamics

The Scrhödinger equations is a function of position and time which is written in its compact form as

$$i\hbar\dot{\psi} = \hat{H}\psi$$

where $\hat{H}$ is known as the Hamiltonian and $\hbar = h/2\pi$ where h is Plank's constant.

Similar to the Hamiltonian in classical mechanics, the Hamiltonian is an linear operator that often encodes energy and in that case, it is written as

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r),$$

where ∇^2 is the Laplacian operator. Furthermore, the expectation of the Hamiltonian, defined by

$$\langle \hat{H} \rangle := \frac{1}{\int_{\mathbb{R}^n} |\psi|^2 \mathrm{d}x^n} \int_{\mathbb{R}^n} \psi^* \hat{H} \psi \mathrm{d}x^n$$

provides the total energy of the system. As $\hat{H}$ is a linear operator, it has eigenfunctions where ϕ_E is said to be an eigenfunction if $\hat{H}\phi_E = E\phi_E$ and this equation is known as the time-independent Schrödinger equation. It is possible to show that this eigenfunctions are orthogonal with respect to the L^2 inner product and form an eigenbasis of all possible states of a system.

As the Schrödinger equation is a linear differential equation, the solution space of the equation is a linear space. In particular, if ψ_i are solutions to the Schrödinger equations, so is $c_1\psi_1 + c_2\psi_2$ for c_1, c_2 constants.

The function ψ is known as the wave function and it is interpreted as the probability of finding the particle it describes at a given time in a certain region. As ψ is a complex functions, it values is known as a probability amplitude by while $|\psi|^2$ is the probability distribution function. Thus, the probability of finding a particle is the interval $[a, b]$ is

$$\int_a^b |\psi(x,t)|^2 \mathrm{d}x,$$

if ψ is normalized, i.e. $\int_{-\infty}^{\infty} |\psi(x,t)| \mathrm{d}x = 1$ for all t. In particular, we note that this interpretation is meaningful only if ψ is square integrable, i.e. $\psi \in L^2$.

Let us consider the following 1-dimensional example. Let $\hat{H}$ be the Hamiltonian as described above, then we have the Schödinger equation

$$i\hbar\dot{\psi}(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t).$$

Then, defining $N(t) := \int_{-\infty}^{\infty} |\psi(x,t)|^2 \mathrm{d}x$, we have

$$\begin{aligned} \frac{\mathrm{d}N}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} \psi^*(x,t)\psi(x,t)\mathrm{d}x \\ &= \int_{-\infty}^{\infty} \dot{\psi}^*\psi + \psi^*\dot{\psi}\mathrm{d}x \end{aligned}$$

substituting $\dot{\psi}$ and $\dot{\psi}^*$ using the Schrödinger equation, we have

$$\begin{aligned}\frac{\mathrm{d}N}{\mathrm{d}t} &= \frac{i}{\hbar}\int_{-\infty}^{\infty}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi^* + V\psi^*\right)\psi - \psi^*\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi + V\psi\right)\mathrm{d}x \\ &= \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\psi\frac{\partial^2}{\partial x^2}\psi^* - \psi^*\frac{\partial^2}{\partial x^2}\psi\mathrm{d}x \\ &= \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\frac{\partial}{\partial x}\left(\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right)\mathrm{d}x \\ &= 0\end{aligned}$$

where the last equality follows by the fundamental theorem of calculus and the fact that $\psi \in L^2$. Thus, N is conserved over time and we may normalize ψ by simply divide by N.

Definition 2.1 (Probability Flux)**.** The probability flux of a wave function ψ is defined as

$$j(x,t) := \frac{i\hbar}{2m}\left(\psi^*\frac{\partial}{\partial x}\psi - \psi\frac{\partial}{\partial x}\psi^*\right).$$

In particular, we see that $\frac{\partial|\psi|^2}{\partial t} = -\frac{\partial j}{\partial x}$, and so, we have the continuity equation

$$\frac{\partial|\psi|^2}{\partial t} + \frac{\partial j}{\partial x} = 0.$$

Unlike the total probability N, the probability in a certain region does fluctuate over time and we see that, if $P_{[a,b]}(t)$ is the probability that a particle is in the region $[a,b]$ at time t, then

$$\frac{\mathrm{d}P_{[a,b]}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\int_a^b|\psi|^2\mathrm{d}x = -\int_a^b\frac{\partial j}{\partial x}\mathrm{d}x = j(a,t) - j(b,t).$$

Similarly, for higher dimensions, we define the probability flux of ψ as

$$j(r,t) = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*),$$

and we have the continuity equation

$$\frac{\partial|\psi|^2}{\partial t} + \nabla\cdot j = 0.$$

Then, if P_V is the probability of finding a particle in the region V, we have

$$\frac{\mathrm{d}P_V}{\mathrm{d}t} = -\int_V\nabla\cdot j\mathrm{d}V = -\int_S j\cdot\mathrm{d}S$$

by the divergence theorem. Thus, the probability change is the total flux through the boundary of the volume.

2.1 Stationary Solution

Let us consider a special family of solutions. Consider the Schrödinger equation

$$i\hbar\dot{\psi} = \hat{H}\psi,$$

where ψ is expressible in the form $\psi(r,t) = \phi(r)\chi(t)$. Then, we have

$$i\hbar\dot{\chi}(t)\phi(r) = i\hbar\dot{\psi} = \hat{H}\phi(r)\chi(t) = \chi(t)\hat{H}\phi(r),$$

and so,

$$i\hbar\frac{\dot{\chi}(t)}{\chi(t)} = \frac{\hat{H}\phi(r)}{\phi(r)}.$$

By observing that the right hand side and the left hand sides of the equation depend on different variables, we conclude that both values must be constants and we denote this constant by E such that

$$\dot{\chi}(t) = -\frac{i}{\hbar}E\chi(t), \text{ and } \hat{H}\phi(r) = E\phi(r).$$

Thus, solving the first differential equation, we have

$$\chi(t) = e^{-iEt/\hbar}\chi(0),$$

while the second is the time-independent Schrödinger equation. The time-independent Schrödinger equation is not always easy to solve though it is solvable analytically in special cases. In particular, for Hamiltonians in of form $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ where the potient V tends to ∞ as $x \to \infty$, normalizable solutions to the time-independent Schrödinger equation only exist for special discrete values of E.

In this case, the wave function is simply

$$\psi(r,t) = \chi_0 e^{-iEt/\hbar}\phi_E(r),$$

and if $\psi(r,0) = \phi(r)$ the probability distribution of the particle is $|\psi(r,t)|^2 = |\phi_E(r)|^2$ which is independent of time, and thus we call solutions of this form stationary states. Note that the superposition of stationary states is not necessarily stationary (exercise).

As an example, let us consider a particle in moving freely in an 1-dimensional interval $[0,L]$. This can be modelled by the potential

$$V(x) = \infty\mathbf{1}_{[0,L]^c}.$$

Then, solving the time-independent Schrödinger equation $\hat{H}\phi_n(x) = E_n\phi_n(x)$, we find

$$E_n = \frac{\pi^2\hbar^2}{2mL^2}n^2, \text{ and } \phi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\mathbf{1}_{[0,L]}.$$