Quantum mechanics summary

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Classical mechanics

- Describe the state of a particle by its position *x(t)* and velocity *v(t)* or momentum *p=mv* as functions of time *t*.
- **Hamilton function**=total energy

$$H(x,p)=T+V=\frac{1}{2}mv^2+V(x)=\frac{p^2}{2m}+V(x)=E$$

- Hamilton equations of motion

$$\dot{x}=\frac{\partial H}{\partial p}\quad,\quad \dot{p}=-\frac{\partial H}{\partial x}$$

- Equivalent to Newtons second law:

$$\dot{x}=\frac{\partial H}{\partial p}=\frac{p}{m}\quad,\quad \dot{p}=-\frac{\partial H}{\partial x}=-\frac{\partial V}{\partial x}=F\quad\Rightarrow\quad ma=F$$

Basic experimental facts about all microscopic systems

- Double slit and diffraction measurements demonstrate wavelike diffraction properties for particles: photons, electrons, neutrons, atoms, molecules, etc
- Photoelectric effect: light consist of particle-like discrete quantities of energy, photons, that obey the **Einstein energy relation**

$$E = hf = \hbar\omega \quad , \quad h = 2\pi\hbar \quad , \quad \omega = 2\pi f$$

This is a basic relation applies to all particles in QM

- Compton effect: photon momentum is

$$p = \hbar k \quad , \quad k = \frac{2\pi}{\lambda} = \text{wavenumber} \quad , \quad \lambda = \text{wavelength}$$

This basic relation associates a **de Broglie wavelength** to any particle

Motivation of Schrödinger equation

- Associate a **wave function** to any particle.
  For a free particle assumed to be a plane wave

  $$\psi(x,t) = Ae^{i(kx-\omega t)}$$

  In the presence of forces the wave function will be more complicated.
- Energy $E\psi = \hbar\omega\psi = i\hbar\frac{\partial}{\partial t}\psi$
- Momentum $p\psi = \hbar k\psi = -i\hbar\frac{\partial}{\partial x}\psi \;\Rightarrow\; p^2\psi = \hbar^2 k^2\psi = -\hbar^2\frac{\partial^2}{\partial x^2}\psi$
- Hamiltonian $H\psi = \left(\frac{p^2}{2m} + V(x)\right)\psi = E\psi$
- **Schrödinger equation** $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = i\hbar\frac{\partial\psi}{\partial t}$

Probability: Discrete case

- Assume that a discrete random process can produce values $x_1, x_2, x_3, \ldots, x_N$ and in a *very large number of observations* x_j is found n_j times.
- The **probability** that an individual measurement of gives the result x_j is defined to be the fraction $P_i = n_i / n$ where $n = \sum_{i=1}^{N} n_i$ is the total number of observations.
- The **probability distribution** P has two basic properties:
  1. Positive definiteness: $P_i \geq 0$
  2. Normalization: $\sum_{i=1}^{N} P_i = \frac{n_1}{n} + \ldots + \frac{n_N}{n} = \frac{\sum_{i=1}^{N} n_i}{n} = 1$
- The average value of all the measured results is given by the **expectation value**

$$\langle x \rangle = \sum_{i=1}^{N} x_i P_i$$

- The likely spread in the outcomes around this expectation value is called **uncertainty** and is defined as the standard deviation whose square is called the variance

$$(\Delta x)^2 = \sum_{i=1}^{N} \left(x_i - \langle x \rangle\right)^2 P_i = \langle x^2 \rangle - \langle x \rangle^2$$

$$\langle x^2 \rangle = \sum_{i=1}^{N} x_i^2 P_i$$

Probability: Continuous case

- Consider a random process that can give any real number *x* as a result of a measurement.
- Divide the range of possible values into finite subintervals, each of length *dx*.
- Let *P(x)dx* be the relative frequency of measured results in *dx* around *x*.
- In the limit when *dx* goes to zero, this procedure defines a continuous function *P(x)* called the **probability density**, and *P(x)dx* is the **probability** to find a value in *dx* around *x*.
- The probability density is positive definite: $P(x) \geq 0$ and normalized: $\int_{-\infty}^{\infty} P(x)dx = 1$
- The **expectation value** of *x* is given by $\langle x \rangle = \int_{-\infty}^{\infty} xP(x)dx$
- The **uncertainty** Δx is the standard deviation, which is the square root of the variance

$$(\Delta x)^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 P(x)dx = \langle x^2 \rangle - \langle x \rangle^2 \quad \text{where} \quad \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x)dx$$

Hermitean operators

- An operator $\hat{A}$ is **Hermitean** if

$$\int \psi^* \hat{A} \varphi dx = \int (\hat{A}\psi)^* \varphi dx \quad \text{for all } \varphi, \psi$$

- The eigenvalue problem $\hat{A}\psi = a\psi$ for Hermitean operators has the following properties

1. The eigenvalues are real
2. Eigenfunctions belonging to different eigenvalues are orthogonal

$$\int \varphi^* \psi dx = 0$$

3. The eigenfunctions form a complete set which means that it is possible to express any wave function as a linear superposition of eigenfunctions, which is a generalized Fourier series of the form

$$\Psi = \sum_{n=1,2,3,\ldots} c_n \psi_n$$

where the coefficients are complex constants.

Postulates of quantum mechanics

Classical rule	**Quantum postulate**
The state of a particle is given by its position $x(t)$ and momentum $p(t)$.	The state of a particle is represented by its wave function $\Psi(x,t)$. Position and momentum are represented by Hermitean operators $\boxed{\hat{x}=x,\ \hat{p}=-i\hbar\frac{\partial}{\partial x}}$
Every dynamical variable is a function of $x(t)$ and $p(t)$: $A=A(x,p)$.	Dynamical variables are represented by Hermitean operators obtained by $\hat{A}=A(\hat{x},\hat{p})$.
The state variables x, p change in time according to Hamilton's equations: $\dot{x}=\frac{\partial H}{\partial p},\ \dot{p}=-\frac{\partial H}{\partial x}$	The state Ψ obeys the time dependent Schrödinger equation $\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V\Psi=i\hbar\frac{\partial\Psi}{\partial t}}$ where $\hat{H}=H(\hat{x},\hat{p})$ is the Hamiltonian, which is a Hermitean operator, and H is the classical Hamilton function.
A measurement of $A(x,p)$ leaves the state $x(t), p(t)$ unchanged.	If the particle is in the state Ψ, then the result of a measurement of A is one of the eigenvalues of A: $\hat{A}\psi_a=a\psi_a$ with probability $\boxed{P(a)\propto\left\|\int\psi_a^*\Psi dx\right\|^2}$ As a result of the measurement the state of the particle changes, or collapses, to ψ_a.

Born probability interpretation and expectation values

- **Probability** of finding a particle in the state Ψ in the interval *dx* around *x*

$$P(x,t)dx = \left|\Psi(x,t)\right|^2 dx$$

- Normalization such that the probability of finding the particle somewhere is one:

$$\int_{-\infty}^{\infty} P(x,t)dx = \int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 dx = 1$$

- Position expectation value $\langle x \rangle = \int_{-\infty}^{\infty} xP(x,t)dx = \int_{-\infty}^{\infty} x\left|\Psi(x,t)\right|^2 dx$

  =average result from measuring the position many times of a particle in that state

- Expectation value of a variable $\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\hat{A}\Psi(x,t)dx$

- Momentum expectation value: $\langle p \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)dx$

Definite observables (opposite to uncertain)

- If the wavefunction is an eigenstate of the operator $\hat{A}\psi_a = a\psi_a$ then *A* is called **definite**, because repeated measurements of it give the same result *a*.
- Expectation value of *A* is

$$\langle A\rangle = \int_{-\infty}^{\infty} \psi_a^* \underbrace{\hat{A}\psi_a}_{=a\psi_a} dx = a\int_{-\infty}^{\infty} \psi_a^* \psi_a dx = a$$

- Uncertainty in *A* is zero, hence definite:

$$(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2 = \int_{-\infty}^{\infty} \psi_a^* \underbrace{\hat{A}^2\psi_a}_{=a^2\psi_a} dx - a^2 = a^2 - a^2 = 0$$

Uncertain variables (opposite to definite)

- If the wavefunction Ψ is NOT an eigenstate of the operator, then $\Delta A > 0$ and *A* is **uncertain**, and a measurement of *A* gives some eigenvalue a_i as result.
- Expand in a superposition of ON eigenfunctions to *A*:

$$\Psi = \sum_i c_i \psi_i \quad , \quad \int_{-\infty}^{\infty} \psi_i^* \Psi dx = \sum_j c_j \underbrace{\int_{-\infty}^{\infty} \psi_i^* \psi_j dx}_{=\delta_{ij}} = c_i$$

- Normalization:

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = \sum_i |c_i|^2 \int_{-\infty}^{\infty} \psi_i^* \psi_i dx = \sum_i |c_i|^2 = 1$$

- Expectation value: $\langle A \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx = \sum_i a_i |c_i|^2$

$$P_i = |c_i|^2 = \left| \int_{-\infty}^{\infty} \psi_i^* \Psi dx \right|^2 = \text{probability to measure } a_i$$

- After a measurement that gives the result a_i the wavefunction changes, or collapses, to the corresponding eigenfunction $\hat{A}\psi_a = a\psi_a$ making A **definite**.

Heisenberg uncertainty relation

- Position-momentum uncertainty relation:

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

- Example of a minimum uncertainty wave function is the Gaussian wave function:

$$\Psi(x) = \frac{1}{\sqrt{\sigma\sqrt{\pi}}} e^{-x^2/2\sigma^2}$$

$$\langle x \rangle = \langle p \rangle = 0 \quad , \quad \langle x^2 \rangle = \frac{\sigma^2}{2} \quad , \quad \langle p^2 \rangle = \frac{\hbar^2}{2\sigma^2}$$

$$\Delta x \Delta x = \frac{\hbar}{2}$$

Time evolution of stationary states

- **Energy eigenstates** $H\psi_E = E\psi_E$
- Time dependence of product state

$$\Psi(x,t) = \psi_E(x)T(t) \Rightarrow$$

$$\frac{1}{\psi_E}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\psi_E = E = i\hbar\frac{1}{T}\frac{\partial T}{\partial t} \Rightarrow$$

$$T(t) = e^{-iEt/\hbar} \Rightarrow$$

$$\Psi(x,t) = \psi_E(x)e^{-iEt/\hbar}$$

- Energy eigenstates are **stationary states**, since the probability density is time independent:

$$P(x,t) = \left|\Psi(x,t)\right|^2 = \left|\psi_E(x)\right|^2$$

Time evolution of nonstationary states

- Expand as superpositions of stationary states.
- Example:

$$\Psi(x,t)=\frac{1}{\sqrt{2}}\psi_{E1}(x)e^{-iE_1t/\hbar}+\frac{1}{\sqrt{2}}\psi_{E2}(x)e^{-iE_2t/\hbar}$$

$$P(x,t)=\frac{1}{2}\left|\psi_{E1}(x)e^{-iE_1t/\hbar}+\psi_{E2}(x)e^{-iE_2t/\hbar}\right|^2=$$

$$=\frac{1}{2}\left[\left|\psi_{E1}(x)\right|^2+\left|\psi_{E2}(x)\right|^2+2\,\mathrm{Re}\left(e^{i(E_1-E_2)t/\hbar}\right)\right]=$$

$$=\frac{1}{2}\left[\left|\psi_{E1}(x)\right|^2+\left|\psi_{E2}(x)\right|^2+2\cos(E_1-E_2)t/\hbar\right]$$

- From this we identify the uncertainty in time as the decay time of the initial state:

$$(E_1-E_2)\Delta t/\hbar\approx 1\;\;\Rightarrow\;\;\Delta E\Delta t\approx\hbar\;\;,\;\;\Delta E\approx E_1-E_2$$

- In accordance with the **energy-time uncertainty relation**

$$\Delta E\Delta t\approx\hbar$$

Current and continuity equation

- Continuity equation

$$\frac{\partial P}{\partial t}+\frac{\partial j}{\partial x}=0$$

$$\frac{\partial P}{\partial t}+\nabla\cdot\bar{j}=0$$

- Probability density

$$P(x,t)=\left|\Psi(x,t)\right|^2$$

- Probability current density

$$j=\frac{\hbar}{2mi}\left[\Psi^*\frac{\partial\Psi}{\partial x}-\Psi\frac{\partial\Psi^*}{\partial x}\right]$$

$$\bar{j}=\frac{\hbar}{2mi}\left[\Psi^*\nabla\Psi-\Psi\nabla\Psi^*\right]$$

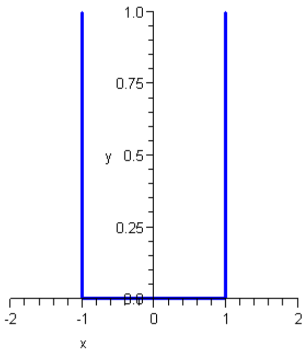
Ehrenfests theorem

- The quantum expectation values obey classical equations of motion, which explain the origin of classical mechanics:

$$m\frac{d\langle x\rangle}{dt}=\langle p\rangle \quad , \quad \frac{d\langle p\rangle}{dt}=\left\langle -\frac{dV}{dx}\right\rangle$$

- These relations apply only for expectation values, not for the operators themselves.

Square well



$$V(x)=\begin{cases}\infty \ , & \mathrm{x}<0\\ 0 \ , & 0<\mathrm{x}<\mathrm{L}\\ \infty \ , & \mathrm{L}<\mathrm{x}\end{cases}$$

$$0<x<L \ \Rightarrow \ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=E\psi \ \Rightarrow \ \psi(x)=A\sin kx+B\cos kx$$

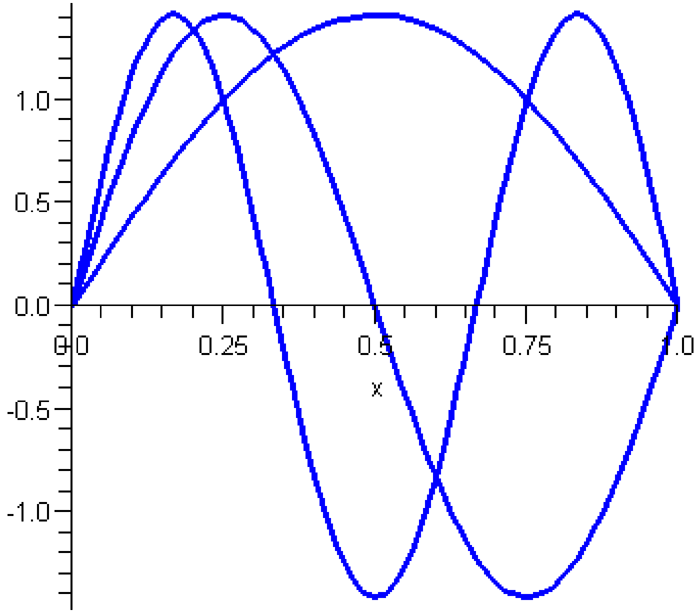
Continuity requirements at endpoints:

$$\psi(0)=0 \ \Rightarrow \ B=0$$

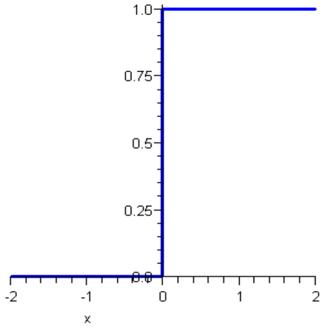
$$\psi(L)=0 \ \Rightarrow \ kL=n\pi \ , \ n=1,2,\ldots$$

$$\Rightarrow \ \psi(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$E_n=\frac{\hbar^2k_n^2}{2m}=\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$



Reflection against a potential step



$$V(x)=\begin{cases}0 & , \quad x<0\\ V_0 & , \quad x>0\end{cases}$$

1. Assume $E<V_0$ Schrödinger equation

$$x<0: \ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=E\psi \ \Rightarrow \ \psi(x)=Ae^{ikx}+Be^{-ikx}$$

$$x>0: \ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V_0\psi=E\psi \ \Rightarrow \ \psi(x)=Ce^{-\kappa x}$$

$$E=\frac{\hbar^2k^2}{2m}=-\frac{\hbar^2\kappa^2}{2m}+V_0 \ \Rightarrow \ k=\frac{\sqrt{2mE}}{\hbar} \ , \ \kappa=\frac{\sqrt{2m(V_0-E)}}{\hbar}$$

- Determines penetration depth $1/\kappa$ into classically forbidden region $x>0$
- The amplitudes can be determined from the incoming amplitude :

  continuity of $\psi(x=0)\Rightarrow$ $A+B=C$

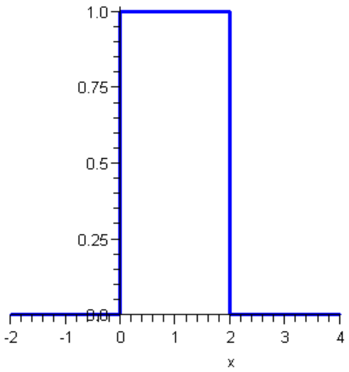
  continuity of $\dfrac{d\psi(x=0)}{dx}\Rightarrow$ $ikA-ikB=-\kappa C$

2. Assume $E>V_0$ Solution is formally the same: $\kappa=\frac{\sqrt{2m(V_0-E)}}{\hbar}=i\frac{\sqrt{2m(E-V_0)}}{\hbar}$

but turns into a plane wave for $x>0$

Tunneling

$$V(x)=\begin{cases}0 & , \ \mathrm{x}<0\\ V_0 & , \ 0<\mathrm{x}<\mathrm{L}\\ 0 & , \ \mathrm{L}<\mathrm{x}\end{cases}$$



- Assume $E<V_0$ Schrödinger equation

$$x<0: \quad -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}=E\psi \quad \Rightarrow \psi(x)=Ae^{ikx}+Be^{-ikx}$$

$$0<x<L: \ -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V_0\psi=E\psi \Rightarrow \psi(x)=Ce^{-\kappa x}+De^{\kappa x}$$

$$L<x: \quad \psi(x)=Fe^{ikx}$$

$$E=\frac{\hbar^2k^2}{2m}=-\frac{\hbar^2\kappa^2}{2m}+V_0 \ \Rightarrow \ k=\frac{\sqrt{2mE}}{\hbar} \quad , \quad \kappa=\frac{\sqrt{2m(V_0-E)}}{\hbar}$$

which determines the penetration depth $1/\kappa$

- Reflection and transmission probabilities: $R=\left|\frac{B}{A}\right|^2 \ , \ T=\left|\frac{F}{A}\right|^2 \ , \ T+R=1$
- Continuity at $x=0 \Rightarrow \quad A+B=C+D \qquad ikA-ikB=\kappa C-\kappa D$
- Continuity at $x=L \Rightarrow \quad Ae^{ikL}+Be^{-ikL}=Ce^{-\kappa L}+De^{\kappa L}$

$$ikAe^{ikL}-ikBe^{-ikL}=-\kappa Ce^{-\kappa L}+\kappa De^{\kappa L}$$

- These equations can be solved to give R,T
- For a wide barrier such that $e^{-2\kappa L}<<1 \quad D\approx 0$ which gives $T\approx\frac{16E(V_0-E)}{V_0^2}e^{-2\kappa L}$
- This explains the exponential dependence of the tunnelling current in Scanning Tunneling Microscopy (STM).

Harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+\frac{1}{2}m\omega^2x^2\psi=i\hbar\frac{\partial\psi}{\partial t}$$

$$\omega^2=\frac{k}{m}$$

$$E_n=\left(n+\tfrac{1}{2}\right)\hbar\omega \quad , \quad n=0,1,2,\ldots$$

$$\psi_0(x)=\left(\frac{1}{a\sqrt{\pi}}\right)^{1/2}e^{-x^2/2a^2} \quad , \quad a^2=\frac{\hbar}{m\omega}$$

- The ground state is a minimum uncertainty wavefunction.

Angular momentum

$$\hat{\bar{L}} = \hat{\bar{r}} \times \hat{\bar{p}} = -i\hbar\bar{r} \times \nabla$$

$$\hat{L}^2 Y_l^m(\theta,\phi) = l(l+1)\hbar^2 Y_l^m(\theta,\phi)$$

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi)$$

$$l = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots$$

$$m = -l, -l+1, \ldots, l-1, l$$

$$\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi \left| Y_l^m \right|^2 = 1$$

Hydrogen atom

- Hydrogen: one electron with charge –*e* and mass *m* bound to one proton with charge *+e*:

$$-\frac{\hbar^2}{2m}\nabla^2\psi-\frac{e^2}{4\pi\varepsilon_0 r}\psi=E\psi$$

$$\psi(r,\theta,\phi)=R(r)Y_l^m(\theta,\phi)$$

$$-\frac{\hbar^2}{2mr}\frac{d^2(rR)}{dr^2}+\left[\frac{l(l+1)\hbar^2}{2mr^2}+V(r)\right]R=ER$$

$$R(r)=\frac{u(r)}{r}$$

$$\int_0^\infty r^2|R|^2\,dr=\int_0^\infty |u|^2\,dr=1$$

$$E_n=-\frac{E_R}{n^2}\quad,\quad n=1,2,3,\ldots,\quad E_R=\frac{e^4m}{2(4\pi\varepsilon_0)^2\hbar^2}=13.6\,\mathrm{eV}$$

$$u_{n=0,l}=\frac{2}{\sqrt{a_0}}\left(\frac{r}{a_0}\right)e^{-r/a_0}\quad,\quad a_0=\frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m}$$

Hydrogen like atom

- One electron with charge *-e* bound to one proton with charge *Ze*, performing relative motion with effective mass : $\mu = \frac{mM}{m+M}$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

$$E_n = -\frac{Z^2 e^4 \mu}{2(4\pi\varepsilon_0)^2\hbar^2 n^2} \quad , \quad n = 1,2,3,\ldots$$

$$u_{n=0,l} = \frac{2}{\sqrt{a_0}}\left(\frac{r}{a_0}\right)e^{-r/a_0}$$

$$a_0 = \frac{4\pi\varepsilon_0}{Ze^2}\frac{\hbar^2}{\mu}$$