QML-Mod3-Quantum Mechanics

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Indice

1 Introduction to Quantum Mechanics -4/04/2025

Newton's laws explained all known macroscopic problems of dynamics of solids. Hamilton had developed a very elegant method to write and solve general mechanical problems. Maxwell's equations could solve almost all known problems related to electricity and magnetism, and of light propagation. However there were a list of thing that couldn't be explained:

- the blackbody radiation

- the photoelectric effect

- the light spectra of gases

- the specific heat of solids

- the stability of matter

1.1 Historical introduction

1.1.1 Blackbody radiation

The experimental evidence was that the emitted light depends only on the temperature of the body. The problem of explaining this phenomenon with classical physics leads to the so called "ultraviolet catastrophe". The solution to this problem arrives when the assumption that the energy is quantized is formulated ($E = h\nu$, where h is the Planck constant).

1.1.2 The photoelectric effect

The experimental evidence was that a metal exposed to light shows a measurable current if the light to witch the metal is exposed is in the UV range (even if it's very weak). Classical physics however predicts that current is proportional to intensity and not to frequency. To explain this phenomenon, Einstein proposed that not only energy was quantized but also light, in this way the photoelectric effect can be explained in the following way: electrons are trapped in the bodies, if a minimum energy is given, the electron is freed form the atom.

1.1.3 Bohr's atomic model

Planetary model of atoms: a nucleus is surrounded by electrons on different orbits. Transitions from two orbits releases energy in form of light.

1.1.4 De Broglie

By combining the Planck's equation and the Einsteins's equation ($E = mc^2$), De Broglie derives:

$$p = \frac{h}{\lambda} = \frac{2\pi h}{\lambda}.$$

The relationship by De Broglie introduce the concept of wave into the atomic problem. The orbits from the Bohr's model are now seen as standing waves, like those formed in drum when you hit it.

1.2 Mathematical fundamentals

We start by formulating the Hamiltonian:

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

We can write the equations of motion as:

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}, \frac{dp}{dt} = -\frac{\partial H}{\partial q}.$$

The Shrodinger's equation is formulated as:

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi.$$

The probabilistic interpretation asserts that

$$\int_a^b |\Psi(x,t)|^2 dt = \{\text{probability of finding particle between a and b at time t}\}$$

Note that: (1) Ψ is complex and (2) measurements can only return squares of amplitudes: if I have Ψ, I need to multiply it by its complex conjugate Ψ^*.

If I have a particle, the probability of measuring the presence of the particle somewhere in space is 100 %.

$$\int |\Psi(x,t)|^2 dt = 1.$$

This sets the condition for a natural interpretation of the probability. Is also sets another requirement for acceptable wavefunctions: their modulus square need to be integrable (i.e. no diverging wavefunctions).

Normalization

$$\int_{-\infty}^{+\infty} |N\psi(x)|^2\, dx = 1.$$

$$N^2 \int_{-\infty}^{+\infty} |\Psi(x)|^2\, dx = 1.$$

$$|N| = \frac{1}{\sqrt{\int_{-\infty}^{+\infty} |\Psi(x)|^2\, dx}}.$$

1.3 The problem of measurement

Electrons were measured as particle-like entities by Thomson and Millikan. Still unresolved as of today, but accepted hand-waving explanation is that, upon a measurement, the wave function collapses. If I measure the position of the particle, the wavefunction collapses. If i quickly measure again the particle, I find it in the same place. For how strange it may seem, there is no way for us to know where the particle was before the measurement.

Double slit experiment
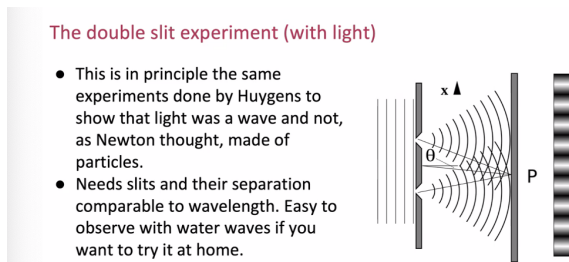
For electrons the wavelenght is small: there is the need for an atomic-scale slits. If I repeat the experiment shooting through the slits one electron at the time I'm still able to observe interference. What is the electron interfering with? **It's interfering with itself**.

Electrons have an inner wavy nature.

All measurements performed on QM particles showed that it was not possible to measure position and momentum with arbitrary precision. Heisenberg expressed it mathematically:

$$\sigma_x \sigma_p \geq \frac{\hbar}{2}.$$

The greater the precision in the measure of one of these two quantities, the greater the uncertainty of the other.

Mathematically, the principle is related to the evidence that there is a minimum value for the product of widths of a function and of its Fourier transform. $\rightarrow$ the concepts of position and momentum are need to be revised, as there is no way to measure accurately both of them. There seems to be a fundamental limit.

Expectation value of position and momentum

$$< x >= \int_{\infty}^{\infty} x|\Psi(x,t)|^2 dx$$

4

More generally we need to know the wavefunction and the operator corresponding to the quantity that we want to calculate. The operator for position and momentum are:

$$\begin{cases} x \to \hat{x}, \\ p \to \hat{p} = -i\hbar \frac{d}{dx}. \end{cases}$$

In this way we have:

$$\begin{cases} <x> = \int \Psi^*[x]\Psi dx, \\ <p> = \int \Psi^*[-i\hbar \frac{\partial}{\partial x}]\Psi dx. \end{cases}$$

For a generic operator:

$$\begin{cases} <Q> = \int \Psi^*(x,t)\hat{Q}\Psi(x,t)dx, \\ <Q^2> = \int \Psi^*(x,t)\hat{Q}^2\Psi(x,t)dx. \end{cases}$$

where $\sigma_Q = \sqrt{<Q^2> - <Q>^2}$.

Solving Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial^2} + V\Psi$$

One of the most used tricks by physicists to simplify this problem is the separation of variables. Hypothesis: the solution you look for can be written as a product of functions $\to \Psi(x,t) = \psi(x)\phi(t)$:

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\phi}{dt}, \frac{\partial^2 \Psi}{\partial^2 x} = \frac{d^2 \psi}{dx^2}\phi$$

We can now rewrite:

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

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

If the left hand side depends only on the variable t, and the right hand side depends only on the variable x, and they are equal, then they must be equal to a constant.

$$\frac{d\phi}{dt} = -\frac{iE}{\hbar}\phi \to \phi(t) = e^{-\frac{iE}{\hbar}t}.$$

The Schrodinger equation can be also expressed with the Hamiltonian operator:

$$\hat{H}\Psi = E\Psi.$$

Solving the time-independent Schrodinger equation returns the stationary states Ψ_n and allowed energies E_n. In mathematical terms, the allowed energies are the eigenvalues associated to the

eigenvectors Ψ_n.

Stationary states, by definition, do not depend on time. Any quantum mechanical state can be expressed as a weighted superposition of stationary states, times a phase factor:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-\frac{iE_n}{\hbar}t}.$$

If for example t=0, then the answer is immediate and moreover all c_n are always constant.

In general

$$c_n = \int \Psi_n^* \Psi(x,0) dx.$$

We'll see later how to have an intuitive understanding.

If the stationary states Ψ_n are normalized, for the total wave function to be normalized then it is required that:

$$\sum_{n=1}^{\inf} |c_n|^2 = 1.$$

Stationary states are orthogonal

$$\int \psi_m^*(x) \psi_n dx = 0,$$

they form a complete set

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

where

$$c_n = \int \psi_n^* \Psi(x,0) dx.$$

2 Introduction to Quantum Mechanics part 2 - 9/05/2025

2.1 The infinite potential well -aka "the particle in a box"

$$V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$

The Shrodinger equation is then:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

The general solution for this problem si:

$$\psi(x) = A\sin(kx) + B\cos(kx), \quad \psi(0) = \psi(a) = 0.$$

The firts conditions implies that B = 0, while the second implies $\sin(ka) = 0 \rightarrow ka = 0, \pm\pi, \pm2\pi, \pm3\pi, ... \rightarrow$ $k_n = \frac{n\pi}{a}$ with $n = 1, 2, 3, ...$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Not all energies are allowed.

Normalization condition: $\int_0^a dx(|A|^2 sin^2(kx)) = |A|^2\frac{a}{2} = 1$ so $|A|^2 = \frac{2}{a}$

$$\rightarrow \psi_n(x) = \sqrt{\frac{2}{a}} sin(\frac{n\pi x}{a}).$$

We now demonstrate how stationary states are orthogonal:

$$\int \psi_m(x)^*\psi_n(x)\,dx = 0, \quad (m \ne n)$$

$$\longrightarrow \int_0^a \psi_m(x)^*\psi_n(x)\,dx = \frac{2}{a}\int_0^a \sin\left(\frac{m\pi x}{a}\right)\sin\left(\frac{n\pi x}{a}\right)dx$$
$$= \frac{1}{a}\int_0^a \left[\cos\left(\frac{(m-n)\pi x}{a}\right) - \cos\left(\frac{(m+n)\pi x}{a}\right)\right]dx$$
$$= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{(m-n)\pi x}{a}\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{(m+n)\pi x}{a}\right)\right\}_0^a$$
$$= \frac{1}{\pi}\left[\frac{\sin((m-n)\pi)}{(m-n)} - \frac{\sin((m+n)\pi)}{(m+n)}\right] = 0,$$

indeed:

$$\int \psi_m(x)^*\psi_n(x)dx = \delta_{mn} \quad \delta_{mn} = \begin{cases} 0, & m \ne n \\ 1 & m = n \end{cases}$$

2.2 Quantum Control

Check out: Q-CTRL

2.3   Finite potential well

$$V(x) = \begin{cases} 0, & -a \le x \le a \\ V_0, & \text{otherwise} \end{cases}$$

$$\rightarrow \psi(x) = \begin{cases} B * \exp(kx) & x \le -a \\ C * \sin(lx) + D * \cos(lx) & -a \le x \le a \\ A * \exp(-kx) & x \ge a \end{cases}$$

2.4   Harmonic Oscillator

$$F = -kx = m\frac{d^2x}{dt^2} \longrightarrow V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \longrightarrow x(t) = A\sin(\omega t) + B\cos(\omega t) \quad \omega = \sqrt{\frac{k}{m}}$$

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

$$\hat{H} = \frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right].$$

$$\frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right]\psi = E\psi,$$

$$u^2 + v^2 = (iu + v)(-iu + v).$$

$$\hat{a}_\pm \equiv \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp i\hat{p} + m\omega x\right)$$

The latter are called the ladder operators.

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}\left(i\hat{p} + m\omega\hat{x}\right)\left(-i\hat{p} + m\omega\hat{x}\right)$$

$$= \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega\hat{x})^2 - im\omega\left(\hat{x}\hat{p} - \hat{p}\hat{x}\right)\right].$$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}.$$

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}. \quad \hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}\left[\hat{p}^2 + (m\omega x)^2\right] - \frac{i}{2\hbar}[x, \hat{p}].$$

$$[x, \hat{p}]\, f(x) = \left[x(-i\hbar)\frac{d}{dx}(f) - (-i\hbar)\frac{d}{dx}(xf)\right] = -i\hbar\left(x\frac{df}{dx} - x\frac{df}{dx} - f\right) = i\hbar f(x).$$

$$\boxed{[x, \hat{p}] = i\hbar}$$

$$\implies \hat{H} = \hbar\omega(\hat{a}_-\hat{a}_+ \frac{1}{2}).$$

$$\boxed{[\hat{a}_-, \hat{a}_+] = 1}$$

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi$$

$$\hat{H}(\hat{a}_+\psi) = \hbar\omega\left(\hat{a}_+\hat{a}_- + \frac{1}{2}\right)(\hat{a}_+\psi) = \hbar\omega\left(\hat{a}_+\hat{a}_-\hat{a}_+ + \frac{1}{2}\hat{a}_+\right)\psi$$

$$= \hbar\omega\hat{a}_+\left(\hat{a}_-\hat{a}_+ + \frac{1}{2}\right)\psi = \hat{a}_+\left[\hbar\omega\left(\hat{a}_-\hat{a}_+ + 1 + \frac{1}{2}\right)\right]\psi$$

$$= \hat{a}_+\left(\hat{H} + \hbar\omega\right)\psi = \hat{a}_+(E + \hbar\omega)\psi = (E + \hbar\omega)(\hat{a}_+\psi). \quad \text{QED}$$

3 Introduction to formalism of Quantum Mechanics -10/05/2025

3.1 Dirac Notation

Ket: $|\psi\rangle \in H$.
Properties:

- $|\psi_1\rangle + |\psi_2\rangle = |\psi_3\rangle$

- $|\psi_1\rangle + |\psi_2\rangle = |\psi_2\rangle + |\psi_1\rangle$

- $(|\psi_1\rangle + |\psi_2\rangle) + |\psi_3\rangle = |\psi_1\rangle + (|\psi_2\rangle + |\psi_3\rangle)$

- $|\psi_1\rangle + 0 = |\psi_1\rangle$

- $|\psi_1\rangle + (-|\psi_1\rangle) = 0$

- $z * |\psi_1\rangle = |z\psi_1\rangle$

Bra: $\langle\psi| \in H$.
The above properties also apply for the bra.
Scalar product: $\langle\psi_1|\psi_2\rangle \equiv \psi_1 \cdot \psi_2 \equiv \int dx(\psi_1^*\psi_2)$.
Properties:

- $\langle\psi_1|(|\psi_2\rangle + |\psi_3\rangle) = \langle\psi_1|\psi_2\rangle + \langle\psi_1|\psi_3\rangle$

- $\langle\psi_1|\psi_2\rangle^* = \langle\psi_2|\psi_1\rangle$

- $\langle\psi|\psi\rangle = \langle\psi|\psi\rangle \qquad \psi \in R.$

If we define $|i\rangle \in H$ with i = 1,...,N such that $\langle i|i\rangle = 1$ and also $\langle i|j\rangle = 0$ with $i \neq j$ ($\to \langle i|j\rangle = \delta_{ij}$)
than we can express a generic $|\psi\rangle \in H$ in terms of the basis:

$$|\psi\rangle = \sum_{i=1}^{N} c_i|i\rangle. \longrightarrow \mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}$$

Similarly: $\langle\psi| = \sum_{i=1}^{N} c_i^*\langle i|$.

$$\langle\psi_\alpha|\psi_\beta\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} c_{\alpha_i}^* c_{\beta_j}^* \langle i|j\rangle = \sum_{i=1}^{N} c_{\alpha_i}^* c_{\beta_j}^* \equiv (c_{\alpha_1}^* c_{\alpha_2}^* c_{\alpha_3}^* c_{\alpha_4}^* ...) \cdot \begin{pmatrix} c_{\beta_1} \\ c_{\beta_2} \\ c_{\beta_3} \\ c_{\beta_4} \\ \vdots \end{pmatrix}$$

In general we can write:
$$\implies \langle \psi | = (c_1^* \dots c_N^*).$$

Given $|\psi\rangle = \sum_j c_j |j\rangle$ than $\langle i|\psi\rangle = \sum_j c_j \langle i|j\rangle = c_i$. In the same way $c_i^* = \langle \psi|i\rangle$.

$$|\psi\rangle = \sum_i c_i |i\rangle = \sum_i |i\rangle\langle i|\psi\rangle \to \sum_i |i\rangle\langle i| = 1.$$

Lets suppose now having a wavefunction $\Psi(x)$ in $0 \le x \le L$ divided N times by a factor Δx such

that $\Psi(x) = \begin{cases} \Psi(x_1) = \Psi_1 = c_1 \\ \vdots \\ \Psi(x_N) = \Psi_N = c_N \end{cases}$. We can rewrite the wavefunction as $|\Psi(x)\rangle = \begin{pmatrix} c_1 \\ \vdots \\ c_N \end{pmatrix}$. The

latter vector can be, in general, expressed on a specific basis $\vec{e}$.