Quantum Mechanics

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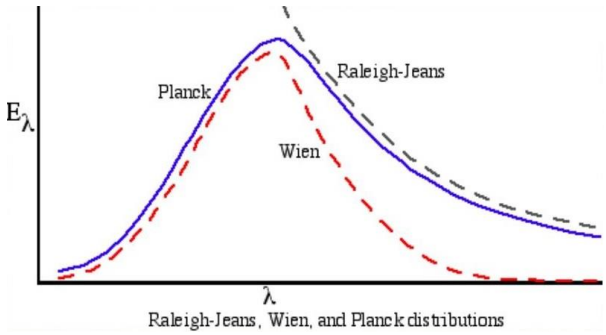
I. What Is Quantum Mechanics?

1.1 Ultraviolet Catastrophe: the necessity of developing quantum mechanics

1.1.1 Ultraviolet Catastrophe

The black-body radiation was extracted from the application of evaluating the temperature in a steel furnace by analyzing the light spectrum coming out from a small window.

The experimental measurements gave the light spectrum of the black-body radiation as the blue line in the figure.



Raleigh-Jeans, Wien, and Planck distributions

Based on the principles of thermodynamics and displacement, Wien derived an empirical formula for black-body radiation:

$$E_\lambda \mathrm{d}\lambda = \frac{C_1}{\lambda^5}\exp\left(-\frac{C_2}{\lambda T}\right)\mathrm{d}\lambda\,, \tag{1.1}$$

where C_1 and C_2 are two constants to be determined by experiment, λ is the wavelength of light, T is the temperature, and E_λ is the energy density in terms of wavelength. Wien's formula qualitatively agrees with the experimental curve, but is quantitatively different at long wavelengths.

On the other hand, J.W. Rayleigh and J. H. Jeans derived from the laws of classical statistical mechanics to obtain the Rayleigh-Jeans formula:

$$E_\nu \mathrm{d}\nu = \frac{8\pi\nu^2}{c^3}\bar{\varepsilon}\mathrm{d}\nu\,, \tag{1.2}$$

where ν is the frequency of light, c is the speed of light, E_ν is the energy density in terms of frequency, and the average energy per degree of freedom is

$$\bar{\varepsilon} = \frac{\int_0^\infty \varepsilon \exp\left(-\varepsilon / k_\mathrm{B}T\right) \mathrm{d}\varepsilon}{\int_0^\infty \exp\left(-\varepsilon / k_\mathrm{B}T\right) \mathrm{d}\varepsilon} = k_\mathrm{B}T \,. \tag{1.3}$$

The Rayleigh-Jeans formula agrees well with the experimental curve at long wavelengths, but diverges at short wavelengths. Therefore, this disagreement of theory with respect to experiment is called “ultraviolet catastrophe”.

Inspired by the two formulas, Plank *postulated* that the energy ε in Eq. (1.3) should not be continuous, but can only be the multiple of a certain “quantum” of energy:

$$\varepsilon = n\varepsilon_0, \quad n = 0,1,2,\cdots, \tag{1.4}$$

so Eq. (1.3) is modified as

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty} n\varepsilon_0 \exp\left(-n\varepsilon_0 / k_\mathrm{B}T\right)}{\sum_{n=0}^{\infty} \exp\left(-n\varepsilon_0 / k_\mathrm{B}T\right)} = \frac{\varepsilon_0}{\exp\left(\varepsilon_0 / k_\mathrm{B}T\right) - 1} \,. \tag{1.5}$$

Putting in Eq. (1.2), we have

$$E_\nu \mathrm{d}\nu = \frac{8\pi\nu^2}{c^3} \frac{\varepsilon_0}{\exp\left(\varepsilon_0 / k_\mathrm{B}T\right) - 1} \mathrm{d}\nu \,. \tag{1.6}$$

Comparing with Eq. (1.1), and note that $\lambda = c / \nu$, we can only choose

$$\varepsilon_0 = h\nu \,. \tag{1.7}$$

where h is a constant, later known as the Plank constant experimentally determined to be

$$h \simeq 6.63 \times 10^{-24} \ \ \mathrm{J{\cdot}s}. \tag{1.8}$$

Therefore, Eq. (1.6) becomes Plank’s formula

$$E_\nu \mathrm{d}\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(h\nu / k_\mathrm{B}T\right) - 1} \mathrm{d}\nu \,, \tag{1.9}$$

Equivalent to

$$E_\lambda \mathrm{d}\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp\left(hc / k_\mathrm{B}T\lambda\right) - 1} \mathrm{d}\lambda \,. \tag{1.10}$$

From Plank’s formula for black-body radiation, we may establish at least three new physical concepts beyond classical mechanics: (1) The energy in the microscopic world can be discrete rather than continuous; (2) The Plank constant is a relative measurement to distinguish the microscopic and macroscopic limits; (3) the wave and particle properties can simultaneously appear in microscopic materials.

Plank’s formula Eq. (1.9) can be rigorously derived by applying the Fermi-Dirac distribution in quantum statistical mechanics to the photon gas model (the statistical model of black body).

1.2 Wave-Particle Duality: De Broglie wave and uncertainty principle

1.2.1 De Broglie Wave

Louis Victor de Broglie has proposed in 1924 that all materials have the wave-particle duality:

$$\lambda = \frac{h}{p} = \frac{h}{mv}, \tag{1.11}$$

where λ is the intrinsic wavelength of the particle, p is the momentum, m is the mass, v is the speed, and $h = 6.626\times10^{-34}\,\mathrm{m^2\cdot Kg/s}$ is the Planck constant.

We may look into two examples to estimate the orders of the de Broglie wavelength for macroscopic and microscopic materials. For a macroscopic matter with $m = 1\,\mathrm{Kg}$ moving at $v = 1\,\mathrm{m/s}$, its intrinsic wave length is $\lambda = \frac{6.626\times10^{-34}\,\mathrm{m^2\cdot Kg/s}}{1\mathrm{Kg}\cdot1\mathrm{m/s}} = 6.626\times10^{-34}\,\mathrm{m}$, which is so small that the waving property of this matter can be neglected. By contrast, for an electron ($m = 9.1\times10^{-31}\,\mathrm{Kg}$) with $E = 10\,\mathrm{eV}$, its momentum $p = \sqrt{2mE} = 4.2\times10^{-24}\,\mathrm{J\cdot s/m}$, so its intrinsic wavelength $\lambda = \frac{h}{p} = 1.6\times10^{-10}\,\mathrm{m}$, much larger than the effective radius of an electron $2.82\times10^{-15}\,\mathrm{m}$. Therefore, the wave nature of electrons is non-negligible.

1.2.2 Commutation Operator

For two observables *A* and *B*, define the *commutation operator*

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{1.12}$$

It is always 0 in classical mechanics, while it can be non-zero in quantum mechanics. For example, $\left[\hat{x}_\alpha, \hat{p}_\beta\right] = i\hbar\delta_{\alpha\beta}$; for the angular momentum $\hat{\vec{l}} = \hat{\vec{r}}\times\hat{\vec{p}}$, $\left[\hat{l}_\alpha,\hat{l}_\beta\right] = \varepsilon_{\alpha\beta}i\hbar\hat{l}_\gamma$, $\left[\hat{\vec{l}}^2,\hat{l}_\alpha\right] = 0$.

1.2.3 Uncertainty Principle

One of the consequences of the wave-particle duality is the *uncertainty principle*, whose position-momentum relation is

$$\Delta x\cdot\Delta p \geq \frac{\hbar}{2}, \tag{1.13}$$

where x is the particle position and $\hbar = \frac{h}{2\pi}$. Another case is the energy-time relation

$$\Delta E\cdot\Delta t \geq \frac{\hbar}{2}. \tag{1.14}$$

Basically, two conjugate non-commutable properties should satisfy the uncertainty principle. Therefore, the concept of deterministic trajectory in classical mechanics is unsuitable for describing microscopic particles, for which we need the concept of *probability wave* whose probability distribution, rather than the specific value is fix in a given time-independent potential.

1.2.4 Probability Wave, Bra, and Ket

If we denote the probability wave of the position of a one-dimensional quantum particle to be $\psi(x)$ in the *x*-representation, then the probability of the particle to appear at the position x is

$$P(x) = |\psi(x)|^2, \tag{1.15}$$

whose normalization condition is

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = \int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\mathrm{d}x = 1. \tag{1.16}$$

The average position of the particle is

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x) x \psi(x)\mathrm{d}x, \tag{1.17}$$

and the average potential

$$\langle V(x) \rangle = \int_{-\infty}^{+\infty} \psi^*(x) V(x) \psi(x)\mathrm{d}x \tag{1.18}$$

Therefore, the position operator in the *x*-representation is $\hat{x}$, and the potential operator is $\hat{V}(x)$.

The probability wave of the particle momentum is

$$\varphi(p) = \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} \psi(x) e^{-ipx/\hbar}\mathrm{d}x, \tag{1.19}$$

so the expectation value of the momentum in the *x*-representation is

$$\langle p \rangle = \int_{-\infty}^{+\infty} \varphi^*(p) p \varphi(p)\mathrm{d}p = \int_{-\infty}^{+\infty} \psi^*(x)(-i\hbar\nabla)\psi(x)\mathrm{d}x. \tag{1.20}$$

From the above equation, we can define the momentum operator in the *x*-representation to be

$$\hat{p} = -i\hbar\nabla, \tag{1.21}$$

the kinetic-energy operator

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \tag{1.22}$$

and the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}. \tag{1.23}$$

In general, the expectation value of an observable *A* can be expressed in the *x*-representation as

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^*(x) \hat{A} \psi(x)\mathrm{d}x, \tag{1.24}$$

1.3 Basic Rule: time-independent Schrödinger equation

In the non-relativistic limit, the mechanical property of a microscopic particle under a time-independent stable potential is described by the *Schrödinger equation of motion*:

$$\hat{H}\psi = E\psi, \tag{1.25}$$

where *E* is just a number. This an eigenequation with the solution of a set of eigenstates $\{\phi_i\}$ and

eigenvalues $\{\varepsilon_i\}$. The eigenstates must satisfy the *orthonormal condition*

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} . \tag{1.26}$$

The particle does not have to always stay at the eigenstate, rather it can stay in an arbitrary state that can be linearly expanded by the eigenstates

$$\psi = \sum_i c_i \phi_i , \tag{1.27}$$

and the energy is

$$E = \sum_i |c_i|^2 \varepsilon_i . \tag{1.28}$$

However, each time the particle is measured, it "collapses" to one of the eigenstates with a certain probability.

When the potential is time-independent, the evolution of the system obeys the time-dependent Schrödinger equation of motion:

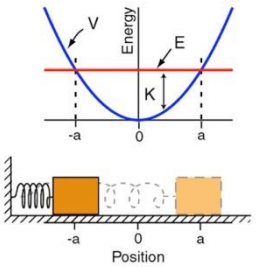
$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi , \tag{1.29}$$

whose solution is

$$\psi(x,t) = \psi(x) \exp\left(-i \frac{Et}{\hbar}\right). \tag{1.30}$$

1.4 Example: one-dimensional classical and quantum harmonic oscillators

1.4.1 Classical Harmonic Oscillator



A classical harmonic oscillator has the relation

$$F(x) = -\frac{\mathrm{d}V}{\mathrm{d}x} = -kx , \tag{1.31}$$

where F is the force, x is the particle position, V is the potential, k is the harmonic coefficient. According to Newton's second law of motion:

$$F = ma , \tag{1.32}$$

where the acceleration $a(x) = \frac{\mathrm{d}^2 x}{\mathrm{d}t^2}$, we have

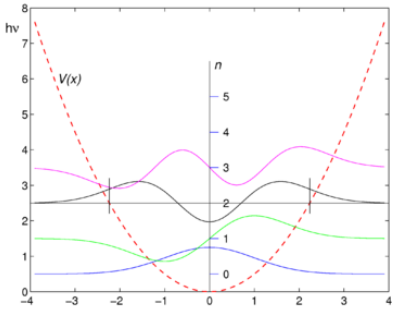
$$-kx = m \frac{\mathrm{d}^2 x}{\mathrm{d}t^2} . \tag{1.33}$$

Given the initial condition $x(t=0) = x_0, \frac{\mathrm{d}x}{\mathrm{d}t}(t=0) = 0$, the solution is

$$x(t) = x_0 \cos(\omega t), \quad \omega = \sqrt{\frac{k}{m}} . \tag{1.34}$$

That is to say, the evolution of the system is deterministic, and thus all physical properties can be accurately predicted in advance.

1.4.1 Quantum Harmonic Oscillator



The potential operator

$$\hat{V}(x)=\frac{1}{2}kx^2=\frac{1}{2}m\omega_0^2x^2,\omega_0=\sqrt{\frac{k}{m}}. \tag{1.35}$$

Correspondingly, the time-independent Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\frac{1}{2}m\omega_0x^2\right)\psi(x)=E\psi(x). \tag{1.36}$$

The solution of the above equation is: the eigenvalues

$$\varepsilon_n=\left(n+\frac{1}{2}\right)\hbar\omega_0,n=0,1,2,\cdots \tag{1.37}$$

and the eigenfunctions

$$\phi_n(x)=N_n\exp\left(-\frac{1}{2}\alpha^2x^2\right)H_n(\alpha x), \tag{1.38}$$

where $\alpha=\sqrt{\frac{m\omega_0}{\hbar}}$, $N_n=\left(\frac{\alpha}{\sqrt{\pi}2^n n!}\right)^{\frac{1}{2}}$, and $H_n(\alpha x)$ are the Hermite polynomials. Note that the ground state have a non-zero energy of $\varepsilon_0=\frac{1}{2}\hbar\omega_0$, which is called the *zero-point energy*.

1.5 Basic Properties: principle of superposition of states, localized and delocalized quantum particles, Boson and Fermion

1.5.1 Principle of Superposition of States

An arbitrary state of a system can be linearly superposed by all other states:

$$\psi=\sum_i c_i\psi_i. \tag{1.39}$$

So is the system energy

$$E=\sum_i|c_i|^2E_i. \tag{1.40}$$

Specifically, an arbitrary state can be linearly expanded by a set of eigenfunctions. Note that the corresponding probability $P = |\psi|^2$ does not obey the linear superposition relation.

1.5.2 Localized and Delocalized Quantum Particles

If particles are so far that their wave functions do not overlap with each other, they may be regarded as *delocalized* quantum particles, which are distinguishable. Otherwise, they are regarded as *localized* and indistinguishable.

The delocalized quantum particles obey the same statistical rules as classical particles, and a group of delocalized quantum particles follow the Maxwell-Boltzmann distribution.

The localized quantum particles follow the Bose-Einstein distribution (bosons with integer spins, symmetry of exchange in wave functions) and the Fermi-Dirac distribution (fermions with half-integer spins, antisymmetry of exchange in wave functions).

1.5.3 Bosons and Fermions

If the spin degree of freedom is considered, quantum particles can be divided into bosons with integer spins and fermions with half-integer spins. The total wave function does not change if two bosons exchange, and many bosons can be in the same quantum state. The wave function of two non-interacting bosons can be written as

$$\psi_{\mathrm{B}}(1,2) \equiv \psi_{\mathrm{B}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2)\right), \tag{1.41}$$

where ϕ_1 and ϕ_2 are the two single-particle wave functions.

The total wave function flips its sign if two fermions exchange, and two fermions cannot stay in the same state simultaneously. The wave function of two non-interacting fermions can be written as

$$\begin{aligned}\psi_{\mathrm{F}}(1,2) &\equiv \psi_{\mathrm{F}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left(\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) - \phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2)\right) \\ &= \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_2(1)\\ \phi_1(2) & \phi_2(2)\end{vmatrix}\end{aligned}. \tag{1.42}$$