

Quantum Mechanics

Lecture Course for 4th Semester Students
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Introduction to Quantum Mechanics

1. Particle-wave duality; Davisson-Germer experiment; de Broglie waves.
2. Schrödinger equation; continuity equation.
3. One-dimensional problems; particle in a square well potential; tunnel effect.
4. Physical interpretation of the wave function.
5. Observables and their representation by hermitian operators.
6. Expectation values; uncertainty principle; Ehrenfest theorem.
7. Three-dimensional problems; central forces; angular momentum.
8. Hydrogen spectrum.
9. Electron spin and magnetic moment; electron magnetic resonance.
10. Perturbation theory.
11. Pauli equation; fine structure of atomic spectra.
12. Zeeman effect.
13. Stark effect.
14. Gamov theory of α -decay.
15. Relativistic wave equations; Klein-Fock-Gordon equation; Dirac equation.

This course will be held in English

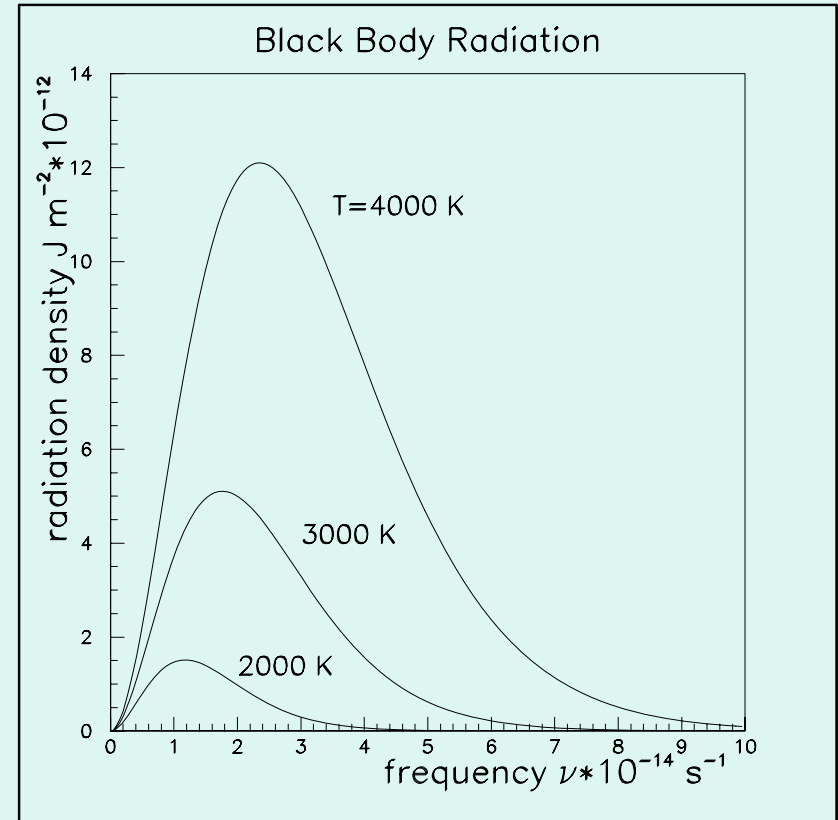
Preliminary Remarks

Quantum mechanics is the extension of classical mechanics into the microscopic world, the world of atoms and molecules and of atomic nuclei and elementary particles. The need for a revision of the foundations of mechanics arises as a result of the wave-particle duality of matter, which manifests itself in systems of atomic dimensions. Wave-particle duality means that particles, such as electrons or protons, have properties characteristic of both waves and particles.

Wave-particle duality was first found for electromagnetic radiation and later understood to be a general property of all matter. It all started with Max Planck's work on black body radiation.

Black Body Radiation

- In 1900 Max Planck found the formula that describes all data on Black Body radiation.
- To do so he had to demand that radiation can be absorbed and emitted only in "*Portions of Energy*" or quanta. This novel concept was the birth of quantum physics.
- This is Planck's formula:



$$\rho(\nu, T) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$$

Planck's idea was further developed by Einstein. First, in 1905, he applied it to explain the photoelectric effect: he showed that the kinetic energy of the electrons emitted from a metal surface illuminated with light of frequency ν is equal to

$$E = h\nu - W$$

where h is the Planck constant and W is a constant specific for the metal (this constant is called the **work function** of the metal).

Later Einstein repeatedly returned to the question of the interaction of radiation with matter. He himself was finally convinced of the reality of light quanta only in 1918. The word photon was coined only in 1926 by the American physical chemist Gilbert Lewis. In today's language the observation of wave properties and particle properties in one and the same object is called **wave-particle duality** (or particle-wave duality, as you like).

Particle-Wave Duality of the Electron.

The wave nature of electrons is demonstrated for instance in the Davisson-Germer experiment. In this experiment a beam of electrons is incident on a crystal; the reflected electrons show a diffraction pattern similar to that observed when x-rays are made to be reflected from a crystal.

Independently Louis de Broglie applied the particle-wave duality of radiation to the electron. This enabled him to deduce the quantum condition introduced by Niels Bohr in an *ad hoc* fashion in order to derive the Balmer formula of the hydrogen spectrum. For this work de Broglie was awarded the Nobel Prize.

Here comes a passage from de Broglie's doctoral thesis in which he proposed the particle-wave duality of the electron:

Louis de Broglie Investigations on Quantum Theory

From the translation of his doctoral thesis published in
***Annales de Physique* 3 (1925) 22**

“Introduction

The history of optical theories shows that the scientific view has for long oscillated between a mechanical and an undulatory conception of light; however, these two views are perhaps less opposed to one another than was previously thought, and the development of quantum theory, in particular, appears to confirm this view. On the basis of the idea of a generally valid relationship between the concepts of frequency and energy, we start in this paper from the existence of a certain periodic process of an as yet not more closely specified nature which must be assigned to each isolated portion of energy and which depends on its eigenmass in accordance with the Planck-Einstein relation. Then the relativity theory requires the assignment to the uniform movement of each material point of the propagation of a certain wave ...

(de Broglie – continued)

...
The basic idea of quantum theory is, of course, the impossibility of considering an isolated fragment of energy without assigning a certain frequency to it. ... which I will call the quantum relation:

$$\text{Energy} = h \cdot \text{frequency}$$

where h is Planck's constant."

* * *

De Broglie's idea remains basic for quantum mechanics; it is alive in the terminology we use: the quantity $\lambda = h/p$, where h is the Planck constant and p is the momentum of a particle, is called the de Broglie wavelength of that particle.

As a consequence of wave-particle duality, the position x and momentum p of a particle cannot be measured simultaneously with absolute precision: the uncertainties Δx and Δp in these measurements satisfy the following relation (**Heisenberg's uncertainty relation**):

$$\Delta x \Delta p \geq \hbar$$

where \hbar is the Planck constant divided by 2π .

The uncertainty relation destroys the basis of Newton's equation of motion which has solutions only if the position and momentum of a particle are simultaneously specified with absolute precision.

However, this does not mean that Classical Mechanics must be completely abandoned:

- (i) Newton's 1st law of mechanics, the relativity principle, remains in force;
- (ii) Newton's 3rd law of mechanics, "action equals reaction", also remains in force.

The first one of these was later extended to electromagnetism: it is one of the postulates of Einstein's (special) theory of relativity.

Newton's second law, the equation of motion, remains valid in an average sense. This is the statement of Ehrenfest's theorem.

A consistent theory, based on the wave nature of matter, was formulated by Schrödinger. For a single particle of mass m in a field of potential energy V the Schrödinger equation is of the form of

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(\vec{r})\psi(\vec{r}, t)$$

where ψ is the wave function and

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Continuity Equation

Consider the 1D the SchEq:

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

and its complex conjugate:

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

Multiply (1) by ψ^* and (2) by ψ , then subtract:

On the l.h.s. we get

$$i\hbar \frac{\partial \psi^* \psi}{\partial t}$$

And on the r.h.s:

$$-\frac{\hbar^2}{2m} \left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2} \right) = -\frac{\hbar^2}{2m} \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right)$$

hence

$$\frac{\partial (\psi^* \psi)}{\partial t} + \frac{\hbar}{2im} \frac{\partial}{\partial x} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) = 0 \quad (3)$$

Define $\rho = \psi^* \psi$ and $j = \frac{\hbar}{2im} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right)$

then Eq. (3) can be written in the form of $\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0$

In 3D the SchEq is

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(\vec{r}) \psi(\vec{r}, t) \quad (4)$$

where

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \quad \text{"nabla" or "del"}$$

and hence $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, and after manipulations

similar to the previous ones we get

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0} \quad \text{continuity equation} \quad (5)$$

where

$$\vec{j} = \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*)$$

Equations like this are also encountered in hydrodynamics and in electromagnetism. They are called **continuity equations**. Now we are going to show that the continuity equation (5) leads to a conservation law.

Integrate Eq. (5) over a volume V with surface S :

$$\int \left(\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} \right) dV = 0$$

or

$$\int \frac{\partial \rho}{\partial t} dV = - \int (\nabla \cdot \vec{j}) dV$$

On the left-hand side we change the order of integration and differentiation:

$$\int \frac{\partial \rho}{\partial t} dV = \frac{d}{dt} \int \rho dV$$

On the right-hand side we use the Gauss-Ostrogradsky theorem:

$$\int (\nabla \cdot \vec{j}) dV = \oint_S j_n dS$$

Where on the r.h.s. j_n is the outward normal component of vector j on the surface S that encloses volume V . Putting things together we get the following:

$$\frac{d}{dt} \int \rho dV = - \oint_S j_n dS$$

Now, we do not yet know what the wave function ψ represents physically. Therefore we also don't know what ρ is. But we do know that it is the mod squared of the wave function, so it cannot be less than nought, and therefore also its integral over the volume V cannot be less than nought.

We also don't know what the vector j represents. But whatever quantity it does represent, the surface integral on the r.h.s. is the outward flux of that quantity. We can therefore summarise our result by the following statement:

The rate of change of the quantity $\int \rho dV$ is equal to the outward flux of the quantity represented by the vector j .

Obviously, the wave function is in some sense connected with the matter it is describing, for instance an electron. It is therefore natural to assume that close to the electron it is bigger than far from it. Anticipating the result we are going to make plausible, and which represents the universally accepted interpretation of the wave function, we shall now say that

$$\rho(\vec{r}, t) dV$$

is the probability of finding the electron in the volume element dV .

ρ is called the **probability density**, and j is the **probability current density**.

Now we must distinguish two cases:

(i) *Bound states* and (ii) *unbound states*.

A typical example of a bound state is an electron bound in an atom;

An example of an unbound state is a beam of particles which may impinge on a target and get deflected but then continues to travel outside any finite volume.

In the former case (bound state) the probability to find the particle is confined to a volume near the particle and falls off rapidly towards infinity. We shall see several examples where the drop of the wfn towards infinity is exponential. Therefore the current density j also drops to zero on the surface enclosing the infinite volume, and drops faster than the surface area increases. So we get

$$\frac{d}{dt} \int_{all\ space} \rho dV = 0$$

hence

$$\int_{all\ space} \rho dV = \int_{all\ space} |\psi|^2 dV = \text{constant}$$

The latter eqn is expressed in the words: “the wfn is square integrable”.

We have seen that the Schrödinger eqn is linear homogeneous in the wfn:

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

Therefore, if ψ is a solution of the Schrödinger eqn, then $c\psi$ is also a solution for any complex constant c . With a suitable choice of c we can therefore **normalise** the wfn, whence

$$\int_{all\ space} \rho dV = \int_{all\ space} |\psi|^2 dV = 1$$

In the probability interpretation of the wfn, the integral over all space of the probability density ρ means the probability of finding the particle *somewhere* in the infinite space, and that is certainty, and in the language of the theory of probability **certainty is a probability equal to one.**

The Schrödinger Equation

Let me now give a heuristic argument to establish the Schrödinger equation.

Recall: Particle-Wave Duality is expressed by the Einstein-de Broglie relations

$$E = h\nu, \quad p = h/\lambda$$

Simplest case: free particle travelling in x direction:

$$\psi(x, t) = e^{i(kx - \omega t)} \quad (1)$$

where $k = 2\pi/\lambda$ and $\omega = 2\pi\nu$.

The wfn should have the complete information on the state of motion of the particle.

We postulate that it contains the info to give the state of motion at the next instant of time, *i.e.* the rate of change of ψ :

$$\frac{\partial \psi}{\partial t} = \hat{O}\psi$$

where \hat{O} is an operator that we must identify.

Take the derivative w.r.t. time of the plane wave fn and use $E = hv = \hbar\omega$:

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial t} e^{i(kx - \omega t)} = -i \frac{E}{\hbar} \psi$$

In nonrelativistic mechanics, the energy E of the free particle is its kinetic energy :

$$E = \frac{p^2}{2m} = \frac{\hbar^2}{2m} k^2$$

For the plane wave we have

$$k^2 \psi(x, t) = -\frac{\partial^2 \psi(x, t)}{\partial x^2}$$

and hence

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

Thus we have identified the operator \hat{O} : up to a factor of $i\hbar$

it is the K.E operator $\hat{T} = \frac{\hat{p}^2}{2m}$ where \hat{p} is the

momentum operator: $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

Schrödinger (postulate!): the wave eqn for matter waves is of the form

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

In 3D and for a single particle the Schrödinger equation is of the form of

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

with the 3D momentum operator

$$\hat{p} = -i\hbar \nabla = -i\hbar \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

Define: $\hat{H} = \hat{T} + \hat{V}$ **Hamiltonian**

then the Schrödinger eqn is:

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

For n particles the K.E. operator is

$$\hat{T} = \sum_{i=1}^n \frac{\hat{p}_i^2}{2m_i}$$