

Quantum Mechanics

Dynamics of matter waves

- We learned that the discoveries such as blackbody radiation and photoelectric effect led to a general conclusion that energy of electromagnetic waves is transferred and transmitted in discrete quanta. The quantization of electromagnetic radiation could be interpreted as a manifestation of particle-like properties of radiation, which was decisively demonstrated by the observation of Compton scattering. A generalization of particle-wave duality to ordinary matter resulted in the de Broglie's proposal that a special kind of wave is associated to ordinary particles, such as atoms or electrons. This proposal found a dramatic confirmation in the observation of electron and neutron diffraction on crystal lattices.
- We described de Broglie's waves by a complex function of coordinates, the wavefunction $\psi(\mathbf{r}, t)$. In order to give it a physical interpretation we confronted the somewhat strange reality of quantum measurements which produce random outcomes in order to accommodate quantization rules. We adopted a probabilistic interpretation of the wavefunction by making an analogy with electromagnetism. This led to the Born's postulate, that $|\psi(\mathbf{r}, t)|^2$ is the probability (density) that the particle would be found in a measurement at location \mathbf{r} at time t .
- If $\psi(\mathbf{r}, t)$ provides the true microscopic description of a particle, we need a wave equation which specifies dynamics, that is how the particle moves in the presence of external forces. Newton's laws specify dynamics in classical physics, but they need to govern only the time dependence of position and momentum of a particle. Now we need an equation of motion which specifies how the entire wavefunction evolves as a function of coordinates and time. Such an equation was formulated by Schrodinger and it gave birth to modern quantum mechanics.

Schrodinger equation

- There are a few physical requirements we must satisfy in constructing the quantum equation of motion (wave equation):
 1. The fundamental requirement of matter wave dynamics is that it be compatible with classical physics. We know that macroscopic objects are governed by Newton's laws, so any quantum mechanical law must have a mathematical limit in which it reduces to classical laws. We will later identify this limit with cases in which one can neglect the Planck's constant, $\hbar \approx 0$.
 2. Another requirement from the quantum mechanical equation of motion is that it have a plane-wave solution $\psi(\mathbf{r}, t) = \exp(i(\mathbf{k}\mathbf{r} - \omega t))$ in the absence of external forces. Such a solution describes a particle with well defined constant momentum $\mathbf{p} = \hbar\mathbf{k}$ and energy $E = \hbar\omega$, according to the de Broglie's and Planck's postulates.
 3. The equation must be linear in the wavefunction $\psi(\mathbf{r}, t)$ in order to allow superpositions of waves.: if $\psi_1(\mathbf{r}, t)$ and $\psi_2(\mathbf{r}, t)$ are solutions, then $\psi(\mathbf{r}, t) = a_1\psi_1(\mathbf{r}, t) + a_2\psi_2(\mathbf{r}, t)$ must also be a solution for arbitrary a_1 and a_2 . The experimentally observed diffraction of matter waves on crystals is completely consistent with such linear superposition. Also, the analogous wave superpositions are familiar in electrodynamics to which matter wave dynamics is very similar.
- We start from the requirement 2 and consider the simplest free motion of a particle in the absence of external forces. The wavefunction $\psi(\mathbf{r}, t) = \exp(i(\mathbf{k}\mathbf{r} - \omega t))$ contains information about the particle's momentum and energy which we can extract by taking appropriate partial derivatives:

$$\begin{aligned} \mathbf{p} = \hbar\mathbf{k} \quad \dots \quad -i\hbar \left(\hat{\mathbf{x}} \frac{\partial}{\partial x} + \hat{\mathbf{y}} \frac{\partial}{\partial y} + \hat{\mathbf{z}} \frac{\partial}{\partial z} \right) e^{i(k_x x + k_y y + k_z z - \omega t)} &\equiv -i\hbar \nabla e^{i(\mathbf{k}\mathbf{r} - \omega t)} = \mathbf{p} e^{i(\mathbf{k}\mathbf{r} - \omega t)} \\ E = \hbar\omega \quad \dots \quad i\hbar \frac{\partial}{\partial t} e^{i(\mathbf{k}\mathbf{r} - \omega t)} &= E e^{i(\mathbf{k}\mathbf{r} - \omega t)} \end{aligned}$$

Now we use the requirement 1 and observe that classical mechanics relates the energy of a (non-relativistic) particle to its momentum:

$$E = \frac{\mathbf{p}^2}{2m}$$

If we multiply this equation by $\psi(\mathbf{r}, t) = e^{i(\mathbf{k}\mathbf{r} - \omega t)}$ and use the formulas above to extract $p^2 = |\mathbf{p}|^2$ and E from the plane-wave function, we obtain the following equation of motion:

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

- This wave equation correctly describes de Broglie waves, but it is applicable only to the uniform motion of free particles. How can we describe acceleration due to external forces? Since the above wave equation naturally deals with energy of the particle, we can use potential energy V to describe forces. Classical physics tells us that the particle's potential energy is converted to kinetic energy when the particle accelerates, but its total energy E is constant:

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

Just as above, we now convert this into a wave equation:

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

The added term is constructed by requiring that the equation be linear in $\psi(\mathbf{r}, t)$ and as similar as possible to its classical counterpart. This is a complete quantum-mechanical equation of motion which Schrodinger wrote in 1925.

- We can demonstrate the compatibility of Schrodinger's equation with classical mechanics by considering a wave-packet. A wave-packet is the wave with as small uncertainty of position and momentum as allowed by the Heisenberg's principle, $\Delta p_x \Delta x \sim \hbar$. Such a wave is localized in space but occupies some small finite volume in order to have a reasonably well defined momentum. We must assume that the potential $V(\mathbf{r})$ varies slowly, so that it can be regarded constant in the volume occupied by the wave-packet. The Schrodinger's equation describes in great detail how the wave-packet evolves and propagates through space. However, if we are not interested in the internal changes of the wave-packet, which anyway occur inside a very small volume, we can apply the Schrodinger's equation to the "carrier" plane wave at the current location of the wave-packet. This gives us precisely the classical equation of motion which governs the evolution of the (most probable) instantaneous momentum \mathbf{p} and position \mathbf{r} of the wave-packet:

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

The assumption that the wave-packet is very small would be exact if the Planck's constant were zero ($\Delta p_x \Delta x \sim \hbar \approx 0$). For all practical purposes, the Planck's constant is indeed extremely small in our macroscopic world. However, inside atoms, the potential $V(\mathbf{r})$ varies extremely rapidly over extremely short distances, which becomes significant despite the smallness of \hbar . This is why we need to apply the full quantum-mechanical theory to study the subatomic world.

Time-independent Schrodinger equation

- The general Schrodinger equation is time-dependent and predicts the full time evolution of a wave-function. However, its full power is needed only in non-equilibrium situations. Most situations that we shall consider occur in equilibrium and can be handled by a simplified time-independent equation. For example, the equilibrium state of a Hydrogen atom should not change in time.
- We seek a stationary solution of the Schrodinger equation in the form:

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$$

Substituting this in the Schrodinger equation yields:

$$-\frac{\hbar^2 \nabla^2}{2m} \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where $E = \hbar\omega$ and the factors of $e^{-i\omega t}$ on both sides were canceled out. This is the time-independent (or stationary) Schrodinger equation. Its solution is a wavefunction $\psi(\mathbf{r})$ which depends only on coordinates. The wavefunction depends not only on the potential $V(\mathbf{r})$, but also on the energy E .

- We distinguish two kinds of solutions $\psi(\mathbf{r})$. *Bound states* are the solutions which can be normalized in a finite volume \mathcal{V} as:

$$\int_{\mathcal{V}} d^3r |\psi(\mathbf{r})|^2 = 1$$

Such states are localized. Since we interpret $|\psi(\mathbf{r}, t)|^2 = |\psi(\mathbf{r})e^{-i\omega t}|^2 = |\psi(\mathbf{r})|^2$ as the probability (density) that the particle be detected in a measurement at location \mathbf{r} , the normalization tells us that the particle can be found inside the finite volume \mathcal{V} with complete certainty. It turns out that such solutions exist only if the energy E belongs to a discrete set of values, called energy levels. We say that the energy spectrum of bound states is discrete.

- *Extended states* are the solutions $\psi(\mathbf{r})$ which cannot be normalized in a finite volume because $\psi(\mathbf{r})$ is finite everywhere in space. A different normalization condition has to be used. Extended states are typically found at high energies, when kinetic energy is so large that the potential $V(\mathbf{r})$ cannot localize the particle. The spectrum of extended states is continuous.
- The stationary Schrodinger equation allows us to calculate the energy spectrum of any quantum system. Substituting a simple Coulomb potential $V(\mathbf{r}) \propto |\mathbf{r}|^{-1}$ for example provides a description of a Hydrogen atom, that is an electron moving in the electric field of a heavy proton. The electron is bound to the proton in a neutral atom, so that its energy spectrum is discrete. The Schrodinger equation predicts the spectrum which is completely consistent with all observations of Hydrogen radiation spectra and hence provides a complete and successful microscopic theory of the Hydrogen atom (Bohr's and Sommerfeld's descriptions were phenomenological). The extended states, on the other hand, describe electron scattering from a Hydrogen ion (bare proton).

Some important properties

- The solutions of the stationary Schrodinger equation are labeled by so called *quantum numbers*. These are either the physical measurable quantities that characterize the stationary quantum states of the system, or their representatives (which are demonstrated in the examples below). Different systems have different quantum numbers.
- Energy E is always a quantum number. In many situations multiple solutions of the stationary Schrodinger equation can be found for the same energy. These solutions are said to be *degenerate*. We must label degenerate solutions by additional quantum numbers. In general, conserved physical quantities provide quantum numbers. For example, the potential $V(\mathbf{r}) \propto |\mathbf{r}|^{-1}$ of a Hydrogen atom is spherically symmetric, so that angular momentum is conserved and represents a good quantum number.
- The Schrodinger equation always has a trivial solution $\psi(\mathbf{r}) = 0$, which describes the absence of a particle.
- If $\psi(\mathbf{r}, t)$ is a solution of the time-dependent Schrodinger equation, so is $A\psi(\mathbf{r}, t)$ for any complex constant A . However, these two solutions are physically equivalent. First, when we normalize the wavefunction $A\psi(\mathbf{r}, t)$ we fix the modulus $|A|$. Only the phase of A remains undetermined. However, this phase does not affect any observable properties as we shall discuss later, and hence is unphysical. Only relative phases matter in quantum mechanics and give rise to various quantum interference phenomena.

- If $\psi_1(\mathbf{r}, t)$ and $\psi_2(\mathbf{r}, t)$ are solutions of the time-dependent Schrodinger equation, so is $A_1\psi_1(\mathbf{r}, t) + A_2\psi_2(\mathbf{r}, t)$. On the other hand, $A_1\psi_1(\mathbf{r}) + A_2\psi_2(\mathbf{r})$ is the solution of the stationary Schrodinger equation only if $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ are degenerate solutions at the same energy E .
- If $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ are the non-degenerate solutions of the stationary Schrodinger equation, with energies E_1 and E_2 respectively, then they are orthogonal:

$$\int d^3r \psi_1^*(\mathbf{r})\psi_2(\mathbf{r}) = 0$$

Quantum-mechanical effects

- This section illustrates a couple of important quantum phenomena which do not have classical analogues. The examples are solved in one-dimensional space to keep things simple and demonstrate some important calculation techniques.

Particle in an infinitely deep quantum well

- Here we solve the one-dimensional Schrodinger equation:

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x)$$

in the potential:

$$V(x) = \left\{ \begin{array}{ll} \infty & , \quad x < 0 \\ 0 & , \quad 0 < x < a \\ \infty & , \quad a < x \end{array} \right\}$$

This potential is an infinitely deep quantum well: a particle can be located only at $0 < x < a$ since it costs infinite potential energy to place it anywhere else.

- We seek solutions at finite values for energy E . Also, $\psi(x)$ must be finite in order to be normalizable. Only such solutions are physically observable.
- Clearly, $\psi(x)$ must be zero outside the potential well, because otherwise we get a finite value $E\psi(x)$ on the right-hand side and infinite value $V(x)\psi(x)$ on the left-hand side for $x < 0$ or $x > a$.
- $\psi(x)$ must vary smoothly with x . Otherwise, the second derivative on the left-hand side blows up and we cannot satisfy the equation inside the well where $V(x)$, $\psi(x)$ and E are finite.
- Consequently, we must require $\psi(0) = 0$ and $\psi(a) = 0$. These are *boundary conditions*.
- Inside the well $V(x) = 0$ so the Schrodinger equation is very simple:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \quad , \quad 0 < x < a$$

The most general solution of this differential equation is:

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

where A and B are complex constants to be determined, and k can be thought of as a quantum number.

- We can immediately use the boundary conditions:

$$\begin{aligned} x = 0 : & \quad \psi(0) = B = 0 \\ x = a : & \quad \psi(a) = A \sin(ka) = 0 \end{aligned}$$

The first condition eliminates B . The second condition could be satisfied by choosing $A = 0$, but this would give us the trivial solution $\psi(x) = 0$. Therefore, we must choose a finite value for A , which still cannot be determined, and select such k that $\sin(ka) = 0$. This is readily accomplished by

$$k = \frac{\pi}{a}n$$

where n is a positive integer. Note that choosing $n = 0$ would also give us the trivial solution $\psi(x) = 0$, so we don't accept it. Furthermore, choosing $n < 0$ is equivalent to choosing a positive value for n and reversing the sign of A . This does not generate a physically different solution: it is merely a non-physical global phase factor $e^{i\pi} = -1$. All physically non-equivalent and non-trivial solutions are generated for positive integers n .

- Now, substitute $\psi(x) = A \sin(kx)$ in the Schrodinger equation:

$$\frac{\hbar^2 k^2}{2m} A \sin(kx) = E \times A \sin(kx) \quad , \quad 0 < x < a$$

We see that energy takes discrete values:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \quad , \quad n \in \{1, 2, 3, \dots\}$$

- We can determine A only from the normalization condition:

$$\int_0^a dx |\psi(x)|^2 = |A|^2 \int_0^a dx \sin^2(kx) = |A|^2 \frac{a}{2} \left(1 - \frac{\sin(2ka)}{2ka}\right) = 1$$

However, since $ka = n\pi$, we find $\sin(2ka) = \sin(2\pi n) = 0$. Therefore:

$$A = \sqrt{\frac{2}{a}} \times e^{i\theta}$$

The value of θ is arbitrary, so set $\theta = 0$.

- The normalized solutions of the Schrodinger equation are:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad , \quad 0 < x < a$$

$$\psi_n(x) = 0 \quad , \quad x < 0 \quad \text{or} \quad x > a$$

with energy levels

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

obtained for $n \in \{1, 2, 3, \dots\}$.

- It is customary to call n a quantum number in a problem of this kind. All states are localized, so the energy spectrum is fully discrete and easily labeled by one dimensionless (integer) number. Physically, n simply represents energy.

Quantum tunneling through a potential barrier

- Here we solve the one-dimensional stationary Schrodinger equation of the potential:

$$V(x) = \left\{ \begin{array}{ll} 0 & , \quad x < 0 \\ V & , \quad 0 < x < a \\ 0 & , \quad a < x \end{array} \right\}$$

where V is finite and positive. This potential describes a barrier. Classically, a particle has larger energy if it sits within $0 < x < a$ than anywhere else. A quantum particle is free on both the left and right side of the barrier, and there is no localization. Therefore, all quantum states will be extended, and the spectrum will be continuous.

- Outside the barrier the Schrodinger equation is simple:

$$-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x) \quad , \quad x < 0 \quad \text{or} \quad x > a$$

and the solutions are plane waves. This time we write the solution in the form

$$\begin{aligned} \psi(x) &= A_R e^{ikx} + A_L e^{-ikx} \quad , \quad x < 0 \\ \psi(x) &= C_R e^{ikx} + C_L e^{-ikx} \quad , \quad x > a \end{aligned}$$

with unknown coefficients A_L, A_R, C_L, C_R . This choice is motivated by the view of a right-moving plane de Broglie wave $A_R e^{ikx}$ approaching the barrier from $x \rightarrow -\infty$ and partially reflecting back as $A_L e^{-ikx}$. The subscripts L, R refer to the direction of wave propagation, left or right. The wave scattering on the barrier is elastic: energy must be conserved, and since $E = \hbar^2 k^2 / 2m$ the incident and reflected wave must have the same wavenumber k . The wave beyond the barrier must have the same form, with possibly different coefficients C_L and C_R . However, we shall seek solutions with $C_L = 0$ and ask only what fraction of the incident wave passes through the barrier and continues to propagate rightwards (C_R). We could have considered a more complicated problem with $C_L \neq 0$, but then we would have two incident waves coming from opposite directions which both partially reflect and partially go through the barrier.

- Since all states are extended, energy spectrum is continuous. In fact, energy E can be arbitrarily small because the barrier occupies only a finite fraction of space and hence has no physical impact in far-away regions. The energy spectrum is simply the same as for free particles.
- In classical physics, a particle can cross the barrier only if its energy is larger than the barrier potential, $E > V$. In that case, a classical particle always crosses the barrier, while for $E < V$ the particle must bounce back. In quantum mechanics even particles (waves) with $E < V$ can partially pass through the barrier and be detected on the other side. This is known as *quantum tunneling*.
- We wish to calculate reflection and transmission probabilities for the incident wave. We need to solve the Schrodinger equation inside the barrier:

$$-\frac{\hbar^2}{2m}\psi''(x) = (E - V)\psi(x) \quad , \quad 0 < x < a$$

We have to distinguish two cases. For $E > V$ we can find solutions in the form:

$$\psi(x) = B_R e^{ik'x} + B_L e^{-ik'x} \quad , \quad 0 < x < a \quad , \quad E - V = \frac{\hbar^2 k'^2}{2m} > 0$$

but for $E < V$ the solutions are:

$$\psi(x) = \beta_R e^{\kappa x} + \beta_L e^{-\kappa x} \quad , \quad 0 < x < a \quad , \quad E - V = -\frac{\hbar^2 \kappa^2}{2m} < 0$$

This can be easily verified by substituting in the Schrodinger equation only one of the two components of $\psi(x)$ and noting that k' and $-k'$ (or κ and $-\kappa$) give the same energy and can be used to form superpositions. Here we assume $k' > 0$ or $\kappa > 0$.

- Now we need to relate the coefficients by writing boundary conditions. The wavefunction must be finite, and have a finite second derivative. This implies that $\psi(x)$ and $\psi'(x)$ must vary smoothly with x , specifically across the points $x = 0$ and $x = a$. We are interested in:

$$\begin{aligned} R &= \frac{|A_L|^2}{|A_R|^2} \quad \dots \quad \text{reflection probability (the probability of bouncing back)} \\ T &= \frac{|C_R|^2}{|A_R|^2} \quad \dots \quad \text{transmission probability (the probability of passing through the barrier)} \end{aligned}$$

- For $E > V$:

$$\begin{aligned}\psi(0) &= A_R + A_L = B_R + B_L \\ \psi'(0) &= ik(A_R - A_L) = ik'(B_R - B_L) \\ \psi(a) &= B_R e^{ik'a} + B_L e^{-ik'a} = C_R e^{ika} \\ \psi'(a) &= ik'(B_R e^{ik'a} - B_L e^{-ik'a}) = ikC_R e^{ika}\end{aligned}$$

These boundary conditions are four linear equations with five unknowns. We can express four coefficients in terms of one coefficient which can be ultimately determined only by normalization. Therefore, we choose to express all coefficients in terms of A_R which we need not determine if we are interested only in the reflection and transmission probabilities. Solving these equations we find:

$$\begin{aligned}R &= \left[1 + \frac{4k^2 k'^2}{(k^2 - k'^2)^2 \sin^2(k'a)} \right]^{-1} \\ T &= \left[1 + \frac{(k^2 - k'^2)^2 \sin^2(k'a)}{4k^2 k'^2} \right]^{-1}\end{aligned}$$

- For $E < V$:

$$\begin{aligned}\psi(0) &= A_R + A_L = \beta_R + \beta_L \\ \psi'(0) &= ik(A_R - A_L) = \kappa(\beta_R - \beta_L) \\ \psi(a) &= \beta_R e^{\kappa a} + \beta_L e^{-\kappa a} = C_R e^{ika} \\ \psi'(a) &= \kappa(\beta_R e^{\kappa a} - \beta_L e^{-\kappa a}) = ikC_R e^{ika}\end{aligned}$$

Solving these equations we find:

$$\begin{aligned}R &= \left[1 + \frac{4k^2 \kappa^2}{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)} \right]^{-1} \\ T &= \left[1 + \frac{(k^2 + \kappa^2)^2 \sinh^2(\kappa a)}{4k^2 \kappa^2} \right]^{-1}\end{aligned}$$

which, of course, can be obtained from the $E > V$ solution by substituting $k' = -i\kappa$. Note that in all cases $R + T = 1$ as it should be: the incoming particle must be either reflected or transmitted. To verify this, note that R and T have the forms $R = 1/(1 + a)$ and $T = 1/(1 + a^{-1})$, which always yields $R + T = 1$.

Born's interpretation of the wavefunction, expectation values and quantum measurements

- According to the Born's interpretation, $P(\mathbf{r}, t) = |\psi(\mathbf{r}, t)|^2$ is the probability density to detect the quantum particle at position \mathbf{r} in a measurement at time t , provided that the wavefunction $\psi(\mathbf{r}, t)$ is properly normalized. We can apply this interpretation to stationary solutions as well, in which case the time dependence drops out: $P(\mathbf{r}, t) = |\psi(\mathbf{r})e^{-i\omega t}|^2 = |\psi(\mathbf{r})|^2 = P(\mathbf{r})$.
- Since $P(\mathbf{r})$ is the probability density of finding the particle at position \mathbf{r} , we can calculate the average position of the particle:

$$\langle \mathbf{r} \rangle = \int d^3r \mathbf{r} P(\mathbf{r}) = \int d^3r \psi^*(\mathbf{r}) \mathbf{r} \psi(\mathbf{r})$$

The result makes sense only if the particle is localized inside a finite volume.

- We can generalize this to calculate expectation values for other physical quantities, for instance momentum. Physical quantities, or *observables*, are represented by *operators* in quantum mechanics which act on the wavefunction. For example, we constructed the Schrodinger equation by extracting momentum and energy from the wavefunction and fitting to the energy conservation law. We took a time derivative to extract energy and spatial derivatives to extract the momentum vector from the wavefunction. We can regard these derivatives as operators which convert the function they act on into another function. Then, we associate the following operators to energy and momentum observables:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} &\longrightarrow \text{energy: } E \\ -i\hbar \frac{\partial}{\partial x} &\longrightarrow \text{momentum in } x \text{ direction: } p_x \end{aligned}$$

The average momentum of a particle in a stationary state is:

$$\langle \mathbf{p} \rangle = \int d^3r \psi^*(\mathbf{r}) (-i\hbar \nabla) \psi(\mathbf{r})$$

where

$$\nabla = \hat{\mathbf{x}} \frac{\partial}{\partial x} + \hat{\mathbf{y}} \frac{\partial}{\partial y} + \hat{\mathbf{z}} \frac{\partial}{\partial z}$$

- In general, the expectation value of an observable $\mathcal{O} = \langle \hat{\mathcal{O}} \rangle$ defined by the operator $\hat{\mathcal{O}}$ can be time-dependent:

$$\mathcal{O}(t) = \int d^3r \psi^*(\mathbf{r}, t) \hat{\mathcal{O}} \psi(\mathbf{r}, t)$$

- Hamiltonian \hat{H} is the operator associated with energy. The Schrodinger equation tells us that

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

If we calculate its expectation value in a stationary state, we find $\langle \hat{H} \rangle = E = \text{const}$ independent of time.

Quantum measurement

- The Schrodinger equation can be written in the compact operator form:

$$\hat{H}\psi = E\psi$$

This is known in mathematics as an eigenproblem. Think of $\psi(\mathbf{r})$ as a vector with a complex element for every point \mathbf{r} in space. Clearly, such a vector has infinitely many elements (uncountable infinity), but the ordering of elements labeled by \mathbf{r} can be fixed (for example, sort the element labels \mathbf{r} by x , then y , then z coordinates). Then, \hat{H} is a matrix defined in the same vector space (called Hilbert space). If we find a vector ψ such that $\hat{H}\psi$ is a constant E times the same vector ψ , then E is called an eigenvalue and ψ an eigenvector. The normalization and orthogonality of wavefunctions we discussed above translates into the normalization and orthogonality of vectors in this vector space.

- If the system is in a stationary state with energy E , then the measurement of energy will produce the result E with complete certainty. Let $\psi_E(\mathbf{r})$ be the eigenvector of \hat{H} corresponding to the eigenvalue E . The stationary state of energy E is given by the full wavefunction $\psi(\mathbf{r}, t) = \psi_E(\mathbf{r})e^{-iEt/\hbar}$. However, any superposition of solutions to the time-dependent Schrodinger equation is also a non-stationary solution:

$$\psi(\mathbf{r}, t) = \sum_E A_E \psi_E(\mathbf{r}) e^{-iEt/\hbar}$$

where A_E are arbitrary energy-dependent complex numbers, and the sum over energies includes both the discrete portions of the spectrum and continuous segments (it becomes an integral in continuous

segments). This time-dependent wavefunction is not an eigenstate of the Hamiltonian. Outcomes of energy measurements in this state are random in accord with many experimental observations. However,

$$P(E) = |A_E|^2 = \left| \int d^3r \psi_E^*(\mathbf{r}, t) \psi(\mathbf{r}, t) \right|^2$$

is the probability (density) that E will be the outcome of a measurement (we use the orthogonality property of wavefunctions to relate A_E with the integral of wavefunctions). If a normalized stationary wavefunction does not exist at some energy E' , $E = E'$ can never be an outcome of a measurement. Therefore, only Hamiltonian eigenvalues can be obtained by measuring energy (but the outcomes are random).

- What about other observables? For any observable represented by the operator \hat{O} we define an eigenproblem:

$$\hat{O}\psi = \mathcal{O}\psi$$

and require by analogy that the measurements can yield only random outcomes from the set of eigenvalues \mathcal{O} of the operator \hat{O} . The probability of measuring \mathcal{O} is given by:

$$P(\mathcal{O}, t) = \left| \int d^3r \psi_{\mathcal{O}}^*(\mathbf{r}, t) \psi(\mathbf{r}, t) \right|^2$$

where $\psi_{\mathcal{O}}(\mathbf{r}, t)$ is the eigenfunction of \mathcal{O} corresponding to its eigenvalue \mathcal{O} , and $\psi(\mathbf{r}, t)$ is the current wavefunction of the system. This is the postulate about quantum measurement in quantum mechanics.