

6. Time Evolution in Quantum Mechanics

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Until now we used quantum mechanics to predict properties of atoms and nuclei. Since we were interested mostly in the equilibrium states of nuclei and in their energies, we only needed to look at a *time-independent* description of quantum-mechanical systems. To describe dynamical processes, such as radiation decays, scattering and nuclear reactions, we need to study how quantum mechanical systems evolve in time.

6.1 Time-dependent Schrödinger equation

When we first introduced quantum mechanics, we saw that the fourth postulate of QM states that:

The evolution of a closed system is unitary (reversible). The evolution is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \mathcal{H}|\psi\rangle$$

where \mathcal{H} is the Hamiltonian of the system (the energy operator) and \hbar is the reduced Planck constant ($\hbar = h/2\pi$ with h the Planck constant, allowing conversion from energy to frequency units).

We will focus mainly on the Schrödinger equation to describe the evolution of a quantum-mechanical system. The statement that the evolution of a closed quantum system is unitary is however more general. It means that the state of a system at a later time t is given by $|\psi(t)\rangle = U(t)|\psi(0)\rangle$, where $U(t)$ is a unitary operator. An operator is unitary if its adjoint U^\dagger (obtained by taking the transpose and the complex conjugate of the operator, $U^\dagger = (U^*)^T$) is equal to its inverse: $U^\dagger = U^{-1}$ or $UU^\dagger = \mathbb{1}$.

Note that the expression $|\psi(t)\rangle = U(t)|\psi(0)\rangle$ is an integral equation relating the state at time zero with the state at time t . For example, classically we could write that $x(t) = x(0) + vt$ (where v is the speed, for constant speed). We can as well write a differential equation that provides the same information: the Schrödinger equation. Classically for example, (in the example above) the equivalent differential equation would be $\frac{dx}{dt} = v$ (more generally we would have Newton's equation linking the acceleration to the force). In QM we have a differential equation that control the evolution of closed systems. This is the Schrödinger equation:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \mathcal{H}\psi(x,t)$$

where \mathcal{H} is the system's Hamiltonian. The solution to this partial differential equation gives the wavefunction $\psi(x,t)$ at any later time, when $\psi(x,0)$ is known.

6.1.1 Solutions to the Schrödinger equation

We first try to find a solution in the case where the Hamiltonian $\mathcal{H} = \frac{\hat{p}^2}{2m} + V(x,t)$ is such that the potential $V(x,t)$ is time independent (we can then write $V(x)$). In this case we can use separation of variables to look for solutions. That is, we look for solutions that are a product of a function of position only and a function of time only:

$$\psi(x,t) = \varphi(x)f(t)$$

Then, when we take the partial derivatives we have that

$$\frac{\partial \psi(x, t)}{\partial t} = \frac{df(t)}{dt} \varphi(x), \quad \frac{\partial \psi(x, t)}{\partial x} = \frac{d\varphi(x)}{dx} f(t) \quad \text{and} \quad \frac{\partial^2 \psi(x, t)}{\partial x^2} = \frac{d^2 \varphi(x)}{dx^2} f(t)$$

The Schrödinger equation simplifies to

$$i\hbar \frac{df(t)}{dt} \varphi(x) = -\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} f(t) + V(x) \varphi(x) f(t)$$

Dividing by $\psi(x, t)$ we have:

$$i\hbar \frac{df(t)}{dt} \frac{1}{f(t)} = -\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} \frac{1}{\varphi(x)} + V(x)$$

Now the LHS is a function of time only, while the RHS is a function of position only. For the equation to hold, both sides have then to be equal to a constant (separation constant):

$$i\hbar \frac{df(t)}{dt} \frac{1}{f(t)} = E, \quad -\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} \frac{1}{\varphi(x)} + V(x) = E$$

The two equations we find are a simple equation in the time variable:

$$\frac{df(t)}{dt} = -\frac{i}{\hbar} E f(t), \quad \rightarrow \quad f(t) = f(0) e^{-i \frac{Et}{\hbar}}$$

and

$$-\frac{\hbar^2}{2m} \frac{d^2 \varphi(x)}{dx^2} \frac{1}{\varphi(x)} + V(x) = E$$

that we have already seen as the time-independent Schrödinger equation. We have extensively studied the solutions of the this last equation, as they are the eigenfunctions of the energy-eigenvalue problem, giving the stationary (equilibrium) states of quantum systems. Note that for these stationary solutions $\varphi(x)$ we can still find the corresponding total wavefunction, given as stated above by $\psi(x, t) = \varphi(x) f(t)$, which does describe also the time evolution of the system:

$$\psi(x, t) = \varphi(x) e^{-i \frac{Et}{\hbar}}$$

Does this mean that the states that up to now we called stationary are instead evolving in time?

The answer is yes, but with a caveat. Although the states themselves evolve as stated above, any measurable quantity (such as the probability density $|\psi(x, t)|^2$ or the expectation values of observable, $\langle A \rangle = \int \psi(x, t)^* A[\psi(x, t)]$) are still time-independent. (Check it!)

Thus we were correct in calling these states **stationary** and neglecting in practice their time-evolution when studying the properties of systems they describe.

Notice that the wavefunction built from one energy eigenfunction, $\psi(x, t) = \varphi(x) f(t)$, is only a particular solution of the Schrödinger equation, but many other are possible. These will be complicated functions of space and time, whose shape will depend on the particular form of the potential $V(x)$. How can we describe these general solutions? We know that in general we can write a basis given by the eigenfunction of the Hamiltonian. These are the functions $\{\varphi(x)\}$ (as defined above by the time-independent Schrödinger equation). The eigenstate of the Hamiltonian do not evolve. However we can write any wavefunction as

$$\psi(x, t) = \sum_k c_k(t) \varphi_k(x)$$

This just corresponds to express the wavefunction in the *basis* given by the energy eigenfunctions. As usual, the coefficients $c_k(t)$ can be obtained at any instant in time by taking the inner product: $\langle \varphi_k | \psi(x, t) \rangle$.

What is the evolution of such a function? Substituting in the Schrödinger equation we have

$$i\hbar \frac{\partial (\sum_k c_k(t) \varphi_k(x))}{\partial t} = \sum_k c_k(t) \mathcal{H} \varphi_k(x)$$

that becomes

$$i\hbar \sum_k \frac{\partial (c_k(t))}{\partial t} \varphi_k(x) = \sum_k c_k(t) E_k \varphi_k(x)$$

For each φ_k we then have the equation in the coefficients only

$$i\hbar \frac{dc_k}{dt} = E_k c_k(t) \quad \rightarrow \quad c_k(t) = c_k(0) e^{-i \frac{E_k t}{\hbar}}$$

A general solution of the Schrödinger equation is then

$$\psi(x, t) = \sum_k c_k(0) e^{-i \frac{E_k t}{\hbar}} \varphi_k(x)$$

Obs. We can define the eigen-frequencies $\hbar\omega_k = E_k$ from the eigen-energies. Thus we see that the wavefunction is a superposition of waves φ_k propagating in time each with a different frequency ω_k .

The behavior of quantum systems –even particles– thus often is similar to the propagation of waves. One example is the diffraction pattern for electrons (and even heavier objects) when scattering from a slit. We saw an example in the electron diffraction video at the beginning of the class.

Obs. What is the probability of measuring a certain energy E_k at a time t ? It is given by the coefficient of the φ_k eigenfunction, $|c_k(t)|^2 = |c_k(0) e^{-i \frac{E_k t}{\hbar}}|^2 = |c_k(0)|^2$. This means that the probability for the given energy is constant, does not change in time. Energy is then a so-called constant of the motion. This is true only for the energy eigenvalues, not for other observables.

Example: Consider instead the probability of finding the system at a certain position, $p(x) = |\psi(x, t)|^2$. This of course changes in time. For example, let $\psi(x, 0) = c_1(0)\varphi_1(x) + c_2(0)\varphi_2(x)$, with $|c_1(0)|^2 + |c_2(0)|^2 = |c_1|^2 + |c_2|^2 = 1$ (and $\varphi_{1,2}$ normalized energy eigenfunctions). Then at a later time we have $\psi(x, t) = c_1(0)e^{-i\omega_1 t}\varphi_1(x) + c_2(0)e^{-i\omega_2 t}\varphi_2(x)$. What is $p(x, t)$?

$$\begin{aligned} & |c_1(0)e^{-i\omega_1 t}\varphi_1(x) + c_2(0)e^{-i\omega_2 t}\varphi_2(x)|^2 \\ &= |c_1(0)|^2 |\varphi_1(x)|^2 + |c_2(0)|^2 |\varphi_2(x)|^2 + c_1^* c_2 \varphi_1^* \varphi_2 e^{-i(\omega_2 - \omega_1)t} + c_1 c_2^* \varphi_1 \varphi_2^* e^{i(\omega_2 - \omega_1)t} \\ &= |c_1|^2 + |c_2|^2 + 2\text{Re} \left[c_1^* c_2 \varphi_1^* \varphi_2 e^{-i(\omega_2 - \omega_1)t} \right] \end{aligned}$$

The last term describes a wave interference between different components of the initial wavefunction.

Obs.: The expressions found above for the time-dependent wavefunction are only valid if the potential is itself time-independent. If this is not the case, the solutions are even more difficult to obtain.

6.1.2 Unitary Evolution

We saw two equivalent formulation of the quantum mechanical evolution, the Schrödinger equation and the Heisenberg equation. We now present a third possible formulation: following the 4th postulate we express the evolution of a state in terms of a unitary operator, called the **propagator**:

$$\psi(x, t) = \hat{U}(t)\psi(x, 0)$$

with $\hat{U}^\dagger \hat{U} = \mathbb{1}$. (Notice that a priori the unitary operator \hat{U} could also be a function of space). We can show that this is equivalent to the Schrödinger equation, by verifying that $\psi(x, t)$ above is a solution:

$$i\hbar \frac{\partial \hat{U}\psi(x, 0)}{\partial t} = \mathcal{H}\hat{U}\psi(x, 0) \quad \rightarrow \quad i\hbar \frac{\partial \hat{U}}{\partial t} = \mathcal{H}\hat{U}$$

where in the second step we used the fact that since the equation holds for any wavefunction ψ it must hold for the operator themselves. If the Hamiltonian is time independent, the second equation can be solved easily, obtaining:

$$i\hbar \frac{\partial \hat{U}}{\partial t} = \mathcal{H}\hat{U} \quad \rightarrow \quad \hat{U}(t) = e^{-i\mathcal{H}t/\hbar}$$

where we set $\hat{U}(t=0) = \mathbb{1}$. Notice that as desired \hat{U} is unitary, $\hat{U}^\dagger \hat{U} = e^{i\mathcal{H}t/\hbar} e^{-i\mathcal{H}t/\hbar} = \mathbb{1}$.

6.2 Evolution of wave-packets

In Section 6.1.1 we looked at the evolution of a general wavefunction under a time-independent Hamiltonian. The solution to the Schrödinger equation was given in terms of a linear superposition of energy eigenfunctions, each acquiring a time-dependent phase factor. The solution was then the superposition of waves each with a different frequency.

Now we want to study the case where the eigenfunctions form a continuous basis, $\{\varphi_k\} \rightarrow \{\varphi(k)\}$. More precisely, we want to describe how a free particle evolves in time. We already found the eigenfunctions of the free particle Hamiltonian ($\mathcal{H} = \hat{p}^2/2m$): they were given by the momentum eigenfunctions e^{ikx} and describe more properly a traveling wave. A particle localized in space instead can be described by wavepacket $\psi(x, 0)$ initially well localized in x -space (for example, a Gaussian wavepacket).

How does this wave-function evolve in time? First, following Section 2.2.1, we express the wavefunction in terms of momentum (and energy) eigenfunctions:

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \bar{\psi}(k) e^{ikx} dk,$$

We saw that this is equivalent to the Fourier transform of $\bar{\psi}(k)$, then $\psi(x, 0)$ and $\bar{\psi}(k)$ are a Fourier pair (can be obtained from each other via a Fourier transform).

Thus the function $\bar{\psi}(k)$ is obtained by Fourier transforming the wave-function at $t = 0$. Notice again that the function $\bar{\psi}(k)$ is the continuous-variable equivalent of the coefficients $c_k(0)$.

The second step is to evolve in time the superposition. From the previous section we know that each energy eigenfunction evolves by acquiring a phase $e^{-i\omega(k)t}$, where $\omega(k) = E_k/\hbar$ is the energy eigenvalue. Then the time evolution of the wavefunction is

$$\psi(x, t) = \int_{-\infty}^{\infty} \bar{\psi}(k) e^{i\varphi(k)} dk,$$

where

$$\varphi(k) = kx - \omega(k)t.$$

For the free particle we have $\omega_k = \frac{\hbar k^2}{2m}$. If the particle encounters instead a potential (such as in the potential barrier or potential well problems we already saw) ω_k could have a more complex form. We will thus consider this more general case.

Now, if $\bar{\psi}(k)$ is **strongly peaked** around $k = k_0$, it is a reasonable approximation to Taylor expand $\varphi(k)$ about k_0 .

We can then approximate $\bar{\psi}(k)$ by $\bar{\psi}(k) \approx e^{-\frac{(k-k_0)^2}{4(\Delta k)^2}}$ and keeping terms up to second-order in $k - k_0$, we obtain

$$\psi(x, t) \propto \int_{-\infty}^{\infty} e^{-\frac{(k-k_0)^2}{4(\Delta k)^2}} \exp\left[-ikx + i\left\{\varphi_0 + \varphi'_0(k-k_0) + \frac{1}{2}\varphi''_0(k-k_0)^2\right\}\right] dk,$$

where

$$\begin{aligned} \varphi_0 &= \varphi(k_0) = k_0 x - \omega_0 t, \\ \varphi'_0 &= \frac{d\varphi(k_0)}{dk} = x - v_g t, \\ \varphi''_0 &= \frac{d^2\varphi(k_0)}{dk^2} = -\alpha t, \end{aligned}$$

$$-ikx + i\left\{k_0 x - \omega_0 t + (x - v_g t)(k - k_0) + \frac{1}{2}\varphi''_0(k - k_0)^2\right\}$$

with

$$\omega_0 = \omega(k_0), \quad v_g = \frac{d\omega(k_0)}{dk}, \quad \alpha = \frac{d^2\omega(k_0)}{dk^2}.$$

As usual, the variance of the initial wavefunction and of its Fourier transform are related: $\Delta k = 1/(2\Delta x)$, where Δx is the initial width of the wave-packet and Δk the spread in the momentum. Changing the variable of integration to $y = (k - k_0)/(2\Delta k)$, we get

$$\psi(x, t) \propto e^{i(k_0 x - \omega_0 t)} \int_{-\infty}^{\infty} e^{i\beta_1 y - (1+i\beta_2)y^2} dy,$$

where

$$\begin{aligned} \beta_1 &= 2\Delta k(x - x_0 - v_g t), \\ \beta_2 &= 2\alpha(\Delta k)^2 t, \end{aligned}$$

The above expression can be rearranged to give

$$\psi(x, t) \propto e^{i(k_0 x - \omega_0 t) - (1+i\beta_2)\beta^2/4} \int_{-\infty}^{\infty} e^{-(1+i\beta_2)(y-y_0)^2} dy,$$

where $y_0 = i\beta/2$ and $\beta = \beta_1/(1+i\beta_2)$.

Again changing the variable of integration to $z = (1+i\beta_2)^{1/2}(y-y_0)$, we get

$$\psi(x, t) \propto (1+i\beta_2)^{-1/2} e^{i(k_0 x - \omega_0 t) - (1+i\beta_2)\beta^2/4} \int_{-\infty}^{\infty} e^{-z^2} dz.$$

The integral now just reduces to a number. Hence, we obtain

$$\psi(x, t) \propto \frac{e^{i(k_0 x - \omega_0 t)} e^{-\frac{(x - x_0 - v_g t)^2 [1 - i2\alpha \Delta k^2 t]}{4\sigma(t)^2}}}{\sqrt{1 + i2\alpha (\Delta k)^2 t}},$$

where

$$\sigma^2(t) = (\Delta x)^2 + \frac{\alpha^2 t^2}{4(\Delta x)^2}.$$

Note that even if we made an approximation earlier by Taylor expanding the phase factor $\varphi(k)$ about $k = k_0$, the above wave-function is still identical to our original wave-function at $t = 0$.

The probability density of our particle as a function of times is written

$$|\psi(x, t)|^2 \propto \sigma^{-1}(t) \exp\left[-\frac{(x - x_0 - v_g t)^2}{2\sigma^2(t)}\right].$$

Hence, the probability distribution is a Gaussian, of characteristic width $\sigma(t)$ (increasing in time), which peaks at $x = x_0 + v_g t$. Now, the most likely position of our particle obviously coincides with the peak of the distribution function. Thus, the particle's most likely position is given by

$$x = x_0 + v_g t.$$

It can be seen that the particle effectively moves at the uniform velocity

$$v_g = \frac{d\omega}{dk},$$

which is known as the **group-velocity**. In other words, a plane-wave travels at the phase-velocity, $v_p = \omega/k$, whereas a wave-packet travels at the group-velocity, $v_g = d\omega/dk$. From the dispersion relation for particle waves the group velocity is

$$v_g = \frac{d(\hbar\omega)}{d(\hbar k)} = \frac{dE}{dp} = \frac{p}{m}.$$

which is identical to the classical particle velocity. Hence, the dispersion relation turns out to be consistent with classical physics, after all, as soon as we realize that particles must be identified with **wave-packets** rather than plane-waves.

Note that the width of our wave-packet grows as time progresses: the characteristic time for a wave-packet of original width Δx to double in spatial extent is

$$t_2 \sim \frac{m(\Delta x)^2}{\hbar}.$$

So, if an electron is originally localized in a region of atomic scale (i.e., $\Delta x \sim 10^{-10}$ m) then the doubling time is only about 10^{-16} s. Clearly, particle wave-packets (for freely moving particles) spread very rapidly.

The rate of spreading of a wave-packet is ultimately governed by the second derivative of $\omega(k)$ with respect to k , $\frac{\partial^2 \omega}{\partial k^2}$. This is why the relationship between ω and k is generally known as a **dispersion relation**, because it governs how wave-packets disperse as time progresses.

If we consider light-waves, then ω is a *linear* function of k and the second derivative of ω with respect to k is zero. This implies that there is no dispersion of wave-packets, wave-packets propagate without changing shape. This is of course true for any other wave for which $\omega(k) \propto k$. Another property of linear dispersion relations is that the phase-velocity, $v_p = \omega/k$, and the group-velocity, $v_g = d\omega/dk$ are identical. Thus a light pulse propagates at the same speed of a plane light-wave; both propagate through a vacuum at the characteristic speed $c = 3 \times 10^8$ m/s.

Of course, the dispersion relation for particle waves is *not* linear in k (for example for free particles is quadratic). Hence, particle plane-waves and particle wave-packets propagate at different velocities, and particle wave-packets also gradually disperse as time progresses.

6.3 Evolution of operators and expectation values

The Schrödinger equation describes how the state of a system evolves. Since via experiments we have access to observables and their outcomes, it is interesting to find a differential equation that directly gives the evolution of expectation values.

6.3.1 Heisenberg Equation

We start from the definition of expectation value and take its derivative wrt time

$$\begin{aligned} \frac{d\langle \hat{A} \rangle}{dt} &= \frac{d}{dt} \int d^3x \psi(x, t)^* \hat{A} \psi(x, t) \\ &= \int d^3x \frac{\partial \psi(x, t)^*}{\partial t} \hat{A} \psi(x, t) + \int d^3x \psi(x, t)^* \frac{\partial \hat{A}}{\partial t} \psi(x, t) + \int d^3x \psi(x, t)^* \hat{A} \frac{\partial \psi(x, t)}{\partial t} \end{aligned}$$

We then use the Schrödinger equation:

$$\frac{\partial \psi(x, t)}{\partial t} = -\frac{i}{\hbar} \mathcal{H} \psi(x, t), \quad \frac{\partial \psi^*(x, t)}{\partial t} = \frac{i}{\hbar} (\mathcal{H} \psi(x, t))^*$$

and the fact $(\mathcal{H} \psi(x, t))^* = \psi(x, t)^* \mathcal{H}^* = \psi(x, t)^* \mathcal{H}$ (since the Hamiltonian is *hermitian* $\mathcal{H}^* = \mathcal{H}$). With this, we have

$$\begin{aligned} \frac{d\langle \hat{A} \rangle}{dt} &= \frac{i}{\hbar} \int d^3x \psi(x, t)^* \mathcal{H} \hat{A} \psi(x, t) + \int d^3x \psi(x, t)^* \frac{\partial \hat{A}}{\partial t} \psi(x, t) - \frac{i}{\hbar} \int d^3x \psi(x, t)^* \hat{A} \mathcal{H} \psi(x, t) \\ &= \frac{i}{\hbar} \int d^3x \psi(x, t)^* [\mathcal{H} \hat{A} - \hat{A} \mathcal{H}] \psi(x, t) + \int d^3x \psi(x, t)^* \frac{\partial \hat{A}}{\partial t} \psi(x, t) \end{aligned}$$

We now rewrite $[\mathcal{H} \hat{A} - \hat{A} \mathcal{H}] = [\mathcal{H}, \hat{A}]$ as a commutator and the integrals as expectation values:

$$\boxed{\frac{d\langle \hat{A} \rangle}{dt} = \frac{i}{\hbar} \langle [\mathcal{H}, \hat{A}] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle}$$

Obs. Notice that if the observable itself is time independent, then the equation reduces to $\frac{d\langle \hat{A} \rangle}{dt} = \frac{i}{\hbar} \langle [\mathcal{H}, \hat{A}] \rangle$. Then if the observable \hat{A} commutes with the Hamiltonian, we have no evolution at all of the expectation value. An observable that commutes with the Hamiltonian is a constant of the motion. For example, we see again why energy is a constant of the motion (as seen before).

Notice that since we can take the expectation value with respect to any wavefunction, the equation above must hold also for the operators themselves. Then we have the **Heisenberg equation**:

$$\boxed{\frac{d\hat{A}}{dt} = \frac{i}{\hbar} [\mathcal{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t}}$$

This is an equivalent formulation of the system's evolution (equivalent to the Schrödinger equation).

Obs. Notice that if the operator A is time independent and it commutes with the Hamiltonian \mathcal{H} then the operator is conserved, it is a constant of the motion (not only its expectation value).

Consider for example the angular momentum operator \hat{L}^2 for a central potential system (i.e. with potential that only depends on the distance, $V(r)$). We have seen when solving the 3D time-independent equation that $[\mathcal{H}, \hat{L}^2] = 0$. Thus the angular momentum is a constant of the motion.

6.3.2 Ehrenfest's theorem

We now apply this result to calculate the evolution of the expectation values for position and momentum.

$$\frac{d\langle \hat{x} \rangle}{dt} = \frac{i}{\hbar} \langle [\mathcal{H}, \hat{x}] \rangle = \frac{i}{\hbar} \left\langle \left[\frac{\hat{p}^2}{2m} + V(x), \hat{x} \right] \right\rangle$$

Now we know that $[V(x), \hat{x}] = 0$ and we already calculated $[\hat{p}^2, \hat{x}] = -2i\hbar\hat{p}$. So we have:

$$\boxed{\frac{d\langle \hat{x} \rangle}{dt} = \frac{1}{m} \langle \hat{p} \rangle}$$

Notice that this is the same equation that links the classical position with momentum (remember $p/m = v$ velocity). Now we turn to the equation for the momentum:

$$\frac{d\langle\hat{p}\rangle}{dt} = \frac{i}{\hbar} \langle[\mathcal{H}, \hat{p}]\rangle = \frac{i}{\hbar} \left\langle \left[\frac{\hat{p}^2}{2m} + V(x), \hat{p} \right] \right\rangle$$

Here of course $[\frac{\hat{p}^2}{2m}, \hat{p}] = 0$, so we only need to calculate $[V(x), \hat{p}]$. We substitute the explicit expression for the momentum:

$$\begin{aligned} [V(x), \hat{p}]f(x) &= V(x) \left[-i\hbar \frac{\partial f(x)}{\partial x} \right] - \left[-i\hbar \frac{\partial (V(x)f(x))}{\partial x} \right] \\ &= -V(x)i\hbar \frac{\partial f(x)}{\partial x} + i\hbar \frac{\partial V(x)}{\partial x} f(x) + i\hbar \frac{\partial f(x)}{\partial x} V(x) = i\hbar \frac{\partial V(x)}{\partial x} f(x) \end{aligned}$$

Then,

$$\boxed{\frac{d\langle\hat{p}\rangle}{dt} = - \left\langle \frac{\partial V(x)}{\partial x} \right\rangle}$$

Obs. Notice that in these two equations \hbar has been canceled out. Also the equation involve only real variables (as in classical mechanics).

Obs. Usually, the derivative of a potential function is a force, so we can write $-\frac{\partial V(x)}{\partial x} = F(x)$. If we could approximate $\langle F(x) \rangle \approx F(\langle x \rangle)$, then the two equations are rewritten:

$$\frac{d\langle\hat{x}\rangle}{dt} = \frac{1}{m} \langle\hat{p}\rangle \quad \frac{d\langle\hat{p}\rangle}{dt} = F(\langle x \rangle)$$

These are two equations in the expectation values only. Then we could just make the substitutions $\langle\hat{p}\rangle \rightarrow p$ and $\langle\hat{x}\rangle \rightarrow x$ (i.e. identify the expectation values of QM operators with the corresponding classical variables). We obtain in this way the usual classical equation of motions. This is **Ehrenfest's theorem**.

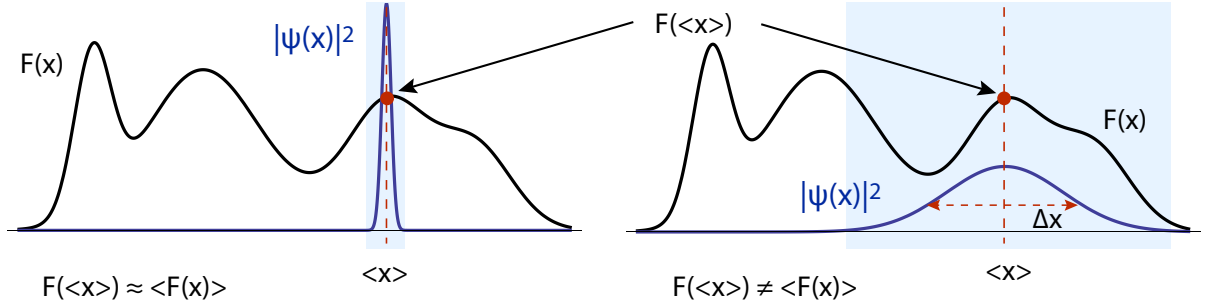


Fig. 40: Localized (left) and spread-out (right) wavefunction. In the plot the absolute value square of the wavefunction is shown in blue (corresponding to the position probability density) for a system approaching the classical limit (left) or showing more quantum behavior. The force acting on the system is shown in black (same in the two plots). The shaded areas indicate the region over which $|\psi(x)|^2$ is non-negligible, thus giving an idea of the region over which the force is averaged. The wavefunctions give the same average position $\langle x \rangle$. However, while for the left one $F(\langle x \rangle) \approx \langle F(x) \rangle$, for the right wavefunction $F(\langle x \rangle) \neq \langle F(x) \rangle$.

When is the approximation above valid? We want $\left\langle \frac{\partial V(x)}{\partial x} \right\rangle \approx \frac{\partial V(\langle x \rangle)}{\partial \langle x \rangle}$. This means that the wavefunction is localized enough such that the width of the position probability distribution is small compared to the typical length scale over which the potential varies. When this condition is satisfied, then the expectation values of quantum-mechanical probability observable will follow a classical trajectory.

Assume for example $\psi(x)$ is an eigenstate of the position operator $\psi(x) = \delta(x - \bar{x})$. Then $\langle\hat{x}\rangle = \int dx x \delta(x - \bar{x}) = \bar{x}$ and

$$\left\langle \frac{\partial V(x)}{\partial x} \right\rangle = \int \frac{\partial V(x)}{\partial x} \delta(x - \langle x \rangle) dx = \frac{\partial V(\langle x \rangle)}{\partial \langle x \rangle}$$

If instead the wavefunction is a packet centered around $\langle x \rangle$ but with a finite width Δx (i.e. a Gaussian function) we no longer have an equality but only an approximation if $\Delta x \ll L = \left| \frac{1}{V} \frac{\partial V(x)}{\partial x} \right|^{-1}$ (or localized wavefunction).

6.4 Fermi's Golden Rule

We consider now a system with an Hamiltonian \mathcal{H}_0 , of which we know the eigenvalues and eigenfunctions:

$$\mathcal{H}_0 u_k(x) = E_k u_k(x) = \hbar \omega_k u_k(x)$$

Here I just expressed the energy eigenvalues in terms of the frequencies $\omega_k = E_k/\hbar$. Then, a general state will evolve as:

$$\psi(x, t) = \sum_k c_k(0) e^{-i\omega_k t} u_k(x)$$

If the system is in its equilibrium state, we expect it to be stationary, thus the wavefunction will be one of the eigenfunctions of the Hamiltonian. For example, if we consider an atom or a nucleus, we usually expect to find it in its ground state (the state with the lowest energy). We consider this to be the initial state of the system:

$$\psi(x, 0) = u_i(x)$$

(where i stands for *initial*). Now we assume that a perturbation is applied to the system. For example, we could have a laser illuminating the atom, or a neutron scattering with the nucleus. This perturbation introduces an extra potential \hat{V} in the system's Hamiltonian (a priori \hat{V} can be a function of both position and time $\hat{V}(x, t)$, but we will consider the simpler case of time-independent potential $\hat{V}(x)$). Now the hamiltonian reads:

$$\mathcal{H} = \mathcal{H}_0 + \hat{V}(x)$$

What we should do, is to find the eigenvalues $\{E_h^v\}$ and eigenfunctions $\{v_h(x)\}$ of this new Hamiltonian and express $u_i(x)$ in this new basis and see how it evolves:

$$u_i(x) = \sum_h d_h(0) v_h \quad \rightarrow \quad \psi'(x, t) = \sum_h d_h(0) e^{-iE_h^v t/\hbar} v_h(x).$$

Most of the time however, the new Hamiltonian is a complex one, and we cannot calculate its eigenvalues and eigenfunctions. Then we follow another strategy.

Consider the examples above (atom+laser or nucleus+neutron): What we want to calculate is the probability of making a transition from an atom/nucleus energy level to another energy level, as induced by the interaction. Since \mathcal{H}_0 is the original Hamiltonian describing the system, it makes sense to always describe the state in terms of its energy levels (i.e. in terms of its eigenfunctions). Then, we *guess* a solution for the state of the form:

$$\psi'(x, t) = \sum_k c_k(t) e^{-i\omega_k t} u_k(x)$$

This is very similar to the expression for $\psi(x, t)$ above, except that now the coefficient c_k are time dependent. The time-dependency derives from the fact that we added an extra potential interaction to the Hamiltonian.

Let us now insert this guess into the Schrödinger equation, $i\hbar \frac{\partial \psi'}{\partial t} = \mathcal{H}_0 \psi' + \hat{V} \psi'$:

$$i\hbar \sum_k [\dot{c}_k(t) e^{-i\omega_k t} u_k(x) - i\omega_k c_k(t) e^{-i\omega_k t} u_k(x)] = \sum_k c_k(t) e^{-i\omega_k t} (\mathcal{H}_0 u_k(x) + \hat{V}[u_k(x)])$$

(where \dot{c} is the time derivative). Using the eigenvalue equation to simplify the RHS we find

$$\begin{aligned} \sum_k \left[i\hbar \dot{c}_k(t) e^{-i\omega_k t} u_k(x) + \cancel{\hbar \omega_k c_k(t) e^{-i\omega_k t} u_k(x)} \right] &= \sum_k \left[\cancel{c_k(t) e^{-i\omega_k t} \hbar \omega_k u_k(x)} + c_k(t) e^{-i\omega_k t} \hat{V}[u_k(x)] \right] \\ \sum_k i\hbar \dot{c}_k(t) e^{-i\omega_k t} u_k(x) &= \sum_k c_k(t) e^{-i\omega_k t} \hat{V}[u_k(x)] \end{aligned}$$

Now let us take the inner product of each side with $u_h(x)$:

$$\sum_k i\hbar \dot{c}_k(t) e^{-i\omega_k t} \int_{-\infty}^{\infty} u_h^*(x) u_k(x) dx = \sum_k c_k(t) e^{-i\omega_k t} \int_{-\infty}^{\infty} u_h^*(x) \hat{V}[u_k(x)] dx$$

In the LHS we find that $\int_{-\infty}^{\infty} u_h^*(x) u_k(x) dx = 0$ for $h \neq k$ and it is 1 for $h = k$ (the eigenfunctions are orthonormal). Then in the sum over k the only term that survives is the one $k = h$:

$$\sum_k i\hbar \dot{c}_k(t) e^{-i\omega_k t} \int_{-\infty}^{\infty} u_h^*(x) u_k(x) dx = i\hbar \dot{c}_h(t) e^{-i\omega_h t}$$

On the RHS we do not have any simplification. To shorten the notation however, we call V_{hk} the integral:

$$V_{hk} = \int_{-\infty}^{\infty} u_h^*(x) \hat{V}[u_k(x)] dx$$

The equation then simplifies to:

$$\dot{c}_h(t) = -\frac{i}{\hbar} \sum_k c_k(t) e^{i(\omega_h - \omega_k)t} V_{hk}$$

This is a differential equation for the coefficients $c_h(t)$. We can express the same relation using an integral equation:

$$c_h(t) = -\frac{i}{\hbar} \sum_k \int_0^t c_k(t') e^{i(\omega_h - \omega_k)t'} V_{hk} dt' + c_h(0)$$

We now make an important **approximation**. We said at the beginning that the potential \hat{V} is a perturbation, thus we assume that its effects are small (or the changes happen slowly). Then we can approximate $c_k(t')$ in the integral with its value at time 0, $c_k(t=0)$:

$$c_h(t) = -\frac{i}{\hbar} \sum_k c_k(0) \int_0^t e^{i(\omega_h - \omega_k)t'} V_{hk} dt' + c_h(0)$$

[Notice: for a better approximation, an iterative procedure can be used which replaces $c_k(t')$ with its first order solution, then second etc.].

Now let's go back to the initial scenario, in which we assumed that the system was initially at rest, in a stationary state $\psi(x,0) = u_i(x)$. This means that $c_k(0) = 0$ for all $k \neq i$. The equation then reduces to:

$$c_h(t) = -\frac{i}{\hbar} \int_0^t e^{i(\omega_h - \omega_i)t'} V_{hi} dt'$$

or, by calling $\Delta\omega_h = \omega_h - \omega_i$,

$$c_h(t) = -\frac{i}{\hbar} V_{hi} \int_0^t e^{i\Delta\omega_h t'} dt' = -\frac{V_{hi}}{\hbar\Delta\omega_h} (1 - e^{i\Delta\omega_h t})$$

What we are really interested in is the probability of making a transition from the initial state $u_i(x)$ to another state $u_h(x)$: $P(i \rightarrow h) = |c_h(t)|^2$. This transition is caused by the extra potential \hat{V} but we assume that both initial and final states are eigenfunctions of the original Hamiltonian \mathcal{H}_0 (notice however that the final state will be a superposition of all possible states to which the system can transition to).

We obtain

$$P(i \rightarrow h) = \frac{4|V_{hi}|^2}{\hbar^2 \Delta\omega_h^2} \sin^2\left(\frac{\Delta\omega_h t}{2}\right)$$

The function $\frac{\sin z}{z}$ is called a sinc function (see figure 41). Take $\frac{\sin(\Delta\omega t/2)}{\Delta\omega/2}$. In the limit $t \rightarrow \infty$ (i.e. assuming we are describing the state of the system after the new potential has had a long time to change the state of the quantum system) the sinc function becomes very narrow, until when we can approximate it with a delta function. The exact limit of the function gives us:

$$P(i \rightarrow h) = \frac{2\pi|V_{hi}|^2 t}{\hbar^2} \delta(\Delta\omega_h)$$

We can then find the transition rate from $i \rightarrow h$ as the probability of transition per unit time, $W_{ih} = \frac{dP(i \rightarrow h)}{dt}$:

$$W_{ih} = \frac{2\pi}{\hbar^2} |V_{hi}|^2 \delta(\Delta\omega_h)$$

This is the so-called **Fermi's Golden Rule**, describing the transition rate between states.

Obs.: This transition rate describes the transition from u_i to a single level u_h with a given energy $E_h = \hbar\omega_h$. In many cases the final state is an unbound state, which, as we saw, can take on a continuous of possible energy available. Then, instead of the point-like delta function, we consider the transition to a set of states with energies in a small interval $E \rightarrow E + dE$. The transition rate is then proportional to the number of states that can be found with this

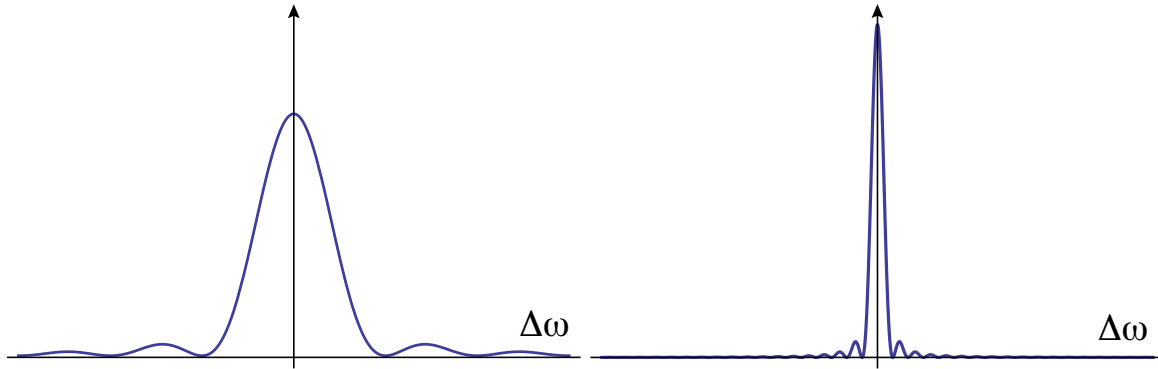


Fig. 41: Sinc function $\frac{\sin(\Delta\omega t/2)}{\Delta\omega/2}$. Left: Sinc function at short times. Right: Sinc function at longer times, the function becoming narrower and closer to a Dirac delta function

energy. The number of state is given by $dn = \rho(E)dE$, where $\rho(E)$ is called the density of states (we will see how to calculate this in a later lecture). Then, Fermi's Golden rule is more generally expressed as:

$$W_{ih} = \frac{2\pi}{\hbar} |V_{hi}|^2 \rho(E_h)|_{E_h=E_i}$$

[Note, before making the substitution $\delta(\Delta\omega) \rightarrow \rho(E)$ we need to write $\delta(\Delta\omega) = \hbar\delta(\hbar\Delta\omega) = \hbar\delta(E_h - E_i) \rightarrow \hbar\rho(E_h)|_{E_h=E_i}$. This is why in the final formulation for the Golden rule we only have a factor \hbar and not its square.]

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