Chapter 12. Time Evolution of Quantum Systems

Section 12.4. The Evolution of the Probability Density $\rho(\vec{r}, t)$

§20 The continuity equation

Section 12.1. The Time-Dependent Schrödinger Equation

§ 1 *Introduction.* Physical chemistry is about change and in quantum mechanics change is described by the time-dependent Schrödinger equation. In this chapter I will introduce you to this equation and some of its consequences. To understand the physical content of the equation and the manner in which it is used, I consider that the world consists of two parts. One is "the system" (here I use this term to mean a molecule, a gas of molecules, a solid surface, or anything else that might be of interest to a physical chemist). The other is the "external agent" which may be a laser, or an electron beam, or a neutron beam, etc. The purpose of the experiment that we examine is to determine what happens to these two parts of the universe when they interact.

It is arbitrary which part we call the system and which one is called the external agent. If we do an experiment in which an electron beam passes through a gas of molecules, a chemist is interested in what happens to the molecules and for him the gas is the system and the electron beam is the external agent. A plasma physicist is interested in knowing what happens to the electron beam if some molecules get in the way; for him the beam is the system. We advocate that this division is arbitrary and arises from overspecialization. It is better, whenever possible, to treat the system nd the external agent on an equal footing. A complete experiment will measure what happens to the system(the gas) *and* what happens to the external agent (the electrons).

Most experiments take place in three steps.

(1) The experimentalists "prepare" the system to have a known quantum state, which I denote either by $|\psi, t_0\rangle$ or by $|\psi_{t_0}\rangle$. This is the state at a time t_0, after preparation.

(b) They then acts with some external agent (laser, electron beam, molecular beam, etc.) on the system in the state $|\psi, t_0\rangle$, to cause it to change. At time t_1, this action stops and the system is in a state $|\psi, t_1\rangle$ (or $|\psi_{t_1}\rangle$).

(c) Then, at a time $t_2 > t_1$, they probes the system to find how it was modified by the action described in (b). This probe may involve looking at the light emitted by the system, or examining the fragments of a reaction, or ionizing the system to count how many molecules of a certain kind were formed in (b).

All three steps in the experiment cause the state of the system to change in time. Such changes are described by the time-dependent Schrödinger equation, which we study in this chapter.

§ **2** *The time-dependent Schrödinger equation.* In his first paper on quantum mechanics, Schrödinger proposed that the evolution of the wave function is given by

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi, t\rangle = \hat{H}|\psi, t\rangle \tag{1}$$

where $\mathrm{i} = \sqrt{-1}$ and $\hat{H}$ is the Hamiltonian of the system.

If the state of the molecule changes, because we act on it with an external agent, then the Hamiltonian $\hat{H}$ consists of the energy of the molecule, the energy of the external agent, and the energy of the interaction between them. The Hamiltonian is time-independent because the total energy is conserved. The ket $|\psi, t\rangle$ describes the state of the molecule and that of the external agent.

In some cases it is a reasonable approximation to treat the evolution of the external agent classically. For example, if the external agent is light, we can treat it as a classical electromagnetic field. When we do this we no longer include in the quantum Hamiltonian the energy of the electromagnetic field but keep the energy of the interaction between the field and the system. Since the classical electromagnetic field is time dependent, the energy of the interaction between the system and the field becomes time-dependent; therefore the Hamiltonian becomes time-dependent. No matter what the system is if you see a time dependent term in the Hamiltonian someone has treated classically either a part of the system or the external agent.

If the external agent is a high-energy electron, we can assume that its position at different times can be described by a classical trajectory. The interaction energy between the molecule and the electron becomes time-dependent because it depends on the position of the electron and this changes in time. This is not a bad approximation if the electron has high energy and you are only interested in what happens to the molecule.

Remember: in general the Hamiltonian operator $\hat{H}$ is time-independent! It becomes time-dependent only when we treat a part of the system (e.g.

the light) classically. If such an approximation is made than the system is described approximately and the evolution of the external agent is described very poorly.

§ 3 *What can we do with the time-dependent Schrödinger equation?* If you know that the state of the system at time t_0 is $|\psi, t_0\rangle$, then you can solve Eq. 1 to obtain the state $|\psi, t\rangle$ at time t.

You can think of this equation as a set of mathematical rules that map an initial state $|\psi, t_0\rangle$ into a final state $|\psi, t\rangle$. Keep in mind that $|\psi, t\rangle$ can be a very different state from $|\psi, t_0\rangle$. For example, $|\psi, t_0\rangle$ could be the ground state of a molecule and $|\psi, t\rangle$ could be an excited state, or the state of the fragments produced by the photodissociation of the molecule.

The information contained in $|\psi, t\rangle$ depends on the approximations made in the Hamiltonian. Consider the example of a molecule interacting with an electromagnetic field (light). An exact treatment will use the Hamiltonian

$$\hat{H} = \hat{H}_{\mathrm{m}} + \hat{H}_{\mathrm{mr}} + \hat{H}_{\mathrm{r}}$$

where $\hat{H}_{\mathrm{m}}$ is the Hamiltonian of the molecule, $\hat{H}_{\mathrm{r}}$ is the Hamiltonian of the electromagnetic radiation (i.e. the energy operator of the electromagnetic field), and $\hat{H}_{\mathrm{mr}}$ is the energy of the interaction between the molecule and the field. *The total energy is conserved*; this is equivalent to saying that $\hat{H}$ must be time-independent.

The energy of the molecule and the energy of the field are not conserved, only their sum is. The molecule can donate energy to the field, by emitting photons, or take energy from the field, by absorbing photons. The total energy must be conserved but the energy of the parts can vary.

The state calculated by using the time-dependent Schrödinger equation with the total, time independent Hamiltonian tells us the state of the molecule *and* the field. For instance, it may tell us that if we start at time t_0 with a ket $|\psi, t_0\rangle$ in which the field contains photons and the molecule is in the ground state, then at a later time t, in the state $|\psi, t\rangle$, the molecule is excited and a photon has disappeared from the field.

Consider now the case in which we treat the field classically. The Hamiltonian operator is

$$\hat{H} = \hat{H}_{\mathrm{m}} + \hat{H}_{\mathrm{mr}}(t)$$

The operator $\hat{H}_{\mathrm{r}}$ has been dropped so the theory has no information about the energy of the field. In this theory we cannot tell how many photons are in the system. The electromagnetic field is treated classically in the operator $\hat{H}_{\mathrm{mr}}$ and because the classical field depends on time t, $\hat{H}_{\mathrm{mr}}(t)$ also does. The energy is no longer conserved, because the molecule can be excited by the classical field, gaining energy, but because $\hat{H}_{\mathrm{r}}$ is no longer present in the Hamiltonian, this energy is not removed from the field. The ket $|\psi, t\rangle$ calculated with this approximate Hamiltonian has information *only about the molecule.* There is no information regarding the state of the field.

§ 4 *Observables.* Let us assume that we have prepared the system in the state $|\psi, t_0\rangle$, acted on it with an agent whose energy is *included in* $\hat{H}$ (the system is conservative), and calculated the state $|\psi, t\rangle$ at time t. What can we do with this? We may want to know whether the molecule has the energy E_n at time t. The operator for the probability that the molecule is in state $|E_n\rangle$ is

$$\hat{P}(E_n) = |E_n\rangle \langle E_n|$$

The probability that the molecule has the energy E_n, when the system is in the state $|\psi, t\rangle$ is

$$P(E_n, t) = \langle \psi, t \,|\, \hat{P}(E_n) \,|\, \psi, t\rangle = \langle \psi, t \,|\, E_n\rangle \, \langle E_n \,|\, \psi, t\rangle \tag{2}$$

Here $|E_n\rangle$ is an energy eigenstate of the molecular Hamiltonian $\hat{H}_{\mathrm{m}}$ and the ket $|\psi, t\rangle$ describes both the state of the molecule *and* the state of the external agent.

If I want to know the average energy of the molecule at time t, I calculate

$$\langle \hat{H}_{\mathrm{m}}\rangle(t) \equiv \langle \psi, t \,|\, \hat{H}_{\mathrm{m}} \,|\, \psi, t\rangle \tag{3}$$

Since $\hat{H}_{\mathrm{m}} = \sum_n |E_n\rangle \, E_n \, \langle E_n|$, one can easily show that

$$\langle \hat{H}_{\mathrm{m}}\rangle(t) = \sum_n P(E_n, t) \, E_n \tag{4}$$

which is indeed the mean energy of the molecule. The energy of the field is not included in this calculation and this is why $\langle \hat{H}_{\mathrm{m}}\rangle(t)$ is time-dependent (in general). The molecule can exchange energy with the external agent.

§ 5 *The propagator.* In many formal manipulations, it is useful to introduce the operator $\hat{U}(t, t_0)$, called *the propagator from time t_0 to time t*. This is defined by

$$\hat{U}(t, t_0)|\psi, t_0\rangle \equiv |\psi, t\rangle \tag{5}$$

If the Hamiltonian is time-independent (the system is conservative) then

$$\hat{U}(t, t_0) = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar} \tag{6}$$

To prove Eq. 6, we start with

$$|\psi, t\rangle = \hat{U}(t, t_0)|\psi, t_0\rangle = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|\psi, t_0\rangle \tag{7}$$

and show that the ket $|\psi, t\rangle$ that it defines satisfies the Schrödinger equation, Eq. 1. To show this, apply $\mathrm{i}\hbar\frac{\partial}{\partial t}$ to both sides of Eq. 7. You get

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial|\psi, t\rangle}{\partial t} &= \mathrm{i}\hbar\frac{\partial}{\partial t}\mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|\psi, t_0\rangle \\
&= \mathrm{i}\hbar\left(\frac{-\mathrm{i}}{\hbar}\right)\hat{H}\frac{\partial}{\partial t}\mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|\psi, t_0\rangle = \hat{H}|\psi, t\rangle
\end{aligned}$$

This means that

$$|\psi, t\rangle = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|\psi, t_0\rangle \equiv \hat{U}(t, t_0)|\psi, t_0\rangle \tag{8}$$

is the solution of the Schrödinger equation. Note that during this derivation, we assumed that $\hat{H}$ does not depend on time, which is true only for conservative systems. Had we treated the external agent classically, $\hat{H}$ would have been time-dependent and Eqs. 6 and 7 would not be applicable.

§ **6** *A few properties of the propagator.*

1. The *group property* asserts that

   $$\hat{U}(t_2, t_1)\hat{U}(t_1, t_0) = \hat{U}(t_2, t_0) \tag{9}$$

   If you propagate from time t_0 to time t_1 and then from t_1 to t_2, you get the same result as when you propagate directly from t_0 to t_2.

2. *Reversibility* asserts that

   $$\hat{U}(t_0, t)\hat{U}(t, t_0)|\psi, t_0\rangle = |\psi, t_0\rangle \tag{10}$$

   If you propagate from t_0 to t and then back, you will obtain the initial wave function. This is true only for conservative systems, which do not lose energy during propagation. Mathematically, Eq. 10 means that[1]

   $$\hat{U}(t_0, t) = \hat{U}(t, t_0)^{-1} \tag{11}$$

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[1] Recall that if $AB = BA = I$ then B is the inverse of A and we denote it by $B \equiv A^{-1}$.

3. $\hat{U}(t,t_0)$ *is a unitary operator.* To derive this property, we start with

$$\langle \psi, t \,|\, \psi, t\rangle = \langle \psi, t_0 \,|\, \psi, t_0\rangle = 1 \tag{12}$$

We impose this condition because in a conservative system, the kets must be normalized at all times.

From the definition of $\hat{U}$ and the fact that $\langle \hat{A}x \,|\, \hat{B}y\rangle = \langle x \,|\, \hat{A}^\dagger \hat{B} \,|\, y\rangle$, we have

$$\langle \psi, t \,|\, \psi, t\rangle = \langle \psi, t_0 \,|\, \hat{U}(t,t_0)^\dagger \hat{U}(t,t_0) \,|\, \psi, t_0\rangle = 1 \tag{13}$$

Since Eq. 12 tells us that $\langle \psi, t_0 \,|\, \psi, t_0\rangle = 1$, Eq. 13 implies that

$$\hat{U}(t,t_0)^\dagger \hat{U}(t,t_0) = \hat{I}, \tag{14}$$

which is one of the definitions of an unitary operator.

Exercise 1 (a) Use the fact that $\hat{U}(t,t_0) = \exp[-\mathrm{i}(t-t_0)\hat{H}/\hbar]$ to prove properties 1–3 above.

(b) Show that

$$\mathrm{i}\hbar \frac{\partial \hat{U}(t,t_0)}{\partial t} = \hat{H}\hat{U}(t,t_0)$$

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§ **7** *The energy eigenstates are stationary.* Let us assume that a molecule absorbs light and is excited into an energy eigenstate $|E_n\rangle$ at time t_0. How does the state $|E_n\rangle$ evolve *after it no longer interacts with the light?*

We will treat the radiation field classically. In a complete treatment the Hamiltonian would be $\hat{H} = \hat{H}_{\mathrm{m}} + \hat{H}_{\mathrm{r}} + \hat{H}_{\mathrm{mr}}$. A classical-field approximation reduces it to $\hat{H} = \hat{H}_{\mathrm{m}} + \hat{H}_{\mathrm{mr}}(t)$. If we look at the molecule *after it* *has interacted with light*, the molecule-field interaction becomes zero because there is no longer a field to interact with. This is an approximation because in reality if a molecule is excited, it will spontaneously emit a photon and create a field. Photon emission is caused by $\hat{H}_{\mathrm{mr}} \neq 0$ and the existence of the emitted photon is possible only if $\hat{H}_{\mathrm{r}}$ is present in $\hat{H}$. Using a classical field theory when no photons are present (after the light is turned off) suppresses photon emission and makes the system conservative. It is the evolution of this false-conservative example that we examine now. I will soon tell you how we correct empirically for the errors caused by this approach.

Using Eq. 8 and the fact that in the absence of light, $\hat{H}|E_n\rangle = E_n|E_n\rangle$ (by the definition of $|E_n\rangle$), we have

$$\begin{aligned} |E_n, t\rangle &= \hat{U}(t, t_0)|E_n, t_0\rangle \\ &= \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|E_n, t_0\rangle = \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar}|E_n\rangle \end{aligned} \tag{15}$$

After the time t_0 the system no longer interacts with light and the Hamiltonian $\hat{H}$ no longer contains the time-dependent light-system interaction. This allows us to use the exponential formula for the propagator.

Eq. 15 says that the state $|E_n, t\rangle$ at time t is proportional to $|E_n\rangle$. The only change caused by the flow of time is multiplication by the phase factor $\exp[-\mathrm{i}(t - t_0)E_n/\hbar]$. In quantum mechanics this is no change at all.

Indeed, the result of any measurement we care to make is calculated through an expression of the form

$$\langle E_n, t \,|\, \hat{O} \,|\, E_n, t\rangle$$

where $\hat{O}$ is the operator describing the quantity being measured. This expression is (use Eq. 15 and $\langle ax \,|\, by\rangle = a^* b\langle x \,|\, y\rangle$ when a and b are complex numbers)

$$\begin{aligned}\langle E_n, t \,|\, \hat{O} \,|\, E_n, t\rangle &= \langle \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar} E_n \,|\, \hat{O} \,|\, \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar} E_n \\ &= \mathrm{e}^{\mathrm{i}(t-t_0)E_n/\hbar} \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar} \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \\ &= \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \end{aligned} \tag{16}$$

The result of the measurement is independent of time, as long as the measurement is made *after* the molecule stopped interacting with light *and* the molecule was left in an energy eigenstate $|E_n\rangle$. This is why the eigenstates of energy are called *stationary states.*

However, the statement that excited energy eigenstates are stationary, which we seem to have proved, is misleading. We know that a molecule in an excited state will emit a photon and go into the ground state. Molecules excited into an energy eigenstate have a fleeting lifetime, of about a nanosecond. Stationary states are not stationary at all!

What is going on? Where did our proof go wrong? The error comes from the Hamiltonian $\hat{H}$ that we used, which was that of the molecule *in isolation.* $\hat{H}$ does not contain the terms that would allow a photon to appear. Had we added to the Hamiltonian a term representing the energy of an electromagnetic field and a term representing the interaction of the molecule with the electromagnetic field, then the time-dependent Schrödinger equation would have led to spontaneous photon emission. The ket describing this system will contain two pieces of information: the state of the molecule and the state of the field. The total energy will be the energy of the molecule and that of the field. The state of the molecule *and* field is stationary, but the state of the molecule alone is not, since energy can be transferred from the molecule to the field.

§ 8 *A comparison to classical theory.* The statement that nothing changes when the state of a closed system (meaning a system that does not interact with the outside world) is an energy eigenstate is quite shocking for a classical-minded person. If a particle has energy how is it possible that its mean position and mean velocity do not change in time? Let us examine the example of a classical harmonic oscillator to try to understand to try to understand whether we can shed some light on the reason for this behavior.

The oscillating particle is not charged, so we do not need to deal with the issue of radiation. An oscillator in an energy eigenstate, say $|E_3\rangle$, has the total energy

$$E_3 = \left(3 + \frac{1}{2}\right)\hbar\omega \tag{17}$$

If no outside forces act on the oscillator then E_3 is constant. In classical physics the total energy is

$$\frac{m\,v(t)^2}{2} + \frac{k\,x(t)^2}{2} \tag{18}$$

where m is the mass, k is the force constant, $v(t)$ is velocity, and $x(t)$ is position. This total energy is also conserved in classical theory, if no outside forces are at work. However, if the total energy is equal to E_3, then the classical oscillator cannot be still. The classical equation of motion for the oscillator is

$$m\frac{\mathrm{d}^2x(t)}{\mathrm{d}t} = -k\,x(t) \tag{19}$$

and its solution is

$$x(t) = A\cos\left(\sqrt{\frac{k}{m}}\;t + \phi\right) \tag{20}$$

where A and ϕ are constants. If we use $x(t)$ from Eq. 20 to calculate the right-hand side of Eq. 18, we obtain

$$E_3 = \frac{A^2 k}{2} \tag{21}$$

As we expected, classical total energy is conserved, as it is in quantum mechanics. However, unlike quantum mechanics, the position $x(t)$ and the momentum $m\,v(t)$ change in time. In quantum mechanics, no observable changes in time if the state is $|E_3\rangle$ and the total energy is fixed.

To make a fair comparison between quantum and classical behavior we need to recognize that if we only specify the total energy the state of the classical system is not described uniquely. Many pairs of values of $x(t)$ and $v(t)$ give the same total energy. The total energy determines the amplitude A in Eq. 20 but the phase ϕ is not determined.

Since we cannot determine the phase, let us assume that all we know about the phase is that any value is equally probable. The probability that the phase has a value between ϕ and $\phi + \mathrm{d}\phi$ is therefore

$$P(\phi)\,\mathrm{d}\phi = \frac{\mathrm{d}\phi}{2\pi}$$

The average value of the position is

$$\langle x(t)\rangle = \int_0^{2\pi} P(\phi)\,x(t)\;\mathrm{d}\phi = \int_0^{2\pi} \frac{\mathrm{d}\phi}{2\pi}\,A\,\cos(\sqrt{\frac{k}{m}}\,t + \phi) = 0$$

The average value of the position is zero! and so is the average value of the velocity. We see that a behavior of a classical oscillator whose state is specified by giving only the total energy is similar to that of a quantum oscillatory. This happens because by knowing only the total energy we know nothing about the phase of the oscillation.

This particular result is specific to a harmonic oscillator but the analysis is more general. A substantial difference between a quantum system whose state is an energy eigenstate we only know the energy. If that is all we know for the classical system then neither the position nor the velocity are determined uniquely. An infinite set of classical trajectories is compatible with the specified energy. The average position over these trajectories is zero, just as in quantum mechanics.

§ 9 *The evolution of a coherent superposition of energy eigenstates.* Let us examine what happens if we act on a system with an external agent and when we stop acting on it, its state is

$$|\psi, t_0\rangle = a_n|E_n\rangle + a_m|E_m\rangle \tag{22}$$

Here $|E_n\rangle$ and $|E_m\rangle$ are eigenstates of the time-independent Hamiltonian $\hat{H}$ of the molecule when we external agent no longer acts on the molecule. They satisfy

$$\hat{H}|E_\beta\rangle = E_\beta|E_\beta\rangle \text{ with } \beta = n \text{ or } m \tag{23}$$

The state $|\psi, t_0\rangle$ defined by Eq. 22 is called a coherent superposition of the states $|E_n\rangle$ and $|E_m\rangle$.

How does the system evolve if, after I have stopped acting on it, it is left in the state given by Eq. 22? Since I no longer act on the system, the Hamiltonian is that of the system alone (we ignore the possibility of photon emission) and it is time-independent. Therefore, the propagator is

$$\hat{U}(t, t_0) = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar} \tag{24}$$

The wave function at time t is

$$\begin{aligned}|\psi, t\rangle &= \hat{U}(t,t_0)|\psi,t_0\rangle = a_n\hat{U}|E_n\rangle + a_m\hat{U}|E_m\rangle \\ &= a_n e^{-i(t-t_0)E_n/\hbar}|E_n\rangle + a_m e^{-i(t-t_0)E_m/\hbar}|E_m\rangle \qquad (25)\end{aligned}$$

This calculation uses the fact that

$$e^{-i(t-t_0)\hat{H}/\hbar}|E_\alpha\rangle = e^{-i(t-t_0)E_\alpha/\hbar}\,|E_\alpha\rangle \qquad (26)$$

Exercise 2 Prove Eq. 26.

I will now answer the following questions. If the system is in the coherent initial state $|\psi, t_0\rangle$ (Eq. 22) and it evolves according to Eq. 25, what is the evolution of

1. the probability P_m that the system is in the state $|E_m\rangle$?
2. the average energy $\langle\psi, t\,|\,\hat{H}\,|\,\psi, t\rangle$?
3. the average value $\langle\psi, t\,|\,\hat{O}\,|\,\psi, t\rangle$ of an arbitrary operator $\hat{O}$?

(1) The probability that the system was in the state $|E_m\rangle$ at time t_0 is

$$\begin{aligned}P_m(t_0) &\equiv |\langle E_m\,|\,\psi, t_0\rangle|^2 = |a_m\langle E_m\,|\,E_m\rangle + a_n\langle E_m\,|\,E_n\rangle|^2 \\ &= |a_m|^2 \qquad (27)\end{aligned}$$

(I used $\langle E_m\,|\,E_m\rangle = 1$ and $\langle E_m\,|\,E_n\rangle = 0$.) Similarly,

$$P_n(t_0) \equiv |\langle E_n\,|\,\psi, t_0\rangle|^2 = |a_n|^2 \qquad (28)$$

What are these probabilities at time t?

$$\begin{aligned} P_m(t) &\equiv |\langle E_m \,|\, \psi, t\rangle|^2 = |a_m \mathrm{e}^{-\mathrm{i}E_m(t-t_0)/\hbar}|^2 \\ &= a_m^* \mathrm{e}^{\mathrm{i}E_m(t-t_0)/\hbar}\, a_m \mathrm{e}^{-\mathrm{i}E_m(t-t_0)/\hbar} = a_m^* a_m = |a_m|^2 \end{aligned} \tag{29}$$

(I used $\langle E_m \,|\, E_m\rangle = 1$, $\langle E_m \,|\, E_n\rangle = 0$, and $\langle ax \,|\, by\rangle = a^* b \langle x \,|\, y\rangle$ if a and b are complex numbers and $|x\rangle$ and $|y\rangle$ are kets.) Thus we see that

$$P_m(t) = P_m(t_0) \tag{30}$$

and, similarly, that $P_n(t) = P_n(t_0)$. If the state of the system is a coherent superposition of energy eigenstates and no external agent acts on it, then the probability that the molecule has the energy E_n (or E_m) does not change in time.

In this calculation we have ignored photon emission (the Hamiltonian $\hat{H}$ does not contain the energy of the electromagnetic field or the energy of the interaction between the molecule and the field). Had we taken these terms into account, the probability that the molecule is in an excited state $|E_n\rangle$ at time $t > t_0$ would decay in time to become zero. In many cases, this decay is exponential:

$$P_n(t) = \mathrm{e}^{-\Gamma_n(t-t_0)} P_n(t_0) \tag{31}$$

The quantity Γ_n^{-1} is called the radiative lifetime of the state $|E_n\rangle$; it is of order 10^{-9} sec for fluorescence and longer for phosphorescence.

I will continue examining the evolution of a coherent state by ignoring, for a while, the decay mentioned above.

(2) The average energy of a system in a coherent state is

$$\langle E\rangle_t \equiv \langle \psi, t \,|\, \hat{H} \,|\, \psi, t\rangle = P_m(t) E_m + P_n(t) E_n \tag{32}$$

Since the probabilities P_m and P_n are time-independent, so is the average energy $\langle E\rangle_t$.

Exercise 3 Prove Eq. 32.

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(3) It would be wrong to conclude, from the fact that $P_n(t)$ is time-independent, that the system does not change in time after being excited to a coherent state. To see why I say that, consider the mean value of an arbitrary operator $\hat{O}$, which happens to have the property that $\langle E_n \,|\, \hat{O} \,|\, E_m\rangle \neq 0$. Its expectation value at time t is

$$\langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle = \langle a_m \mathrm{e}^{-\mathrm{i}(t-t_0)E_m/\hbar} + a_n \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar} \,|\, \hat{O} \,|\, a_m \mathrm{e}^{-\mathrm{i}(t-t_0)E_m/\hbar} + a_n \mathrm{e}^{-\mathrm{i}(t-t_0)E_n/\hbar}\rangle$$

By using the properties of the scalar product, this can be written as

$$\begin{aligned} \langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle &= a_m^* a_m \langle E_m \,|\, \hat{O} \,|\, E_m\rangle + a_n^* a_n \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \\ &\quad + a_m^* a_n \mathrm{e}^{-\mathrm{i}(E_n-E_m)(t-t_0)/\hbar} \langle E_m \,|\, \hat{O} \,|\, E_n\rangle \\ &\quad + a_n^* a_m \mathrm{e}^{+\mathrm{i}(E_n-E_m)(t-t_0)/\hbar} \langle E_n \,|\, \hat{O} \,|\, E_m\rangle \end{aligned} \tag{33}$$

Note that the fourth term is the complex conjugate of the third. Therefore we can write the last two terms in Eq. 33 as (use $z + z^* = 2\Re z$ where $\Re z$ is the real part of the complex number z)

$$2\Re\left\{a_m^* a_n \mathrm{e}^{-\mathrm{i}(E_n-E_m)(t-t_0)/\hbar} \langle E_m \,|\, \hat{O} \,|\, E_n\rangle\right\} \tag{34}$$

In addition $a_n^* a_n = P_n$ and $a_m^* a_m = P_m$. Using all these facts in Eq. 33 gives

$$\begin{aligned} \langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle &= P_m \langle E_m \,|\, \hat{O} \,|\, E_m\rangle + P_n \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \\ &\quad + 2\Re\left\{a_m^* a_n \mathrm{e}^{-\mathrm{i}(E_n-E_m)(t-t_0)/\hbar} \langle E_m \,|\, \hat{O} \,|\, E_n\rangle\right\} \end{aligned} \tag{35}$$

This is a very interesting result. If the operator $\hat{O}$ is the Hamiltonian $\hat{H}$, then $\langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle \equiv \langle \psi, t \,|\, \hat{H} \,|\, \psi, t\rangle$ and

$$\langle E_m \,|\, \hat{H} \,|\, E_n\rangle = E_n \langle E_m \,|\, E_n\rangle = E_n \delta_{mn} = 0$$

The time-dependent term in Eq. 35 becomes zero and the mean energy is independent of time. However, since $\hat{O}$ is such that

$$\langle E_m \,|\, \hat{O} \,|\, E_n\rangle \neq 0, \tag{36}$$

$\langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle$ contains a term that oscillates with the frequency

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \tag{37}$$

This additional term is very similar to the one causing interference when two waves overlap. Because of this, we say that when the state of a system is a coherent superposition of two energy eigenstates, these two states ‘interfere’. The fact that $\langle E_m \,|\, \hat{O} \,|\, E_n\rangle \neq 0$ leads to *quantum interference* or to *coherent oscillations.*

What are the physical consequences of this mathematical observation? Let us take

$$\hat{O} = |x\rangle \langle x| \equiv \hat{P}(x) \tag{38}$$

which is the probability operator that the particle is located at point x. Introducing this into Eq. 35 gives

$$\begin{aligned}\langle \psi, t \,|\, \hat{P}(x) \,|\, \psi, t\rangle &= P_m \langle E_m \,|\, x\rangle \langle x \,|\, E_m\rangle + P_n \langle E_n \,|\, x\rangle \langle x \,|\, E_n\rangle \\ &\quad + 2\Re\left\{a_m^* a_n \mathrm{e}^{-\mathrm{i}\omega_{nm}(t-t_0)} \langle E_m \,|\, x\rangle \langle x \,|\, E_n\rangle\right\}\end{aligned} \tag{39}$$

But

$$\langle x \,|\, E_m\rangle \equiv \psi_{E_m}(x) \tag{40}$$

is the wave function in the Schrödinger representation and

$$\langle E_m \,|\, x \rangle = \psi_{E_m}^*(x) \tag{41}$$

Using Eqs. 40 and 41 in Eq. 39 gives

$$\begin{aligned} \langle \psi, t \,|\, \hat{P}(x) \,|\, \psi, t \rangle \;&=\; P_m \psi_{E_m}(x)^* \, \psi_{E_m}(x) + P_n \psi_{E_n}(x)^* \, \psi_{E_n}(x) \\ &\quad + 2\Re \left\{ \psi_{E_m}(x)^* \, \psi_{E_n}(x) \, \mathrm{e}^{-\mathrm{i}\omega_{nm}(t-t_0)} a_m^* a_n \right\} \end{aligned} \tag{42}$$

The probability that the particle is located at x *changes in time.* The first term on the right-hand side in Eq. 42 is the probability P_m that the system is in an energy eigenstate $|E_m\rangle$ times the probability $\psi_{E_m}(x)^* \, \psi_{E_m}(x)$ that, when the particle is in the state $|E_m\rangle$, its location is x. The term $P_n \psi_{E_n}(x)^* \, \psi_{E_n}(x)$ has a similar interpretation. These first two terms in Eq. 42 are exactly what one would expect from classical probability theory. Note that they are independent of time. The third term, the time-dependent one, has no analog in classical probability theory! Its presence makes the probability that a particle is located at a position x oscillate in time with the frequency ω_{nm}.

This time evolution is characterized by one frequency ω_{nm} because the initial wave function

$$|\psi, t_0\rangle = a_m |E_m\rangle + a_n |E_n\rangle$$

was a coherent superposition of *two* energy eigenstates. You can easily show that if

$$|\psi, t_0\rangle = \sum_{n=0}^{M} a_n |E_n\rangle \tag{43}$$

then

$$\begin{aligned}\langle \psi, t \,|\, \hat{O}(x) \,|\, \psi, t\rangle &= \sum_{n=0}^{M} a_n^* a_n \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \\ &\quad + 2\Re\left\{\sum_{n=0}^{M}\sum_{m>n}^{M} a_n^* a_m \langle E_n \,|\, \hat{O} \,|\, E_m\rangle \mathrm{e}^{-\mathrm{i}(E_m-E_n)(t-t_0)/\hbar}\right\} \qquad (44)\end{aligned}$$

Now $\langle \psi, t \,|\, \hat{O}(x) \,|\, \psi, t\rangle$ has a large number of terms, oscillating at many frequencies $\omega_{mn} \equiv (E_m - E_n)/\hbar$.

Note also that if the coefficients a_n and $\langle E_m \,|\, \hat{O} \,|\, E_n\rangle$ are *real numbers*, then

$$\begin{aligned}\langle \psi, t \,|\, \hat{O}(x) \,|\, \psi, t\rangle &= \sum_{n=0}^{M} a_n^2 \langle E_n \,|\, \hat{O} \,|\, E_n\rangle \\ &\quad + 2\sum_{n=0}^{M}\sum_{m>n}^{M} a_n a_m \langle E_n \,|\, \hat{O} \,|\, E_m\rangle \cos[\omega_{mn}(t-t_0)] \qquad (45)\end{aligned}$$

§ 10 *Coherent spectroscopy.* Coherent oscillations are used in spectroscopy to measure differences between the energy eigenstates of a molecule. If we use a short pulse of light (say, a picosecond or less) to excite a molecule, there is an uncertainty in the energy of the photon. If this range is such that two energy eigenstates can be excited, the principle of linear superposition tells us that the state created by photon absorption must be a coherent superposition of these two energy eigenstates. We will prove that this is true when we study the interaction of light with molecules. Let us accept for now that this is the case and ask what we can say about the light emitted by a molecule in such state. One can show that the emission intensity is proportional to

$$|\langle E_g \,|\, \hat{\mu} \,|\, \psi, t\rangle|^2, \qquad (46)$$

where $\hat{\mu}$ is the dipole operator, $|E_g\rangle$ is the ground state of the molecule, and

$|\psi, t\rangle$ is the coherent state of the molecule *after* it interacted with a very short pulse of light.

If the duration of the excitation pulse and its frequency are chosen so that the excited state is

$$|\psi, t\rangle = a_1|E_1\rangle + a_2|E_2\rangle \tag{47}$$

then we have

$$\langle E_g \,|\, \hat{\mu} \,|\, \psi, t\rangle = a_1 \mathrm{e}^{-\mathrm{i}E_1 t/\hbar}\langle E_g \,|\, \hat{\mu} \,|\, E_1\rangle + a_2 \mathrm{e}^{-\mathrm{i}E_2 t/\hbar}\langle E_g \,|\, \hat{\mu} \,|\, E_2\rangle \tag{48}$$

and Eq. 46 becomes

$$\begin{aligned} |\langle E_g \,|\, \hat{\mu} \,|\, \psi, t\rangle|^2 \;\; = \;\; & |a_1|^2|\langle E_g \,|\, \hat{\mu} \,|\, E_1\rangle|^2 + |a_2|^2|\langle E_g \,|\, \hat{\mu} \,|\, E_2\rangle|^2 \\ & + 2\Re\left\{a_1^* a_2 \langle E_g \,|\, \hat{\mu} \,|\, E_1\rangle^* \langle E_g \,|\, \hat{\mu} \,|\, E_2\rangle \mathrm{e}^{-\mathrm{i}(E_2 - E_1)t/\hbar}\right\} \end{aligned} \tag{49}$$

The intensity of the emitted light oscillates in time, with the frequency $\omega_{12} \equiv (E_2 - E_1)/\hbar$.

Eq. 49 contains part of the truth but not all of it. Experiments tell us that the intensity of light decays exponentially because a molecule that emitted light goes into the ground state. After a while all molecules have emitted light and emission is no longer possible. A better theory than the one leading to Eq. 48 will predict an oscillating, exponential decay (Fig. 1). The dotted line shows the prediction of Eq. 49 and the solid line shows the correct evolution. However the two curves oscillate at the same frequency. The frequency of these oscillations give us the energy difference $E_2 - E_1$ between the two excited states. This method of finding the energy difference is more accurate than others when the energy difference is very small, because

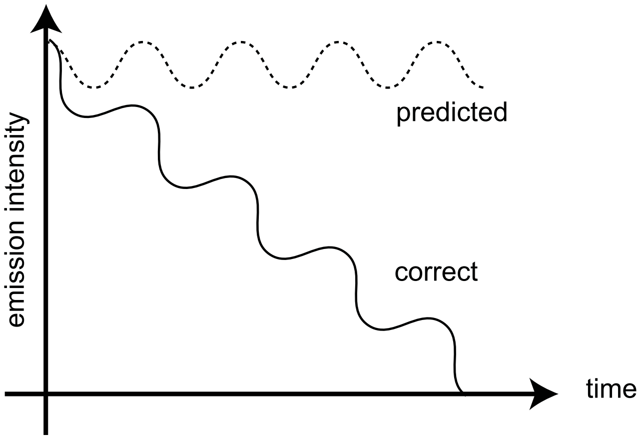

Figure 1: Oscillating decay: the dotted line is the behavior predicted by Eq. 49 and the solid line is the correct behavior

the period of oscillation is long and easy to measure. Measuring this small difference by absorption spectroscopy requires very stable lasers that have a very narrow line width, so that one and only one eigenstate is excited. The smaller the energy difference between two energy levels, the easier it is to measure it by coherent spectroscopy and the harder it is to measure it by absorption spectroscopy.

§ 11 *The time scale on which an observable changes.* Because the eigenstates of the Hamiltonian form a complete basis set, Eq. 43 is valid for any state $|\psi, t_0\rangle$, provided that M is large enough. Therefore Eq. 44 is valid in general. This has an interesting consequence, sometimes called the time-energy uncertainty relation. The time evolution of $\langle\psi, t\,|\,\hat{O}\,|\,\psi, t\rangle$ depends on the set of frequencies ω_{mn}. In this set there is a largest frequency, which I call $\omega_{\max}$, and a smallest one called $\omega_{\min}$. When $t = t_0$, the argument of the cosine in Eq. 45 is zero and all cosines in the expression are equal to one. $\langle \psi, t \,|\, \hat{O} \,|\, \psi, t \rangle$ will differ noticeably from $\langle \psi, t_0 \,|\, \hat{O} \,|\, \psi, t_0 \rangle$ only when $\omega_{\max}(t - t_0)$ reaches a sufficiently high value. For example, if $\omega_{\max}(t - t_0) = \pi/10$ then $\cos(\omega_{\max}(t - t_0)) = \cos(\pi/10) = 0.951$. All other cosines will change by a smaller amount. Therefore we will notice a change in the value of $\langle \psi, t \,|\, \hat{O} \,|\, \psi, t \rangle$ only at a time t that satisfies

$$\omega_{\max}(t - t_0) \geq \frac{\pi}{10}$$

This means (since $\omega_{\max} = \max |E_m - E_n|/\hbar$) that

$$[\max |E_m - E_n|] \, \Delta t/\hbar \geq \frac{\pi}{10} \tag{50}$$

Here $\max |E_m - E_n|$ is the largest energy difference in Eq. 45 as m and n vary.

If the state of the system is represented by two energy eigenstates then the condition in Eq. 50 is

$$\Delta E \, \Delta t \approx \frac{\hbar \pi}{10} \tag{51}$$

with $\Delta E = E_2 - E_1$.

This looks like a Heisenberg uncertainty principle but it is nothing of the kind. Heisenberg uncertainty is a relationship between measurements of observables whose operators do not commute. Eq. 50 tells us that the time interval required for noticing a change in the state of the system is of order $\hbar/\Delta E$ where ΔE is the largest difference between the energies involved in the excited state. The energies E_m and E_n are those energies that appear in the expansion $|\psi, t_0\rangle = \sum_n c_n |E_n\rangle$.

Section 12.2. Time Evolution of Mean Values: Heisenberg and Schrödinger Representation

§ **12** *Time evolution of observables.* If we know the time evolution of the state $|\psi, t\rangle$, we can calculate the evolution of the average value of an observable A from the definition

$$\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle \equiv \langle\hat{A}\rangle_t \tag{52}$$

It is convenient to define a *new operator* $\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}$ through the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle \overset{\text{def}}{=} \langle\psi, t\,|\,\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\,|\,\psi, t\rangle \tag{53}$$

Below I will show that

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{A}] + \frac{\partial\hat{A}}{\partial t} \tag{54}$$

where $[\hat{H},\hat{A}]$ is the commutator

$$[\hat{H}, \hat{A}] \equiv \hat{H}\hat{A} - \hat{A}\hat{H}$$

The last term in Eq. 54 appears only if $\hat{A}$ is a time-dependent operator.

For example, $\hat{A} = \hat{\vec{\boldsymbol{\mu}}} \cdot \vec{E}(t)$ couples the electric field of light to a molecule, where $\vec{E}(t)$ is the classical electric field of light and $\hat{\vec{\boldsymbol{\mu}}}$ is the dipole moment operator of the molecule. For this case $\frac{\partial\hat{A}}{\partial t} = \hat{\vec{\boldsymbol{\mu}}} \cdot \frac{\partial\vec{E}(t)}{\partial t}$. The time dependence of $\hat{A}$ appears because we treat the electric field classically.

To prove Eq. 54, start from Eq. 53 (it is more convenient here to use the notation $|\psi_t\rangle$ for $|\psi, t\rangle$):

$$\begin{aligned}\langle\psi_t\,|\,\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\,|\,\psi_t\rangle &\equiv \frac{\mathrm{d}}{\mathrm{d}t}(\langle\psi_t\,|\,\hat{A}\,|\,\psi_t\rangle)\\ &= \left(\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi_t|\right)\hat{A}\,|\,\psi_t\rangle + \langle\psi_t\,|\,\hat{A}\left(\frac{\mathrm{d}}{\mathrm{d}t}|\psi_t\rangle\right) + \langle\psi_t\,|\,\frac{\partial\hat{A}}{\partial t}\,|\,\psi_t\rangle \quad (55)\end{aligned}$$

Now we use the time-dependent Schrödinger equation to rewrite Eq. 55. Since

$$\frac{\mathrm{d}|\psi_t\rangle}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}\hat{H}|\psi_t\rangle, \tag{56}$$

the middle term in the right-hand side of Eq. 55 is

$$\langle\psi_t\,|\,\hat{A}\frac{\mathrm{d}}{\mathrm{d}t}\,|\,\psi_t\rangle = -\frac{\mathrm{i}}{\hbar}\langle\psi_t\,|\,\hat{A}\hat{H}\,|\,\psi_t\rangle \tag{57}$$

The first term in the right-hand side of Eq. 55 is[2]

$$\begin{aligned}\left(\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi_t|\right)\hat{A}|\psi_t\rangle &= \langle\hat{A}\psi_t\,|\,\frac{\mathrm{d}|\psi_t\rangle}{\mathrm{d}t}\rangle^* = \langle\hat{A}\psi_t\,|\left(\frac{-\mathrm{i}}{\hbar}\right)\hat{H}\psi_t\rangle^* \\ &= \frac{\mathrm{i}}{\hbar}\langle\hat{H}\psi_t\,|\,\hat{A}\psi_t\rangle = \frac{\mathrm{i}}{\hbar}\langle\psi_t\,|\,\hat{H}\hat{A}\,|\,\psi_t\rangle \qquad (58)\end{aligned}$$

Using Eqs. 57 and 58 in Eq. 55 gives

$$\frac{\partial}{\partial t}\langle\psi_t\,|\,\hat{A}\,|\,\psi_t\rangle = \langle\psi_t\,|\left(\frac{\mathrm{i}}{\hbar}[\hat{H},\hat{A}] + \frac{\partial\hat{A}}{\partial t}\right)|\,\psi_t\rangle \tag{59}$$

Comparing this to the definition in Eq. 53 proves Eq. 54.

In summary, the time evolution of the expectation (i.e. average) value of an observable A is given by the equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi,t\,|\,\hat{A}\,|\,\psi,t\rangle = \langle\psi,t\,|\,\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\,|\,\psi,t\rangle \tag{60}$$

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{A}] + \frac{\partial\hat{A}}{\partial t} \tag{61}$$

Exercise 4 (a) From a mathematical point of view, the definition of $\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}$ as a *time derivative* must be consistent with the known properties of

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[2] use the properties of the scalar product such as $\langle x\,|\,y\rangle = \langle y\,|\,x\rangle^*$ and $\langle x\,|\,\mathrm{i}y\rangle = \mathrm{i}\langle x\,|\,y\rangle$ and $\langle\hat{H}x\,|\,y\rangle = \langle x\,|\,\hat{H}\,|\,y\rangle$

the time-derivative operation. For the definitions

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle = \langle \psi, t \,|\, \frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \,|\, \psi, t\rangle \tag{62}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \psi, t \,|\, \hat{A}^2 \,|\, \psi, t\rangle = \langle \psi, t \,|\, \frac{\mathrm{d}\hat{A}^2}{\mathrm{d}t} \,|\, \psi, t\rangle \tag{63}$$

to be consistent with the properties of the time derivative, we must have

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{A}^2 = \frac{\mathrm{d}\hat{A}}{\mathrm{d}t}\,\hat{A} + \hat{A}\,\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \tag{64}$$

Prove that the definitions Eqs. 62 and 63 imply Eq. 64. Why didn't I use $\frac{\mathrm{d}}{\mathrm{d}t}\hat{A}^2 = 2\hat{A}(\frac{\mathrm{d}}{\mathrm{d}t}\hat{A})$?

(b) Show that if $\hat{A} = \hat{I}$ then $\mathrm{d}\hat{A}/\,\mathrm{d}t = 0$.

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§ 13 *Conserved observables.* We call an observable *conserved* if

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle = 0 \tag{65}$$

This means that if we prepare the system in the initial state $|\psi, 0\rangle$ and the initial average value of $\hat{A}$ is $\langle \psi, 0 \,|\, \hat{A} \,|\, \psi, 0\rangle$, then as the state evolves in time, the average value of $\hat{A}$, given by $\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle$, *does not change.*

Since

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle \equiv \langle \psi, t \,|\, \frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \,|\, \psi, t\rangle \tag{66}$$

an observable is conserved if and only if

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = 0 \tag{67}$$

In turn, if $\hat{A}$ is time-independent, Eq. 61 gives

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{A}] \tag{68}$$

and we have that (when $\hat{A}$ is time-independent)

$$\hat{A} \text{ is conserved if and only if } [\hat{H}, \hat{A}] = 0 \tag{69}$$

We know further that $[\hat{H}, \hat{A}] = 0$ (i.e. the two operators commute) if and only if they have common eigenstates.

Let us look at some examples of conserved/non-conserved observables. For the electron in a hydrogen atom, $\hat{\mathbf{L}}^2$, $\hat{L}_z$, and $\hat{H}$ commute (where $\hat{\mathbf{L}}$ is the angular momentum operator and $\hat{L}_z$ is its component on the OZ axis). Therefore angular momentum squared is conserved and so is $\hat{L}_z$. If we have a magnetic field along the OX axis, $\hat{L}_z$ no longer commutes with the Hamiltonian and is no longer conserved: its average value will change in time.

Another example is given by symmetry operations $\hat{R}$, which have the property

$$\hat{H}\hat{R}|\psi\rangle = \hat{R}\hat{H}|\psi\rangle \tag{70}$$

This means that we can apply the symmetry transform first and then apply $\hat{H}$ or vice versa, and get the same result. Therefore $\hat{R}$ is conserved. We conclude that if the wave function is an eigenstate of the symmetry operator $\hat{R}$ then it will be an eigenstate of $\hat{R}$ for the same eigenvalue, *forever.*

We have based our definition of conservation of $\hat{A}$ on the average value of $\hat{A}$. Is it possible that $\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle$ is unchanged in time (i.e. conserved) but some $\langle \psi, t \,|\, f(\hat{A}) \,|\, \psi, t\rangle$ is not? On physical grounds one can see immediately that if $\hat{A}$ is conserved then so is $f(\hat{A})$. This is borne out by mathematics.

Since

$$\hat{A} = \sum_{\alpha} |\alpha\rangle\, \alpha\, \langle\alpha| \tag{71}$$

where $|\alpha\rangle$ are the pure states of $\hat{A}$, we can write

$$\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle = \sum_{\alpha} \langle\psi, t\,|\,\alpha\rangle\, \langle\alpha\,|\,\psi, t\rangle\, \alpha = \sum_{\alpha} P_{\psi}(\alpha; t)\alpha \tag{72}$$

Here $P(\alpha; t)$ is the probability of getting the result α if you measure $\hat{A}$ when the system is in state $|\psi, t\rangle$. Note that if $\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle = 0$ then $P_{\psi}(\alpha; t)$ must be zero.

Also note that

$$\frac{\mathrm{d}\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle}{\mathrm{d}t} = 0 \;\text{ if and only if }\; \frac{\mathrm{d}P_{\psi}(\alpha; t)}{\mathrm{d}t} = 0$$

Hence, the time-independence of $\langle\psi, t\,|\,\hat{A}\,|\,\psi, t\rangle$ implies the time-independence of $P_{\psi}(\alpha; t)$.

Now, since

$$f(\hat{A}) = \sum_{\alpha} |\alpha\rangle\, f(\alpha)\, \langle\alpha|$$

and

$$\langle\psi, t\,|\,f(\hat{A})\,|\,\psi, t\rangle = \sum_{\alpha} P_{\psi}(\alpha; t) f(\alpha)$$

the time-independence of P_{ψ} implies the time-independence of $\langle\psi, t\,|\,f(\hat{A})\,|\,\psi, t\rangle$. Therefore if $\hat{A}$ is conserved, then so is $f(\hat{A})$.

A simpler way of showing this is to note that

$$[\hat{A}, \hat{H}] = 0 \;\text{ if and only if }\; [f(\hat{A}), \hat{H}] = 0$$

Exercise 5 (1) Do in detail the calculations sketched above.

(2) Show that $\frac{\mathrm{d}f(\hat{A})}{\mathrm{d}t} = \frac{\mathrm{d}f(\hat{A})}{\mathrm{d}\hat{A}}\frac{\mathrm{d}\hat{A}}{\mathrm{d}t}$. This indicates that if $\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = 0$ then $\frac{\mathrm{d}f(\hat{A})}{\mathrm{d}t} = 0$. Hence if $\hat{A}$ is conserved then so is $f(\hat{A})$.

(3) Show that $[\hat{H}, \hat{A}] = 0$ implies $[\hat{H}, f(\hat{A})] = 0$. Hence if $\hat{A}$ is conserved, so is $f(\hat{A})$.

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§ 14 *Heisenberg representation.* All observables are matrix elements of some operator, such as

$$\langle A \rangle_t \equiv \langle \psi, t \,|\, \hat{A} \,|\, \psi, t \rangle \tag{73}$$

Because $|\psi, t\rangle = \hat{U}(t)|\psi, 0\rangle$ we can rewrite this expression as

$$\langle A \rangle_t = \langle \psi, 0 \,|\, \hat{U}^\dagger(t)\hat{A}\hat{U}(t) \,|\, \psi, 0 \rangle \tag{74}$$

where $|\psi, 0\rangle$ is the initial state (at time 0) and $\hat{U}(t)$ is the propagator

$$\hat{U}(t) = \exp[-\mathrm{i}t\hat{H}/\hbar] \tag{75}$$

This is valid if $\hat{H}$ is time-independent. Using the notation

$$\hat{A}_{\mathrm{H}}(t) \equiv \hat{U}^\dagger(t)\hat{A}\hat{U}(t) = \exp[\mathrm{i}t\hat{H}/\hbar]\,\hat{A}\,\exp[-\mathrm{i}t\hat{H}/\hbar] \tag{76}$$

we can write Eq. 74 as

$$\langle A \rangle_t = \langle \psi, 0 \,|\, \hat{A}_{\mathrm{H}}(t) \,|\, \psi, 0 \rangle \tag{77}$$

The expression $\hat{A}_{\mathrm{H}}(t)$ defined by

$$\hat{A}_{\mathrm{H}}(t) = \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{A}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \tag{78}$$

is called $\hat{A}$ *in the Heisenberg picture.*

When we need to distinguish $\hat{A}_{\mathrm{H}}(t)$ from $\hat{A}$, we say that $\hat{A}$ is the operator in the Schrödinger picture. We have now two ways of writing the time evolution of the mean value of $\hat{A}$. In the Heisenberg picture,

$$\langle A\rangle_t = \langle \psi, 0 \,|\, \hat{A}_{\mathrm{H}}(t) \,|\, \psi, 0\rangle; \tag{79}$$

the state does not change in time but the operator does. In the Schrödinger picture,

$$\langle A\rangle_t = \langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle; \tag{80}$$

the wave function evolves while the operator is time-independent.

You will sometimes encounter expressions of the form

$$\langle A\rangle_t \equiv \langle \psi, t \,|\, \hat{A}(t) \,|\, \psi, t\rangle \tag{81}$$

where $\hat{A}(t)$ depends explictly on time. This happens when we approximate $\hat{A}(t)$ by using a classical expression. For example, it is common to use the operator $\hat{\vec{\boldsymbol{\mu}}} \cdot \vec{E}(t)$ for the interaction of light with a molecule. $\hat{\vec{\boldsymbol{\mu}}}$ is the dipole operator of the molecule and $\vec{E}(t)$ is the *classical* electric field of the light wave. This formula is an approximation. The correct procedure quantizes the electromagnetic field, and the classical electromagnetic field is replaced by the *time-independent* operator $\hat{\vec{E}}$. When the field is quantized, the interaction energy $\hat{\vec{\boldsymbol{\mu}}} \cdot \hat{\vec{E}}$ is time-independent, in the Schrödinger picture. The evolution of the electric field is given by the ket describing the state of radiation.

§ 15 *Time evolution in Heisenberg representation.* It is a matter of taste or convenience to use the Heisenberg or Schrödinger picture. If you decide to use the Heisenberg picture, it is easy to derive an equation of motion for

$\hat{A}_{\mathrm{H}}(t)$:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\hat{A}_{\mathrm{H}}(t) &= \left(\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{+\mathrm{i}t\hat{H}/\hbar}\right)\hat{A}\,\mathrm{e}^{-\mathrm{i}t\hat{H}/\hbar} + \mathrm{e}^{+\mathrm{i}t\hat{H}/\hbar}\,\hat{A}\left(\frac{\mathrm{d}}{\mathrm{d}t}\mathrm{e}^{-\mathrm{i}t\hat{H}/\hbar}\right) \\ &= \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{A}_{\mathrm{H}}(t)] \qquad (82)\end{aligned}$$

§ 16 *Summary.* In the Schrödinger picture, the operators are time-independent and the evolution of the system is described by changes in the wave function. The time-dependent state $|\psi,t\rangle$ satisfies the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial|\psi,t\rangle}{\partial t} = \hat{H}|\psi,t\rangle \qquad (83)$$

To solve this, we need to know $|\psi,t\rangle$ at one time (usually, but not necessarily, the "initial time"). The forces acting on the system are contained in $\hat{H}$. The changes in the properties of the system are encoded in $|\psi,t\rangle$.

If $\hat{H}$ is time-independent, this equation has the formal solution

$$|\psi,t\rangle = \mathrm{e}^{-\mathrm{i}(t-t_0)\hat{H}/\hbar}|\psi,t_0\rangle \qquad (84)$$

where $|\psi,t_0\rangle$ is the state at time t_0 and $|\psi,t\rangle$ is the state at time t.

If a classical approximation is made, the Hamiltonian can be time-dependent. In that case

$$\mathrm{i}\hbar\frac{\partial|\psi,t\rangle}{\partial t} = \hat{H}(t)|\psi,t\rangle \qquad (85)$$

is still valid, but Eq. 84 is not.

If a system is *closed* (no outside forces act on it) and has a Hamiltonian $\hat{H}$ and its state is an eigenstate $|E_n\rangle$ of $\hat{H}$, none of the measurable properties of the system will change in time; $|E_n\rangle$ is a stationary state of the system.

If a state $|\psi\rangle$ can be represented as a coherent superposition of energy eigenstates, then its average energy and the probability that a measurement yields a particular value for the energy are both independent of time. However, if $|\psi\rangle$ is a coherent superposition of energy eigenstates $|E_n\rangle$, the average value of a quantity A varies in time if for at least two states $|E_\alpha\rangle$ and $|E_\beta\rangle$ that appear in the representation of $|\psi\rangle$, we have

$$\langle E_\alpha \,|\, \hat{A} \,|\, E_\beta\rangle \neq 0 \tag{86}$$

The time derivative $\mathrm{d}\hat{A}/\,\mathrm{d}t$ of an operator was defined so that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \psi, t \,|\, \hat{A} \,|\, \psi, t\rangle \equiv \langle \psi, t \,|\, \frac{\mathrm{d}\hat{A}}{\mathrm{d}t} \,|\, \psi, t\rangle \tag{87}$$

and it was shown that

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{A}] \tag{88}$$

If a classical approximation makes $\hat{A}$ time-dependent, then

$$\frac{\mathrm{d}\hat{A}}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t} \tag{89}$$

Eqs. 88 and 89 do not hold if a classical approximation made $\hat{H}$ time-dependent.

From Eq. 88 it follows that an observable is conserved (i.e. its average value and the probability of having a particular value are constant) if its operator commutes with the Hamiltonian. This statement is true only if the system is closed (the Hamiltonian is time-independent).

There are two ways of expressing time evolution. In the Schrödinger picture, the operators are time-independent (except when approximations are made), the expectation value of an operator $\hat{O}$ is

$$\langle O\rangle_\psi(t) \equiv \langle \psi, t \,|\, \hat{O} \,|\, \psi, t\rangle, \tag{90}$$

and the state of the system evolves according to

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi,t\rangle = \hat{H}|\psi,t\rangle \tag{91}$$

In the Heisenberg picture, the mean value at time t, of a system that was at time t_0 in the state $|\psi,t_0\rangle$, is given by

$$\langle O\rangle_\psi(t) \equiv \langle \psi, t_0\,|\,\hat{O}_{\mathrm{H}}(t-t_0)\,|\,\psi,t_0\rangle \tag{92}$$

with

$$\hat{O}_{\mathrm{H}}(\tau) \equiv \mathrm{e}^{\mathrm{i}\tau\hat{H}/\hbar}\,\hat{O}\,\mathrm{e}^{-\mathrm{i}\tau\hat{H}/\hbar} \tag{93}$$

and

$$\frac{\mathrm{d}\hat{O}_{\mathrm{H}}(t)}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H},\hat{O}_{\mathrm{H}}(t)] \tag{94}$$

These two pictures give the same values for any observable.

Section 12.3. The Ehrenfest Equations of Motion

§ 17 *Derivation.* Eq. 59 allows us to derive equations of motion for the average values of any observable. We are going to use this capability to find how the mean position and the mean momentum change in time. We want to know this because in classical mechanics the state of a system is described by position and momentum. So it is possible to examine how quantum mechanics differs from or resembles classical mechanics.

For an arbitrary observable A and the corresponding operator $\hat{A}$, we have (combine Eqs. 60 and 61)

$$\begin{aligned}\frac{\mathrm{d}A_t}{\mathrm{d}t} &\equiv \frac{\mathrm{d}}{\mathrm{d}t}\langle\psi_t\,|\,\hat{A}\,|\,\psi_t\rangle \\ &= \frac{\mathrm{i}}{\hbar}\langle\psi_t\,|\,[\hat{H},\hat{A}]\,|\,\psi_t\rangle + \langle\psi_t\,|\,\frac{\partial\hat{A}}{\partial t}\,|\,\psi_t\rangle \end{aligned}\tag{95}$$

Let us use this equation for $\hat{A} = \hat{x}$. We obtain

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} \equiv \frac{\mathrm{d}}{\mathrm{d}t}\langle \psi_t \,|\, \hat{x} \,|\, \psi_t \rangle = \frac{\mathrm{i}}{\hbar}\langle \psi_t \,|\, [\hat{H}, \hat{x}] \,|\, \psi_t \rangle \tag{96}$$

The position operator is time-independent and therefore $\mathrm{d}\hat{x}/\,\mathrm{d}t = 0$.

If we choose $\hat{A} = \hat{p}$, then

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} \equiv \frac{\mathrm{d}}{\mathrm{d}t}\langle \psi_t \,|\, \hat{p} \,|\, \psi_t \rangle = \frac{\mathrm{i}}{\hbar}\langle \psi_t \,|\, [\hat{H}, \hat{p}] \,|\, \psi_t \rangle \tag{97}$$

Let us work out the consequences of these equations for a system with the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \tag{98}$$

Here $V(\hat{x})$ is the potential energy operator, which defines the force acting on the particle. To convert Eq. 96 into an equivalent form that is simpler or easier to interpret, we can use a number of relations involving commutators:

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \tag{99}$$

$$[a\hat{A} + b\hat{B}, c\hat{C}] = ac[\hat{A}, \hat{C}] + bc[\hat{B}, \hat{C}] \tag{100}$$

$$[\hat{A}, \hat{B}^2] = [\hat{A}, \hat{B}]\hat{B} + \hat{B}[\hat{A}, \hat{B}] \tag{101}$$

$$[\hat{A}, f(\hat{A})] = 0 \;\text{ for any function } f \tag{102}$$

Eqs. 99–101 can be easily verified by expanding the commutators (using the definition $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$). Eq. 102 follows from the facts that (since A is observable)

$$\hat{A} = \sum_n |a_n\rangle\, a_n\, \langle a_n|$$

where $|a_n\rangle$ are the pure states of $\hat{A}$ and a_n are its eigenvalues and that

$$f(\hat{A}) = \sum_n |a_n\rangle\, f(a_n)\, \langle a_n|$$

If you take into account the orthonormality condition $\langle a_n \,|\, a_m\rangle = \delta_{nm}$, you can easily prove Eq. 102.

Let us put these relations to use and simplify Eq. 96.

$$\begin{aligned}
\frac{\mathrm{d}x_t}{\mathrm{d}t} &= \frac{\mathrm{i}}{\hbar}\langle\psi_t \,|\, [\hat{H}, \hat{x}] \,|\, \psi_t\rangle \\
&= \frac{\mathrm{i}}{\hbar}\langle\psi_t \,|\, [\frac{\hat{p}^2}{2m} + V(\hat{x}), \hat{x}] \,|\, \psi_t\rangle \quad \text{(used Eq. 98)} \\
&= \frac{\mathrm{i}}{\hbar}\langle\psi_t \,|\, [\frac{\hat{p}^2}{2m}, \hat{x}] \,|\, \psi_t\rangle \quad \text{(used Eqs. 100 and 102)} \\
&= \frac{-\mathrm{i}}{2m\hbar}\langle\psi_t \,|\, [\hat{x}, \hat{p}^2] \,|\, \psi_t\rangle \quad \text{(used Eqs. 99 and 100)} \\
&= \frac{-\mathrm{i}}{2m\hbar}\langle\psi_t \,|\, [\hat{x}, \hat{p}]\hat{p} + \hat{p}[\hat{x}, \hat{p}] \,|\, \psi_t\rangle \quad \text{(used Eqs. 100 and 101)}
\end{aligned}$$

When we use in this equation the definition of momentum

$$[\hat{x}, \hat{p}] = \mathrm{i}\hbar \tag{103}$$

we obtain

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = \frac{-\mathrm{i}}{2m\hbar}(2\mathrm{i}\hbar)\langle\psi_t \,|\, \hat{p} \,|\, \psi_t\rangle$$

and therefore (recall that $\mathrm{i}^2 = -1$)

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = \frac{\langle\psi_t \,|\, \hat{p}\psi_t\rangle}{m} = \frac{p_t}{m} \tag{104}$$

This is a very surprising result: the equation of motion for x_t is identical to the equation from classical mechanics. This result is independent of the nature of the potential energy, hence of the forces acting on the particle.

Of course, to find how x_t evolves, we need to know how p_t evolves. So, let us evaluate $\mathrm{d}p_t/\,\mathrm{d}t$, by starting with Eq. 97 and using Eqs. 98–102:

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}\langle\psi_t \,|\, [\hat{H}, \hat{p}] \,|\, \psi_t\rangle$$

$$
\begin{aligned}
&= \frac{\mathrm{i}}{\hbar}\langle\psi_t\,|\,[\frac{\hat{p}^2}{2m}+V(\hat{x}),\hat{p}]\,|\,\psi_t\rangle \\
&= \frac{\mathrm{i}}{\hbar}\langle\psi_t\,|\,[V(\hat{x}),\hat{p}]\,|\,\psi_t\rangle \qquad (105)
\end{aligned}
$$

The only way we know how to evaluate $V(\hat{x})$ is to go to the coordinate representation where

$$\langle x\,|\,V(\hat{x})\,|\,\psi\rangle = V(x)\langle x\,|\,\psi\rangle \qquad (106)$$

and

$$\langle x\,|\,\hat{p}\,|\,\psi\rangle = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\langle x\,|\,\psi\rangle \qquad (107)$$

Using the representation of the unit operator $\hat{I}$ as

$$\int_{-\infty}^{+\infty}\mathrm{d}x\,|x\rangle\,\langle x| = \hat{I} \qquad (108)$$

in Eq. 105 and then using Eqs. 106 and 107 leads to

$$
\begin{aligned}
\frac{\mathrm{d}p_t}{\mathrm{d}t} &= \frac{\mathrm{i}}{\hbar}\int_{-\infty}^{+\infty}\mathrm{d}x\,\langle\psi_t\,|\,x\rangle\,\langle x\,|\,(V(\hat{x})\hat{p}-\hat{p}V(\hat{x}))\,|\,\psi_t\rangle \\
&= \frac{\mathrm{i}}{\hbar}\int_{-\infty}^{+\infty}\mathrm{d}x\,\langle\psi_t\,|\,x\rangle\left\{V(x)\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\langle x\,|\,\psi_t\rangle-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\left[V(x)\langle x\,|\,\psi_t\rangle\right]\right\} \\
&= \frac{\hbar}{\mathrm{i}}\left(-\frac{\hbar}{\mathrm{i}}\right)\int_{-\infty}^{+\infty}\mathrm{d}x\,\langle\psi_t\,|\,x\rangle\,\frac{\partial V}{\partial x}\,\langle x\,|\,\psi_t\rangle \\
&= -\int_{-\infty}^{+\infty}\mathrm{d}x\,\langle\psi_t\,|\,x\rangle\,\frac{\partial V}{\partial x}\,\langle x\,|\,\psi_t\rangle \qquad (109)
\end{aligned}
$$

This is the equation we were looking for.

This result has a simple physical interpretation.

$$P(x,t)\equiv\langle\psi_t\,|\,x\rangle\,\langle x\,|\,\psi_t\rangle = \psi_t(x)^*\psi_t(x) \qquad (110)$$

is the probability that the particle is at position x, at time t.

$$-\frac{\partial V}{\partial x}\equiv F(x) \qquad (111)$$

is the force acting on the particle when it is located at x. Using Eqs. 110 and 111, we can rewrite Eq. 109 as

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = \int_{-\infty}^{+\infty} \mathrm{d}x\, P(x,t)\, F(x) \equiv \langle F(x) \rangle_t \tag{112}$$

where the right-hand side is the *average force* acting on the particle at time t.

Note that

$$\int_{-\infty}^{+\infty} \langle \psi_t \,|\, x \rangle \, \frac{\partial V}{\partial x} \, \langle x \,|\, \psi_t \rangle \equiv \langle \psi_t \,|\, \frac{\partial V(\hat{x})}{\partial \hat{x}} \,|\, \psi_t \rangle$$

and therefore we can rewrite Eq. 109 as

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = -\langle \psi_t \,|\, \frac{\partial V(\hat{x})}{\partial \hat{x}} \,|\, \psi_t \rangle \tag{113}$$

This and the equation

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = \frac{p_t}{m} \tag{114}$$

are called the Ehrenfest equations of motion. If we know $V(x)$ and $|\psi_t\rangle$, we can use the Ehrenfest equations to calculate x_t and p_t. Of course, if we know $|\psi_t\rangle$, it is easier to directly evaluate $\langle \psi_t \,|\, \hat{x} \,|\, \psi_t \rangle$ and $\langle \psi_t \,|\, \hat{p} \,|\, \psi_t \rangle$. Nevertheless, the Ehrenfest equations are often useful, as you will see in other sections of these lectures.

§ **18** *The classical limit.* The classical equation of motion is

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = F(x_t) \tag{115}$$

It may seem that Eq. 112 is very close to that of the classical theory. In fact, if we assume that

$$\langle F(x) \rangle_t \cong F(x_t) \tag{116}$$

then Eq. 112 is the same as the classical equation, Eq. 115. In a different notation, Eq. 116 is

$$\int P(x,t)\,F(x)\;\mathrm{d}x \cong F(\int P(x,t)\,x\;\mathrm{d}x) \tag{117}$$

We replaced the average of force over positions with the force at the average position. This is rarely a good idea. When might it work?

In some limit, classical mechanics ought to work, but taking the classical limit is always tricky. In this context, the classical limit is valid if we can assume that Eq. 117 is valid. The latter is the case if we can set

$$P(x,t) = \delta(x - x_t) \tag{118}$$

Indeed, using this in Eq. 112 gives

$$\frac{\mathrm{d}p}{\mathrm{d}t} = F(x_t) \tag{119}$$

which is exactly the classical Newton equation. Is Eq. 118 reasonable? Strictly speaking, no. Using a δ-function for probability violates Heisenberg's principle. Therefore assuming that we can create a state in which Eq. 118 is valid is not consistent with quantum mechanics.

Let us abandon Eq. 118 and assume the situation shown in Fig. 2. The wave function is such that $P(x,t)$ *is sharply peaked around* x_t. In addition, the force $F(x)$ *varies smoothly* in the region around x_t. In that case

$$\begin{aligned}
\frac{\mathrm{d}p_t}{\mathrm{d}t} &= \int P(x)\,F(x)\;\mathrm{d}x \\
&\cong \int P(x,t)\left[F(x_t) + \frac{\partial F}{\partial x_t}(x - x_t) + \frac{1}{2}\frac{\partial^2 F}{\partial x_t^2}(x - x_t)^2\right]\;\mathrm{d}x \\
&= F(x_t) + \frac{\partial F}{\partial x_t}\int P(x,t)(x - x_t)\,\mathrm{d}x + \frac{1}{2}\frac{\partial^2 F}{\partial x_t^2}\int P(x)(x - x_t)^2\,\mathrm{d}x
\end{aligned}$$

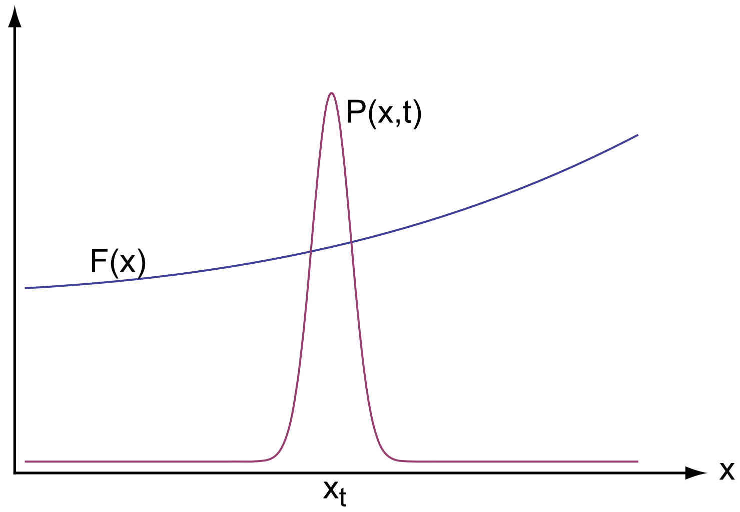

Figure 2: The situation in which classical and quantum mechanical equations of motion are close

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If $P(x,t)$ is symmetric around x_t, the first integral is zero. The classical equation $\mathrm{d}p_t/\,\mathrm{d}t = F_t$ holds if we can neglect the last term, which is possible if

$$F(x_t) \gg \frac{1}{2}\frac{\partial^2 F}{\partial x_t^2}\langle (x-x_t)^2\rangle$$

Essentially, classical mechanics is valid if the location of the particle is localized over a region δ in which the force is almost constant. We expect large deviations from classical theory when the particle is very delocalized (its position is very uncertain) and/or the forces vary rapidly in space.

§ 19 *The evolution of quantum mean position and momentum for a harmonic oscillator.*[3] I will first show that, for the harmonic oscillator, Newton's classical equations of motion appear to be identical to the Ehrenfest

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[3] In what follows I use a number of results for a harmonic oscillator. If $|E_m\rangle$ is an

equations for the mean position $x_t \equiv \langle \psi, t \,|\, \hat{x} \,|\, \psi, t \rangle$ and the mean momentum $p_t \equiv \langle \psi, t \,|\, \hat{p} \,|\, \psi, t \rangle$. Then I will show that this analogy is very misleading.

The potential energy for the oscillator is

$$V(\hat{x}) = \frac{k\hat{x}^2}{2} \tag{120}$$

I will denote the classical position by $x(t)$ and the classical momentum by $p(t)$, to distinguish them from the quantum mean values. Newton's equation is

$$\frac{\mathrm{d}p(t)}{\mathrm{d}t} = -\frac{\partial V}{\partial x(t)} = -k\, x(t) \tag{121}$$

We also have, from the definition of momentum,

$$p(t) = m\frac{\mathrm{d}x(t)}{\mathrm{d}t} \tag{122}$$

The Ehrenfest equation for x_t is (see Eq. 114)

$$m\frac{\mathrm{d}x_t}{\mathrm{d}t} = p_t = \langle \psi, t \,|\, \hat{p} \,|\, \psi, t \rangle \tag{123}$$

The other Ehrenfest equation, Eq. 113, gives

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = -\langle \psi, t \,|\; \frac{\partial V(\hat{x})}{\partial \hat{x}} \,|\, \psi, t \rangle = -\langle \psi, t \,|\; k\hat{x} \,|\, \psi, t \rangle = -k\, x_t \tag{124}$$

Except for notation ($x(t)$, $p(t)$ versus x_t, p_t), the Ehrenfest equations, Eqs. 123 and 124, *appear to be identical* to Newton's equations, Eqs. 121 and 122.

Should we conclude that p_t and x_t evolve classically? Absolutely not. The notation x_t and p_t hides the fact that x_t and p_t depend on $|\psi, t\rangle$ and this dependence is essential and makes the quantum results very different from the classical results.

---

energy eigenstate then $\langle E_m \,|\, \hat{x} \,|\, E_m \rangle = \langle E_m \,|\, \hat{p} \,|\, E_m \rangle = 0$ and neither $\langle E_{m+1} \,|\, \hat{x} \,|\, E_m \rangle$ nor $\langle E_{m+1} \,|\, \hat{p} \,|\, E_m \rangle$ is equal to zero.

Consider, for example, the case in which

$$|\psi, t\rangle = \mathrm{e}^{-\mathrm{i}E_3 t/\hbar}|E_3\rangle \tag{125}$$

The oscillator is in the excited eigenstate having the energy

$$E_3 = \hbar\omega(3 + 1/2) \tag{126}$$

Let us examine the Ehrenfest equations in this case. Eq. 123 becomes

$$m\frac{\mathrm{d}x_t}{\mathrm{d}t} = \langle E_3 \,|\, \mathrm{e}^{\mathrm{i}E_3 t/\hbar}\, \hat{p}\, \mathrm{e}^{-\mathrm{i}E_3 t/\hbar} \,|\, E_3\rangle = \langle E_3 \,|\, \hat{p} \,|\, E_3\rangle$$

We can calculate the matrix element and find that $\langle E_3 \,|\, \hat{p} \,|\, E_3\rangle = 0$. Therefore

$$\frac{\mathrm{d}x_t}{\mathrm{d}t} = 0$$

The mean position is a constant: it does not change in time! Eq. 124 gives

$$\frac{\mathrm{d}p_t}{\mathrm{d}t} = -k\, x_t = -k\langle E_3 \,|\, \hat{x} \,|\, E_3\rangle = 0$$

The mean momentum p_t is also constant.

Now let us look at the classical results. The energy of the oscillator is E_3 given by Eq. 126. We do not need to solve Newton's equation to know that this oscillator will oscillate, and $x(t)$ and $p(t)$ will change with time. If we solve Newton's equation, we find that

$$x(t) = A\cos(\omega t + \phi) \tag{127}$$

$$p(t) = -A\omega\sin(\omega t + \phi) \tag{128}$$

with

$$\omega = \sqrt{\frac{k}{m}} \tag{129}$$

You can see the derivation in the file `harmonic oscillator.nb`. Obviously the classical oscillator oscillates, with a frequency ω. The amplitude A and the phase ϕ are determined by the initial conditions.

There seems to be a complete disconnect between classical and quantum theory even though the Ehrenfest and Newton equations appear to be identical. However, the chasm is not as wide as it appears to be. The system is in the state $|E_3\rangle$ and we know that its energy is

$$E_3 = \hbar\omega(3 + 1/2) = 7\hbar\omega/2 \tag{130}$$

In classical mechanics this is not sufficient to determine the position and the momentum. We need two conditions (e.g. initial momentum and position) but we are only given one,

$$E_{\text{tot}} = \frac{p(t)^2}{2m} + \frac{k\,x(t)^2}{2} = 7\hbar\omega/2 \tag{131}$$

Using $x(t)$ and $p(t)$ given by Eqs. 127 and 128 in this equation for the total energy gives (see the file `harmonic oscillator.nb`)

$$E_{\text{tot}} = \frac{A^2 k}{2} = 7\hbar\omega/2$$

This one condition determines the amplitude A (since k is known). However, the phase ϕ cannot be determined from the information that we have.

Out of desperation, let us assume that the probability that the phase is between ϕ and $\phi +\, \mathrm{d}\phi$ is

$$P(\phi)\,\mathrm{d}\phi = \frac{\mathrm{d}\phi}{2\pi}$$

This means that any phase is as likely as any other phase. If we now average the position over the phase we obtain

$$\int_0^{2\pi} x(t)\frac{\mathrm{d}\phi}{2\pi} = 0$$

The average position and momentum are zero, just as in quantum mechanics.

From this example, we learn that when we compare quantum mechanics to classical mechanics, we must ensure that the two treatments make use of the same amount of information. In this example, when we specified that the state is $|E_3\rangle$, we only knew the total energy. This should not be compared to a usual classical calculation in which we know the initial momentum and position an information that is impossible to have if the particle obeys quantum mechanics).

Exercise 6 Show that if $|\psi_{t=0}\rangle$ is an energy eigenstate and $|\psi_t\rangle$ is evolved from it, then $\mathrm{d}\langle\psi_t\,|\,\hat{A}\,|\,\psi_t\rangle/\,\mathrm{d}t = 0$ regardless of what $\hat{A}$ is.

Let us now explore further paradoxes regarding the equations of motion for the harmonic oscillator.

Consider the case in which $|\psi_t\rangle$ is the coherent superposition of energy eigenstates

$$|\psi_t\rangle = \mathrm{e}^{-\mathrm{i}E_0 t/\hbar} a_0 |E_0\rangle + \mathrm{e}^{-\mathrm{i}E_1 t/\hbar} a_1 |E_1\rangle \tag{132}$$

Since $|\psi_t\rangle$ must be normalized, the coefficients a_0 and a_1 must satisfy

$$|a_0|^2 + |a_1|^2 = 1 \tag{133}$$

I choose them to be

$$a_0 = a_1 = \frac{1}{\sqrt{2}} \tag{134}$$

Also, since

$$|\langle E_0\,|\,\psi_t\rangle|^2 = |a_0|^2 = a_0^2,$$

a_0^2 is the probability that the system is in the state $|E_0\rangle$. The quantity a_1^2 has a similar meaning.

In §9, we have seen that for any operator $\hat{O}$, when $|\psi_t\rangle$ is given by Eq. 132, we have

$$\begin{aligned}\langle \psi_t \,|\, \hat{O} \,|\, \psi_t \rangle &= a_0^2 \langle E_0 \,|\, \hat{O} \,|\, E_0 \rangle + a_1^2 \langle E_1 \,|\, \hat{O} \,|\, E_1 \rangle \\ &\quad + 2 a_0 a_1 \langle E_0 \,|\, \hat{O} \,|\, E_1 \rangle \cos(\omega t) \end{aligned} \tag{135}$$

where

$$\omega = \frac{E_1 - E_0}{\hbar}$$

This is true because a_0, a_1, and $\langle E_0 \,|\, \hat{O} \,|\, E_1 \rangle$ are real numbers.

If we apply this to $\hat{O} \equiv \hat{x}$, we obtain (use $\langle E_0 \,|\, \hat{x} \,|\, E_0 \rangle = \langle E_1 \,|\, \hat{x} \,|\, E_1 \rangle = 0$)

$$x_t \equiv \langle \psi_t \,|\, \hat{x} \,|\, \psi_t \rangle = 2 a_0 a_1 \langle E_0 \,|\, \hat{x} \,|\, E_1 \rangle \cos(\omega t) \tag{136}$$

The matrix element $\langle E_0 \,|\, \hat{x} \,|\, E_1 \rangle$ is nonzero and the quantum mechanical oscillator oscillates, like in classical mechanics! The oscillation frequency ω is the same as the frequency in classical mechanics, $\omega = \sqrt{k/m}$. The same is true for

$$p_t = 2 a_0 a_1 \langle E_0 \,|\, \hat{p} \,|\, E_1 \rangle \cos(\omega t) \tag{137}$$

Before we claim that the oscillator behaves classically, let us note a number of anomalies. First, x_t and p_t have no phase in Eqs. 136 and 137, unlike the classical equations, Eqs. 127 and 128.

Second, if the state $|\psi_t\rangle$ had been

$$|\psi_t\rangle = a_0 |E_0\rangle \mathrm{e}^{-\mathrm{i} E_0 t/\hbar} + a_2 |E_2\rangle \mathrm{e}^{-\mathrm{i} E_2 t/\hbar} \tag{138}$$

then Eqs. 136 and 137 become

$$x_t = a_0 a_2 \langle E_0 \,|\, \hat{x} \,|\, E_2 \rangle \cos(2\omega t) \tag{139}$$

with

$$\frac{E_2 - E_0}{\hbar} = \frac{\hbar\omega(2 + 1/2) - \hbar\omega/2}{\hbar} = 2\omega$$

Having twice the frequency of the classical oscillator is baffling enough but in addition, $\langle E_0 \,|\, \hat{x} \,|\, E_2 \rangle = 0$, so $x_t = 0$ and the quantum oscillator does not oscillate at all. The same type of argument gives $p_t = 0$ in this case.

It seems that the classical-like behavior of x_t and p_t is peculiar to the state defined by Eq. 132. But even that is not true.

Consider next the evolution of x^2 (the potential energy is $kx^2/2$). From Eq. 135 we have

$$\begin{aligned} \langle \psi_t \,|\, \hat{x}^2 \,|\, \psi_t \rangle &= a_0^2 \langle E_0 \,|\, \hat{x}^2 \,|\, E_0 \rangle + a_1^2 \langle E_1 \,|\, \hat{x}^2 \,|\, E_1 \rangle \\ &\quad + 2a_0 a_1 \langle E_0 \,|\, \hat{x}^2 \,|\, E_1 \rangle \cos(\omega t) \end{aligned} \tag{140}$$

The classical result is $x^2(t) = A^2 \cos(\omega t + \phi)^2$ where A and ϕ are real numbers. Eq. 140 has no resemblance to the classical result. Even more embarrassing is the fact that

$$\langle E_0 \,|\, \hat{x}^2 \,|\, E_1 \rangle = 0$$

and therefore $\langle \psi_t \,|\, \hat{x}^2 \,|\, \psi_t \rangle$ given by Eq. 140 is time-independent! So $\langle \psi_t \,|\, \hat{x} \,|\, \psi_t \rangle$ oscillates as in classical mechanics but $\langle \psi_t \,|\, \hat{x}^2 \,|\, \psi_t \rangle$ is constant. You can also show that $\langle \psi_t \,|\, \hat{p}^2 \,|\, \psi_t \rangle$ is constant.

I am of the opinion that attempts to discuss quantum mechanics in terms of classical mechanics are often wrong-headed. Sometimes some quantities appear to behave as in classical mechanics but this is often a coincidence due to a special choice of state or to a superficial examination of the behavior of the other quantities in the system. In the case of the harmonic oscillator, there is a special state, called a coherent state, in which the motion is very close to classical theory. We will discuss it in a future chapter because it describes the photons produced by a laser.

Section 12.4. The Evolution of the Probability Density $\rho(\vec{r}, t)$

§ **20** *The continuity equation.* The probability that a particle is located in the volume $\mathrm{d}\vec{r}$ centered at the point $\vec{r}$ is

$$\psi^*(\vec{r}, t)\psi(\vec{r}, t)\,\mathrm{d}\vec{r} \equiv \rho(\vec{r}, t)\,\mathrm{d}\vec{r} \tag{141}$$

We want to find out how $\rho(\vec{r}, t)$ changes in time. From the time-dependent Schrödinger equation, we have

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\partial \psi^*}{\partial t}\psi + \psi^*\frac{\partial \psi}{\partial t} = \left(-\frac{\mathrm{i}}{\hbar}\hat{H}\psi^*\right)\psi + \psi^*\left(\frac{\mathrm{i}}{\hbar}\hat{H}\psi\right) \\ &= \frac{\mathrm{i}}{\hbar}[\psi^*\hat{H}\psi - \psi(\hat{H}\psi^*)] \end{aligned} \tag{142}$$

In this derivation, I used $\mathrm{i}\hbar\partial\psi/\partial t = \hat{H}\psi$ and $-\mathrm{i}\hbar\partial\psi^*/\partial t = \hat{H}\psi^*$. If

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{\vec{r}}) \tag{143}$$

then Eq. 142 becomes

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\mathrm{i}}{\hbar}[\psi^*\frac{\hat{p}^2}{2m}\psi - \psi\frac{\hat{p}^2}{2m}\psi^*] \\ &= \frac{\mathrm{i}}{\hbar}\left(-\frac{\hbar^2}{2m}\right)[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*] \end{aligned} \tag{144}$$

It is easy to verify that

$$\psi^*\nabla^2\psi - \psi\nabla^2\psi^* = \nabla\cdot\{\psi^*\nabla\psi - \psi\nabla\psi^*\} \tag{145}$$

Hence, if we use the notation

$$\vec{J} = \frac{\hbar}{2\mathrm{i}m}(\psi^*\nabla\psi - \psi\nabla\psi^*), \tag{146}$$

we can write

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \vec{J} \tag{147}$$

This is called the continuity equation and it ensures that probability is conserved.

The probability that the particle is in a volume V is

$$\int_{\mathrm{V}} \rho \, \mathrm{d}\vec{r}$$

The time derivative of this probability is

$$\frac{\partial}{\partial t} \int_{\mathrm{V}} \rho \, \mathrm{d}\vec{r} = \int_{\mathrm{V}} \frac{\partial \rho}{\partial t} \, \mathrm{d}\vec{r} = \int_{\mathrm{V}} \nabla \cdot \vec{J} \, \mathrm{d}\vec{r} = \int_{\mathrm{S}} \vec{J}(\vec{r}) \vec{n} \, \mathrm{dA}$$

In the last step, I used Gauss's Theorem. S is the surface of the volume V, and $\vec{n}$ is a unit vector perpendicular to the surface and pointing outward (from inside the volume towards the outside). The surface integral requires knowing $\vec{J}(\vec{r})$ for $\vec{r}$ at the points on the surface. $\vec{J}(\vec{r})\vec{n} \, \mathrm{dA}$ is the rate of flow of probability out of the volume, through the area dA.

$\vec{J}$ is an important quantity in scattering theory, in the theory of electrical conductivity, and in the theory of superfluidity.

We can write the flux as

$$\begin{aligned}
\vec{J}(\vec{r}, t) &= \langle \psi \,|\, \frac{\hat{p}\delta(\hat{\vec{r}} - \vec{r}\,') + \delta(\hat{\vec{r}} - \vec{r}\,')\hat{p}}{2m} \,|\, \psi \rangle \\
&= \frac{1}{2m} \langle p\psi \,|\, \delta(\vec{r} - \vec{r}\,') \,|\, \psi \rangle + \langle \psi \,|\, \delta(\hat{\vec{r}} - \vec{r}\,')\hat{p} \,|\, \psi \rangle \\
&= \frac{1}{2m} \left[\langle \psi \,|\, \delta(\hat{\vec{r}} - \vec{r}\,')\hat{p} \,|\, \psi \rangle \right]^* + \frac{1}{2m} \langle \psi \,|\, \delta(\hat{\vec{r}} - \vec{r}\,')\hat{\vec{p}} \,|\, \psi \rangle \\
&= \frac{1}{2m} \left(\int \mathrm{d}\vec{r} \, \psi(\vec{r})^* \, \delta(\vec{r} - \vec{r}\,') \frac{\hbar}{\mathrm{i}} \frac{\partial \psi}{\partial \vec{r}} \right)^* + \frac{1}{2m} \int \psi(\vec{r})^* \, \mathrm{d}\vec{r} \, \delta(\vec{r} - \vec{r}\,') \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \vec{r}} \psi(\vec{r}) \\
&= \frac{\hbar}{2\mathrm{i}m} \left[\psi(\vec{r}\,')^* \nabla_{\vec{r}\,'} \psi(\vec{r}\,') + \psi(\vec{r}\,')^* \nabla_{\vec{r}\,'} \psi(\vec{r}\,') \right]
\end{aligned}$$

Therefore the flux is the expectation value of the operator

$$\hat{\vec{J}}(\vec{r}\,') = \frac{1}{2}\left[\frac{\hat{p}}{m}\delta(\hat{\vec{r}} - \vec{r}\,') + \delta(\vec{r} - \vec{r}\,'\frac{\hat{p}}{m}\right] \tag{148}$$

Since $\delta(\hat{\vec{r}} - \vec{r}\,')$ is the density operator and $\hat{p}/m$ is velocity, this formula resembles the classical expression for the flux,

$$\vec{J}(\vec{r}\,') = \vec{v}\,\rho(\vec{r}\,') = \frac{1}{2}\left[\vec{v}\,\rho(\vec{r}\,') + \rho(\vec{r}\,')\,\vec{v}\right]$$

In classical physics, $\vec{v}\rho = \rho\vec{v}$, but in quantum mechanics these two quantities do not commute. The "symmetrization" in Eq. 148 is necessary because without it, $\hat{\vec{J}}$ would not be a Hermitian operator. Since the flux is an observable, $\hat{\vec{J}}$ must be Hermitian.