

## Chapter 10. The Time Evolution of Quantum Systems

### Section 10.1. Generalities

§ 1 *Introduction.* A typical experiment involving a quantum system has three stages:

- (a) The experimentalist “prepares” 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) After that he 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 denoted by  $|\psi, t_1\rangle$  or  $|\psi_{t_1}\rangle$ .
- (c) Then, at a time  $t_2 > t_1$ , he probes the system to find out what the action in (b) did to it. 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 *An example: a pump-probe experiment.* To illustrate this kind of procedure, we examine a pump-probe experiment performed with femtosecond pulses.

Consider a molecule that has the energy-level diagram shown in Fig. 1. Initially the molecule is in the ground state  $|g\rangle$ . Step (a) is very simple: use a cold gas and the molecule will be in the ground state.<sup>1</sup> Step (b) consists of exposing the molecule to a very short pulse of light at time  $t_1$ . We choose the light frequency  $\omega_1$  so that photon absorption is possible and the molecule is

---

<sup>1</sup>Many of the molecules in a cold gas are in an excited state of rotation. We ignore this in order to simplify the explanation. The discussion in the text applies to the molecules that are in some particular rotational state. The signal measured by the experimentalist in a real gas is the sum of the signals produced by the molecules in different rotational states.

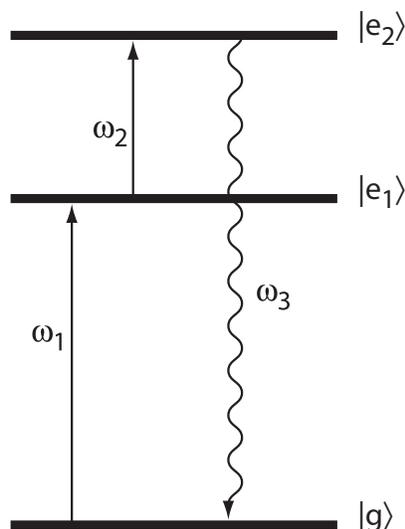


Figure 1: A pump-probe experiment

excited to the state  $|e_1\rangle$ . This state is such that the molecule will dissociate. To find out how long it takes for the molecule to fall apart, we expose it, at time  $t_2$ , to a short *probe pulse*, of frequency  $\omega_2$ , which excites the molecule to state  $|e_2\rangle$ . This excitation is possible only if the molecule is still in state  $|e_1\rangle$  (i.e. it has not dissociated). We measure the fluorescence (frequency  $\omega_3$ ) from the state  $|e_2\rangle$ , which is proportional to the number of molecules that have been excited at  $t_1$  and were not dissociated at  $t_2$ . By repeating the experiment with different times  $t_2$ , we monitor the rate of photodissociation. If  $t_2 - t_1$  is very small, most molecules are still in state  $|e_1\rangle$ , hence they absorb light and the emission from  $|e_2\rangle$  is intense. If  $t_2 - t_1$  is large, most molecules have dissociated and can no longer absorb light of frequency  $\omega_2$ . The emission from  $|e_2\rangle$  will be weak.

This is one among a large number of examples of experiments in which we act on a molecule to change its state. To interpret such experiments, we need an equation that tells us how the wave function changes in time when the molecule interacts with the agent of change.

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

is given by

$$i\hbar \frac{\partial}{\partial t} |\psi, t\rangle = \hat{H} |\psi, t\rangle \quad (1)$$

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

For the experiment described in §2,  $\hat{H}$  is the Hamiltonian of the molecule plus the Hamiltonian of the probe (light), plus the interaction energy between the probe and the molecule. In the case of light or the magnetic fields used in NMR, we assume that we can treat the fields by classical electromagnetic theory. Because of this, the Hamiltonian is simplified: the energy of the light or magnetic field no longer appears in  $\hat{H}$  and the interaction between light and molecule becomes *time-dependent*. It is possible to treat light quantum mechanically, and sometimes it is necessary to do so, but we do not do this in these introductory lectures.

In general the Hamiltonian is time-independent! It becomes time-dependent only because we treat a part of the whole system (e.g. the light) classically .

§ 4 *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  $t$ . If, between times  $t_0$  and  $t$ , you have acted on the system with light, this calculation will tell you the state of the system at time  $t$  that results from this action.

You can think of this equation as a set of mathematical rules that map an initial state  $|\psi, t_0\rangle$  into  $|\psi, t\rangle$ . 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.

Let us assume that we have prepared the system in the state  $|\psi, t_0\rangle$ , acted on it with an agent whose presence is included in  $\hat{H}$ , 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 probability that this is the case is

$$P(E_n, t) = |\langle E_n | \psi, t \rangle|^2 \quad (2)$$

where  $|E_n\rangle$  is an energy eigenstate of the molecular Hamiltonian. For the experiment illustrated in Fig. 1,  $|\langle e_1 | \psi, t_1 \rangle|^2$  is the probability that the molecule is in state  $|e_1\rangle$ , at time  $t_1$ ,  $|\langle e_2 | \psi, t_1 \rangle|^2$  is the probability that the molecule is excited to state  $|e_2\rangle$  at time  $t_1$ , and  $|\langle g | \psi, t_1 \rangle|^2$  is the probability that the molecule is not excited at time  $t_1$ .

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

$$\langle \hat{H} \rangle(t) \equiv \langle \psi, t | \hat{H} | \psi, t \rangle \quad (3)$$

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

$$\langle \hat{H} \rangle(t) = \sum_n P(E_n, t) E_n \quad (4)$$

which is indeed the mean energy.

### § 5 A few properties of the propagator.

1. The *group property* asserts that

$$\hat{U}(t_2, t_1) \hat{U}(t_1, t_0) = \hat{U}(t_2, t_0) \quad (5)$$

This is physically transparent: 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

$$\hat{U}(t_0, t) \hat{U}(t, t_0) | \psi, t_0 \rangle = | \psi, t_0 \rangle \quad (6)$$

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. 6 means that<sup>2</sup>

$$\hat{U}(t_0, t) = \hat{U}(t, t_0)^{-1} \quad (7)$$

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

$$\langle \psi, t | \psi, t \rangle = \langle \psi, t_0 | \psi, t_0 \rangle = 1 \quad (8)$$

We impose this condition because kets must be normalized at all times if all physical agents acting on the system are included in the Hamiltonian (this ensures that no energy is lost during propagation).

From the definition of  $\hat{U}$ ,

$$\langle \psi, t | \psi, t \rangle = \langle \psi, t_0 | \hat{U}(t, t_0)^\dagger \hat{U}(t, t_0) | \psi, t_0 \rangle = 1 \quad (9)$$

Since Eq. 8 tells us that  $\langle \psi, t_0 | \psi, t_0 \rangle = 1$ , we conclude that

$$\hat{U}(t, t_0)^\dagger \hat{U}(t, t_0) = \hat{I} \quad (10)$$

which is the definition of a unitary operator.

---

<sup>2</sup>Recall that if  $AB = BA = I$  then  $B$  is the inverse of  $A$  and we denote it by  $B \equiv A^{-1}$ .

The unitarity of the propagator follows from the demand that the wave function stay normalized throughout its evolution. Physically this means that the Hamiltonian includes all possible interactions so that energy and probability are conserved.

---

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

(b) Show that

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


---

**§ 6 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

$$\hat{U}(t, t_0)|\psi, t_0\rangle \triangleq |\psi, t\rangle \quad (11)$$

If the Hamiltonian is time-independent, it is easy to prove that

$$\hat{U}(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar} \quad (12)$$

Often one writes  $\exp[-i\hat{H}(t - t_0)/\hbar]$  but I changed the order of  $\hat{H}$  and the time to make sure that you don't think that  $\hat{H}$  is a function of time.

To prove Eq. 12, start with

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

and show that it satisfies Eq. 1. To do this, apply  $i\hbar \frac{\partial}{\partial t}$ . You get

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

This means that Eq. 12 is equivalent to the time-dependent Schrödinger equation. In other words,

$$|\psi, t\rangle = e^{-i(t-t_0)\hat{H}/\hbar} |\psi, t_0\rangle \equiv \hat{U}(t, t_0) |\psi, t_0\rangle \quad (13)$$

is the solution of the Schrödinger equation.

§ 7 *The energy eigenstates are stationary.* Let us assume that a molecule absorbs light and is excited into an energy eigenstate  $|E_n\rangle$ . How does the state  $|E_n\rangle$  evolve after it no longer interacts with the light? Using Eq. 13 and the fact that  $\hat{H}|E_n\rangle = E_n|E_n\rangle$  (by the definition of  $|E_n\rangle$ ), we have

$$\begin{aligned} |E_n, t\rangle &= \hat{U}(t, t_0)|E_n, t_0\rangle \\ &= e^{-i(t-t_0)\hat{H}/\hbar}|E_n, t_0\rangle = e^{-i(t-t_0)E_n/\hbar}|E_n\rangle \end{aligned} \quad (14)$$

Here  $|E_n, t_0\rangle$  is the state when the light is turned off and it is equal to  $|E_n\rangle$ .  $|E_n, t\rangle$  is the state at a later time  $t$  (no external agent acts between time  $t_0$  and time  $t$ ). Eq. 14 says that the state  $|E_n, t\rangle$  at time  $t$  is proportional to  $|E_n\rangle$ . The only change is multiplication by the phase factor  $\exp[-i(t-t_0)E_n/\hbar]$ . 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. 14)

$$\begin{aligned} \langle E_n, t | \hat{O} | E_n, t \rangle &= \langle e^{-i(t-t_0)E_n/\hbar} E_n | \hat{O} | e^{-i(t-t_0)E_n/\hbar} E_n \rangle \\ &= e^{i(t-t_0)E_n/\hbar} e^{-i(t-t_0)E_n/\hbar} \langle E_n | \hat{O} | E_n \rangle \\ &= \langle E_n | \hat{O} | E_n \rangle \end{aligned} \quad (15)$$

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*.

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 photons until it reaches 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*. It 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. This “expanded” state is stationary, but the state of the molecule alone is not, since energy can be transferred from the molecule to the field. The excited state is no longer stationary.

§ 8 *A comparison to classical theory.* The statement that nothing changes when the state of a closed system is an energy eigenstate is quite shocking for a classical-minded person. Consider the example of a harmonic oscillator. Let us assume that the oscillating particle is not charged, so we do not have to deal with the issue of radiation. Let us consider such an oscillator in the energy eigenstate  $|E_3\rangle$ . The energy of the oscillator is

$$E_3 = \left(3 + \frac{1}{2}\right) \hbar\omega \quad (16)$$

This is the total energy. If the oscillator is classical and “closed” (no outside forces act on it),  $E_3$  is constant. However, in classical physics

$$E_3 = \frac{m v(t)^2}{2} + \frac{k x(t)^2}{2} \quad (17)$$

where  $m$  is the mass,  $k$  is the force constant,  $v(t)$  is velocity, and  $x(t)$  is position. If all I know is that the energy is equal to  $E_3$ , then the classical oscillator cannot be still. The equation of motion for the oscillator is

$$m \frac{d^2 x(t)}{dt^2} = -k x(t) \quad (18)$$

and the solution of the equation of motion is

$$x(t) = A \cos \left( \sqrt{\frac{k}{m}} t + \phi \right) \quad (19)$$

where  $A$  and  $\phi$  are constants. If we use  $x(t)$  from Eq. 19 to calculate the right-hand side of Eq. 17, we obtain

$$E_3 = \frac{A^2 k}{2} \quad (20)$$

The total energy is constant, and fixing it to be  $(3 + \frac{1}{2})\hbar\omega$  tells us what  $A^2$  is. The value of  $\phi$  remains undetermined, if all we know is the total energy. Nevertheless, no matter what we take for  $\phi$ , the values of  $x$  and  $v$  change in time. Quantum mechanics says that no such time dependence is observable, meaning that  $\langle \psi_3, t | \hat{x} | \psi_3, t \rangle$  and  $\langle \psi_3, t | \hat{p} | \psi_3, t \rangle$  are time-independent, and so are  $P_{\psi_3}(x)$  and  $P_{\psi_3}(p)$ .

---

**Exercise 2** What is the average value of  $x(t)$  and  $v(t)$  if you assume that the probability that the phase  $\phi$  is in the interval between  $\phi$  and  $\phi + d\phi$ , is given by  $\frac{1}{2\pi}d\phi$  (all phase values between zero and  $2\pi$  are equally probable)? What are the average values of  $mv^2/2$  and of  $kx^2/2$ ? Do they vary in time?

---

**§ 9** *The evolution of a coherent superposition of energy eigenstates.* Let us examine what happens if we act on a system and we change its state to

$$|\psi, t_0\rangle = a_n|E_n\rangle + a_m|E_m\rangle \quad (21)$$

Here  $|E_n\rangle$  and  $|E_m\rangle$  are eigenstates of the Hamiltonian of the isolated system:

$$\hat{H}|E_\beta\rangle = E_\beta|E_\beta\rangle \text{ with } \beta = n \text{ or } m \quad (22)$$

How does the system evolve after I have stopped acting on it? Since I no longer act on the system, the Hamiltonian is that of the system alone (we ignore photon emission). Therefore, the propagator is

$$\hat{U}(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar} \quad (23)$$

The wave function at time  $t$  is

$$\begin{aligned} |\psi, t\rangle &= \hat{U}(t, t_0)|\psi, t_0\rangle = a_n\hat{U}|E_n\rangle + a_m\hat{U}|E_m\rangle \\ &= a_n e^{-i(t-t_0)E_n/\hbar}|E_n\rangle + a_m e^{-i(t-t_0)E_m/\hbar}|E_m\rangle \end{aligned} \quad (24)$$

This calculation uses the facts that

$$e^{-i(t-t_0)\hat{H}/\hbar} = \sum_{\alpha} |E_{\alpha}\rangle e^{-i(t-t_0)E_{\alpha}/\hbar} \langle E_{\alpha}| \quad (25)$$

and

$$\langle E_{\alpha} | E_{\beta} \rangle = \delta_{\alpha\beta} \quad (26)$$

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

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

Similarly,

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

What are these probabilities at time  $t$ ?

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

Thus we see that

$$P_m(t) = P_m(t_0) \quad (30)$$

and, similarly, that  $P_n(t) = P_n(t_0)$ . The probability that the molecule has the energy  $E_n$  (or  $E_m$ ) does not change in time. If we measure the energy of the state  $|\psi, t\rangle$ , we get at time  $t$  the same result as at time  $t_0$ .

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

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

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

Let us continue examining the evolution of a coherent state by first ignoring the decay mentioned above.

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 operator  $\hat{O}$ :

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

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

$$\begin{aligned} \langle \psi, t | \hat{O} | \psi, t \rangle &= a_m^* a_m \langle E_m | \hat{O} | E_m \rangle + a_n^* a_n \langle E_n | \hat{O} | E_n \rangle \\ &\quad + a_m^* a_n e^{-i(E_n - E_m)(t-t_0)/\hbar} \langle E_m | \hat{O} | E_n \rangle \end{aligned} \quad (32)$$

$$+ a_n^* a_m e^{+i(E_n - E_m)(t-t_0)/\hbar} \langle E_n | \hat{O} | E_m \rangle \quad (33)$$

Now use (Eqs. 28 and 29)

$$P_n = a_n^* a_n, \quad P_m = a_m^* a_m \quad (34)$$

and note that the fourth term is the complex conjugate of the third. Therefore we can write the last two terms together as (use  $z + z^* = 2\Re z$ )

$$2\Re \left\{ a_m^* a_n e^{-i(E_n - E_m)(t - t_0)/\hbar} \langle E_m | \hat{O} | E_n \rangle \right\} \quad (35)$$

Using Eqs. 34 and 35 in Eq. 33 gives

$$\begin{aligned} \langle \psi, t | \hat{O} | \psi, t \rangle &= P_m \langle E_m | \hat{O} | E_m \rangle + P_n \langle E_n | \hat{O} | E_n \rangle \\ &\quad + 2\Re \left\{ a_m^* a_n e^{-i(E_n - E_m)(t - t_0)/\hbar} \langle E_m | \hat{O} | E_n \rangle \right\} \end{aligned} \quad (36)$$

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. 36 becomes zero and the mean energy is independent of time. However, if  $\hat{O}$  is such that

$$\langle E_m | \hat{O} | E_n \rangle \neq 0 \quad (37)$$

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

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \quad (38)$$

This additional term is very similar to the one causing interference when two waves are overlapping. Because of this, we say that the two states  $|E_n\rangle$  and  $|E_m\rangle$  interfere. The presence of this term leads to *quantum interference* or to *coherent oscillations*.

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

$$\hat{O} = |x\rangle \langle x| \equiv \hat{P}(x) \quad (39)$$

which is the probability operator that the particle is located at point  $x$ . Introducing this into Eq. 36 gives

$$\begin{aligned} \langle \psi, t | \hat{P}(x) | \psi, t \rangle &= P_m \langle E_m | x \rangle \langle x | E_m \rangle + P_n \langle E_n | x \rangle \langle x | E_n \rangle \\ &\quad + 2\Re \left\{ a_m^* a_n e^{-i\omega_{nm}(t - t_0)} \langle E_m | x \rangle \langle x | E_n \rangle \right\} \end{aligned} \quad (40)$$

But

$$\langle x | E_m \rangle \equiv \psi_{E_m}(x) \quad (41)$$

is the wave function in the Schrödinger representation and

$$\langle E_m | x \rangle = \psi_{E_m}^*(x) \quad (42)$$

Using Eqs. 41 and 42 in Eq. 40 gives

$$\begin{aligned} \langle \psi, t | \hat{P}(x) | \psi, t \rangle &= P_m \psi_{E_m}(x)^* \psi_{E_m}(x) + P_n \psi_{E_n}(x)^* \psi_{E_n}(x) \\ &\quad + 2\Re \left\{ \psi_{E_m}(x)^* \psi_{E_n}(x) e^{-i\omega_{nm}(t-t_0)} a_m^* a_n \right\} \end{aligned} \quad (43)$$

The probability that the particle is located at  $x$  *changes in time*. The first term on the right-hand side in Eq. 43 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. 43 are exactly what one would expect from classical probability theory. The third term, the time-dependent one, is not! This is a term present only in quantum theory. Its presence makes the particle position oscillate with the frequency  $\omega_{nm}$ .

This movement is characterized by one frequency 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

$$|\psi, t_0\rangle = \sum_{n=0}^M a_n |E_n\rangle \quad (44)$$

then

$$\begin{aligned} \langle \psi, t | \hat{O}(x) | \psi, t \rangle &= \sum_{n=0}^M a_n^* a_n \langle E_n | \hat{O} | E_n \rangle \\ &\quad + 2\Re \left\{ \sum_{n=0}^M \sum_{m>n}^M a_n^* a_m \langle E_n | \hat{O} | E_m \rangle e^{-i(E_m - E_n)(t-t_0)/\hbar} \right\} \end{aligned} \quad (45)$$

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

$$\begin{aligned} \langle \psi, t | \hat{O}(x) | \psi, t \rangle &= \sum_{n=0}^M a_n^2 \langle E_n | \hat{O} | E_n \rangle \\ &+ 2 \sum_{n=0}^M \sum_{m>n}^M a_n a_m \langle E_n | \hat{O} | E_m \rangle \cos[\omega_{mn}(t - t_0)] \end{aligned} \quad (46)$$

**§ 10 Coherent spectroscopy.** Coherent oscillations are used in spectroscopy to measure differences between the energy eigenstates of a molecule. I discuss here one example.

If we use a short pulse (say, a picosecond or less) to excite a molecule, there is an uncertainty in the energy of the photons. Because of this, there is an uncertainty in the energy of the states being excited, and this means that we excite a coherent superposition of states. We will prove this soon, when we study the interaction of light with molecules. Let us accept for now that this is the case and ask how the molecules excited in this way emit light. One can show that the emission intensity is proportional to

$$|\langle E_g | \hat{\mu} | \psi, t \rangle|^2, \quad (47)$$

where  $\hat{\mu}$  is the dipole operator,  $|E_g\rangle$  is the ground state of the molecule, and  $|\psi, t\rangle$  is the state of the molecule *after* it interacted with a very short pulse of light.

If the duration of the pulse and its frequency are chosen so that

$$|\psi, t\rangle = a_1 |E_1\rangle + a_2 |E_2\rangle \quad (48)$$

then we have

$$\langle E_g | \hat{\mu} | \psi, t \rangle = a_1 e^{-iE_1 t/\hbar} \langle E_g | \hat{\mu} | E_1 \rangle + a_2 e^{-iE_2 t/\hbar} \langle E_g | \hat{\mu} | E_2 \rangle \quad (49)$$

and Eq. 47 becomes

$$\begin{aligned} |\langle E_g | \hat{\mu} | \psi, t \rangle|^2 &= |a_1|^2 |\langle E_g | \hat{\mu} | E_1 \rangle|^2 + |a_2|^2 |\langle E_g | \hat{\mu} | E_2 \rangle|^2 \\ &+ 2\Re \left\{ a_1^* a_2 \langle E_g | \hat{\mu} | E_1 \rangle^* \langle E_g | \hat{\mu} | E_2 \rangle e^{-i(E_2 - E_1)t/\hbar} \right\} \end{aligned} \quad (50)$$

The intensity of the emitted light oscillates in time.

Eq. 50 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

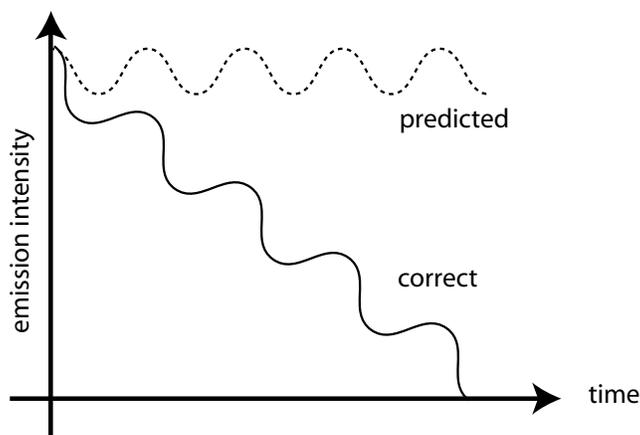


Figure 2: Oscillating decay: the dotted line is the behavior predicted by Eq. 50 and the solid line is the correct behavior

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. 49 will predict an oscillating, exponential decay (Fig. 2). The dotted line shows the prediction of Eq. 50 and the solid line shows the correct evolution. However the two curves oscillate at the same frequency. 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 the period of oscillation is long and easy to measure. On the other hand, measuring this small difference by absorption spectroscopy requires very high accuracy.

**§ 11** *The time scale on which an observable changes.* Eq. 46 has an interesting consequence sometimes called the time and energy uncertainty relation. The time evolution of  $\langle \psi, t | \hat{O} | \psi, t \rangle$  depends on the set of frequencies  $\omega_{mn}$ . 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. 46 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 when

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

This means

$$[\max(E_m - E_n)] \Delta t / \hbar \geq \frac{\pi}{10} \quad (51)$$

Here  $\max(E_m - E_n)$  is the largest energy difference in Eq. 46 as  $m$  and  $n$  vary.

If the state of the system is represented by two energy eigenstates then the condition is

$$\Delta E \Delta t \approx \frac{\hbar \pi}{10} \quad (52)$$

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. 51 tells us that the time in which we will notice a change in the state of the system is of order  $\hbar/\Delta E$  where  $\Delta E$  is the largest difference between the energies involved in the excited state. In other words, 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 10.2. 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

$$\langle \psi, t | \hat{A} | \psi, t \rangle \equiv \langle \hat{A} \rangle_t \quad (53)$$

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

$$\frac{d}{dt} \langle \psi, t | \hat{A} | \psi, t \rangle \stackrel{\text{def}}{=} \langle \psi, t | \frac{d\hat{A}}{dt} | \psi, t \rangle \quad (54)$$

Below we will find that

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t} \quad (55)$$

The last term appears only if  $\hat{A}$  is a time-dependent operator. For example,  $\hat{A} = \hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t)$  couples the electric field of light to a molecule and depends on time through  $\mathbf{E}(t)$ , the *classical* electric field. In this case  $\frac{\partial \hat{A}}{\partial t} = \hat{\boldsymbol{\mu}} \cdot \frac{\partial \mathbf{E}(t)}{\partial t}$ .

To prove Eq. 55, start from Eq. 54 (it is more convenient here to use the notation  $|\psi_t\rangle$  for  $|\psi, t\rangle$ ):

$$\begin{aligned} \langle \psi_t | \frac{d\hat{A}}{dt} | \psi_t \rangle &\equiv \frac{d}{dt} (\langle \psi_t | \hat{A} | \psi_t \rangle) \\ &= \left( \frac{d}{dt} \langle \psi_t | \right) \hat{A} | \psi_t \rangle + \langle \psi_t | \hat{A} \left( \frac{d}{dt} | \psi_t \rangle \right) + \langle \psi_t | \frac{\partial \hat{A}}{\partial t} | \psi_t \rangle \end{aligned} \quad (56)$$

Now we use the time-dependent Schrödinger equation to rewrite Eq. 56. Since

$$\frac{d|\psi_t\rangle}{dt} = -\frac{i}{\hbar} \hat{H} |\psi_t\rangle, \quad (57)$$

the middle term in the right-hand side of Eq. 56 is

$$\langle \psi_t | \hat{A} \frac{d}{dt} | \psi_t \rangle = -\frac{i}{\hbar} \langle \psi_t | \hat{A} \hat{H} | \psi_t \rangle \quad (58)$$

The first term in the right-hand side of Eq. 56 is

$$\begin{aligned} \left( \frac{d}{dt} \langle \psi_t | \right) \hat{A} | \psi_t \rangle &= \langle \hat{A} \psi_t | \frac{d|\psi_t\rangle}{dt} \rangle^* = \langle \hat{A} \psi_t | \left( \frac{-i}{\hbar} \right) \hat{H} \psi_t \rangle^* \\ &= \frac{i}{\hbar} \langle \hat{A} \psi_t | \hat{H} \psi_t \rangle = \frac{i}{\hbar} \langle \psi_t | \hat{A} \hat{H} | \psi_t \rangle \end{aligned} \quad (59)$$

Using Eqs. 58 and 59 in Eq. 56 gives

$$\frac{\partial}{\partial t} \langle \psi_t | \hat{A} | \psi_t \rangle = \langle \psi_t | \left( \frac{i}{\hbar} [\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t} \right) | \psi_t \rangle \quad (60)$$

Comparing this to the definition in Eq. 54 proves Eq. 55.

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

$$\frac{d}{dt} \langle \psi, t | \hat{A} | \psi, t \rangle = \langle \psi, t | \frac{d\hat{A}}{dt} | \psi, t \rangle \quad (61)$$

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t} \quad (62)$$


---

**Exercise 3** (a) From a mathematical point of view, the definition of  $\frac{d\hat{A}}{dt}$  as a *time derivative* must be consistent with the known properties of the time-derivative operation. For the definitions

$$\frac{d}{dt}\langle\psi, t|\hat{A}|\psi, t\rangle = \langle\psi, t|\frac{d\hat{A}}{dt}|\psi, t\rangle \quad (63)$$

$$\frac{d}{dt}\langle\psi, t|\hat{A}^2|\psi, t\rangle = \langle\psi, t|\frac{d\hat{A}^2}{dt}|\psi, t\rangle \quad (64)$$

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

$$\frac{d}{dt}\hat{A}^2 = \frac{d\hat{A}}{dt}\hat{A} + \hat{A}\frac{d\hat{A}}{dt} \quad (65)$$

Prove that the definitions Eqs. 63 and 64 imply Eq. 65. Why didn't I use  $\frac{d}{dt}\hat{A}^2 = 2\hat{A}(\frac{d}{dt}\hat{A})$ ?

(b) Show that if  $\hat{A} = \hat{I}$  then  $\frac{d\hat{A}}{dt} = 0$ .

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

$$\frac{d}{dt}\langle\psi, t|\hat{A}|\psi, t\rangle = 0 \quad (66)$$

This means that if we prepare the system in the state  $|\psi, 0\rangle$  and the 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

$$\frac{d}{dt}\langle\psi, t|\hat{A}|\psi, t\rangle \equiv \langle\psi, t|\frac{d\hat{A}}{dt}|\psi, t\rangle \quad (67)$$

an observable is conserved if and only if

$$\frac{d\hat{A}}{dt} = 0 \quad (68)$$

In turn, if  $\hat{A}$  is not time-dependent,

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{A}] \quad (69)$$

and we have that (if  $\hat{A}$  is not time-dependent)

$$\hat{A} \text{ is conserved if and only if } [\hat{H}, \hat{A}] = 0 \quad (70)$$

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,  $\hat{L}^2$ ,  $\hat{L}_z$ , and  $\hat{H}$  commute (where  $\hat{L}$  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. If we have a symmetry operator  $\hat{R}$  then

$$\hat{H}\hat{R}|\psi\rangle = \hat{R}\hat{H}|\psi\rangle \quad (71)$$

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

$$\hat{A} = \sum_{\alpha} |\alpha\rangle \alpha \langle\alpha| \quad (72)$$

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

$$\langle\psi, t|\hat{A}|\psi, t\rangle = \sum_{\alpha} \langle\psi, t|\alpha\rangle \langle\alpha|\psi, t\rangle \alpha = \sum_{\alpha} P_{\psi}(\alpha; t) \alpha \quad (73)$$

Here  $P(\alpha; t)$  is the probability of getting the result  $\alpha$  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

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

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  $P_\psi$  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 4** (1) Do in detail the calculations sketched above.

- (2) Show that  $\frac{df(\hat{A})}{dt} = \frac{df(\hat{A})}{d\hat{A}} \frac{d\hat{A}}{dt}$ . This indicates that if  $\frac{d\hat{A}}{dt} = 0$  then  $\frac{df(\hat{A})}{dt} = 0$ . 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  $f(\hat{A})$ .

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

$$\langle A \rangle_t \equiv \langle \psi, t | \hat{A} | \psi, t \rangle \quad (74)$$

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

$$\langle A \rangle_t = \langle \psi, 0 | \hat{U}^\dagger(t) \hat{A} \hat{U}(t) | \psi, 0 \rangle \quad (75)$$

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

$$\hat{U}(t) = \exp[-it\hat{H}/\hbar] \quad (76)$$

Using the notation

$$\hat{A}_H(t) \equiv \hat{U}^\dagger(t) \hat{A} \hat{U}(t) = \exp[it\hat{H}/\hbar] \hat{A} \exp[-it\hat{H}/\hbar] \quad (77)$$

we can write Eq. 75 as

$$\langle A \rangle_t = \langle \psi, 0 | \hat{A}_H(t) | \psi, 0 \rangle \quad (78)$$

The expression  $\hat{A}_H(t)$  is called the Heisenberg picture of  $\hat{A}$ .

When we need to distinguish  $\hat{A}_H(t)$  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,

$$\langle A \rangle_t = \langle \psi, 0 | \hat{A}_H(t) | \psi, 0 \rangle; \quad (79)$$

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

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

the wave function evolves while the operator is time-independent. You will sometimes encounter expressions of the form

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

where  $\hat{A}(t)$  depends explicitly on time. This happens when we approximate  $\hat{A}(t)$  by using a classical expression. For example, it is common to use the operator  $\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(t)$  for the interaction of light with a molecule.  $\hat{\boldsymbol{\mu}}$  is the dipole operator of the molecule and  $\mathbf{E}(t)$  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  $\hat{\mathbf{E}}$ . When the field is quantized, the interaction energy  $\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}}$  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  $\hat{A}_H(t)$ :

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

**§ 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

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

The forces acting on the system are contained in  $\hat{H}$ . The changes in the system are contained in  $|\psi, t\rangle$ .

This equation has the formal solution

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

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

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

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 again  $|\psi\rangle$  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

$$\langle E_\alpha | \hat{A} | E_\beta \rangle \neq 0 \quad (86)$$

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

$$\frac{d}{dt} \langle \psi, t | \hat{A} | \psi, t \rangle \equiv \langle \psi, t | \frac{d\hat{A}}{dt} | \psi, t \rangle \quad (87)$$

and it was shown that

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{A}] \quad (88)$$

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

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t} \quad (89)$$

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.

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

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

and the state of the system evolves according to

$$i\hbar \frac{\partial}{\partial t} |\psi, t\rangle = \hat{H} |\psi, t\rangle \quad (91)$$

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

$$\langle O \rangle_\psi(t) \equiv \langle \psi, t_0 | \hat{O}_H(t - t_0) | \psi, t_0 \rangle \quad (92)$$

with

$$\hat{O}_H(\tau) \equiv e^{i\tau\hat{H}/\hbar} \hat{O} e^{-i\tau\hat{H}/\hbar} \quad (93)$$

and

$$\frac{d\hat{O}_H(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{O}_H(t)] \quad (94)$$

These two pictures give the same values for any observable.

### Section 10.3. The Ehrenfest equations of motion

§ 17 *Derivation.* Eq. 60 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.

For an arbitrary observable  $A$  and corresponding operator  $\hat{A}$ , we have (combine Eqs. 61 and 62)

$$\begin{aligned}\frac{dA_t}{dt} &\equiv \frac{d}{dt}\langle\psi_t|\hat{A}|\psi_t\rangle \\ &= \frac{i}{\hbar}\langle\psi_t|[\hat{H},\hat{A}]|\psi_t\rangle + \langle\psi_t|\frac{\partial\hat{A}}{\partial t}|\psi_t\rangle\end{aligned}\quad (95)$$

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

$$\frac{dx_t}{dt} \equiv \frac{d}{dt}\langle\psi_t|\hat{x}|\psi_t\rangle = \frac{i}{\hbar}\langle\psi_t|[\hat{H},\hat{x}]|\psi_t\rangle \quad (96)$$

The position operator is not time-dependent and therefore  $d\hat{x}/dt = 0$ . If we choose instead  $\hat{A} = \hat{p}$ , then we obtain

$$\frac{dp_t}{dt} \equiv \frac{d}{dt}\langle\psi_t|\hat{p}|\psi_t\rangle = \frac{i}{\hbar}\langle\psi_t|[\hat{H},\hat{p}]|\psi_t\rangle \quad (97)$$

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

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

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:

$$[\hat{A},\hat{B}] = -[\hat{B},\hat{A}] \quad (99)$$

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

$$[\hat{A},\hat{B}^2] = [\hat{A},\hat{B}]\hat{B} + \hat{B}[\hat{A},\hat{B}] \quad (101)$$

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

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 in simplifying Eq. 96.

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

When we use in this equation the definition of momentum

$$[\hat{x}, \hat{p}] = i\hbar \quad (103)$$

we obtain

$$\frac{dx_t}{dt} = \frac{-i}{2m\hbar} (2i\hbar) \langle \psi_t | \hat{p} | \psi_t \rangle$$

and therefore (recall that  $i^2 = -1$ )

$$\frac{dx_t}{dt} = \frac{p_t}{m} \quad (104)$$

This is a very surprising result: the equation of motion for  $x_t$  is identical to the equation from classical mechanics.

Of course, to find how  $x_t$  evolves, we need to know how  $p_t$  evolves. So, let us evaluate  $dp_t/dt$ , by starting with Eq. 97 and using Eqs. 98–102:

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

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

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

and

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

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

$$\int_{-\infty}^{+\infty} dx |x\rangle \langle x| = \hat{I} \quad (108)$$

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

$$\begin{aligned} \frac{dp_t}{dt} &= \frac{i}{\hbar} \int_{-\infty}^{+\infty} dx \langle \psi_t | x \rangle \langle x | (V(\hat{x})\hat{p} - \hat{p}V(\hat{x})) | \psi_t \rangle \\ &= \frac{i}{\hbar} \int_{-\infty}^{+\infty} dx \langle \psi_t | x \rangle \left\{ V(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \langle x | \psi_t \rangle - \frac{\hbar}{i} \frac{\partial}{\partial x} V(x) \langle x | \psi_t \rangle \right\} \\ &= -\frac{\hbar}{i} \int_{-\infty}^{+\infty} dx \langle \psi_t | x \rangle \frac{\partial V}{\partial x} \langle x | \psi_t \rangle \end{aligned} \quad (109)$$

This is the equation we were looking for

This result has a simple physical interpretation.

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

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

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

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

$$\frac{dp_t}{dt} = \int_{-\infty}^{+\infty} dx P(x, t) F(x) \quad (112)$$

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

The classical equation of motion is

$$\frac{dp_t}{dt} = F(x_t) \quad (113)$$

This differs from the quantum mechanical equation, Eq. 112. The two equations are very close to each other only in the situation shown in Fig. 3, where

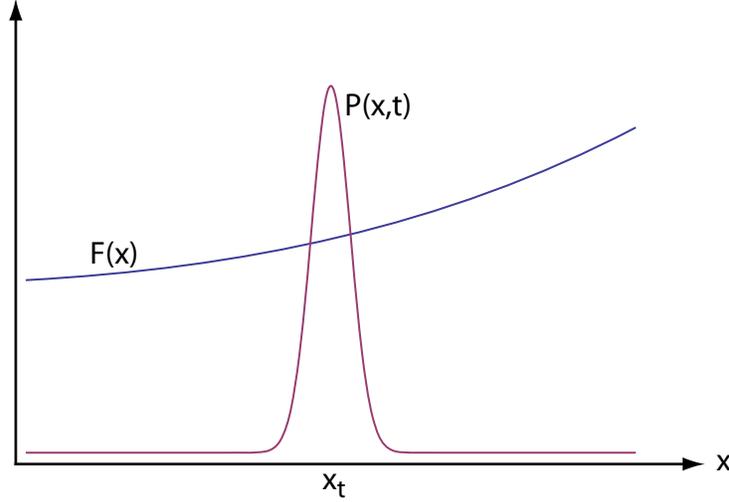


Figure 3: @@The unlikely situation in which classical and quantum mechanical equations of motion are close@@

$P(x, t)$  has a narrow peak at  $x = x_t$  and the force  $F(x)$  is almost constant within the width of the peak. This condition must be satisfied for all values of  $t$ . This is not likely to happen. Often  $P(x, t)$  has no sharp peak, or has more than one peak, or the peak is not located at  $x_t$ . Furthermore, often the force varies rapidly with the distance  $x$ .

Before leaving the subject, I 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

$$\frac{dp_t}{dt} = -\langle \psi_t | \frac{\partial V(\hat{x})}{\partial \hat{x}} | \psi_t \rangle \quad (114)$$

This and the equation

$$\frac{dx_t}{dt} = \frac{p_t}{m} \quad (115)$$

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, in general, it is easier to directly evaluate  $\langle \psi_t | \hat{x} | \psi_t \rangle$  and  $\langle \psi_t | \hat{p} | \psi_t \rangle$ .

§ 18 *The evolution of  $x_t$  and  $p_t$  for a harmonic oscillator.* Let us apply these equations to the case of a harmonic oscillator, for which

$$V(x) = \frac{kx^2}{2} \quad (116)$$

and

$$\frac{\partial V(x)}{\partial x} = kx \quad (117)$$

Inserting Eq. 117 in Eq. 114 gives

$$\frac{dp_t}{dt} = -k\langle\psi_t|\hat{x}|\psi_t\rangle = -kx_t \quad (118)$$

Let us see what classical mechanics gives us. Start with Newton's equation

$$F = ma_t \quad (119)$$

( $a$  = acceleration,  $m$  = mass). We have

$$a_t = \frac{dv_t}{dt} \quad (120)$$

where  $v_t$  is the velocity and  $F = -kx_t$ . Furthermore,  $p_t = mv_t$ . These allow us to write Eq. 119 as

$$-kx_t = \frac{dp_t}{dt} \quad (121)$$

But this is exactly the same as the quantum mechanical equation, Eq. 118!

Should we conclude that the harmonic oscillator is described by classical mechanics? Absolutely not! We know that the oscillator has discrete eigenvalues, which is not possible in classical mechanics. Should we conclude that  $x_t$  and  $p_t$  evolve according to classical mechanics? This too would be incorrect! (even though the equations of motion are the same as the ones in classical mechanics)

Let me explain why I say this. The quantum mechanics equations of motion contain  $|\psi_t\rangle$  and this is a non-classical object. Let us see what happens if we take

$$|\psi_t\rangle = e^{-iE_3t/\hbar}|E_3\rangle \quad (122)$$

where  $|E_3\rangle$  is the energy eigenstate corresponding to the eigenvalue

$$E_3 = \hbar\omega(3 + \frac{1}{2}) \quad (123)$$

The equation

$$\frac{dx_t}{dt} = p_t = \langle \psi_t | \hat{p} | \psi_t \rangle$$

becomes

$$\begin{aligned} \frac{dx_t}{dt} &= \frac{1}{m} \langle e^{-iE_3t/\hbar} E_3 | \hat{p} | e^{-iE_3t/\hbar} E_3 \rangle \\ &= \frac{1}{m} e^{iE_3t/\hbar} e^{-iE_3t/\hbar} \langle E_3 | \hat{p} | E_3 \rangle = \frac{1}{m} \langle E_3 | \hat{p} | E_3 \rangle \end{aligned} \quad (124)$$

Obviously  $p_t$  becomes time-independent (it is equal to  $\langle E_3 | \hat{p} | E_3 \rangle$ ). This is impossible in classical mechanics. The oscillator has the energy  $\hbar\omega(3 + \frac{1}{2})$  and therefore it must move. Its position and momentum will oscillate in time.

**Exercise 5** The classical energy is

$$E = \frac{p^2}{2m} + \frac{kx^2}{2}$$

Pick a pair,  $p_0$  and  $x_0$ , of initial values of  $p$  and  $x$  (take  $\omega = 1$ ) so that

$$E = \hbar\omega(3 + \frac{1}{2})$$

Solve the classical equations of motion

$$\begin{aligned} \frac{dx(t)}{dt} &= \frac{p(t)}{m} \\ \frac{dp(t)}{dt} &= -kx(t) \end{aligned}$$

with the initial conditions  $x(0) = x_0$  and  $p(0) = p_0$ . Show that  $x(t)$  and  $p(t)$  oscillate in time with frequency  $\sqrt{k/m}$ .

If the momentum  $p_t$  is time-independent then  $dx_t/dt = p_t/m$  integrates to

$$x_t = x_{t=0} + t \frac{p_t}{m} \quad (125)$$

It appears that  $x_t$  grows indefinitely. This is not possible for an oscillator! What is going on? Well, we obtained the equation  $dx_t/dt = p_t/m =$

$\langle E_3 | \hat{p} | E_3 \rangle / m$  and declared  $p_t$  to be constant, which it is. However, if you evaluate  $\langle E_3 | \hat{p} | E_3 \rangle$ , you will find that it is not just constant: it is equal to zero. Moreover,

$$x_t = \langle \psi_t | \hat{x} | \psi_t \rangle = \langle E_3 | \hat{x} | E_3 \rangle$$

and this is also zero. The equations of motion become, for this particular choice of  $|\psi_t\rangle$  (Eq. 122),

$$\frac{dx_t}{dt} = \frac{p_t}{m} \quad \text{and} \quad \frac{dp_t}{dt} = -kx_t$$

with  $x_t = 0$  and  $p_t = 0$  at all times. The equations of motion look classical, but the time evolution of  $x_t$  and  $p_t$  in quantum mechanics has no resemblance to their classical evolution.

How can this be? The probability  $|\langle x | E_3 \rangle|^2$  that the position has the value  $x$  is *equal to* the probability that it has the value  $-x$ . Therefore,  $x_t$ , which is the average position, is zero. The same goes for  $p_t$ : the probability that the momentum is  $p$  is equal to the probability that it is  $-p$ ; the average momentum is zero.

**Exercise 6** Calculate the probabilities  $P_3(x) \equiv |\langle x | E_3 \rangle|^2$  and  $P_3(p) \equiv |\langle p | E_3 \rangle|^2$  and show that  $P_3(-x) = P_3(x)$  and  $P_3(-p) = P_3(p)$ .

There is another way to convince yourself that

$$\frac{d\langle \psi_t | \hat{x} | \psi_t \rangle}{dt} = \frac{d\langle \psi_t | \hat{p} | \psi_t \rangle}{dt} = 0 \quad (126)$$

when

$$|\psi_t\rangle = e^{-iE_n t/\hbar} |E_n\rangle \quad (127)$$

and

$$\hat{H}|E_n\rangle = E_n|E_n\rangle \quad (128)$$

We have<sup>3</sup>

$$\begin{aligned} \frac{dx_t}{dt} &= \frac{i}{\hbar} \langle E_n | [\hat{H}, \hat{x}] | E_n \rangle = \frac{i}{\hbar} \langle E_n | \hat{H}\hat{x} - \hat{x}\hat{H} | E_n \rangle \\ &= \frac{i}{\hbar} (E_n \langle E_n | \hat{x} | E_n \rangle - E_n \langle E_n | \hat{x} | E_n \rangle) = 0 \end{aligned}$$

<sup>3</sup>Phase factors are irrelevant and can be dropped.

This is true for any operator, not just  $\hat{x}$ , and therefore it is true for  $\hat{p}$ .

The equations of motion look classical but the motion is not classical at all if the state of the system is an eigenvalue of energy.

**Exercise 7** Show that if  $|\psi_{t=0}\rangle$  is an energy eigenstate and  $|\psi_t\rangle$  is evolved from it, then  $d\langle\psi_t|\hat{A}|\psi_t\rangle/dt = 0$  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

$$|\psi_t\rangle = e^{-iE_0t/\hbar}a_0|E_0\rangle + e^{-iE_1t/\hbar}a_1|E_1\rangle \quad (129)$$

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

$$|a_0|^2 + |a_1|^2 = 1 \quad (130)$$

I choose them to be

$$a_0 = a_1 = \frac{1}{\sqrt{2}} \quad (131)$$

Also, since

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

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

In §9, we have seen that for any operator  $\hat{O}$ , when  $|\psi_t\rangle$  is given by Eq. 129,

$$\langle\psi_t|\hat{O}|\psi_t\rangle = a_0^2\langle E_0|\hat{O}|E_0\rangle + a_1^2\langle E_1|\hat{O}|E_1\rangle + 2a_0a_1\langle E_0|\hat{O}|E_1\rangle \cos(\omega t) \quad (132)$$

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  $\langle E_0|\hat{x}|E_0\rangle = \langle E_1|\hat{x}|E_1\rangle = 0$ )

$$x_t \equiv \langle\psi_t|\hat{x}|\psi_t\rangle = 2a_0a_1\langle E_0|\hat{x}|E_1\rangle \cos(\omega t) \quad (133)$$

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  $\omega$  is

the same as the frequency in classical mechanics,  $\omega = \sqrt{k/m}$ . The same is true for

$$p_t = 2a_0a_1\langle E_0 | \hat{p} | E_1 \rangle \cos(\omega t) \quad (134)$$

Before we claim that the oscillator behaves classically, let us note a number of anomalies.

If the state  $|\psi_t\rangle$  had been

$$|\psi_t\rangle = a_0|E_0\rangle e^{-iE_0t/\hbar} + a_2|E_2\rangle e^{-iE_2t/\hbar} \quad (135)$$

then Eqs. 133 and 134 would be correct but

$$x_t = a_0a_2\langle E_0 | \hat{x} | E_2 \rangle \cos(2\omega t) \quad (136)$$

with

$$2\omega = \frac{E_2 - E_0}{\hbar}$$

Having twice the frequency 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. 129. But even that is not true.

Consider next the evolution of  $x^2$  (the potential energy is  $kx^2/2$ ). From Eq. 132 we have

$$\langle \psi_t | \hat{x}^2 | \psi_t \rangle = a_0^2\langle E_0 | \hat{x}^2 | E_0 \rangle + a_1^2\langle E_1 | \hat{x}^2 | E_1 \rangle + 2a_0a_1\langle E_0 | \hat{x}^2 | E_1 \rangle \cos(\omega t) \quad (137)$$

The classical result is  $x^2(t) = A^2 \cos(\omega t + \phi)^2$  where  $A$  and  $\phi$  are real numbers. Eq. 137 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. 137 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 misguided. 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.