

## TILLEGG 4

## 4. Important theorems in quantum mechanics

Before attacking three-dimensional potentials in the next chapter, we shall in chapter 4 of this course discuss a few important quantum-mechanical theorems.

### 4.1 Compatible observables, simultaneous eigenfunctions and commuting operators

When two observables of a system can have sharp values simultaneously, we say that these two observables are **compatible**. As an example, if we consider a free particle with mass  $m$ , then the momentum  $p_x$  and the kinetic energy  $K_x = p_x^2/2m$  are compatible observables: In the state  $\psi_p(x) = (2\pi\hbar)^{-1/2}e^{ipx/\hbar}$ , both  $p_x$  and  $K_x$  are sharp, with the values  $p$  and  $p^2/2m$ :

$$\begin{aligned}\hat{p}_x \psi_p &= p \psi_p, \\ \hat{K}_x \psi_p &= \frac{p^2}{2m} \psi_p. \end{aligned} \quad \left( \hat{K}_x = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right)$$

We then say that  $\psi_p(x)$  is a **simultaneous eigenfunction**; it is *simultaneously* an eigenfunction of both  $\hat{p}_x$  and  $\hat{K}_x$ . We shall see that this implies that the two operators must *commute*;  $[\hat{p}_x, \hat{K}_x] = 0$ .

It is of course easy to check the last relation directly, but it is more interesting to show that it does in fact follow from the compatibility of the corresponding observables, as we shall now see.

Suppose that the observables  $F$  and  $G$  are compatible. From the example above we then understand that there must exist a simultaneous set of eigenfunctions of the corresponding operators:

$$\hat{F} \Psi_n = f_n \Psi_n, \quad \hat{G} \Psi_n = g_n \Psi_n. \quad (\text{T4.1})$$

It is then easy to prove the following rule:

**A.** If the observables  $F$  and  $G$  are compatible, that is, if there exists a simultaneous set of eigenfunctions of the operators  $\hat{F}$  and  $\hat{G}$ , then these operators must commute;

$$[\hat{F}, \hat{G}] = 0.$$

(T4.2)

This rule can also be “turned around”:

**B.** If the operators  $\hat{F}$  and  $\hat{G}$  commute, then it is possible to find a simultaneous set of eigenfunctions.

(T4.3)

From rule **A** it follows directly that

**C.** If the operators  $\hat{F}$  and  $\hat{G}$  *do not* commute, that is, if  $[\hat{F}, \hat{G}] \neq 0$ , then there does *not* exist a common set of eigenfunctions of the two operators. This means that the corresponding observables can not have sharp values simultaneously; they are *not* compatible.

(T4.4)

Proof of rule A: When the two observables  $F$  and  $G$  are compatible, we must as mentioned have a simultaneous set of eigenfunctions; cf (T4.1). From these eigenvalue equations it follows that

$$(\hat{F}\hat{G} - \hat{G}\hat{F})\Psi_n = (f_n g_n - g_n f_n)\Psi_n = 0 \quad (\text{for all } n).$$

Because the operators are hermitian, the set  $\Psi_n$  is complete. Then, for an arbitrary function  $\Psi = \sum_n c_n \Psi_n$  we have:

$$(\hat{F}\hat{G} - \hat{G}\hat{F})\Psi = \sum_n c_n (\hat{F}\hat{G} - \hat{G}\hat{F})\Psi_n = 0.$$

We have now proved the following operator identity:

$$\hat{F}\hat{G} - \hat{G}\hat{F} \equiv [\hat{F}, \hat{G}] = 0, \quad \text{q.e.d.}$$

Proof of rule B: Let  $\Psi_n$  be one of the eigenfunctions of the operator  $\hat{F}$ , with the eigenvalue  $f$ :

$$\hat{F}\Psi_n = f\Psi_n.$$

Since the two operators  $\hat{F}$  and  $\hat{G}$  are supposed to commute, we then have

$$\hat{F}(\hat{G}\Psi_n) = \hat{G}\hat{F}\Psi_n = f(\hat{G}\Psi_n).$$

This equation states that the function  $\hat{G}\Psi_n$  is an eigenfunction of the operator  $\hat{F}$  with the eigenvalue  $f$ , together with the function  $\Psi_n$ . For the remaning part of this proof we have to distinguish between two possibilities:

(i) One of the possibilities is that the eigenvalue  $f$  of the operator  $\hat{F}$  is non-degenerate, which means that there *is* only one eigenfunction with this eigenvalue. In that case the function  $\hat{G}\Psi_n$  can differ from the function  $\Psi_n$  only by a constant factor  $g$ :

$$\hat{G}\Psi_n = g\Psi_n.$$

This equation expresses that  $\Psi_n$  is an eigenfunction also of  $\hat{G}$ , and that is what we wanted to prove.

(ii) The other possibility is that the eigenvalue  $f$  is degenerate, so that there is more than one egenfunction of  $\hat{F}$  with this eigenvalue. The proof of rule **B** then is a little bit more complicated, as you can see in section 4.1 in Hemmer, or in section 5.4 in B&J.

### Example 1

The momentum operators  $\hat{p}_x$ ,  $\hat{p}_y$  and  $\hat{p}_z$  commute with each other. Then, according to rule **B**, there exists a simultaneous set of eigenfunctions. These are the momentum wave functions

$$\psi_{p_x}(x)\psi_{p_y}(y)\psi_{p_z}(z) = (2\pi\hbar)^{-1/2}e^{ip_x x/\hbar} \cdot (2\pi\hbar)^{-1/2}e^{ip_y y/\hbar} \cdot (2\pi\hbar)^{-1/2}e^{ip_z z/\hbar} = (2\pi\hbar)^{-3/2}e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}.$$

In such a state, all three components of the momentum vector  $\mathbf{p}$  have sharp values; the three components are compatible.

**Example 2**

The operators  $\hat{x} = x$  (multiplication by  $x$ ) and  $\hat{p}_y = (\hbar/i)\partial/\partial y$  commute. Their simultaneous set of eigenfunctions is

$$\psi_{x'}(x)\psi_{p_y}(y) = \delta(x - x')(2\pi\hbar)^{-1/2}e^{ip_y y/\hbar} \quad (-\infty < x' < \infty; -\infty < p_y < \infty).$$

**Example 3**

From the important commutator  $[x, \hat{p}_x] = i\hbar$  and rule **C** it follows that the observables  $x$  and  $p_x$  can not have sharp values simultaneously; they are not compatible. This is also expressed in Heisenberg's uncertainty relation,

$$\Delta x \Delta p_x \geq \frac{1}{2}\hbar. \quad (\text{T4.5})$$

**Example 4**

We saw in Tillegg 2 that the Cartesian components of the angular momentum operator  $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$  do not commute; they satisfy the so-called **angular-momentum algebra**, which consists of the commutator relation

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad (\text{T4.6})$$

together with two additional relations which follow from (T4.6) by cyclic interchange of the indices. This means that the components of the *observable*  $\mathbf{L}$  are not compatible. This has the following consequence: Even if the size  $|\mathbf{L}|$  of the angular momentum has a sharp value, the *components* can not be sharp simultaneously. This means that according to quantum mechanics the *direction* of  $\mathbf{L}$  cannot be sharply defined, contrary to what is the case in classical mechanics.

We have also seen that each of the Cartesian components  $\hat{L}_x$  etc commute with the square  $\hat{\mathbf{L}}^2$  of the angular-momentum operator,

$$[\hat{\mathbf{L}}^2, \hat{L}_x] = [\hat{\mathbf{L}}^2, \hat{L}_y] = [\hat{\mathbf{L}}^2, \hat{L}_z] = 0. \quad (\text{T4.7})$$

According to the rules above, this means that  $\hat{\mathbf{L}}^2$  is compatible with for example  $\hat{L}_z$ . Thus it is possible to find simultaneous eigenfunctions of these two operators, as we shall see in the next chapter.

## 4.2 Parity

The concept of **parity** is a simple and important remedy of quantum mechanics.

**The parity operator and its eigenvalues:**

When the parity operator  $\hat{\mathcal{P}}$  acts on a function  $\psi(\mathbf{r})$ , its effect is defined as

$$\hat{\mathcal{P}}\psi(\mathbf{r}) = \psi(-\mathbf{r}).$$

Thus the parity operator corresponds to reflection with respect to the origin, or **space inversion**, as we also call it.

We have previously seen examples of wave functions that are either symmetric or antisymmetric with respect to the origin, e.g. for the harmonic oscillator;  $\psi(-x) = \pm\psi(x)$ . Such examples occur also in three dimensions:  $\psi(-\mathbf{r}) = \pm\psi(\mathbf{r})$ . For such a function,

$$\hat{\mathcal{P}}\psi(\mathbf{r}) = \psi(-\mathbf{r}) = \pm\psi(\mathbf{r}).$$

A function which is symmetric (or antisymmetric) with respect to space inversion thus is an eigenfunction of the parity operator with the eigenvalue  $+1$  (or  $-1$ ). This eigenvalue is called the parity of the wave function. It turns out that the eigenvalues  $\pm 1$  are the only possible ones, which means that the spectrum of the parity operator is  $\pm 1$ .

**Proof:** Let  $\psi$  be an eigenfunction of  $\hat{\mathcal{P}}$  with the eigenvalue  $p$ ,

$$\hat{\mathcal{P}}\psi(\mathbf{r}) = p\psi(\mathbf{r}).$$

Then

$$\hat{\mathcal{P}}^2\psi(\mathbf{r}) = \hat{\mathcal{P}}(\hat{\mathcal{P}}\psi(\mathbf{r})) = p\hat{\mathcal{P}}\psi(\mathbf{r}) = p^2\psi(\mathbf{r}).$$

Here, the operator  $\hat{\mathcal{P}}^2$  corresponds to *two* space inversions; we have that

$$\hat{\mathcal{P}}^2\psi(\mathbf{r}) = \hat{\mathcal{P}}\psi(-\mathbf{r}) = \psi(\mathbf{r}).$$

This means that

$$\psi(\mathbf{r}) = p^2\psi(\mathbf{r}),$$

that is,  $p^2 = 1$ . Thus, the only possible eigenevalues of  $\hat{\mathcal{P}}$  are

$$p = \begin{cases} +1 & \text{(even parity)} \\ -1 & \text{(odd parity)} \end{cases} \quad \text{q.e.d.}$$

**For a symmetric potential,  $[\hat{\mathcal{P}}, \hat{H}] = 0$**

For a symmetric potential,

$$\hat{\mathcal{P}}V(\mathbf{r}) = V(-\mathbf{r}) = V(\mathbf{r}),$$

we note that the Hamiltonian is left unchanged by the parity operator. This means that the parity operator commutes with the Hamiltonian:

$$V(-\mathbf{r}) = V(\mathbf{r}) \quad \implies \quad \hat{\mathcal{P}}\hat{H}(\mathbf{r}) = \hat{H}(-\mathbf{r}) = \hat{H}(\mathbf{r}) \quad \implies \quad [\hat{\mathcal{P}}, \hat{H}] = 0.$$

**Proof:** We have for an arbitrary function  $\psi(\mathbf{r})$

$$[\hat{\mathcal{P}}, \hat{H}(\mathbf{r})]\psi(\mathbf{r}) = \hat{\mathcal{P}}\hat{H}(\mathbf{r})\psi(\mathbf{r}) - \hat{H}(\mathbf{r})\hat{\mathcal{P}}\psi(\mathbf{r}) = \hat{H}(-\mathbf{r})\psi(-\mathbf{r}) - \hat{H}(\mathbf{r})\psi(-\mathbf{r}) = 0, \quad \text{q.e.d.}$$

According to rule **B** above, it is then possible to find simultaneous eigenstates of the two operators  $\hat{\mathcal{P}}$  and  $\hat{H}$ , that is, energy eigenfunctions  $\psi_E(\mathbf{r})$  with well-defined parity (i.e, symmetric or antisymmetric):

Following the procedure in the proof of rule **B** we have that

$$\hat{H}(\hat{\mathcal{P}}\psi_E) = \hat{\mathcal{P}}\hat{H}\psi_E = E(\hat{\mathcal{P}}\psi_E).$$

Thus  $\hat{\mathcal{P}}\psi_E$  is an eigenfunction with energy  $E$ , together with  $\psi_E$ :

- (i) If this energy is non-degenerate, the function  $\hat{\mathcal{P}}\psi_E$  must be proportional to  $\psi_E$ ,

$$\hat{\mathcal{P}}\psi_E = p\psi_E.$$

Here  $p$  is either  $+1$  or  $-1$ , since these are the only possible eigenvalues of  $\hat{\mathcal{P}}$ . Thus, for the non-degenerate energy  $E$  the eigenfunction  $\psi_E$  necessarily has a well-defined parity; it is either symmetric or antisymmetric.

- (ii) The other possibility is that the energy  $E$  is degenerate, with several energy eigenfunctions  $\psi_{Ei}$  ( $i = 1, \dots, g$ ). Then these eigenfunctions do not *need* to have well-defined parities, but rule **B** tells us that they can be **combined linearly** into parity eigenstates.

To remember the contents of the above discussion, it is sufficient to remember a couple of well-known examples:

- (i) the harmonic oscillator has non-degenerate energy levels and eigenstates with well-defined parity,

- (ii) the free particle. In this case we can *choose* to work with symmetric or antisymmetric solutions ( $\cos kx$  and  $\sin kx$ ), but we can also use *asymmetric* solutions ( $e^{\pm ikx}$ ).

A third example is the square well

$$V(x) = \begin{cases} 0 & \text{for } |x| < l, \\ V_0 & \text{for } |x| > l. \end{cases}$$

For  $0 < E < V_0$ , the energy levels are discrete and non-degenerate, and the energy eigenfunctions have well-defined parity, as we have seen. For  $E > V_0$ , we have two independent eigenfunctions for each energy. Here, according to rule **B**, these can be chosen so that one is symmetric and the other one is antisymmetric. However, it is more interesting to work with an asymmetric linear combination of these, on the form

$$\psi_E(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & \text{for } x < -l, \\ De^{iqx} + Fe^{-iqx} & \text{for } -l < x < l, \\ Ce^{ikx} & \text{for } x > l. \end{cases} \quad (\text{T4.8})$$

This is called a **scattering solution**, because it contains an incoming and a reflected wave to the left of the well, and a transmitted wave on the right. (It can be shown that the probability of transmission is  $T = |C/A|^2$ .)

### 4.3 Time development of expectation values

The time development of a state  $\Psi(\mathbf{r}, t)$  is determined by the Schrödinger equation, which of course also determines how the expectation values of the various observables,

$$\langle F \rangle_\Psi = \int \Psi^* \hat{F} \Psi d\tau,$$

behave as functions of  $t$ .

It turns out that certain aspects of this time dependence can be clarified without solving the Schrödinger equation explicitly. This can be shown by taking the derivative ( $d/dt$ ) of the left and right sides of the equation above. On the right, we can move the differentiation inside the integral, provided that we take the *partial* derivative with respect to  $t$ , that is, keep the other variables fixed. The partial derivative of the integrand is

$$\frac{\partial}{\partial t}[\Psi^*(\hat{F}\Psi)] = \frac{\partial\Psi^*}{\partial t}\hat{F}\Psi + \Psi^*\frac{\partial(\hat{F}\Psi)}{\partial t}.$$

If  $\hat{F}$  does not depend *explicitly* on  $t$ , it acts as a constant under the last differentiation. If it *does* depend on  $t$ , the last differentiation gives two terms, so that the result becomes

$$\frac{d}{dt} \langle F \rangle_{\Psi} = \int \frac{\partial \Psi^*}{\partial t} \hat{F} \Psi d\tau + \int \Psi^* \hat{F} \frac{\partial \Psi}{\partial t} d\tau + \int \Psi^* \frac{\partial \hat{F}}{\partial t} \Psi d\tau.$$

Using the Schrödinger equation we have

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi.$$

The first and the second terms in the above equation then become respectively

$$\int \left( -\frac{i}{\hbar} \hat{H} \Psi \right)^* \hat{F} \Psi d\tau = \frac{i}{\hbar} \int \Psi^* \hat{H} \Psi d\tau \quad \text{and} \quad -\frac{i}{\hbar} \int \Psi^* \hat{F} \hat{H} \Psi d\tau.$$

The resulting formula for the time development of expectation values then is

$$\boxed{\frac{d}{dt} \langle F \rangle_{\Psi} = \frac{i}{\hbar} \langle [\hat{H}, \hat{F}] \rangle_{\Psi} + \left\langle \frac{\partial \hat{F}}{\partial t} \right\rangle_{\Psi}.} \quad (\text{T4.9})$$

Here,  $\hat{F}$  will usually *not* depend explicitly on  $t$ , so that we can remove the last term.

If  $\hat{F}$ , in addition to being time independent, also commutes with  $\hat{H}$ , that is, if the observable  $F$  is compatible with the energy  $E$ , we find the interesting result that

$$\frac{d}{dt} \langle F \rangle_{\Psi} = 0.$$

In such a case  $\langle F \rangle_{\Psi}$  thus is time independent, and we note that this holds for any state  $\Psi$  of the system. We then say that the observable  $F$  is a **quantum-mechanical constant of the motion**. All observables which are compatible with the energy thus are constants of motion. (Note the definition of a constant of motion: It is the *expectation value* of the observable that stays constant.)

### Example 1: Conservative system

An example is the energy itself. With  $F = E$  we find that

$$\frac{d}{dt} \langle E \rangle_{\Psi} = \frac{i}{\hbar} \langle [\hat{H}, \hat{H}] \rangle_{\Psi} = 0.$$

This holds provided that  $\partial \hat{H} / \partial t = 0$ , that is, if we have a **conservative system**. For such a conservative system we can thus state that the energy is a constant of the motion for an arbitrary state, whether it is stationary or non-stationary.

### Example 2: Non-conservative system

If the potential depends on time, we have a case where the Hamiltonian depends explicitly on time,

$$\hat{H} = \hat{K} + V(\mathbf{r}, t).$$

By returning to the derivation on pages 4 and 5 we then see that

$$\begin{aligned}\frac{\partial}{\partial t} [\Psi^* (\widehat{H} \Psi)] &= \frac{\partial \Psi^*}{\partial t} \widehat{H} \Psi + \Psi^* \widehat{H} \frac{\partial \Psi}{\partial t} + \Psi^* \frac{\partial \widehat{H}}{\partial t} \Psi \\ &= \frac{i}{\hbar} \Psi^* (\widehat{H} \widehat{H} - \widehat{H} \widehat{H}) \Psi + \Psi^* \frac{\partial \widehat{H}}{\partial t} \Psi,\end{aligned}$$

so that

$$\frac{d}{dt} \langle E \rangle_{\Psi} = \left\langle \frac{\partial \widehat{H}}{\partial t} \right\rangle_{\Psi} = \left\langle \frac{\partial V}{\partial t} \right\rangle_{\Psi}.$$

### Example 3: Parity conservation

For a symmetric potential we have seen that  $[\widehat{H}, \widehat{\mathcal{P}}] = 0$ . Then it follows that the parity is a constant of the motion, in the sense that  $\langle \widehat{\mathcal{P}} \rangle_{\Psi} = \int \Psi^* \widehat{\mathcal{P}} \Psi d\tau$  is time independent. As a special case we can assume that the state is symmetric (or antisymmetric) at some initial time, so that this integral is equal to 1 (or  $-1$ ). The parity conservation then means that the symmetry is conserved for all times (also in cases where the state is non-stationary).

### Example 4: Free particle

For a free particle, with  $\widehat{H} = \widehat{\mathbf{p}}^2/2m$ , we have  $[\widehat{H}, \widehat{\mathbf{p}}] = 0$ , so that  $(d/dt) \langle \mathbf{p} \rangle_{\Psi} = 0$ . This means that the momentum is a constant of the motion (that is,  $\langle \mathbf{p} \rangle_{\Psi} = \text{constant}$ ) for an arbitrary time-dependent free-particle state  $\Psi(\mathbf{r}, t)$ . This is the quantum-mechanical parallel to Newton's first law.

How will the expectation value  $\langle \mathbf{r} \rangle_{\Psi}$  of the *position* behave for a free-particle wave  $\Psi(\mathbf{r}, t)$ ? The answer is that

$$\frac{d}{dt} \langle \mathbf{r} \rangle_{\Psi} = \frac{\langle \mathbf{p} \rangle_{\Psi}}{m},$$

which is the quantum-mechanical parallel to the classical relation  $d\mathbf{r}/dt = \mathbf{v} = \mathbf{p}/m$ . It turns out that this relation holds also for a particle in a potential  $V(\mathbf{r})$ . This is a part of **Ehrenfest's theorem**, which has *more* to say about the connection between classical and quantum mechanics:

## 4.4 The Ehrenfest theorem

(The Ehrenfest theorem is described in section 5.11 in B&J, and in section 4.4 in Hemmer.)

We shall see that (T4.9) can also be used to derive the **Ehrenfest theorem**. This theorem is concerned with the connection between classical and quantum mechanics, or with the so-called **classical limit** of the latter, if you like.

We know that classical mechanics works perfectly for macroscopic objects (with certain exceptions; cf superfluidity), but we also know that this theory fails when applied to the really small things in nature, like molecules, atoms and sub-atomic particles. On the other hand,

the dynamics of these sub-microscopic objects is described perfectly by quantum mechanics. The question then is: What happens if we apply quantum mechanics to larger objects? Can it be that it fails when the objects become large?

The answer is that quantum mechanics has no such limitation. When the scale is increased, it turns out that the quantum-mechanical description converges towards the classical one (except for a few cases where the classical description in fact fails; cf superfluidity and superconductivity, where quantum effects are observed even on macroscopic scales). We can therefore state that quantum mechanics contains classical mechanics as a limiting case. This gradual convergence of quantum and classical mechanics can to some extent be illustrated by the Ehrenfest theorem.

Let us consider a particle moving in a potential  $V(\mathbf{r})$ . Classically the motion is described by the equations

$$\frac{d\mathbf{p}}{dt} = -\nabla V \quad , \quad \frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{m}. \quad (\text{Newton}) \quad (\text{T4.10})$$

In quantum mechanics we describe this motion in terms of a wave function  $\Psi(\mathbf{r}, t)$  — a wave packet which follows the particle on its “journey” in the potential  $V(\mathbf{r})$ . What must then be compared with the classical position  $\mathbf{r}$  and the momentum  $\mathbf{p}$  are the quantum-mechanical expectation values

$$\langle \mathbf{r} \rangle_\Psi = \int \Psi^* \mathbf{r} \Psi d^3r \quad \text{and} \quad \langle \mathbf{p} \rangle_\Psi = \int \Psi^* \hat{\mathbf{p}} \Psi d^3r. \quad (\text{T4.11})$$

If the particle is heavy (macroscopic), we must expect that these expectation values behave exactly like the classical quantities in (T4.10). For microscopic particles, on the other hand, we cannot expect (T4.10) to be more than a very poor approximation to (T4.11).

We shall now investigate if this actually is the case. From (T4.9) we have:

$$\frac{d}{dt} \langle \mathbf{r} \rangle = \frac{i}{\hbar} \langle [H, \mathbf{r}] \rangle \quad \text{and} \quad \frac{d}{dt} \langle \mathbf{p} \rangle = \frac{i}{\hbar} \langle [H, \hat{\mathbf{p}}] \rangle, \quad (\text{T4.12})$$

where<sup>1</sup>

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}, t).$$

We note that  $\mathbf{r}$  commutes with the potential, and that  $\hat{\mathbf{p}}$  commutes with the kinetic term  $\hat{\mathbf{p}}^2/2m$ . Thus we need the commutators  $[\hat{\mathbf{p}}^2, \mathbf{r}]$  and  $[V, \hat{\mathbf{p}}]$ . In the calculation of these and other commutators we can use the general rules (T2.24):

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}.$$

We then find that

$$[\hat{p}_x^2, x] = \hat{p}_x[\hat{p}_x, x] + [\hat{p}_x, x]\hat{p}_x = -2i\hbar\hat{p}_x, \quad (\text{T4.13})$$

so that

$$[\hat{H}, x] = [\frac{\hat{\mathbf{p}}^2}{2m}, x] = \frac{1}{2m}[\hat{p}_x^2, x] = -i\hbar\frac{\hat{p}_x}{m}, \quad (\text{T4.14})$$

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<sup>1</sup>We can allow the potential to be time dependent.



and

$$[\widehat{H}, \mathbf{r}] = -i\hbar \frac{\widehat{\mathbf{p}}}{m}. \quad (\text{T4.15})$$

Furthermore,

$$[V, \nabla]\Psi = V\nabla\Psi - \nabla(V\Psi) = -(\nabla V)\Psi, \quad (\text{T4.16})$$

so that

$$[\widehat{H}, \widehat{\mathbf{p}}] = [V, \widehat{\mathbf{p}}] = i\hbar \nabla V. \quad (\text{T4.17})$$

Inserting into (T4.12) we get the two equations

$$\frac{d}{dt} \langle \mathbf{r} \rangle_\Psi = \frac{\langle \mathbf{p} \rangle_\Psi}{m}, \quad (\text{T4.18})$$

$$\frac{d}{dt} \langle \mathbf{p} \rangle_\Psi = -\langle \nabla V \rangle_\Psi, \quad (\text{T4.19})$$

which together are known as the Ehrenfest theorem:

*The quantum-mechanical “equations of motion” for  $\langle \mathbf{r} \rangle$  and  $\langle \mathbf{p} \rangle$  are found by replacing the quantities in the classical equations (T4.10) by their expectation values.*

Here, it may look as if the expectation values follow the same trajectories as the classical orbits  $\mathbf{r}$  and  $\mathbf{p}$ , — but it is not quite as simple as that: The trajectories *are* the same if the right-hand side of (T4.19), which is the expectation value of the force  $\mathbf{F} = -\nabla V$ , is equal to the force precisely at the mean position  $\langle \mathbf{r} \rangle$ . In general, however, this condition is not satisfied. This is seen by expanding the force in a Taylor series around the mean position. In one dimension, we have

$$F(x) = F(\langle x \rangle) + (x - \langle x \rangle)F'(\langle x \rangle) + \frac{1}{2}(x - \langle x \rangle)^2 F''(\langle x \rangle) + \dots,$$

so that the right side of (T4.19) corresponds to

$$\begin{aligned} \langle F(x) \rangle &= F(\langle x \rangle) + \frac{1}{2} \langle (x - \langle x \rangle)^2 \rangle F''(\langle x \rangle) + \dots \\ &= F(\langle x \rangle) + \frac{1}{2} (\Delta x)^2 F''(\langle x \rangle) + \dots. \end{aligned} \quad (\text{T4.20})$$

We can then summarize as follows:

(i) For macroscopic particles,  $\Delta x$  and  $\Delta p_x$  will be negligible compared to  $\langle x \rangle$  and  $\langle p_x \rangle$ . At the same time, the variation of  $F$  over the extension of the wave packet will be insignificant, so that  $\langle F(x) \rangle = F(\langle x \rangle)$ , to a very good approximation. In this case, the expectation values  $\langle x \rangle$  and  $\langle p_x \rangle$  satisfy Newton’s equation (T4.10); thus classical mechanics is a limiting case of quantum mechanics.

(ii) Even for microscopic particles we are in some cases allowed to set  $\langle F(x) \rangle = F(\langle x \rangle)$  and to use the classical equations. This requires that the variation of the potential over the wave packet can be neglected. This is in fact very well satisfied e.g. in particle accelerators.

(iii) The condition  $\langle F(x) \rangle = F(\langle x \rangle)$  can also be satisfied for particles moving in potentials of sub-microscopic extension. This requires that  $F''(x) = 0$ , that is, the force must either be constant (as in the gravitational field) or vary linearly, as in the harmonic oscillator. For these kinds of potentials we can thus conclude that  $\langle x \rangle$  and  $\langle p_x \rangle$  will follow classical trajectories. In an oscillator, e.g.,  $\langle x \rangle$  will oscillate harmonically (as  $\cos \omega t$ ).