Chapter 10
General Methods of Quantum Mechanics

10.1 Introduction

The preceding chapters have provided the introductory information about Quantum Mechanics. Here the general principles of the theory are illustrated, and the methods worked out for the Hamiltonian operator are extended to the operators associated to dynamical variables different from energy. The important concept of separable operator is introduced, and the property of some operators to commute with each other is related to the mutual compatibility of measurements of the corresponding dynamical variables. Then, the concepts of expectation value and uncertainty are introduced, and the Heisenberg uncertainty principle is worked out. This leads in turn to the analysis of the time derivative of the expectation values, showing that the latter fulfill relations identical to those of Classical Mechanics. The form of the minimum-uncertainty wave packet is worked out in the complements.

10.2 General Methods

The discussion carried out in Sect. 9.2 has led to a number of conclusions regarding the eigenvalues of the time-independent Schrödinger equation (7.45). They are:

- The energy of a particle subjected to a conservative force is one of the eigenvalues of the time-independent equation $\mathcal{H}w = Ew$, where $\mathcal{H}$ is derived from the corresponding Hamiltonian function by replacing p_i with $-\mathrm{i}\,\hbar\,\partial/\partial x_i$. Any other energy different from an eigenvalue is forbidden.
- The wave function of a conservative case (taking by way of example the discrete-eigenvalue case) is $\psi = \sum_n c_n\, w_n\, \exp(-\mathrm{i}\, E_n\, t/\hbar)$. The particle's localization is given by $|\psi|^2$, where it is assumed that ψ is normalized to unity. The probability that a measurement of energy finds the eigenvalue E_m is $|c_m|^2$; an energy measurement that finds the eigenvalues E_m forces c_n to become δ_{nm}.
- The time evolution of ψ is found by solving the time-dependent Schrödinger equation $\mathrm{i}\,\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$. The latter holds also in the non-conservative situations; although in such cases the wave function ψ is not expressible as a superposition of monochromatic waves, it can still be expanded using an orthonormal set like in (9.10) or (9.11).

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An important issue is now extending the conclusions listed above to the dynamical quantities different from energy (e.g., momentum, angular momentum, and so on). The extension is achieved by analogy, namely, it is assumed that for any dynamical variable one can construct an eigenvalue equation whose solution provides the possible values of the variable itself. This line of reasoning yields the procedures listed below, that are called *general methods of Quantum Mechanics*:

1. Given a dynamical variable A, an operator $\mathcal{A}$ is associated to it. It is found, first, by expressing A in terms of canonical coordinates q_i, p_i (Sect. 1.6), then, by replacing the momentum's components p_i with $\hat{p}_i = -\mathrm{i}\,\hbar\,\partial/\partial q_i$ in such a way that $\mathcal{A}$ is Hermitean.
2. It is checked whether the eigenvalue equation $\mathcal{A}v = Av$ possesses a complete, orthonormal set of eigenfunctions. If the check fails, the operator is not considered; otherwise it is accepted, and is called *observable* [78, Chap. V.9]. The eigenvalue equation is subjected to the same boundary or asymptotic conditions as $\mathcal{H}w = Ew$.
3. Let A_n or A_β be the eigenvalues of $\mathcal{A}v = Av$, with n (β) a set of discrete (continuous) indices. Such eigenvalues are the only values that a measure of the dynamical variable A can find.
4. Thanks to completeness, the wave function ψ describing the particle's localization can be written, respectively for discrete or continuous spectra,

$$\psi = \sum_n a_n(t)\, v_n(\mathbf{r}), \qquad \psi = \int_\beta a_\beta(t)\, v_\beta(\mathbf{r})\, \mathrm{d}\beta, \tag{10.1}$$

   with $a_n = \langle v_n|\psi\rangle$, $a_\beta = \langle v_\beta|\psi\rangle$.
5. If the wave function in (10.1) is normalizable, then $\sum_n |a_n|^2 = 1$, $\int_\beta |a_\beta|^2\, \mathrm{d}\beta = 1$ at all times. For a discrete spectrum, $P_n = |a_n(t_A)|^2$ is the probability that a measurement of A finds the eigenvalue A_n at $t = t_A$. For a continuous spectrum, the infinitesimal probability that at $t = t_A$ the domain of A_β is found in the interval $\mathrm{d}\beta$ around β is $\mathrm{d}P = |a_\beta(t_A)|^2\, \mathrm{d}\beta$.
6. When the measurement is carried out at $t = t_A$ and an eigenvalue, say, A_m, is found, the coefficients of the first expansion in (10.1) are forced by the measurement to become $|a_n(t_A^+)|^2 = \delta_{mn}$, and the wave function at that instant[1] becomes $\psi(\mathbf{r}, t_A^+) = v_m(\mathbf{r})$. The time evolution of ψ starting from t_A^+ is prescribed by the time-dependent Schrödinger equation $\mathrm{i}\,\hbar\,\partial\psi/\partial t = \mathcal{H}\psi$, with $\psi(\mathbf{r}, t_A^+)$ as the initial condition. In this respect there is a neat parallel with Classical Mechanics, where the time evolution of the canonical variables starting from the initial conditions is prescribed by the Hamilton equations (1.42).

According to the general methods listed above, the eigenvalues of $\mathcal{A}$ are the only possible outcome of a measurement of the dynamical variable A. As the eigenvalues

[1] Measurements are not instantaneous (refer to the discussion in Sect. 9.2). Here it is assumed that the duration of a measurement is much shorter than the time scale of the whole experiment.

represent a physical quantity, they must be real; this makes the requirement that $\mathcal{A}$ must be Hermitean easily understood: if an operator is Hermitean, then its eigenvalues are real (Sect. 8.4.1). The inverse is also true: if the eigenfunctions of $\mathcal{A}$ form a complete set and its eigenvalues are real, then $\mathcal{A}$ is Hermitean. In fact, for any pair of functions f, g, considering the discrete spectrum by way of example, one has

$$\langle g|\mathcal{A}f\rangle - \langle \mathcal{A}g|f\rangle = \sum_n \sum_m g_n^*\, f_m\, [\langle v_n|\mathcal{A}v_m\rangle - \langle \mathcal{A}v_n|v_m\rangle] =$$

$$= \sum_n \sum_m g_n^*\, f_m\, \langle v_n|v_m\rangle\, \left(A_m - A_n^*\right) = \sum_n g_n^*\, f_n\, \left(A_n - A_n^*\right) = 0, \tag{10.2}$$

which holds for all f, g because the eigenfunctions v_n are mutually orthogonal and the eigenvalues A_n are real.

As indicated at point 1 above, the dynamical variable A is transformed into the operator $\mathcal{A}$ by replacing p_i with $\hat{p}_i$. The operator obtained from such a replacement is not necessarily Hermitean: its hermiticity must be checked on a case-by-case basis. For instance, the dynamical variable $A = x\, p_x$ can be written in equivalent ways as $x\, p_x$, $p_x\, x$, and $(x\, p_x + p_x\, x)/2$. However, their quantum counterparts

$$-\mathrm{i}\,\hbar x\,\frac{\partial}{\partial x}, \qquad -\mathrm{i}\,\hbar\,\frac{\partial}{\partial x}\,x, \qquad -\mathrm{i}\,\frac{\hbar}{2}\left(x\,\frac{\partial}{\partial x} + \frac{\partial}{\partial x}\,x\right) \tag{10.3}$$

are different from each other, and only the third one is Hermitean (compare with Sect. 9.5).

10.3 Separable Operators

Let $\mathcal{A}$ be an operator acting only on the x coordinate. Similarly, let $\mathcal{B}$ and $\mathcal{C}$ two operators acting only on y and z, respectively. The eigenvalue equations for the discrete-spectrum case read

$$\mathcal{A}u_k = A_k\, u_k, \qquad \mathcal{B}v_m = B_m\, v_m, \qquad \mathcal{C}w_n = C_n\, w_n, \tag{10.4}$$

where $u_k(x)$, $v_m(y)$, and $w_n(z)$ are three complete and orthonormal sets of eigenfunctions. Given a function $f(x, y, z)$, thanks to the completeness of the three sets the following expansion holds:

$$f(x,y,z) = \sum_n a_n(x,y)\, w_n = \sum_n \left[\sum_m b_{mn}(x)\, v_m\right] w_n =$$

$$= \sum_n \left\{\sum_m \left[\sum_k c_{kmn}\, u_k\right] v_m\right\} w_n = \sum_{kmn} c_{kmn}\, u_k\, v_m\, w_n, \tag{10.5}$$

showing that the set made of the products $u_k\, v_m\, w_n$ is complete. Also, for any linear combination of the above operators, with $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ constant vectors, it is

$$(\mathbf{a}\,\mathcal{A} + \mathbf{b}\,\mathcal{B} + \mathbf{c}\,\mathcal{C})\; u_k\, v_m\, w_n = (\mathbf{a}\,A_k + \mathbf{b}\,B_m + \mathbf{c}\,C_n)\; u_k\, v_m\, w_n, \tag{10.6}$$

that is, $u_k\, v_m\, w_n$ is an eigenfunction corresponding to eigenvalue $\mathbf{a}\, A_k + \mathbf{b}\, B_m + \mathbf{c}\, C_n$. It is important to add that in (10.4) it is implied that the boundary conditions of $\mathcal{A}u_k = A_k\, u_k$ depend on x alone, those of $\mathcal{B}v_m = B_m\, v_m$ on y alone, and the like for the third equation. In other terms, separability means that at least one set of coordinates exists, such that both the equation and boundary conditions are separable.

As a first example of application of (10.6), consider the classical position of a particle, $\mathbf{r} = x_1\, \mathbf{i}_1 + x_2\, \mathbf{i}_2 + x_3\, \mathbf{i}_3$. Such a dynamical variable does not contain the components of momentum; as a consequence, the operator associated to it is $\mathbf{r}$ itself, and generates the eigenvalue equation $\mathbf{r}\, g(\mathbf{r}) = \mathbf{r}_0\, g(\mathbf{r})$. Separating the latter and considering the eigenvalue equation for x_i, one finds $x_i\, v_i(x_i) = x_{i0}\, v_i(x_i)$, namely, $(x_i - x_{i0})\, v_i(x_i) = 0$ for all $x_i \neq x_{i0}$. It follows $v_i = \delta(x_i - x_{i0})$, whence $\mathbf{r}_0 = x_{10}\, \mathbf{i}_1 + x_{20}\, \mathbf{i}_2 + x_{30}\, \mathbf{i}_3$, and

$$g_{\mathbf{r}_0}(\mathbf{r}) = \delta(x_1 - x_{10})\, \delta(x_2 - x_{20})\, \delta(x_3 - x_{30}) = \delta(\mathbf{r} - \mathbf{r}_0). \tag{10.7}$$

As a second example consider the classical momentum of a particle, $\mathbf{p} = p_1\, \mathbf{i}_1 + p_2\, \mathbf{i}_2 + p_3\, \mathbf{i}_3$. Remembering the discussion of Sect. 8.5 one finds for the operator associated to $\mathbf{p}$,

$$\hat{\vec{p}} = -\mathrm{i}\, \hbar \left(\mathbf{i}_1\, \frac{\partial}{\partial x_1} + \mathbf{i}_2\, \frac{\partial}{\partial x_2} + \mathbf{i}_3\, \frac{\partial}{\partial x_3} \right) = -\mathrm{i}\, \hbar\, \mathrm{grad}, \tag{10.8}$$

whose eigenvalue equation reads $-\mathrm{i}\, \hbar\, \mathrm{grad}\, f = \mathbf{p}_0\, f$. Separation yields for the ith eigenvalue equation, with $v_i = v_i(x_i)$, the first-order equation $-\mathrm{i}\, \hbar\, \mathrm{d}v_i/\mathrm{d}x_i = p_{i0}\, v_i$ (compare with (8.49)), whence $v_i = (2\,\pi)^{-1/2}\, \exp(\mathrm{i}\, k_i\, x_i)$, with $k_i = p_{i0}/\hbar$, so that $\mathbf{k} = \mathbf{p}/\hbar = k_1\, \mathbf{i}_1 + k_2\, \mathbf{i}_2 + k_3\, \mathbf{i}_3$, and

$$f_{\mathbf{k}}(\mathbf{r}) = (2\,\pi)^{-3/2}\, \exp(\mathrm{i}\, \mathbf{k} \cdot \mathbf{r}). \tag{10.9}$$

Neither (10.7) nor (10.9) are square integrable. The indices of the eigenvalues ($\mathbf{r}_0$ in (10.7) and $\mathbf{k}$ in (10.9)) are continuous in both cases. Also, from the results of Sects. C.2 and C.5 one finds that $g_{\mathbf{r}_0}(\mathbf{r}) = g(\mathbf{r}, \mathbf{r}_0)$ is the Fourier transform of $f_{\mathbf{k}}(\mathbf{r}) = f(\mathbf{r}, \mathbf{k})$.

10.4 Eigenfunctions of Commuting Operators

It has been shown in Sect. 10.2 that a measurement of the dynamical variable A at time t_A yields one of the eigenvalues of the equation $\mathcal{A}a = A\, a$. Considering for instance a discrete spectrum, let the eigenvalue be A_m. The initial condition $\psi(\mathbf{r}, t_A^+)$ for the time evolution of the particle's wave function after the measurement is one of the eigenfunctions of $\mathcal{A}$ corresponding to A_m. If a measurement of another dynamical variable B is carried out at a later time t_B, the wave function at $t = t_B$ is forced to become one of the eigenfunctions of $\mathcal{B}b = B\, b$, say, b_k. The latter can in turn be expanded in terms of the complete set derived from $\mathcal{A}$, namely, $b_k = \sum_n \langle a_n | b_k \rangle\, a_n$. As the coefficients of the expansion are in general different from zero, there is a finite

probability that a new measurement of A at $t_C > t_B$ finds a value different from A_m. In principle this could be due to the fact that, if A is not conserved, its value has evolved, from the outcome A_m of the measurement carried out at $t = t_A$, into something different, as prescribed by the time-dependent Schrödinger equation having $\psi(\mathbf{r}, t_A^+)$ as initial condition.[2] However, the instant t_B of the second measurement can in principle be brought as close to t_A as we please, so that the two measurements can be thought of as simultaneous. As a consequence, the loss of information about the value of A must be ascribed to the second measurement, specifically, to its interference with the wave function, rather than to a natural evolution[3] of the value of A: the gain in information about the eigenvalue of B produces a loss of information about that of A; for this reason, the two measurements are said to be *incompatible*.

From the discussion above one also draws the conclusion that, if it were $b_k = a_m$, the two measurements of outcome A_m and B_k would be compatible. This is in itself insufficient for stating that the measurements of A and B are compatible in all cases; for this to happen it is necessary that the whole set of eigenfunctions of A coincides with that of B: in this case, in fact, the condition $b_k = a_m$ is fulfilled no matter what the outcome of the two measurements is.

It would be inconvenient to check the eigenfunctions to ascertain whether two observables A, B are compatible or not. In fact, this is not necessary thanks to the following property: if two operators $\mathcal{A}$ and $\mathcal{B}$ have a common, complete set of eigenfunctions, then they commute, and vice versa (as indicated in Sect. 8.6.2, two operators commute if their commutator (8.71) is the null operator). Still assuming a discrete spectrum, for any eigenfunction v_n it is $\mathcal{A}\mathcal{B}v_n = \mathcal{A}B_n\, v_n = B_n\mathcal{A}v_n = B_n\, A_n\, v_n$. Similarly, $\mathcal{B}\mathcal{A}v_n = \mathcal{B}A_n\, v_n = A_n\mathcal{B}v_n = A_n\, B_n\, v_n$, showing that $\mathcal{A}$ and $\mathcal{B}$ commute for all eigenfunctions. Then, using the completeness of the common set v_n to expand any function f as $f = \sum_n f_n\, v_n$, one finds

$$\mathcal{A}\mathcal{B}f = \sum_n f_n \mathcal{A}\mathcal{B}v_n = \sum_n f_n \mathcal{B}\mathcal{A}v_n = \mathcal{B}\mathcal{A}\sum_n f_n\, v_n = \mathcal{B}\mathcal{A}f. \tag{10.10}$$

This proves that if two operators have a complete set of eigenfunctions in common, then they commute. Conversely, assume that $\mathcal{A}$ and $\mathcal{B}$ commute and let v_n be an eigenfunction of $\mathcal{A}$; then, $\mathcal{A}\mathcal{B}v_n = \mathcal{B}\mathcal{A}v_n$ and $\mathcal{A}v_n = A_n\, v_n$. Combining the latter relations yields $\mathcal{A}\mathcal{B}v_n = \mathcal{B}A_n\, v_n$ which, letting $g_n = \mathcal{B}v_n$, is recast as $\mathcal{A}g_n = A_n g_n$. In conclusion, both v_n and g_n are eigenfunctions of $\mathcal{A}$ belonging to the same eigenvalue A_n.

If A_n is not degenerate, the eigenfunctions v_n and g_n must be the same function, apart from a multiplicative constant due to the homogeneity of the eigenvalue equation. Let such a constant be B_n; combining $g_n = B_n\, v_n$ with the definition $g_n = \mathcal{B}v_n$ yields $\mathcal{B}v_n = B_n\, v_n$, this showing that v_n is an eigenfunction of $\mathcal{B}$ as well. The

[2] By way of example one may think of A as the position x, that typically evolves in time from the original value $x_A = x(t_A)$ even if the particle is not perturbed.

[3] In any case, the evolution would be predicted exactly by the Schrödinger equation. Besides, the eigenvalue would not change if A were conserved.

property holds also when A_n is degenerate, although the proof is somewhat more involved [77, Chap. 8-5]. This proves that if two operators commute, then they have a complete set of eigenfunctions in common. Examples are given in Sect. 8.6.3.

10.5 Expectation Value and Uncertainty

The discussion carried out in Sect. 10.2 has led to the conclusion that the wave function ψ describing the particle's localization can be expanded as in (10.1), where v_n or v_β are the eigenfunctions of a Hermitean operator $\mathcal{A}$ that form a complete, orthonormal set. Considering a discrete spectrum first, the coefficients of the expansion are $a_n = \langle v_n|\psi\rangle$; assuming that the wave function is normalizable, it is $\sum_n |a_n|^2 = 1$.

The meaning of the coefficients is that $P_n = |a_n(t)|^2$ is the probability that a measurement of A finds the eigenvalue A_n at t. From this it follows that the statistical average of the eigenvalues is

$$\langle A\rangle(t) = \sum_n P_n\, A_n. \tag{10.11}$$

The average (10.11) is called *expectation value*.[4] It can be given a different form by observing that $P_n = a_n^*\, a_n = (\sum_m a_m^*\, \delta_{mn})\, a_n$ and that, due to the orthonormality of the eigenfunctions of $\mathcal{A}$, it is $\delta_{mn} = \langle v_m|v_n\rangle$; then,

$$\sum_n \left(\sum_m a_m^*\, \langle v_m|v_n\rangle\right) a_n\, A_n = \langle \sum_m a_m v_m| \sum_n a_n A_n v_n\rangle = \langle \sum_m a_m v_m| \sum_n a_n \mathcal{A} v_n\rangle. \tag{10.12}$$

Combining (10.12) with (10.11) and remembering that $\mathcal{A}$ is Hermitean yields

$$\langle A\rangle = \langle\psi|\mathcal{A}|\psi\rangle. \tag{10.13}$$

The same result holds for a continuous spectrum:

$$\langle A\rangle = \int_\alpha P_\alpha\, A_\alpha\, \mathrm{d}\alpha = \int_\alpha |a_\alpha|^2\, A_\alpha\, \mathrm{d}\alpha = \langle\psi|\mathcal{A}|\psi\rangle, \tag{10.14}$$

where

$$\int_\alpha |a_\alpha|^2\, A_\alpha\, \mathrm{d}\alpha = \int_\alpha \left(\int_\beta a_\beta^*\, \delta(\beta-\alpha)\, \mathrm{d}\beta\right) a_\alpha\, A_\alpha\, \mathrm{d}\alpha, \tag{10.15}$$

and $\int_\beta |a_\beta|^2\, \mathrm{d}\beta = 1$ at all times. The expectation values of Hermitean operators are real because they are the statistical averages of the eigenvalues, themselves real.

[4] If the wave function is normalized to a number different from unity, the definition of the expectation value is $\sum_n P_n\, A_n / \sum_n P_n$, and the other definitions are modified accordingly.

Using (8.57) one extends the definition of expectation value to the powers of the eigenvalues; for instance,

$$\langle A^2\rangle = \langle\psi|\mathcal{A}^2|\psi\rangle = \int_\Omega \psi^*\,\mathcal{A}\mathcal{A}\psi\,\mathrm{d}\Omega = \langle\mathcal{A}\psi|\mathcal{A}\psi\rangle = ||\mathcal{A}\psi||^2 \geq 0, \qquad (10.16)$$

where the hermiticity of $\mathcal{A}$ is exploited. The *variance* of the eigenvalues is given by

$$(\Delta A)^2 = \left\langle (A - \langle A\rangle)^2 \right\rangle = \left\langle A^2 - 2\,\langle A\rangle\, A + \langle A\rangle^2 \right\rangle = \langle A^2\rangle - \langle A\rangle^2, \qquad (10.17)$$

real and non negative by construction; as a consequence, $\langle A^2\rangle \geq \langle A\rangle^2$. The general term used to indicate the positive square root of the variance, $\Delta A = \sqrt{(\Delta A)^2} \geq 0$, is *standard deviation*. When it is used with reference to the statistical properties of the eigenvalues, the standard deviation is called *uncertainty*.

Assume by way of example that the wave function at $t = t_A$ coincides with one of the eigenfunctions of $\mathcal{A}$. With reference to a discrete spectrum (first relation in (10.1)), let $\psi(t_A) = v_m$. From (10.13) and (10.17) it then follows $\langle A\rangle(t_A) = A_m$, $\Delta A(t_A) = 0$. The standard deviation of the eigenvalues is zero in this case, because the measurement of A can only find the eigenvalue A_m. As a second example consider a continuous spectrum in one dimension, and let $\psi(t_A) = \exp(\mathrm{i}\,k\,x)/\sqrt{2\,\pi}$, namely, an eigenfunction of the momentum operator. In this case the wave function is not square integrable, so one must calculate the expectation value as

$$\langle A\rangle(t_A) = \lim_{x_0\to\infty} \frac{\int_{-x_0}^{+x_0} \psi^*(t_A)\,\mathcal{A}\psi(t_A)\,\mathrm{d}x}{\int_{-x_0}^{+x_0} \psi^*(t_A)\,\psi(t_A)\,\mathrm{d}x}. \qquad (10.18)$$

If one lets $\mathcal{A} = \hat{p} = -\mathrm{i}\,\hbar\,\mathrm{d}/\mathrm{d}x$, the result is $\langle p\rangle(t_A) = \hbar\,k$, $\Delta p(t_A) = 0$. In fact, like in the previous example, the wave function coincides with one of the eigenfunctions of the operator. If, however, one applies another operator to the same wave function, its variance does not necessarily vanish. A remarkable outcome stems from applying $\hat{x} = x$, that is, the operator associated to the dynamical variable canonically conjugate to p: one finds $\langle x\rangle(t_A) = 0$, $\Delta x(t_A) = \infty$.

In conclusion, the examples above show that the term "uncertainty" does not refer to an insufficient precision of the measurements (which in principle can be made as precise as we please), but to the range of eigenvalues that is covered by the form of $\psi(t_A)$. In the last example above all positions x are equally probable because $|\psi(t_A)|^2 = \text{const}$, whence the standard deviation of position diverges.

10.6 Heisenberg Uncertainty Relation

Consider the wave function ψ describing the dynamics of a particle, and let $\mathcal{A}$ and $\mathcal{B}$ be Hermitean operators. A relation exists between the standard deviations of these operators, calculated with the same wave function. Defining the complex functions $f = (\mathcal{A} - \langle A\rangle)\,\psi$ and $g = (\mathcal{B} - \langle B\rangle)\,\psi$ yields

$$||f||^2 = (\Delta A)^2, \qquad ||g||^2 = (\Delta B)^2, \qquad \langle f|g\rangle - \langle g|f\rangle = \mathrm{i}\,\langle C\rangle, \qquad (10.19)$$

where the first two relations derive from (10.17) while $\langle C \rangle$ in the third one is the expectation value of the commutator $\mathcal{C} = -\mathrm{i}\,(\mathcal{AB} - \mathcal{BA})$. Letting $\mu = \mathrm{i}\,\nu$ in (8.16), with ν real, and using (10.19) provides

$$(\Delta A)^2 + \nu^2\,(\Delta B)^2 - \nu\,\langle C \rangle \geq 0, \tag{10.20}$$

namely, a second-degree polynomial in the real parameter ν. In turn, the coefficients of the polynomial are real because they derive from Hermitean operators. For the polynomial to be non negative for all ν, the discriminant $\langle C \rangle^2 - 4\,(\Delta A)^2\,(\Delta B)^2$ must be non positive. The relation between the standard deviations then reads

$$\Delta A\;\Delta B \geq \frac{1}{2}\,|\langle C \rangle|. \tag{10.21}$$

The interpretation of this result follows from the discussion carried out at the end of Sect. 10.5. If $\mathcal{A}$ and $\mathcal{B}$ commute, then their commutator is the null operator, whose eigenvalue is zero. As a consequence it is $\Delta A\;\Delta B \geq 0$, namely, the minimum of the product is zero. Remembering the result of Sect. 10.4, when two operators commute they have a common, complete set of eigenfunctions. If the wave function used for calculating the variance (10.17) is an eigenfunction of $\mathcal{A}$ and $\mathcal{B}$, then both standard deviations ΔA and ΔB vanish and $\Delta A\;\Delta B = 0$, namely, the minimum can in fact be attained. If, instead, $\mathcal{A}$ and $\mathcal{B}$ do not commute, the minimum of the product $\Delta A\;\Delta B$ must be calculated on a case-by-case basis. The most interesting outcome is found when the two operators are associated to conjugate dynamical variables: $\mathcal{A} = q_i$ and $\mathcal{B} = -\mathrm{i}\,\hbar\,\partial/\partial q_i$. Remembering (8.72) one finds $\mathcal{C} = \hbar\,\mathcal{I}$, $C = \hbar$, $\langle C \rangle = \hbar$, whence

$$\Delta A\;\Delta B \geq \frac{\hbar}{2}. \tag{10.22}$$

Inequality (10.22) is also called *Heisenberg principle* or *uncertainty principle*, because it was originally deduced by Heisenberg from heuristic arguments [48].[5] The more formal deduction leading to (10.21) was given shortly after in [61] and [116].

10.7 Time Derivative of the Expectation Value

The expectation value (10.11) of a Hermitean operator is a real function of time. In Classical Mechanics, the generalized coordinates and momenta are also functions of time, whose evolution is given by the Hamilton equations (1.42); the latter express the time derivatives of coordinates and momenta in terms of the Hamiltonian function. Then, for an arbitrary function ρ of the canonical coordinates, the total derivative with respect of time is expressed through the Poisson bracket as in (1.53). A relation

[5] Namely, (10.22) is a theorem rather than a principle. A similar comment applies to the Pauli principle (Sect. 15.6). The English translation of [48] is in [117].

of the same form as (1.53) is found in Quantum Mechanics by calculating the time derivative of the expectation value (10.13). It is assumed that operator $\mathcal{A}$ depends on time, but does not operate on it; as a consequence, the symbol $\partial\mathcal{A}/\partial t$ indicates the operator resulting from differentiating $\mathcal{A}$ with respect to its functional dependence on t. With these premises one finds

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \psi^*\,\mathcal{A}\psi\,\mathrm{d}\Omega = \int_\Omega \left(\frac{\partial\psi^*}{\partial t}\,\mathcal{A}\psi + \psi^*\,\frac{\partial\mathcal{A}}{\partial t}\psi + \psi^*\,\mathcal{A}\frac{\partial\psi}{\partial t}\right)\mathrm{d}\Omega. \tag{10.23}$$

The time derivative of ψ is obtained from the time-dependent Schrödinger equation (9.9). Considering the case where $\mathcal{H}$ is real yields $\partial\psi/\partial t = -\mathrm{i}\,\mathcal{H}\psi/\hbar$ and $\partial\psi^*/\partial t = \mathrm{i}\,\mathcal{H}\psi^*/\hbar$, whence

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \int_\Omega \psi^*\frac{\partial\mathcal{A}}{\partial t}\psi\,\mathrm{d}\Omega + \frac{\mathrm{i}}{\hbar}\int_\Omega \psi^*\,(\mathcal{H}\mathcal{A}-\mathcal{A}\mathcal{H})\,\psi\,\mathrm{d}\Omega, \tag{10.24}$$

which has the same structure as (1.53). Other relations similar to those of Sect. 1.8 are also deduced from (10.24). For instance, letting $\mathcal{A} = \mathcal{H}$ yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle H\rangle = \left\langle\frac{\partial\mathcal{H}}{\partial t}\right\rangle, \tag{10.25}$$

similar to (1.44). If $\langle A\rangle$ is a constant of motion, then

$$\int_\Omega \psi^*\frac{\partial\mathcal{A}}{\partial t}\psi\,\mathrm{d}\Omega + \frac{\mathrm{i}}{\hbar}\int_\Omega \psi^*\,(\mathcal{H}\mathcal{A}-\mathcal{A}\mathcal{H})\,\psi\,\mathrm{d}\Omega = 0, \tag{10.26}$$

similar to (1.54) while, if $\mathcal{A}$ does not depend on time, (10.24) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \frac{\mathrm{i}}{\hbar}\int_\Omega \psi^*\,(\mathcal{H}\mathcal{A}-\mathcal{A}\mathcal{H})\,\psi\,\mathrm{d}\Omega, \tag{10.27}$$

similar to (1.55). Finally, if $\mathcal{A}$ does not depend on time and commutes with $\mathcal{H}$, (10.24) yields $\mathrm{d}\langle A\rangle/\mathrm{d}t = 0$, namely, the expectation value $\langle A\rangle$ is a constant of motion.

10.8 Ehrenfest Theorem

An important application of (10.27) is found by replacing $\mathcal{A}$ with either a position operator or a momentum operator. The calculation is shown here with reference to the Hamiltonian operator $\mathcal{H} = -\hbar^2/(2\,m)\nabla^2 + V$, where the potential energy V is independent of time. Letting first $\mathcal{A} = x$ yields

$$(\mathcal{H}\,x - x\,\mathcal{H})\,\psi = \frac{\hbar^2}{2\,m}\left(x\,\frac{\partial^2\psi}{\partial x^2} - \frac{\partial^2 x\,\psi}{\partial x^2}\right) = \frac{\hbar^2}{2m}\left(-2\frac{\partial\psi}{\partial x}\right) \tag{10.28}$$

whence, using $\hat{p}_x = -\mathrm{i}\,\hbar\,\partial/\partial x$, it follows

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\mathrm{i}}{\hbar}\int_\Omega \psi^*\,\frac{\hbar^2}{2\,m}\left(-2\frac{\partial\psi}{\partial x}\right)\mathrm{d}\Omega = \frac{1}{m}\,\langle\psi|\hat{p}_x|\psi\rangle = \frac{\langle p_x\rangle}{m}. \tag{10.29}$$

In conclusion, the relation $\mathrm{d}\langle x\rangle/\mathrm{d}t = \langle p_x\rangle/m$ holds, similar to the one found in a classical case when the Hamiltonian function has the form $H = p^2/(2\,m) + V$ (compare with the second relation in (1.33)). Still with $\mathcal{H} = -\hbar^2/(2\,m)\nabla^2 + V$, consider as a second example $\mathcal{A} = \hat{p}_x = -\mathrm{i}\,\hbar\,\partial/\partial x$, to find

$$\left(\mathcal{H}\,\hat{p}_x - \hat{p}_x\,\mathcal{H}\right)\psi = -\mathrm{i}\,\hbar\left(V\,\frac{\partial\psi}{\partial x} - \frac{\partial(V\,\psi)}{\partial x}\right) = \mathrm{i}\,\hbar\,\psi\,\frac{\partial V}{\partial x}. \tag{10.30}$$

From this, letting $F_x = -\partial V/\partial x$ be the component of the force along x, it follows

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\langle p_x\rangle = \frac{\mathrm{i}}{\hbar}\int_\Omega \psi^*\,\mathrm{i}\,\hbar\,\psi\,\frac{\partial V}{\partial x}\,\mathrm{d}\Omega = \langle F_x\rangle, \tag{10.31}$$

also in this case similar to the classical one. Combining (10.29) and (10.31) shows that the expectation values fulfill a relation similar to Newton's law,

$$m\,\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle x\rangle = \langle F_x\rangle. \tag{10.32}$$

This result is called *Ehrenfest theorem*. If the dependence of F_x on position is weak in the region where ψ is significant, the normalization of the wave function yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p_x\rangle \simeq F_x\int_\Omega \psi^*\,\psi\,\mathrm{d}\Omega = F_x. \tag{10.33}$$

In this case, called *Ehrenfest approximation*, the expectation value of position fulfills Newton's law exactly. If, on the contrary, F_x depends strongly on position in the region where ψ is significant (as happens, e.g., when the potential energy has the form of a step or a barrier), then the outcome of the quantum calculation is expected to be different from the classical one (see, e.g., Sects. 11.2 and 11.3).

10.9 Complements

10.9.1 Minimum-Uncertainty Wave Function

It has been shown in Sect. 10.6 that when the two operators are associated to conjugate dynamical variables, $\mathcal{A} = q$ and $\mathcal{B} = -\mathrm{i}\,\hbar\,\mathrm{d}/\mathrm{d}q$, the relation between their standard deviations is given by (10.22). It is interesting to seek a form of the wave function such that the equality $\Delta A\,\Delta B = \hbar/2$ holds. If it exists, such a form is called *minimum-uncertainty wave function*. To proceed one notes that the equality yields the value $\nu_m = (|\langle C\rangle|/2)/(\Delta B)^2$ corresponding to the minimum of the polynomial (10.20); moreover, such a minimum is zero. On the other hand, imposing the equality in (8.16) after letting $\mu = \mathrm{i}\,\nu_m$ yields the more compact form $||f + \mathrm{i}\,\nu_m\,g||^2 = 0$, equivalent to $f + \mathrm{i}\,\nu_m\,g = 0$. Remembering the definitions given in Sect. 10.6, it is $f = (\mathcal{A} - \langle A\rangle)\,\psi$, $g = (\mathcal{B} - \langle B\rangle)\,\psi$. Now, letting $q_0 = \langle A\rangle$, $p_0 = \hbar\,k_0 = \langle B\rangle$,

from the relation $f + \mathrm{i}\,\nu_m\, g = 0$ one obtains the first-order differential equation $\nu_m\,\hbar\,\mathrm{d}\psi/\mathrm{d}q = [\mathrm{i}\,\nu_m\, p_0 - (q - q_0)]\,\psi$, whose solution is

$$\psi(q) = \psi_0\, \exp\left[\mathrm{i}\, k_0\, q - (q - q_0)^2/(2\,\nu_m\,\hbar)\right]. \tag{10.34}$$

The normalization condition $\langle\psi|\psi\rangle = 1$ yields $\psi_0 = (\pi\,\nu_m\,\hbar)^{-1/4}$. Using $\langle C\rangle = \hbar$ and combining the expression of ν_m with the equality $\Delta A\,\Delta B = \hbar/2$ provides $\nu_m = 2\,(\Delta A)^2/\hbar$ whence, letting $\Delta q = \Delta A$,

$$\psi(q) = \frac{1}{\sqrt[4]{2\,\pi}\,\sqrt{\Delta q}}\, \exp\left[\mathrm{i}\, k_0\, q - \frac{(q - q_0)^2}{(2\,\Delta q)^2}\right]. \tag{10.35}$$

The minimum-uncertainty wave function turns out to be proportional to a Gaussian function centered at q_0. The factor $\exp(\mathrm{i}\, k_0\, q)$ disappears from $|\psi|^2$, whose peak value and width are determined by Δq. Note that this calculation leaves the individual values of Δq and $\Delta p = \Delta B$ unspecified.

Problems

10.1 Starting from the wave packet (9.5) describing a free particle, determine the time evolution of its position without resorting to the approximation used in Sect. 9.6.

10.2 Using the results of Prob. 10.1, determine the time evolution of the standard deviation of position.

10.3 Starting from the wave packet (9.5) describing a free particle, determine the time evolution of its momentum without resorting to the approximation used in Sect. 9.6.

10.4 Using the results of Prob. 10.3, determine the time evolution of the standard deviation of momentum.

10.5 Consider a one-dimensional wave function that at some instant of time is given by a minimum-uncertainty packet (10.35) whose polar form is

$$\alpha = \frac{1}{\sqrt[4]{2\,\pi}\,\sqrt{\sigma}}\, \exp\left[-\frac{(x - x_0)^2}{4\,\sigma^2}\right], \qquad \beta = k_0\, x. \tag{10.36}$$

The wave packet is normalized to 1. Using the concepts introduced in Sect. 9.7.3, find the "convective" and "thermal" parts of the expectation value of the kinetic energy.