Postulate 1:
The state of a system is completely determined by a 'state vector' $|\,\Psi\,\rangle$, which develops in time according to

$$\widehat{H}\,|\,\Psi\,\rangle = \mathrm{i}\hbar\frac{\partial}{\partial t}|\,\Psi\,\rangle \qquad \Leftrightarrow \qquad \left(\widehat{H} - \mathrm{i}\hbar\frac{\partial}{\partial t}\right)|\,\Psi\,\rangle = |\,o\,\rangle \tag{102}$$

where $\widehat{H}$ is the *Hamilton operator* (or *Hamiltonian*) associated with the classical Hamilton function H. This equation applies *except* at the instant of observation, intervention of an observer being assumed to produce discontinuous and unpredictable changes.

The terms 'vector' and 'operator' are used here in the widest sense. The vector $|\,\Psi\,\rangle$ is an element of a Hilbert space, and the operator $\widehat{H}$ transforms it into another element of the Hilbert space.

In the Schrödinger language, the vector $|\,\Psi\,\rangle$ is a function of time t and all (space and spin) coordinates $\boldsymbol{x} = (\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$, $\boldsymbol{x}_i = (\boldsymbol{r}_i, \sigma_i)$, of the particles comprising the system under study, and the first postulate is simply the generalization of the time-dependent Schrödinger equation.

Corollary 1:
If $|\,\Psi\,\rangle$ satisfies the basic equation (102), then so does $c|\,\Psi\,\rangle = |\,c\Psi\,\rangle$, where c is any (constant) complex number. ● ● ●

This is simply a consequence of the fact that $\widehat{H}$ and the other operators in quantum mechanics are linear operators.

By making use of the scalar product defined in a Hilbert space, the magnitude of c (but not the phase) can be fixed by normalization of the state vector (for all values of the time t):

$$\langle\, c\Psi\,|\,c\Psi\,\rangle = c^*\,c\,\langle\,\Psi\,|\,\Psi\,\rangle = |c|^2\,\langle\,\Psi\,|\,\Psi\,\rangle = 1 \qquad (103)$$

$$c = \frac{\mathrm{e}^{\mathrm{i}\,\theta}}{\langle\,\Psi\,|\,\Psi\,\rangle^{1/2}} \qquad (0 \le \theta < 2\pi)$$

In the Schrödinger language:

$$\langle\,\Psi\,|\,\Psi\,\rangle = \int \Psi^*(\boldsymbol{x},t)\,\Psi(\boldsymbol{x},t)\,\mathrm{d}\boldsymbol{x}$$

Corollary 2:
When $\widehat{H}$ does not depend on time, equation (102) has special solutions representing *stationary states*

$$|\,\Psi\,\rangle = |\,\Phi\,\rangle\;\exp\left(-\mathrm{i}Et/\hbar\right) \qquad (104)$$

in which the time appears only in the 'phase factor' $\mathrm{e}^{-\mathrm{i}Et/\hbar}$, provided the 'amplitude factor' $|\,\Phi\,\rangle$ satisfies the time-independent equation

$$\widehat{H}\,|\,\Phi\,\rangle = E\,|\,\Phi\,\rangle \qquad \Leftrightarrow \qquad \left(\widehat{H} - E\right)|\,\Phi\,\rangle = |\,o\,\rangle \qquad (105)$$

● ● ●

This generalizes the time-independent Schrödinger equation (note, however, that at present E is merely a 'separation constant' with the dimension of energy).

It is also remarkable that equation (105) has the form of an eigenvalue equation, i.e. the vector $|\,\Phi\,\rangle$ recovers under the action of the operator $\widehat{H}$, being merely rescaled by a factor called E.

The second postulate provides a rule for the arithmetic mean value of any physical quantity (observable) A for a system in a given state $|\,\Psi\,\rangle$, which would be obtained from a large number of observations conducted under identical conditions.

Postulate 2:
With every physical observable A may be associated a (suitably chosen) Hermitian operator $\hat{A}$ such that

$$\langle\, A \,\rangle = \langle\, \hat{A} \,\rangle = \langle\, \Psi \,|\, \hat{A} \,|\, \Psi \,\rangle = \langle\, \Psi \,|\, \hat{A}\,\Psi \,\rangle \in \mathbb{R} \tag{106}$$

where $\langle\, A \,\rangle$ denotes the expectation value of A at time t in the state described by the normalized state vector $|\,\Psi\,\rangle$.

For a Hermitian operator $\hat{A}$:

$$\langle\, \Psi_1 \,|\, \hat{A} \,|\, \Psi_2 \,\rangle = \langle\, \Psi_1 \,|\, \hat{A}\,\Psi_2 \,\rangle = \langle\, \hat{A}\,\Psi_1 \,|\, \Psi_2 \,\rangle \tag{107}$$

which is a relation between scalar products. The basic property $\langle\, \Psi \,|\, \Psi' \,\rangle = \langle\, \Psi' \,|\, \Psi \,\rangle^*$ then leads to the fact that all expectation values of physical observables are real, i.e. $\langle\, A \,\rangle \in \mathbb{R}$.

In the Schrödinger language:

$$\langle\, A \,\rangle = \langle\, \Psi \,|\, \hat{A} \,|\, \Psi \,\rangle = \int \Psi^*(\boldsymbol{x},t)\, \hat{A}\, \Psi(\boldsymbol{x},t)\, \mathrm{d}\boldsymbol{x}$$

Examples of physical observables and associated Hermitian operators (in the Schrödinger language):

$$\boldsymbol{r}_i \longrightarrow \hat{\boldsymbol{r}}_i = \boldsymbol{r}_i \tag{108}$$

$$\boldsymbol{p}_i \longrightarrow \hat{\boldsymbol{p}}_i = -\,\mathrm{i}\,\hbar\,\nabla_i \tag{109}$$

$$\boldsymbol{l}_i = \boldsymbol{r}_i \times \boldsymbol{p}_i \longrightarrow \hat{\boldsymbol{l}}_i = \hat{\boldsymbol{r}}_i \times \hat{\boldsymbol{p}}_i = -\,\mathrm{i}\,\hbar\,\hat{\boldsymbol{r}}_i \times \nabla_i \tag{110}$$

$$T = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} \longrightarrow \hat{T} = \sum_{i=1}^{N} \frac{(-\mathrm{i}\,\hbar\,\nabla_i)^2}{2m_i} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\Delta_i \tag{111}$$

$$V = V(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) \longrightarrow \hat{V} = V(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N) \tag{112}$$

$$H = T + V \longrightarrow \hat{H} = \hat{T} + \hat{V} \tag{113}$$

According to Postulate 2, the energy at any instant has an expectation value

$$\langle E \rangle = \langle \Psi | \widehat{H} | \Psi \rangle$$

(since $\widehat{H}$ is the operator associated with the observable 'energy'). Restoring the phase factor in equation (105) and taking the scalar product with $|\Psi\rangle$ (from the left), the expectation value reduces to

$$\langle E \rangle = \langle \Psi | \widehat{H} | \Psi \rangle = E \langle \Psi | \Psi \rangle = E$$

which implies

Corollary 3:
The parameter E appearing in the stationary-state equations (104) and (105) is the expectation value of the energy of the system. •••

We consider, for a single-particle system in a state $|\psi\rangle$, the expectation value for any (multiplicative!) function of position, $f(x, y, z)$:

$$\begin{aligned}\langle f \rangle &= \iiint \psi^*(x, y, z, t)\, f(x, y, z)\, \psi(x, y, z, t)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \\ &= \iiint f(x, y, z)\, |\psi(x, y, z, t)|^2\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \qquad (114)\end{aligned}$$

This result implies the statistical interpretation of the Schrödinger wave function (first proposed by M. Born), which can be generalized to a many-particle system as follows:

Corollary 4:
For a many-particle system, the Schrödinger wave function has the significance that

$$|\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N; t)|^2\, \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \ldots \mathrm{d}\boldsymbol{x}_N \qquad (115)$$

gives the probability to find particle 1 in volume element $\mathrm{d}\boldsymbol{x}_1$ at $\boldsymbol{x}_1$, particle 2 simultaneously in $\mathrm{d}\boldsymbol{x}_2$ at $\boldsymbol{x}_2$, etc., at time t. Here $\boldsymbol{x}_i$ denotes collectively all the (space and spin) coordinates of particle i. •••

As an example, consider a particle (with mass m) in a cubic box with side length L:

$$\psi(\boldsymbol{r},t) = \phi(\boldsymbol{r})\,\mathrm{e}^{-\mathrm{i}\,E\,t/\hbar}$$

$$\phi(\boldsymbol{r}) = \phi_{nkl}(\boldsymbol{r}) = \left(\frac{2}{L}\right)^{3/2} \sin\left(k_x\,x\right)\,\sin\left(k_y\,y\right)\,\sin\left(k_z\,z\right)$$

$$E = E_{nkl} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right), \qquad p_x = \hbar\,k_x \text{ etc.}$$

$$k_x = n\pi/L\,, \qquad k_y = k\pi/L\,, \qquad k_z = l\pi/L$$

Although the energy is consistent with a momentum component p_x of magnitude $\hbar\,k_x$, the average momentum in x direction vanishes:

$$\langle\, p_x \,\rangle_{nkl} = \int_0^L \int_0^L \int_0^L \phi_{nkl}(\boldsymbol{r}) \left(-\,\mathrm{i}\,\hbar\,\frac{\partial}{\partial x}\right) \phi_{nkl}(\boldsymbol{r})\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 0\,,$$

indicating equal likelihood of positive and negative values.

Corollary 5:

A physical observable A has a definite value in state $|\,\Psi\,\rangle$ if and only if $|\,\Psi\,\rangle$ is an eigenfunction of the operator $\widehat{A}$ associated with A, this definite value being the corresponding eigenvalue. In symbols, this condition becomes

$$\widehat{A}\,|\,\Psi\,\rangle = A\,|\,\Psi\,\rangle \tag{116}$$

If $|\,\Psi_n\,\rangle$ is a solution, for which A takes the value A_n, the state represented by $|\,\Psi_n\,\rangle$ is one in which measurement of A is certain to yield the definite value A_n. •••

It is thus evident, that the separation parameter E in equation (105), which may be written

$$\widehat{H}\,|\,\Psi\,\rangle = E\,|\,\Psi\,\rangle$$

after restoring the phase factor $\mathrm{e}^{-\mathrm{i}Et/\hbar}$, is not only an energy expectation value for a stationary state, but also the precise energy value that will always be observed when the state function has the form of equation (104).

For stationary states, equation (116) may be reduced to

$$\hat{A}\,|\,\Phi\,\rangle = A\,|\,\Phi\,\rangle \tag{117}$$

provided the operator $\hat{A}$ is time-independent. The special case $\hat{A} = \widehat{H}$ gives the time-independent Schrödinger equation.

Proof of equation (116):
Firstly, a criterion for the variable A to possess a definite value is required. We define
$\overline{A} = \langle\, A\,\rangle$ — the average value of A (by Postulate 2)
A — a value from a particular observation (measurement)
$A - \overline{A}$ — the deviation of the measured value from the average

Then the mean-square deviation is the average value of $(A - \overline{A})^2$ (by Postulate 2):

$$\Delta A^2 = \langle\,(A - \overline{A})^2\,\rangle = \langle\,\Psi\,|\,(\hat{A} - \overline{A})^2\,|\,\Psi\,\rangle \tag{118}$$

Condition for a definite value:

$$\langle\,\Psi\,|\,(\hat{A} - \overline{A})^2\,|\,\Psi\,\rangle = \langle\,(\hat{A} - \overline{A})\Psi\,|\,(\hat{A} - \overline{A})\Psi\,\rangle = 0$$

where we used that $\hat{A} - \overline{A}$ is a Hermitian operator.

This requires (excluding the trivial case $|\,\Psi\,\rangle = |\,o\,\rangle$, and using a basic property of the scalar product)

$$(\hat{A} - \overline{A})\,|\,\Psi\,\rangle = |\,o\,\rangle$$

which is equivalent to equation (116), if $A = \overline{A} = \langle\,A\,\rangle$ is any one of the eigenvalues of $\hat{A}$, A_n, for instance. Such a value is reproducible without deviation in the corresponding state $|\,\Psi_n\,\rangle$. ■

Corollary 6 (the uncertainty principle):
The root-mean-square deviations, ΔA and ΔB, obtained by repeated measurement of observables A and B for a system in state $|\,\Psi\,\rangle$ are related by

$$\Delta A\,\Delta B \geq \frac{1}{2}\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle \tag{119}$$

where

$$\mathrm{i}\widehat{C} = \widehat{A}\widehat{B} - \widehat{B}\widehat{A} = [\widehat{A},\widehat{B}] = -[\widehat{B},\widehat{A}] \tag{120}$$

is the 'commutator' of the operators associated with A and B. •••

Proof of the uncertainty principle:
If $\widehat{X} = \widehat{A} + \lambda\,\widehat{B}$, $\lambda = a + \mathrm{i}b \in \mathbb{C}$, then

$$\begin{aligned}\langle\,\widehat{X}\Psi\,|\,\widehat{X}\Psi\,\rangle &= \langle\,\Psi\,|\,\widehat{A}^2\,|\,\Psi\,\rangle + \lambda^*\lambda\,\langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle \\ &\qquad + \lambda\,\langle\,\Psi\,|\,\widehat{A}\widehat{B}\,|\,\Psi\,\rangle + \lambda^*\,\langle\,\Psi\,|\,\widehat{B}\widehat{A}\,|\,\Psi\,\rangle \\ &= \langle\,\Psi\,|\,\widehat{A}^2\,|\,\Psi\,\rangle + (a^2+b^2)\,\langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle \\ &\qquad + a\,\langle\,\Psi\,|\,\widehat{D}\,|\,\Psi\,\rangle - b\,\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle \\ &\geq 0\end{aligned}$$

where we introduced the Hermitian operators

$$\widehat{A}\widehat{B} - \widehat{B}\widehat{A} = \mathrm{i}\,\widehat{C}\,, \qquad \widehat{A}\widehat{B} + \widehat{B}\widehat{A} = \widehat{D}$$

Taking $a = 0$ and 'completing the square' for the terms in b leads to:

$$\langle\,\Psi\,|\,\widehat{A}^2\,|\,\Psi\,\rangle + \left[\,b - \frac{\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle}{2\,\langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle}\,\right]^2 \langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle - \frac{\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle^2}{4\,\langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle} \geq 0$$

The value of b may be chosen so that the second term vanishes, to obtain:

$$\langle\,\Psi\,|\,\widehat{A}^2\,|\,\Psi\,\rangle\,\langle\,\Psi\,|\,\widehat{B}^2\,|\,\Psi\,\rangle \geq \frac{1}{4}\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle^2$$

The operators $\widehat{A} - \overline{A}$ and $\widehat{B} - \overline{B}$ have the same commutator, namely $\mathrm{i}\,\widehat{C}$, as $\widehat{A}$ and $\widehat{B}$ themselves. With equation (118) follows

$$\Delta A^2\,\Delta B^2 \geq \frac{1}{4}\langle\,\Psi\,|\,\widehat{C}\,|\,\Psi\,\rangle^2$$

which establishes equation (119). ■

As an example, we consider uncertainties in x and p_x. In Schrödinger language, the commutator has the effect

$$\mathrm{i}\,\widehat{C}\,\Psi = -\,\mathrm{i}\,\hbar\left(x\,\frac{\partial\Psi}{\partial x} - \frac{\partial}{\partial x}(x\,\Psi)\right) = +\,\mathrm{i}\,\hbar\,\Psi$$

on any operand Ψ, and thus

$$\mathrm{i}\,\widehat{C} = [\widehat{x},\widehat{p}_x] = \widehat{x}\,\widehat{p}_x - \widehat{p}_x\,\widehat{x} = \mathrm{i}\,\hbar\,\widehat{1}$$

($\widehat{1}$ is the unit operator), so that in this case equation (119) gives

$$\Delta x\,\Delta p_x \geq \frac{1}{2}\,\hbar$$

Important remark: If the operators $\widehat{A}$ and $\widehat{B}$ commute, the lower bound on $\Delta A\,\Delta B$ for the associated quantities is zero, and thus ΔA, or ΔB, or both may vanish. The latter possibility suggests the existence of states in which two variables could simultaneously be assigned perfectly definite values.

Another important example of non-commuting operators are the operators for the components of angular momentum. For ordinary, i.e. orbital angular momentum, $\widehat{\boldsymbol{l}} = \widehat{\boldsymbol{r}} \times \widehat{\boldsymbol{p}}$, the operators for the cartesian components are found to be (in Schrödinger language)

$$\widehat{l}_x = \widehat{y}\,\widehat{p}_z - \widehat{z}\,\widehat{p}_y = -\,\mathrm{i}\,\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right) = +\,\mathrm{i}\,\hbar\left(\sin\phi\,\frac{\partial}{\partial\theta} + \cot\theta\,\cos\phi\,\frac{\partial}{\partial\phi}\right)$$

$$\widehat{l}_y = \widehat{z}\,\widehat{p}_x - \widehat{x}\,\widehat{p}_z = -\,\mathrm{i}\,\hbar\left(z\,\frac{\partial}{\partial x} - x\,\frac{\partial}{\partial z}\right) = -\,\mathrm{i}\,\hbar\left(\cos\phi\,\frac{\partial}{\partial\theta} - \cot\theta\,\sin\phi\,\frac{\partial}{\partial\phi}\right)$$

$$\widehat{l}_z = \widehat{x}\,\widehat{p}_y - \widehat{y}\,\widehat{p}_x = -\,\mathrm{i}\,\hbar\left(x\,\frac{\partial}{\partial y} - y\,\frac{\partial}{\partial x}\right) = -\,\mathrm{i}\,\hbar\,\frac{\partial}{\partial\phi}$$

and for the squared orbital angular momentum

$$\widehat{l}^2 = \widehat{l}_x^2 + \widehat{l}_y^2 + \widehat{l}_z^2 = -\,\hbar^2\left\{\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\,\sin\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right\} \tag{121}$$

The following commutator relations hold:

$$[\widehat{l}_x,\widehat{l}_y] = \mathrm{i}\,\hbar\,\widehat{l}_z\,,\quad [\widehat{l}_y,\widehat{l}_z] = \mathrm{i}\,\hbar\,\widehat{l}_x\,,\quad [\widehat{l}_z,\widehat{l}_x] = \mathrm{i}\,\hbar\,\widehat{l}_y$$
$$[\widehat{l}^2,\widehat{l}_x] = [\widehat{l}^2,\widehat{l}_y] = [\widehat{l}^2,\widehat{l}_z] = 0 \tag{122}$$

Corollary 7:
The time rate of change of any expectation value is given by

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle = \langle \Psi \,|\, \hat{A}\widehat{H} - \widehat{H}\hat{A} \,|\, \Psi \rangle + i\hbar \langle \Psi \,|\, \left(\frac{\partial \hat{A}}{\partial t} \right) |\, \Psi \rangle \tag{123}$$

where the system is described by the state vector $|\,\Psi\,\rangle$, whose time development is determined by Postulate 1. •••

Proof of equation (123): With eqs. (106) and (102), and the Hermitian property of the operators involved, one finds:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle &= \langle (\partial\Psi/\partial t) \,|\, \hat{A} \,|\, \Psi \rangle + \langle \Psi \,|\, \hat{A} \,|\, (\partial\Psi/\partial t) \rangle + \langle \Psi \,|\, (\partial\hat{A}/\partial t) \,|\, \Psi \rangle \\
&= \langle \hat{A}\Psi \,|\, (\partial\Psi/\partial t) \rangle^{*} + \langle \Psi \,|\, \hat{A} \,|\, (\partial\Psi/\partial t) \rangle + \langle \Psi \,|\, (\partial\hat{A}/\partial t) \,|\, \Psi \rangle \\
&= \left[\frac{1}{i\hbar} \langle \hat{A}\Psi \,|\, \widehat{H}\Psi \rangle \right]^{*} + \frac{1}{i\hbar} \langle \Psi \,|\, \hat{A}\,\widehat{H}\Psi \rangle + \langle \Psi \,|\, (\partial\hat{A}/\partial t) \,|\, \Psi \rangle \\
&= \frac{1}{i\hbar} \langle \Psi \,|\, \hat{A}\,\widehat{H} - \widehat{H}\,\hat{A} \,|\, \Psi \rangle + \langle \Psi \,|\, (\partial\hat{A}/\partial t) \,|\, \Psi \rangle
\end{aligned}$$

which establishes equation (123). ■

If the operator $\hat{A}$ does not depend explicitly on time ($\partial\hat{A}/\partial t = 0$), and if it commutes with the Hamiltonian ($[\hat{A}, \widehat{H}] = 0$), then its expectation value will also be independent of time, i.e. the corresponding physical quantity is a **constant of motion** [compare also to eq. (12)].

The simple choice $\hat{A} = \widehat{H}$ (for a conservative system, i.e. $\partial\widehat{H}/\partial t = 0$) gives the quantum mechanical analogue of the classical principle of energy conservation.

When we consider a state of a single particle with $\widehat{H} = \hat{T} + \hat{V}$ and choose the components of linear momentum as operators, i.e. $\hat{A} = \hat{p}_x$ etc., we obtain Ehrenfest's theorem*

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \boldsymbol{p} \rangle = -\langle \nabla V \rangle = \langle \boldsymbol{F} \rangle$$

since $[\hat{\boldsymbol{p}}, \widehat{H}] = [\hat{\boldsymbol{p}}, \hat{V}] = -i\hbar(\nabla\hat{V})$. This constitutes the quantum mechanical analogue of Newton's second law of motion.

* P. Ehrenfest (1880-1933)

An uncertainty principle connecting energy and time can be obtained from equations (119) and (123). Assuming $\widehat{A}$ is not explicitly dependent on time and taking $\widehat{B} = \widehat{H}$, this leads to

$$\Delta E \, \Delta A \geq \frac{1}{2} \langle \Psi | -\mathrm{i} \left(\widehat{A}\widehat{H} - \widehat{H}\widehat{A} \right) | \Psi \rangle = \frac{\hbar}{2} \frac{\mathrm{d}\langle A \rangle}{\mathrm{d}t}$$

With the definition of

$$\Delta t = \frac{\Delta A}{\mathrm{d}\langle A \rangle / \mathrm{d}t} \qquad (124)$$

(which certainly has the dimension of time) we obtain

Corollary 8:
There is an energy-time uncertainty relation

$$\Delta E \, \Delta t \geq \frac{1}{2} \hbar \qquad (125)$$

where ΔE is the (root-mean-square) uncertainty in the energy of the system and Δt is the time needed for the average value of a dynamical variable A to change by an amount comparable with its uncertainty ΔA and is defined precisely by equation (124). • • •

It is instructive to consider the uncertainty relations from the (non-rigorous) point of view of dimensional analysis:

Uncertainty relation for position x and linear momentum p_x:

$$\Delta x \, \Delta p_x \geq \hbar/2$$

Uncertainty relation for rotation angle α and angular momentum j:

$$\Delta \alpha \, \Delta j \geq \hbar/2$$

Uncertainty relation for time t and energy E:

$$\frac{\Delta x}{c} c \, \Delta p_x = \Delta t \, \Delta E \geq \hbar/2$$

Uncertainty relation for time t and frequency ν ($\omega = 2\pi\nu$):

$$\Delta t \frac{\Delta E}{h} = \Delta t \, \Delta \nu \geq 1/(4\pi) \quad \Rightarrow \quad \Delta t \, \Delta \omega \geq 1/2$$

($\rightarrow$ Fourier analysis; $\rightarrow$ generation / detection of oscillations or frequencies requires time [coloratura and bass singers])

Postulate 3:
The solutions of the eigenvalue problem

$$\widehat{H} \,|\, \Phi \,\rangle = E \,|\, \Phi \,\rangle \tag{126}$$

for a system with Hamiltonian operator $\widehat{H}$ constitute a complete set, closed under the action of all the operators of the system.

This postulate and the following corollary reformulate — in quantum mechanical terminology — some well-known results from the theory of linear vector spaces and Hermitian operators.

Corollary 9:
The solutions $|\, \Phi_k \,\rangle$ of the eigenvalue equation

$$\widehat{H} \,|\, \Phi \,\rangle = E \,|\, \Phi \,\rangle \tag{127}$$

may be chosen so as to form an orthonormal set:

$$\langle\, \Phi_i \,|\, \Phi_j \,\rangle = \delta_{ij} \tag{128}$$

•••

Completeness of the set means simply that any state vector may be expanded in the form

$$|\, \Psi \,\rangle = \sum_k a_k \,|\, \Phi_k \,\rangle \tag{129}$$

where the numerical coefficients a_k may, in general, depend on time.

The property of 'closure' means that an expansion as in equation (129) exists also for any state $\hat{A} \,|\, \Psi \,\rangle$ obtained from action of an operator $\hat{A}$ on the state vector $|\, \Psi \,\rangle$, i.e.

$$\hat{A} \,|\, \Psi \,\rangle = \sum_k b_k \,|\, \Phi_k \,\rangle \tag{130}$$

Corollary 10:
Two operators $\hat{A}$ and $\hat{B}$, defined within a given space, possess a complete set of common eigenvectors if and only if they commute:

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \tag{131}$$

The eigenvectors then describe states in which variables A and B have simultaneously definite values. •••

If $|\Psi_k\rangle$ is a common eigenvector of $\hat{A}$ and $\hat{B}$, then $(\hat{A}\hat{B} - \hat{B}\hat{A})|\Psi_k\rangle = |o\rangle$ because

$$\hat{A}\hat{B}|\Psi_k\rangle = \hat{A}(B_k|\Psi_k\rangle) = B_k\hat{A}|\Psi_k\rangle = A_k B_k|\Psi_k\rangle$$
$$\hat{B}\hat{A}|\Psi_k\rangle = \hat{B}(A_k|\Psi_k\rangle) = A_k\hat{B}|\Psi_k\rangle = A_k B_k|\Psi_k\rangle$$

If valid for all k, this establishes the condition (131) for arbitrary states $|\Psi\rangle = \sum_k c_k|\Psi_k\rangle$, and proves the necessity of the condition (131). See the references for the proof of sufficiency, which allows us to assert that if $\hat{A}$ and $\hat{B}$ commute then a complete set of simultaneous eigenfunctions can be found.

Commuting operators provide a means of classification for stationary states of a system in terms of constants of the motion. One operator is the Hamiltonian $\widehat{H}$ itself. If another operator $\hat{A}$ commutes with $\widehat{H}$, then we can find states in which the observable A has a definite value along with the energy. When a third operator $\hat{B}$ can be found, there exists a complete set of states in which the three quantities E, A, and B have simultaneously definite values.

When the largest set of mutually commuting operators has been found, the corresponding simultaneous eigenvalues give a complete specification of any state in the associated complete set. No more complete specification of the state can be obtained, it is a 'state of maximal knowledge'.

As an example, consider a free particle. The operators (in Schrödinger language)

$$\widehat{H} = -\frac{\hbar^2}{2m}\Delta = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\widehat{p}_x = -\mathrm{i}\,\hbar\frac{\partial}{\partial x}, \quad \widehat{p}_y = -\mathrm{i}\,\hbar\frac{\partial}{\partial y}, \quad \widehat{p}_z = -\mathrm{i}\,\hbar\frac{\partial}{\partial z}$$

all commute with each other. The stationary wave function

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = C\,\exp\left(\mathrm{i}\,\boldsymbol{k}\,\boldsymbol{r}\right)$$

is an eigenfunction of all four operators, with eigenvalues

$$E = \frac{\hbar^2 k^2}{2m}, \quad p_x = \hbar\,k_x\,, \quad p_y = \hbar\,k_y\,, \quad p_z = \hbar\,k_z$$

This is a state of maximal knowledge for a free particle, energy and momentum components all being constants of the motion.

Corollary 11:

If the state vector $|\,\Psi\,\rangle$ of a system is expressed in terms of the eigenvectors $|\,\Psi_k\,\rangle$ describing states of maximal knowledge,

$$|\,\Psi\,\rangle = \sum_k c_k\,|\,\Psi_k\,\rangle = \sum_k |\,\Psi_k\,\rangle\,c_k \qquad (132)$$

then the probability that, in an experiment designed to yield maximal knowledge, the system will be found in state $|\,\Psi_k\,\rangle$ is

$$w_k = |c_k|^2 = |\langle\,\Psi_k\,|\,\Psi\,\rangle|^2 \qquad (133)$$

The scalar products $\langle\,\Psi_k\,|\,\Psi\,\rangle$ in this way acquire a physical meaning.

• • •

We consider, as an illustrative example, a particle in a one-dimensional box of length L (see Part 2). This system is supposed to be in an artificial state with normalized state function

$$\phi(x) = N\,\frac{x}{L}\left(1 - \frac{x}{L}\right), \qquad N = \sqrt{\frac{30}{L}}$$

for which the expection value of the energy is

$$\langle E \rangle = \langle \phi \,|\, \widehat{H} \,|\, \phi \rangle = \int_0^L \phi(x)\, \widehat{H}\, \phi(x)\, \mathrm{d}x = \frac{h^2}{8\,m\,L^2}\frac{10}{\pi^2} > \frac{h^2}{8\,m\,L^2} = E_1$$

i.e. the energy is higher than the energy eigenvalue E_n for the ground state ($n = 1$).

According to Corollary 11, this state function $\phi(x)$ can be expanded in terms of the eigenfunctions $X_n(x) = \sqrt{2/L}\sin(k_n\, x)$ ($k_n = n\pi/L$) as follows (see similarity to Fourier series expansion):

$$\phi(x) = \sum_{n=1}^{\infty} c_n\, X_n(x)$$

$$c_n = \langle X_n \,|\, \phi \rangle = \int_0^L X_n(x)\, \phi(x)\, \mathrm{d}x = \frac{4\sqrt{15}}{(n\,\pi)^3}\,[\,1 - (-1)^n\,]$$

It thus follows, that a measurement of the energy will never give E_n with n even (where $X_n(x)$ is 'ungerade' with respect to $x = L/2$), whereas the ground state energy E_1 will be detected with probability $w_1 = |c_1|^2 = 960/\pi^6 \approx 0.9986$.

Postulate 4:
The operators associated with the position and the momentum variables of a particle commute, with the following exceptions (using $\widehat{1}$ for the unit operator)

$$[\widehat{x}, \widehat{p}_x] = [\widehat{y}, \widehat{p}_y] = [\widehat{z}, \widehat{p}_z] = \mathrm{i}\hbar\widehat{1} \qquad (134)$$

while those for two different particles always commute.

This postulate generalizes the properties obtained so far only in Schrödinger language, and makes them independent from the particular representation that has been chosen.

Corollary 12:
The operators associated with multiples, sums, and products of observables are as follows

$$\begin{array}{lll} c\,A & \longrightarrow & c\,\widehat{A} \\ A+B & \longrightarrow & \widehat{A}+\widehat{B} \\ AB & \longrightarrow & \frac{1}{2}(\widehat{A}\widehat{B}+\widehat{B}\widehat{A}) \end{array} \tag{135}$$

where the $\longrightarrow$ means that the operator on the right is associated with the observable on the left. • • •

This summarizes in a formal way the rules already adopted previously within the Schrödinger language.

The following postulate and corollary are related to the 'spin'. They are included here for completeness, and will not be commented on further.

Postulate 5:
An electron possesses an intrinsic angular momentum, represented by a 'spin' vector $\boldsymbol{s}$ with components s_x, s_y, s_z, each being a 'two-valued' observable, the possible values being $\pm 1/2$ (in units of $\hbar$). The related magnetic dipole moment is $\boldsymbol{\mu} = g_{\mathrm{e}}\mu_{\mathrm{B}}\boldsymbol{s}$, where $\mu_{\mathrm{B}} = e\hbar/(2m_{\mathrm{e}})$ is the Bohr magneton, and $g_{\mathrm{e}} \approx -2.0023$ is an observed 'free-electron g value'. The associated spin operators commute with all the operators representing classical quantities, but not with each other.

Corollary 13:
The spin operators for an electron satisfy the commutation relations

$$\begin{array}{lll} [\widehat{s}_x,\widehat{s}_y] = \widehat{s}_x\widehat{s}_y - \widehat{s}_y\widehat{s}_x & = & \mathrm{i}\,\hbar\,\widehat{s}_z \\ [\widehat{s}_y,\widehat{s}_z] = \widehat{s}_y\widehat{s}_z - \widehat{s}_z\widehat{s}_y & = & \mathrm{i}\,\hbar\,\widehat{s}_x \\ [\widehat{s}_z,\widehat{s}_x] = \widehat{s}_z\widehat{s}_x - \widehat{s}_x\widehat{s}_z & = & \mathrm{i}\,\hbar\,\widehat{s}_y \end{array} \tag{136}$$

which are a necessary consequence of the isotropy of space under rotations of the coordinate axes. • • •

The Pauli principle, which follows from experimental evidence, has to be added to the postulates of quantum mechanics.

The Pauli principle:
The wave function $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ describing any state of a system of N identical particles must behave, under permutation $\widehat{P}$ of the particle variables, according to

$$\widehat{P}\,\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \Psi(\boldsymbol{x}_{i_1}, \boldsymbol{x}_{i_2}, \ldots, \boldsymbol{x}_{i_N}) = \varepsilon_P \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \quad (137)$$

where the 'parity factor' ε_P depends on the nature of the particles.
For electrons, protons, neutrons, and other 'fermions'

$$\begin{array}{ll} \varepsilon_P = +1 & (\widehat{P} \text{ even}) \\ \varepsilon_P = -1 & (\widehat{P} \text{ odd}) \end{array} \quad (138)$$

and the wave function is *totally antisymmetric*.
For photons, α particles, ^{4}He atoms, and other 'bosons' $\varepsilon_P = +1$ for all permutations and the wave function is *totally symmetric*.

On a visit to Leiden, Holland, Einstein wrote the following in a special memory book for Professor Kammerlingh-Onnes:

11 November 1922

Der theoretisch arbeitende Naturforscher ist nicht zu beneiden, denn die Natur, oder genauer gesagt: das Experiment, ist eine unerbittliche und wenig freundliche Richterin seiner Arbeit. Sie sagt zu einer Theorie nie "ja" sondern im günstigsten Falle "vielleicht", in den meisten Fällen aber einfach "nein". Stimmt ein Experiment zur Theorie, bedeutet es für letztere "vielleicht", stimmt es nicht, so bedeutet es "nein". Wohl jede Theorie wird einmal ihr "nein" erleben, die meisten Theorien schon bald nach ihrer Entstehung.

The scientific theorist is not to be envied. For Nature, or more precisely experiment, is an inexorable and not very friendly judge of his work. It never says "Yes" to a theory. In the most favourable cases it says "Maybe", and in the great majority of cases simply "No". If an experiment agrees with a theory it means for the latter "Maybe", and if it does not agree it means "No". Probably every theory will some day experience its "No" — most theories soon after conception.

Albert Einstein (1879–1955, 1921 Nobel Prize for Physics), *The Human Side*, selected and edited by Helen Dukas and Banesh Hoffmann, Princeton University Press, Princeton, New Jersey, 1979, p. 18 & p. 125