The postulates of quantum mechanics

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A. INTRODUCTION

In classical mechanics, the motion of any physical system is determined if the position $\mathbf{r}(x, y, z)$ and velocity $\mathbf{v}(\dot{x}, \dot{y}, \dot{z})$ of each of its points are known as a function of time. In general (appendix III), to describe such a system, one introduces generalized coordinates $q_i(t)$ $(i = 1, 2, ..., N)$, whose derivatives with respect to time, $\dot{q}_i(t)$, are the generalized velocities. Specifying the $q_i(t)$ and $\dot{q}_i(t)$ enables us to calculate, at any given instant, the position and velocity of any point of the system. Using the Lagrangian $\mathscr{L}(q_i, \dot{q}_i, t)$, one defines the conjugate momentum p_i of each of the generalized coordinates q_i:

$$p_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i} \tag{A-1}$$

The $q_i(t)$ and $p_i(t)$ $(i = 1, 2, ..., N)$ are called the fundamental dynamical variables. All the physical quantities associated with the system (energy, angular momentum, etc.) can be expressed in terms of the fundamental dynamical variables. For example, the total energy of the system is given by the classical Hamiltonian $\mathscr{H}(q_i, p_i, t)$. The motion of the system can be studied by using either Lagrange's equations or the Hamilton-Jacobi canonical equations, which are written:

$$\frac{dq_i}{dt} = \frac{\partial \mathscr{H}}{\partial p_i} \tag{A-2-a}$$

$$\frac{dp_i}{dt} = -\frac{\partial \mathscr{H}}{\partial q_i} \tag{A-2-b}$$

In the special case of a system consisting of a single physical point of mass m, the q_i are simply the three coordinates of this point, and the $\dot{q}_i$ are the components of its velocity $\mathbf{v}$. If the forces acting on this particle can be derived from a scalar potential $V(\mathbf{r}, t)$, the three conjugate momenta of its position $\mathbf{r}$ (that is, the components of its linear momentum $\mathbf{p}$) are equal to the components of its mechanical momentum $m\mathbf{v}$. The total energy is then written:

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t) \tag{A-3}$$

and the angular momentum with respect to the origin:

$$\mathscr{L} = \mathbf{r} \times \mathbf{p} \tag{A-4}$$

Since $\mathscr{H}(\mathbf{r}, \mathbf{p}, t) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}, t)$, the Hamilton-Jacobi equations (A-2) here take on the well-known form:

$$\frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}}{m} \tag{A-5-a}$$

$$\frac{d\mathbf{p}}{dt} = -\nabla V \tag{A-5-b}$$

The classical description of a physical system can therefore be summarized as follows:

(*i*) The state of the system at a fixed time t_0 is defined by specifying N generalized coordinates $q_i(t_0)$ and their N conjugate momenta $p_i(t_0)$.

(*ii*) The value, at a given time, of the various physical quantities is completely determined when the state of the system at this time is known: knowing the state of the system, one can predict with certainty the result of any measurement performed at time t_0.

(*iii*) The time evolution of the state of the system is given by the Hamilton-Jacobi equations. Since these are first-order differential equations, their solution $\{ q_i(t), p_i(t) \}$ is unique if the value of these functions at a given time t_0 is fixed, $\{ q_i(t_0), p_i(t_0) \}$. The state of the system is known for all time if its initial state is known.

In this chapter, we shall study the postulates on which the quantum description of physical systems is based. We have already introduced them, in a qualitative and partial way, in chapter I. Here we shall discuss them explicitly, within the framework of the formalism developed in chapter II. These postulates will provide us with an answer to the following questions (which correspond to the three points enumerated above for the classical description):

(*i*) How is the state of a quantum system at a given time described mathematically?

(*ii*) Given this state, how can we predict the results of the measurement of various physical quantities?

(*iii*) How can the state of the system at an arbitrary time t be found when the state at time t_0 is known?

We shall begin by stating the postulates of quantum mechanics (§ B). Then we shall analyze their physical content and discuss their consequences (§§ C, D, E).

B. STATEMENT OF THE POSTULATES

1. Description of the state of a system

In chapter I, we introduced the concept of the quantum state of a particle. We first characterized this state at a given time by a square-integrable wave function. Then, in chapter II, we associated a ket of the state space $\mathscr{E}_r$ with each wave function: choosing $|\psi\rangle$ belonging to $\mathscr{E}_r$ is equivalent to choosing

the corresponding function $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$. Therefore, the quantum state of a particle at a fixed time is characterized by a ket of the space $\mathscr{E}_\mathbf{r}$. In this form, the concept of a state can be generalized to any physical system.

First Postulate: At a fixed time t_0, the state of a physical system is defined by specifying a ket $| \psi(t_0) \rangle$ belonging to the state space $\mathscr{E}$.

It is important to note that, since $\mathscr{E}$ is a vector space, this first postulate implies a superposition principle : a linear combination of state vectors is a state vector. We shall discuss this fundamental point and its relations to the other postulates in §E.

2. Description of physical quantities

We have already used, in §D-1 of chapter I, a differential operator H related to the total energy of a particle in a scalar potential. This is simply a special case of the second postulate.

Second Postulate: Every measurable physical quantity $\mathscr{A}$ is described by an operator A acting in $\mathscr{E}$; this operator is an observable.

COMMENTS :

(*i*) The fact that A is an observable (*cf.* chap. II, §D-2) will be seen below (§3) to be essential.

(*ii*) Unlike classical mechanics (*cf.* §A), quantum mechanics describes in a fundamentally different manner the state of a system and the associated physical quantities : a state is represented by a vector, a physical quantity by an operator.

3. The measurement of physical quantities

a. POSSIBLE RESULTS

The connection between the operator H and the total energy of the particle appeared in §D-1 of chapter I in the following form: the only energies possible are the eigenvalues of the operator H. Here as well, this relation can be extended to all physical quantities.

Third Postulate: The only possible result of the measurement of a physical quantity $\mathscr{A}$ is one of the eigenvalues of the corresponding observable A.

COMMENTS :

(*i*) A measurement of $\mathscr{A}$ always gives a real value, since A is by definition Hermitian.

(*ii*) If the spectrum of A is discrete, the results that can be obtained by measuring $\mathscr{A}$ are quantized (§ C-2).

b. PRINCIPLE OF SPECTRAL DECOMPOSITION

We are going to generalize and discuss in more detail the conclusions of § A-3 of chapter I, where we analyzed a simple experiment performed on polarized photons.

Consider a system whose state is characterized, at a given time, by the ket $|\psi\rangle$, assumed to be normalized to 1:

$$\langle\psi|\psi\rangle = 1 \tag{B-1}$$

We want to predict the result of the measurement, at this time, of a physical quantity $\mathscr{A}$ associated with the observable A. This prediction, as we already know, is of a probabilistic sort. We are now going to give the rules which allow us to calculate the probability of obtaining any given eigenvalue of A.

α. *Case of a discrete spectrum*

First, let us assume that the spectrum of A is entirely discrete. If all the eigenvalues a_n of A are non-degenerate, there is associated with each of them a unique (to within a constant factor) eigenvector $|u_n\rangle$:

$$A|u_n\rangle = a_n|u_n\rangle \tag{B-2}$$

Since A is an observable, the set of the $|u_n\rangle$, which we shall take to be normalized, constitutes a basis in $\mathscr{E}$, and the state vector $|\psi\rangle$ can be written:

$$|\psi\rangle = \sum_n c_n|u_n\rangle \tag{B-3}$$

We postulate that the probability $\mathscr{P}(a_n)$ of finding a_n when $\mathscr{A}$ is measured is:

$$\mathscr{P}(a_n) = |c_n|^2 = |\langle u_n|\psi\rangle|^2 \tag{B-4}$$

> *Fourth Postulate (case of a discrete non-degenerate spectrum)*: When the physical quantity $\mathscr{A}$ is measured on a system in the *normalized* state $|\psi\rangle$, the probability $\mathscr{P}(a_n)$ of obtaining the *non-degenerate* eigenvalue a_n of the corresponding observable A is:
>
> $$\mathscr{P}(a_n) = |\langle u_n|\psi\rangle|^2$$
>
> where $|u_n\rangle$ is the normalized eigenvector of A associated with the eigenvalue a_n.

If, now, some of the eigenvalues a_n are degenerate, several orthonormalized eigenvectors $|u_n^i\rangle$ correspond to them:

$$A|u_n^i\rangle = a_n|u_n^i\rangle; \quad i = 1, 2, \ldots g_n \tag{B-5}$$

$|\psi\rangle$ can still be expanded in the orthonormal basis $\{|u_n^i\rangle\}$:

$$|\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i|u_n^i\rangle \tag{B-6}$$

In this case, the probability $\mathscr{P}(a_n)$ becomes:

$$\mathscr{P}(a_n) = \sum_{i=1}^{g_n} |c_n^i|^2 = \sum_{i=1}^{g_n} |\langle u_n^i \mid \psi \rangle|^2 \tag{B-7}$$

(B-4) is then seen to be a special case of (B-7), which can therefore be considered to be the general formula.

Fourth Postulate (case of a discrete spectrum): When the physical quantity $\mathscr{A}$ is measured on a system in the *normalized* state $|\psi\rangle$, the probability $\mathscr{P}(a_n)$ of obtaining the eigenvalue a_n of the corresponding observable A is:

$$\mathscr{P}(a_n) = \sum_{i=1}^{g_n} |\langle u_n^i \mid \psi \rangle|^2$$

where g_n is the degree of degeneracy of a_n and $\{ |u_n^i\rangle \}$ $(i = 1, 2, ..., g_n)$ is an orthonormal set of vectors which forms a basis in the eigensubspace $\mathscr{E}_n$ associated with the eigenvalue a_n of A.

For this postulate to make sense, it is obviously necessary that, if the eigenvalue a_n is degenerate, the probability $\mathscr{P}(a_n)$ be independent of the choice of the $\{ |u_n^i\rangle \}$ basis in $\mathscr{E}_n$. To verify this, consider the vector:

$$|\psi_n\rangle = \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle \tag{B-8}$$

where the coefficients c_n^i are the same as those appearing in the expansion (B-6) of $|\psi\rangle$:

$$c_n^i = \langle u_n^i \mid \psi \rangle \tag{B-9}$$

$|\psi_n\rangle$ is the part of $|\psi\rangle$ which belongs to $\mathscr{E}_n$, that is, the projection of $|\psi\rangle$ onto $\mathscr{E}_n$. This is, moreover, what we find when we substitute (B-9) into (B-8):

$$\begin{aligned} |\psi_n\rangle &= \sum_{i=1}^{g_n} |u_n^i\rangle \langle u_n^i \mid \psi \rangle \\ &= P_n |\psi\rangle \end{aligned} \tag{B-10}$$

where:

$$P_n = \sum_{i=1}^{g_n} |u_n^i\rangle \langle u_n^i| \tag{B-11}$$

is the projector onto $\mathscr{E}_n$ (§ B-3-b of chapter II). Let us now calculate the square of the norm of $|\psi_n\rangle$. From (B-8):

$$\langle \psi_n \mid \psi_n \rangle = \sum_{i=1}^{g_n} |c_n^i|^2 \tag{B-12}$$

Therefore, $\mathscr{P}(a_n)$ *is the square of the norm of* $|\psi_n\rangle = P_n|\psi\rangle$, the projection of $|\psi\rangle$ onto $\mathscr{E}_n$. From this expression, it is clear that a change in the basis in $\mathscr{E}_n$ does not affect $\mathscr{P}(a_n)$. This probability is written:

$$\mathscr{P}(a_n) = \langle \psi | P_n^\dagger P_n | \psi \rangle \tag{B-13}$$

or, using the fact that P_n is Hermitian ($P_n^\dagger = P_n$) and that it is a projector ($P_n^2 = P_n$):

$$\mathscr{P}(a_n) = \langle \psi | P_n | \psi \rangle \tag{B-14}$$

β. *Case of a continuous spectrum*

Now let us assume that the spectrum of A is continuous and, for the sake of simplicity, non-degenerate. The system, orthonormal in the extended sense, of eigenvectors $|v_\alpha\rangle$ of A:

$$A|v_\alpha\rangle = \alpha|v_\alpha\rangle \tag{B-15}$$

forms a continuous basis in $\mathscr{E}$, in terms of which $|\psi\rangle$ can be expanded:

$$|\psi\rangle = \int d\alpha\, c(\alpha)|v_\alpha\rangle \tag{B-16}$$

Since the possible results of a measurement of $\mathscr{A}$ form a continuous set, we must define a probability density, just as we did for the interpretation of the wave function of a particle (§ B-2 of chapter I). The probability $d\mathscr{P}(\alpha)$ of obtaining a value included between α and $\alpha + d\alpha$ is given by:

$$d\mathscr{P}(\alpha) = \rho(\alpha)\, d\alpha$$

with:

$$\rho(\alpha) = |c(\alpha)|^2 = |\langle v_\alpha|\psi\rangle|^2 \tag{B-17}$$

Fourth Postulate (case of a continuous non-degenerate spectrum): When the physical quantity $\mathscr{A}$ is measured on a system in the *normalized* state $|\psi\rangle$, the probability $d\mathscr{P}(\alpha)$ of obtaining a result included between α and $\alpha + d\alpha$ is equal to:

$$d\mathscr{P}(\alpha) = |\langle v_\alpha|\psi\rangle|^2\, d\alpha$$

where $|v_\alpha\rangle$ is the eigenvector corresponding to the eigenvalue α of the observable A associated with $\mathscr{A}$.

COMMENTS:

(*i*) It can be verified explicitly, in each of the cases considered above, that the total probability is equal to 1. For example, starting with formula (B-7), we find:

$$\sum_n \mathscr{P}(a_n) = \sum_n \sum_{i=1}^{g_n} |c_n^i|^2 = \langle \psi | \psi \rangle = 1 \tag{B-18}$$

since $|\psi\rangle$ is normalized. This last condition is therefore indispensable if the statements we have made are to be coherent. Nevertheless, it is not essential : if it is not fulfilled, it suffices to replace (B-7) and (B-17), respectively, by:

$$\mathscr{P}(a_n) = \frac{1}{\langle \psi | \psi \rangle} \sum_{i=1}^{g_n} |c_n^i|^2 \tag{B-19}$$

and:

$$\rho(\alpha) = \frac{1}{\langle \psi | \psi \rangle} |c(\alpha)|^2 \tag{B-20}$$

(*ii*) For the fourth postulate to be coherent, it is necessary for the operator A associated with any physical quantity to be an observable: it must be possible to expand any state on the eigenvectors of A.

(*iii*) We have not given the fourth postulate in its most general form. Starting with the discussion of the cases we have envisaged, it is simple to extend the principle of spectral decomposition to any situation (continuous degenerate spectrum, partially continuous and partially discrete spectrum, etc...). In § E, and later in chapter IV, we shall apply this fourth postulate to a certain number of examples, pointing out certain implications of the superposition principle mentioned in § B-1.

γ. *An important consequence*

Consider two kets $|\psi\rangle$ and $|\psi'\rangle$ such that:

$$|\psi'\rangle = e^{i\theta} |\psi\rangle \tag{B-21}$$

where θ is a real number. If $|\psi\rangle$ is normalized, so is $|\psi'\rangle$:

$$\langle \psi' | \psi' \rangle = \langle \psi | e^{-i\theta} e^{i\theta} | \psi \rangle = \langle \psi | \psi \rangle \tag{B-22}$$

The probabilities predicted for an arbitrary measurement are the same for $|\psi\rangle$ and $|\psi'\rangle$ since, for any $|u_n^i\rangle$:

$$|\langle u_n^i | \psi' \rangle|^2 = |e^{i\theta} \langle u_n^i | \psi \rangle|^2 = |\langle u_n^i | \psi \rangle|^2 \tag{B-23}$$

Similarly, we can replace $|\psi\rangle$ by:

$$|\psi''\rangle = \alpha e^{i\theta} |\psi\rangle \tag{B-24}$$

without changing any of the physical results: there appear, in both the numerator and denominator of (B-19) and (B-20), factors of $|\alpha|^2$ which cancel. Therefore, *two proportional state vectors represent the same physical state.*

Care must be taken to interpret this result correctly. For example, let us assume that:

$$|\psi\rangle = \lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle \tag{B-25}$$

where λ_1 and λ_2 are complex numbers. It is true that $e^{i\theta_1} |\psi_1\rangle$ represents, for all real θ_1, the same physical state as $|\psi_1\rangle$, and $e^{i\theta_2} |\psi_2\rangle$ represents the same state as $|\psi_2\rangle$. But, in general:

$$|\varphi\rangle = \lambda_1 e^{i\theta_1} |\psi_1\rangle + \lambda_2 e^{i\theta_2} |\psi_2\rangle \tag{B-26}$$

does not describe the same state as $|\psi\rangle$ (we shall see in § E-1 that the *relative* phases of the expansion coefficients of the state vector play an important role). This is not true for the special case where $\theta_1 = \theta_2 + 2n\pi$, that is, where:

$$|\varphi\rangle = e^{i\theta_1} [\lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle] = e^{i\theta_1} |\psi\rangle \tag{B-27}$$

In other words: *a global phase factor does not affect the physical predictions, but the relative phases of the coefficients of an expansion are significant.*

c. REDUCTION OF THE WAVE PACKET

We have already introduced this concept in speaking of the measurement of the polarization of photons in the experiment described in § A-3 of chapter I. We are now going to generalize it, confining ourselves, nevertheless, to the case of a discrete spectrum (we shall take up the case of a continuous spectrum in § E).

Assume that we want to measure, at a given time, the physical quantity $\mathscr{A}$. If the ket $|\psi\rangle$, which represents the state of the system immediately before the measurement, is known, the fourth postulate allows us to predict the probabilities of obtaining the various possible results. But when the measurement is actually performed, it is obvious that only one of these possible results is obtained. Immediately after this measurement, we cannot speak of the "probability of having obtained" this or that value: we know which one was actually obtained. We therefore possess additional information, and it is understandable that the state of the system after the measurement, which must incorporate this information, should be different from $|\psi\rangle$.

Let us first consider the case where the measurement of $\mathscr{A}$ yields a simple eigenvalue a_n of the observable A. We then postulate that the state of the system immediately after this measurement is the eigenvector $|u_n\rangle$ associated with a_n:

$$|\psi\rangle \xRightarrow{(a_n)} |u_n\rangle \tag{B-28}$$

COMMENTS:

(*i*) We have been speaking about states "immediately before" the measurement ($|\psi\rangle$) and "immediately after" ($|u_n\rangle$). The precise meaning of these expressions is the following: assume that the measurement takes place at the time $t_0 > 0$, and that we know the state $|\psi(0)\rangle$ of the system at the time $t = 0$. The sixth postulate (see § 4) describes how the system evolves

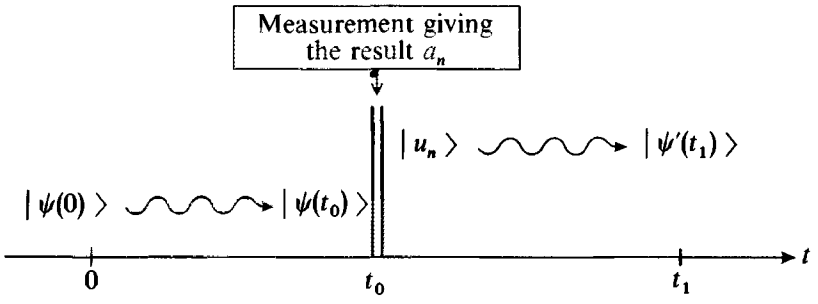

FIGURE 1

When a measurement at time t_0 of the observable A gives the result a_n, the state vector of the system undergoes an abrupt modification and becomes $|u_n\rangle$. This new initial state then evolves.

over time, that is, enables us to calculate from $|\psi(0)\rangle$ the state $|\psi(t_0)\rangle$ "immediately before" the measurement. If the measurement has yielded the non-degenerate eigenvalue a_n, the state $|\psi'(t_1)\rangle$ at a time $t_1 > t_0$ must be calculated from $|\psi'(t_0)\rangle = |u_n\rangle$, the state "immediately after" the measurement, using the sixth postulate to determine the evolution of the state vector between the times t_0 and t_1 (fig. 1).

(*ii*) If we perform a second measurement of $\mathscr{A}$ immediately after the first one (that is, before the system has had time to evolve), we shall always find the same result a_n, since the state of the system immediately before the second measurement is $|u_n\rangle$, and no longer $|\psi\rangle$.

When the eigenvalue a_n given by the measurement is degenerate, postulate (B-28) can be generalized as follows. If the expansion of the state $|\psi\rangle$ immediately before the measurement is written, with the same notation as in section b:

$$|\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle \tag{B-29}$$

the modification of the state vector due to the measurement is written:

$$|\psi\rangle \xrightarrow{(a_n)} \frac{1}{\sqrt{\sum_{i=1}^{g_n} |c_n^i|^2}} \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle \tag{B-30}$$

$\sum_{i=1}^{g_n} c_n^i |u_n^i\rangle$ is the vector $|\psi_n\rangle$ defined above [formula (B-8)], that is, the projection of $|\psi\rangle$ onto the eigensubspace associated with a_n. In (B-30), we normalized this vector since it is always more convenient to use state vectors of norm 1 [comment (*i*) of § b above]. With the notation of (B-10) and (B-11), we can therefore write (B-30) in the form:

$$|\psi\rangle \xrightarrow{(a_n)} \frac{P_n |\psi\rangle}{\sqrt{\langle\psi| P_n |\psi\rangle}} \tag{B-31}$$

Fifth Postulate: If the measurement of the physical quantity $\mathscr{A}$ on the system in the state $|\psi\rangle$ gives the result a_n, the state of the system immediately after the measurement is the normalized projection, $\frac{P_n |\psi\rangle}{\sqrt{\langle\psi| P_n |\psi\rangle}}$, of $|\psi\rangle$ onto the eigensubspace associated with a_n.

The state of the system immediately after the measurement is therefore always an eigenvector of A with the eigenvalue a_n. We stress the fact, however, that *it is not an arbitrary ket of the subspace* $\mathscr{E}_n$, but the part of $|\psi\rangle$ which belongs to $\mathscr{E}_n$ (suitably normalized, for convenience). In the light of § 3-b-γ above, equation (B-28) can be seen to be a special case of (B-30). When $g_n = 1$, the summation over i disappears from (B-30), which becomes:

$$\frac{1}{|c_n|} c_n |u_n\rangle = e^{i \operatorname{Arg} c_n} |u_n\rangle \tag{B-32}$$

This ket indeed describes the same physical state as $|u_n\rangle$.

4. Time evolution of systems

We have already presented, in § B-2 of chapter I, the Schrödinger equation for one particle. Here we shall write it in the general case.

Sixth Postulate: The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle$$

where $H(t)$ is the observable associated with the total energy of the system.

H is called the *Hamiltonian operator* of the system, as it is obtained from the classical Hamiltonian (appendix III and §5 below).

5. Quantization rules

We are finally going to discuss how to construct, for a physical quantity $\mathscr{A}$ already defined in classical mechanics, the operator A which describes it in quantum mechanics.

a. STATEMENT

Let us first consider a system composed of a single particle, without spin, subject to a scalar potential. In this case:

With the position $\mathbf{r}(x, y, z)$ of the particle is associated the observable $\mathbf{R}(X, Y, Z)$. With the momentum $\mathbf{p}(p_x, p_y, p_z)$ of the particle is associated the observable $\mathbf{P}(P_x, P_y, P_z)$.

Recall that the components of **R** and **P** satisfy the canonical commutation relations [chap. II, equations (E-30)]:

$$[R_i, R_j] = [P_i, P_j] = 0$$
$$[R_i, P_j] = i\hbar\delta_{ij} \tag{B-33}$$

Any physical quantity $\mathscr{A}$ related to this particle is expressed in terms of the fundamental dynamical variables **r** and **p**: $\mathscr{A}(\mathbf{r}, \mathbf{p}, t)$. To obtain the corresponding observable A, one could simply replace, in the expression for $\mathscr{A}(\mathbf{r}, \mathbf{p}, t)$, the variables **r** and **p** by the observables **R** and **P***:

$$A(t) = \mathscr{A}(\mathbf{R}, \mathbf{P}, t) \tag{B-34}$$

* See, in complement B_{II}, the definition of a function of an operator.

However, this mode of action would be, in general, ambiguous. Assume, for example, that in $\mathscr{A}(\mathbf{r}, \mathbf{p}, t)$ there appears a term of the form :

$$\mathbf{r} \cdot \mathbf{p} = xp_x + yp_y + zp_z \tag{B-35}$$

In classical mechanics, the scalar product $\mathbf{r} \cdot \mathbf{p}$ is commutative, and one can just as well write :

$$\mathbf{p} \cdot \mathbf{r} = p_x x + p_y y + p_z z \tag{B-36}$$

But when $\mathbf{r}$ and $\mathbf{p}$ are replaced by the corresponding observables $\mathbf{R}$ and $\mathbf{P}$, the operators obtained from (B-35) and (B-36) are not identical [see relations (B-33)] :

$$\mathbf{R} \cdot \mathbf{P} \neq \mathbf{P} \cdot \mathbf{R} \tag{B-37}$$

Moreover, neither $\mathbf{R} \cdot \mathbf{P}$ nor $\mathbf{P} \cdot \mathbf{R}$ is Hermitian :

$$(\mathbf{R} \cdot \mathbf{P})^\dagger = (XP_x + YP_y + ZP_z)^\dagger = \mathbf{P} \cdot \mathbf{R} \tag{B-38}$$

To the preceding postulates, therefore, must be added a symmetrization rule. For example, the observable associated with $\mathbf{r} \cdot \mathbf{p}$ will be :

$$\frac{1}{2}(\mathbf{R} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{R}) \tag{B-39}$$

which is indeed Hermitian. For an observable which is more complicated than $\mathbf{R} \cdot \mathbf{P}$, an analogous symmetrization is to be performed.

> The observable A which describes a classically defined physical quantity $\mathscr{A}$ is obtained by replacing, in the suitably symmetrized expression for $\mathscr{A}$, $\mathbf{r}$ and $\mathbf{p}$ by the observables $\mathbf{R}$ and $\mathbf{P}$ respectively.

We shall see, however, that there exist quantum physical quantities which have no classical equivalent and which are therefore defined directly by the corresponding observables (this is the case, for example, for particle spin).

COMMENT :

The preceding rules, and commutation rules (B-33) in particular, are valid only in cartesian coordinates. It would be possible to generalize them to other coordinate systems ; however, they would no longer have the same simple form as they do above.

b. IMPORTANT EXAMPLES

α. *The Hamiltonian of a particle in a scalar potential*

Consider a (spinless) particle of charge q and mass m, placed in an electric field derived from a scalar potential $U(\mathbf{r})$. The potential energy of the particle is therefore $V(\mathbf{r}) = qU(\mathbf{r})$, and the corresponding classical Hamiltonian is written [appendix III, formula (29)] :

$$\mathscr{H}(\mathbf{r}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \tag{B-40}$$