In the present state of scientific knowledge, quantum mechanics plays a fundamental role in the description and understanding of natural phenomena. In fact, phenomena which occur on a very small (atomic or subatomic) scale cannot be explained outside the framework of quantum physics. For example, the existence and the properties of atoms, the chemical bond and the propagation of an electron in a crystal cannot be understood in terms of classical mechanics. Even when we are concerned only with macroscopic physical objects (that is, whose dimensions are comparable to those encountered in everyday life), it is necessary, in principle, to begin by studying the behavior of their various constituent atoms, ions, electrons, in order to arrive at a complete scientific description. There are many phenomena which reveal, on a macroscopic scale, the quantum behaviour of nature. It is in this sense that it can be said that quantum mechanics is the basis of our present understanding of all natural phenomena, including those traditionally treated in chemistry, biology, etc...

From a historical point of view, quantum ideas contributed to a remarkable unification of the concepts of fundamental physics by treating material particles and radiation on the same footing. At the end of the nineteenth century, people distinguished between two entities in physical phenomena : matter and radiation. Completely different laws were used for each one. To predict the motion of material bodies, the laws of *Newtonian mechanics* (*cf.* appendix III) were utilized. Their success, though of long standing, was none the less impressive. With regard to radiation, the *theory of electromagnetism*, thanks to the introduction of Maxwell's equations, had produced a unified interpretation of a set of phenomena which had previously been considered as belonging to different domains : electricity, magnetism and optics. In particular, the electromagnetic theory of radiation had been spectacularly confirmed experimentally by the discovery of Hertzian waves. Finally, *interactions between radiation and matter* were well explained by the Lorentz force. This set of laws had brought physics to a point which could be considered satisfactory, in view of the experimental data at the time.

However, at the beginning of the twentieth century, physics was to be marked by the profound upheaval that led to the introduction of relativistic mechanics and quantum mechanics. The relativistic " revolution" and the quantum " revolution" were, to a large extent, independent, since they challenged classical physics on different points. Classical laws cease to be valid for material bodies travelling at very high speeds, comparable to that of light (relativistic domain). In addition, they are also found to be wanting on an atomic or subatomic scale (quantum domain). However, it is important to note that classical physics, in both cases, can be seen as an approximation of the new theories, an approximation which is valid for most phenomena on an everyday scale. For example, Newtonian mechanics enables us to predict correctly the motion of a solid body, providing it is non-relativistic (speeds much smaller than that of light) and macroscopic (dimensions much greater than atomic ones). Nevertheless, from a fundamental point of view, quantum theory remains indispensable. It is the only theory which enables us to understand the very existence of a solid body and the values of the macroscopic parameters (density, specific heat, elasticity, etc...) associated with it. At the present time, we do not yet have at our disposal a fully satisfactory theory unifying quantum and relativistic mechanics since difficulties have arisen in this

domain. However, most atomic and molecular phenomena are well explained by the *non-relativistic quantum mechanics* that we intend to examine here.

This chapter is an introduction to quantum ideas and "vocabulary". *No attempt is made here to be rigorous or complete.* The essential goal is to awaken the curiosity of the reader. Phenomena will be described which unsettle ideas as firmly anchored in our intuition as the concept of a trajectory. We want to render the quantum theory "plausible" for the reader by showing simply and qualitatively how it enables us to solve the problems which are encountered on an atomic scale. We shall later return to the various ideas introduced in this chapter and go into further detail, either from the point of view of the mathematical formalism (chap. II) or from the physical point of view (chap. III).

In the first section (§A), we introduce the basic quantum ideas (wave-particle duality, the measurement process), relying on well-known optical experiments. Then we show (§ B) how these ideas can be extended to material particles (wave function, Schrödinger equation). We next study in more detail the characteristics of the "wave packet" associated with a particle, and we introduce the Heisenberg uncertainty relations (§ C). Finally, we discuss some simple cases of typical quantum effects (§ D).

A. ELECTROMAGNETIC WAVES AND PHOTONS

1. Light quanta and the Planck-Einstein relations

Newton considered light to be a beam of particles, able, for example, to bounce back upon reflection from a mirror. During the first half of the nineteenth century, the wavelike nature of light was demonstrated (interference, diffraction). This later enabled optics to be integrated into electromagnetic theory. In this framework, the speed of light, c, is related to electric and magnetic constants and light polarization phenomena can be interpreted as manifestations of the vectorial character of the electric field.

However, the study of *blackbody* radiation, which electromagnetic theory could not explain, led Planck to suggest the hypothesis of the *quantization of energy* (1900): for an electromagnetic wave of frequency ν, the only possible energies are integral multiples of the quantum $h\nu$, where h is a new fundamental constant. Generalizing this hypothesis, Einstein proposed a return to the particle theory (1905): light consists of a beam of *photons*, each possessing an energy $h\nu$. Einstein showed how the introduction of photons made it possible to understand, in a very simple way, certain as yet unexplained characteristics of the photoelectric effect. Twenty years had to elapse before the photon was actually shown to exist, as a distinct entity, by the Compton effect (1924).

These results lead to the following conclusion: the interaction of an electromagnetic wave with matter occurs by means of *elementary indivisible processes*, in which the radiation appears to be composed of particles, the photons. Particle parameters (the energy E and the momentum $\mathbf{p}$ of a photon) and wave parameters

(the angular frequency $\omega = 2\pi\nu$ and the wave vector $\mathbf{k}$, where $|\mathbf{k}| = 2\pi/\lambda$, with ν the frequency and λ the wavelength) are linked by the fundamental relations:

$$\boxed{\begin{array}{c} E = h\nu = \hbar\omega \\ \\ \mathbf{p} = \hbar\mathbf{k} \end{array}} \qquad \text{(Planck-Einstein relations)} \tag{A-1}$$

where $\hbar = h/2\pi$ is defined in terms of the Planck constant h:

$$h \simeq 6.62\ 10^{-34}\ \text{Joule} \times \text{second} \tag{A-2}$$

During each elementary process, energy and total momentum must be conserved.

2. Wave-particle duality

Thus we have returned to a particle conception of light. Does this mean that we must abandon the wave theory? Certainly not. We shall see that typical wave phenomena such as interference and diffraction could not be explained in a purely particle framework. Analyzing Young's well-known double-slit experiment will lead us to the following conclusion: a complete interpretation of the phenomena can be obtained only by conserving *both* the wave aspect and the particle aspect of light (although they seem *a priori* irreconcilable). We shall then show how this paradox can be resolved by the introduction of the fundamental quantum concepts.

a. ANALYSIS OF YOUNG'S DOUBLE-SLIT EXPERIMENT

The device used in this experiment is shown schematically in figure 1. The monochromatic light emitted by the source $\mathscr{S}$ falls on an opaque screen $\mathscr{P}$ pierced by two narrow slits F_1 and F_2, which illuminate the observation screen $\mathscr{E}$ (a photographic plate, for example). If we block F_2, we obtain on $\mathscr{E}$ a light intensity distribution $I_1(x)$ which is the diffraction pattern of F_1. In the same way, when F_1 is obstructed, the diffraction pattern of F_2 is described by $I_2(x)$. When the two slits F_1 and F_2 are open at the same time, we observe a system of interference fringes on the screen. In particular, we note that the corresponding intensity $I(x)$ is not the sum of the intensities produced by F_1 and F_2 separately:

$$I(x) \neq I_1(x) + I_2(x) \tag{A-3}$$

How could one conceive of explaining, in terms of a particle theory (seen, in the preceding section, to be necessary), the experimental results just described? The existence of a diffraction pattern when only one of the two slits is open could, for example, be explained as being due to photon collisions with the edges of the slit. Such an explanation would, of course, have to be developed more precisely, and a more detailed study would show it to be insufficient. Instead, let us concentrate on the interference phenomenon. We could attempt to explain it by an interaction between the photons which pass through the slit F_1 and those which pass through the slit F_2. Such an explanation would lead to the following predic-

tion : if the intensity of the source $\mathscr{S}$ (the number of photons emitted per second) is diminished until the photons strike the screen practically one by one, the interaction between the photons must diminish and, eventually, vanish. The interference fringes should therefore disappear.

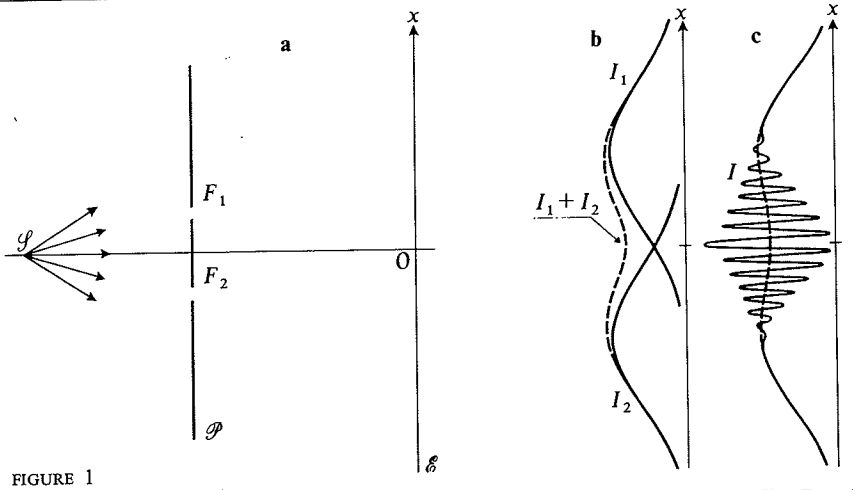

FIGURE 1

Diagram of Young's double-slit light interference experiment (fig. a). Each of the slits F_1 and F_2 produces a diffraction pattern on the screen $\mathscr{E}$. The corresponding intensities are $I_1(x)$ and $I_2(x)$ (solid lines in figure b). When the two slits F_1 and F_2 are open simultaneously, the intensity $I(x)$ observed on the screen is not the sum $I_1(x) + I_2(x)$ (dashed lines in figures b and c), but shows oscillations due to the interference between the electric fields radiated by F_1 and F_2 (solid line in figure c).

Before we indicate the answer given by experiment, recall that the wave theory provides a completely natural interpretation of the fringes. The light intensity at a point of the screen $\mathscr{E}$ is proportional to the square of the amplitude of the electric field at this point. If $E_1(x)$ and $E_2(x)$ represent, in complex notation, the electric fields produced at x by slits F_1 and F_2 respectively (the slits behave like secondary sources), the total resultant field at this point when F_1 and F_2 are both open is ★ :

$$E(x) = E_1(x) + E_2(x) \tag{A-4}$$

Using complex notation, we then have :

$$I(x) \propto |E(x)|^2 = |E_1(x) + E_2(x)|^2 \tag{A-5}$$

Since the intensities $I_1(x)$ and $I_2(x)$ are proportional, respectively, to $|E_1(x)|^2$ and $|E_2(x)|^2$, formula (A-5) shows that $I(x)$ differs from $I_1(x) + I_2(x)$ by an interference term which depends on the phase difference between E_1 and E_2 and whose presence explains the fringes. The wave theory thus predicts that diminishing the intensity of the source $\mathscr{S}$ will simply cause the fringes to diminish in intensity but not to vanish.

★ Since the experiment studied here is performed with unpolarized light, the vectorial character of the electric field does not play an essential role. For the sake of simplicity, we ignore it in this paragraph.

What actually happens when $\mathscr{S}$ emits photons practically one by one? *Neither the predictions of the wave theory nor those of the particle theory are verified.* In fact :

(*i*) If we cover the screen $\mathscr{E}$ with a photographic plate and increase the exposure time so as to capture a large number of photons on each photograph, we observe when we develop them that *the fringes have not disappeared. Therefore, the purely corpuscular interpretation,* according to which the fringes are due to an interaction between photons, *must be rejected.*

(*ii*) On the other hand, we can expose the photographic plate during a time so short that it can only receive a few photons. We then observe that each photon produces a *localized impact* on $\mathscr{E}$ and not a very weak interference pattern. *Therefore, the purely wave interpretation must also be rejected.*

In reality, as more and more photons strike the photographic plate, the following phenomenon occurs. Their individual impacts seem to be distributed in a *random manner*, and only when a great number of them have reached $\mathscr{E}$ does the distribution of the impacts begin to have a continuous aspect. The density of the impacts at each point of $\mathscr{E}$ corresponds to the interference fringes : maximum on a bright fringe and zero on a dark fringe. It can thus be said that the photons, as they arrive, build up the interference pattern.

The result of this experiment therefore leads, apparently, to a paradox. Within the framework of the particle theory, for example, it can be expressed in the following way. Since photon-photon interactions are excluded, each photon must be considered separately. But then it is not clear why the phenomena should change drastically according to whether only one slit or both slits are open. For a photon passing through one of the slits, why should the fact that the other is open or closed have such a critical importance?

Before we discuss this problem, note that in the preceding experiment we did not seek to determine through which slit each photon passed before it reached the screen. In order to obtain this information, we can imagine placing detectors (photomultipliers) behind F_1 and F_2. It will then be observed that, if the photons arrive one by one, each one passes through a well-determined slit (a signal is recorded either by the detector placed behind F_1 or by the one covering F_2 but not by both at once). But, obviously, the photons detected in this way are absorbed and do not reach the screen. Remove the photomultiplier which blocks F_1, for example. The one which remains behind F_2 tells us that, out of a large number of photons, about half pass through F_2. We conclude that the others (which can continue as far as the screen) pass through F_1. But the pattern that they gradually construct on the screen is not an interference pattern, since F_2 is blocked. It is only the diffraction pattern of F_1.

b. QUANTUM UNIFICATION OF THE TWO ASPECTS OF LIGHT

The preceding analysis shows that it is impossible to explain all the phenomena observed if only one of the two aspects of light, wave or particle, is considered. Now these two aspects seem to be mutually exclusive. To overcome this difficulty, it thus becomes indispensable to reconsider in a critical way the concepts of classical physics. We must accept the possibility that these concepts, although our

everyday experience leads us to consider them well-founded, may not be valid in the new ("microscopic") domain which we are entering. For example, an essential characteristic of this new domain appeared when we placed counters behind Young's slits : *when one performs a measurement on a microscopic system, one disturbs it in a fundamental fashion.* This is a new property since, in the macroscopic domain, we always have the possibility of conceiving measurement devices whose influence on the system is practically as weak as one might wish. This critical revision of classical physics is imposed by experiment and must of course be guided by experiment.

Let us reconsider the "paradox" stated above concerning the photon which passes through one slit but behaves differently depending on whether the other slit is open or closed. We saw that if we try to detect the photons when they cross the slits, we prevent them from reaching the screen. More generally, a detailed experimental analysis shows that *it is impossible to observe the interference pattern and to know at the same time through which slit each photon has passed* (*cf.* complement D_I). Thus it is necessary, in order to resolve the paradox, to give up the idea that a photon inevitably passes through a particular slit. We are then led to question the concept, which is a fundamental one of classical physics, of a particle's trajectory.

Moreover, as the photons arrive one by one, their impacts on the screen gradually build up the interference pattern. This implies that, for a particular photon, we are not certain in advance where it will strike the screen. Now these photons are all emitted under the same conditions. Thus another classical idea has been destroyed : that the initial conditions completely determine the subsequent motion of a particle. We can only say, when a photon is emitted, that the probability of its striking the screen at x is proportional to the intensity $I(x)$ calculated using wave theory, that is, to $|E(x)|^2$.

After many tentative efforts that we shall not describe here, the concept of *wave-particle duality* was formulated. We can summarize it schematically as follows* :

(*i*) The particle and wave aspects of light are inseparable. *Light behaves simultaneously like a wave and like a flux of particles, the wave enabling us to calculate the probability of the manifestation of a particle.*

(*ii*) Predictions about the behavior of a photon can only be probabilistic.

(*iii*) The information about a photon at time t is given by the wave $E(\mathbf{r}, t)$, which is a solution of Maxwell's equations. We say that this wave characterizes the state of the photons at time t. $E(\mathbf{r}, t)$ is interpreted as the *probability amplitude* of a photon appearing, at time t, at the point $\mathbf{r}$. This means that the corresponding probability is proportional to $|E(\mathbf{r}, t)|^2$.

COMMENTS :

(*i*) Since Maxwell's equations are linear and homogeneous, we can use a *superposition principle* : if E_1 and E_2 are two solutions of these equations, then $E = \lambda_1 E_1 + \lambda_2 E_2$, where λ_1 and λ_2 are constants, is also a solution.

* It is worth noting that this interpretation of physical phenomena, generally considered to be "orthodox" at the present time, is still being contested today by certain physicists.

It is this superposition principle which explains wave phenomena in classical optics (interference, diffraction). In quantum physics, the interpretation of $E(\mathbf{r}, t)$ as a probability amplitude is thus essential to the persistence of such phenomena.

(*ii*) The theory merely allows one to calculate the probability of the occurence of a given event. Experimental verifications must thus be founded on the repetition of a large number of identical experiments. In the above experiment, a large number of photons, all produced in the same way, are emitted successively and build up the interference pattern, which is the manifestation of the calculated probabilities.

(*iii*) We are talking here about "the photon state" so as to be able to develop in § B an analogy between $E(\mathbf{r}, t)$ and the wave function $\psi(\mathbf{r}, t)$ which characterizes the quantum state of a material particle. This "optical analogy" is very fruitful. In particular, as we shall see in § D, it allows us to understand, simply and without recourse to calculation, various quantum properties of material particles. However, we should not push it too far and let it lead us to believe that it is rigorously correct to consider $E(\mathbf{r}, t)$ as characterizing the quantum state of a photon.

Furthermore, we shall see that the fact that $\psi(\mathbf{r}, t)$ is complex is essential in quantum mechanics, while the complex notation $E(\mathbf{r}, t)$ is used in optics purely for convenience (only its real part has a physical meaning). The precise definition of the (complex) quantum state of radiation can only be given in the framework of quantum electrodynamics, a theory which is simultaneously quantum mechanical and relativistic. We shall not consider these problems here (we shall touch on them in complement K_V).

3. The principle of spectral decomposition

Armed with the ideas introduced in § 2, we are now going to discuss another simple optical experiment, whose subject is the polarization of light. This will permit us to introduce the fundamental concepts which concern the measurement of physical quantities.

The experiment consists of directing a polarized plane monochromatic light wave onto an analyzer A. Oz designates the direction of propagation of this wave and $\mathbf{e}_p$, the unit vector describing its polarization (*cf.* fig. 2). The analyzer A transmits light polarized parallel to Ox and absorbs light polarized parallel to Oy.

The classical description of this experiment (a description which is valid for a sufficiently intense light beam) is the following. The polarized plane wave is characterized by an electric field of the form:

$$\mathbf{E}(\mathbf{r}, t) = E_0 \mathbf{e}_p \, e^{i(kz - \omega t)} \tag{A-6}$$

where E_0 is a constant. The light intensity I is proportional to $|E_0|^2$. After its passage through the analyzer A, the plane wave is polarized along Ox:

$$\mathbf{E}'(\mathbf{r}, t) = E'_0 \mathbf{e}_x e^{i(kz - \omega t)} \tag{A-7}$$

and its intensity I', proportional to $|E'_0|^2$, is given by *Malus' law*:

$$I' = I \cos^2 \theta \tag{A-8}$$

[$\mathbf{e}_x$ is the unit vector of the Ox axis and θ is the angle between $\mathbf{e}_x$ and $\mathbf{e}_p$].

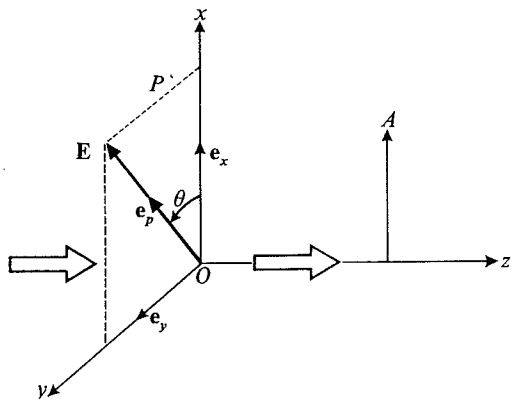

FIGURE 2

A simple measurement experiment relating to the polarization of a light wave. A beam of light propagates along the direction Oz and crosses successively the polarizer P and the analyzer A. θ is the angle between Ox and the electric field of the wave transmitted by P. The vibrations transmitted by A are parallel to Ox.

What will happen on the quantum level, that is, when I is weak enough for the photons to reach the analyzer one by one? (We then place a photon detector behind this analyser.) First of all, the detector never registers a "fraction of a photon". Either the photon crosses the analyzer or it is entirely absorbed by it. Next (except in special cases that we shall examine in a moment), we cannot predict with certainty whether a given incident photon will pass or be absorbed. We can only know the corresponding probabilities. Finally, if we send out a large number N of photons one after the other, the result will correspond to the classical law, in the sense that about $N \cos^2 \theta$ photons will be detected after the analyzer.

We shall retain the following ideas from this description :

(*i*) The measurement device (the analyzer, in this case) can give only certain privileged results, which we shall call *eigen* (or proper) *results*★. In the above experiment, there are only two possible results : the photon crosses the analyzer or it is stopped. One says that there is quantization of the result of the measurement, in contrast to the classical case [*cf.* formula (A-8)] where the transmitted intensity I' can vary continuously, according to the value of θ, between 0 and I.

★ The reason for this name will appear in chapter III.

(*ii*) To each of these eigen results corresponds an *eigenstate*. Here, the two eigenstates are characterized by:

$$\begin{aligned} &\mathbf{e}_p = \mathbf{e}_x \\ \text{or} \quad &\mathbf{e}_p = \mathbf{e}_y \end{aligned} \tag{A-9}$$

($\mathbf{e}_y$ is the unit vector of the Oy axis). If $\mathbf{e}_p = \mathbf{e}_x$, we know with certainty that the photon will traverse the analyzer; if $\mathbf{e}_p = \mathbf{e}_y$, it will, on the contrary, definitely be stopped. The correspondence between eigen results and eigenstates is therefore the following. If the particle is, before the measurement, in one of the eigenstates, the result of this measurement is certain: it can only be the associated eigen result.

(*iii*) When the state before the measurement is arbitrary, only the probabilities of obtaining the different eigen results can be predicted. To find these probabilities, one decomposes the state of the particles into a linear combination of the various eigenstates. Here, for an arbitrary $\mathbf{e}_p$, we write:

$$\mathbf{e}_p = \mathbf{e}_x \cos\theta + \mathbf{e}_y \sin\theta \tag{A-10}$$

The probability of obtaining a given eigen result is then proportional to the square of the absolute value of the coefficient of the corresponding eigenstate. The proportionality factor is determined by the condition that the sum of all these probabilities must be equal to 1. We thus deduce from (A-10) that each photon has a probability $\cos^2\theta$ of traversing the analyzer and a probability $\sin^2\theta$ of being absorbed by it (we know that $\cos^2\theta + \sin^2\theta = 1$). This is indeed what was stated above. This rule is called in quantum mechanics the *principle of spectral decomposition*. Note that the decomposition to be performed depends on the type of measurement device being considered, since one must use the eigenstates which correspond to it: in formula (A-10), the choice of the axes Ox and Oy is fixed by the analyzer.

(*iv*) After passing through the analyzer, the light is completely polarized along $\mathbf{e}_x$. If we place, after the first analyzer A, a second analyzer A', having the same axis, all the photons which traversed A will also traverse A'. According to what we have just seen in point (*ii*), this means that, after they have crossed A, the state of the photons is the eigenstate characterized by $\mathbf{e}_x$. There has therefore been an abrupt change in the state of the particles. Before the measurement, this state was defined by a vector $\mathbf{E}(\mathbf{r}, t)$ which was collinear with $\mathbf{e}_p$. After the measurement, we possess an additional piece of information (the photon has passed) which is incorporated by describing the state by a different vector, which is now collinear with $\mathbf{e}_x$. This expresses the fact, already pointed out in § A-2, that *the measurement disturbs the microscopic system* (here, the photon) *in a fundamental fashion.*

COMMENT:

The certain prediction of the result when $\mathbf{e}_p = \mathbf{e}_x$ or $\mathbf{e}_p = \mathbf{e}_y$ is only a special case. The probability of one of the possible events is then indeed equal to 1. But, in order to verify this prediction, one must perform a large number of experiments. One must be sure that *all* the photons pass (or are stopped), since the fact that a particular photon crosses the analyzer (or is absorbed) is not characteristic of $\mathbf{e}_p = \mathbf{e}_x$ (or $\mathbf{e}_p = \mathbf{e}_y$).

B. MATERIAL PARTICLES AND MATTER WAVES

1. The de Broglie relations

Parallel to the discovery of photons, the study of atomic emission and absorption spectra uncovered a fundamental fact, which classical physics was unable to explain : these spectra are composed of *narrow lines*. In other words, a given atom emits or absorbs only photons having well-determined frequencies (that is, energies). This fact can be interpreted very easily if one accepts that *the energy of the atom is quantized*, that is, it can take on only certain discrete values $E_i (i = 1, 2, ..., n, ...)$: the emission or absorption of a photon is then accompanied by a "jump" in the energy of the atom from one permitted value E_i to another E_j. Conservation of energy implies that the photon has a frequency ν_{ij} such that:

$$h\nu_{ij} = |E_i - E_j| \tag{B-1}$$

Only frequencies which obey (B-1) can therefore be emitted or absorbed by the atom.

The existence of such discrete energy levels was confirmed independently by the Franck-Hertz experiment. Bohr interpreted this in terms of privileged electronic orbits and stated, with Sommerfeld, an empirical rule which permitted the calculation of these orbits for the case of the hydrogen atom. But the fundamental origin of these quantization rules remained mysterious.

In 1923, however, de Broglie put forth the following hypothesis : *material particles, just like photons, can have a wavelike aspect*. He then derived the Bohr-Sommerfeld quantization rules as a consequence of this hypothesis, the various permitted energy levels appearing as analogues of the normal modes of a vibrating string. Electron diffraction experiments (Davisson and Germer, 1927) strikingly confirmed the existence of a wavelike aspect of matter by showing that *interference patterns could be obtained with material particles such as electrons*.

One therefore associates with a material particle of energy E and momentum $\mathbf{p}$, a wave whose angular frequency $\omega = 2\pi\nu$ and wave vector $\mathbf{k}$ are given by the same relations as for photons (*cf.* § A-1) :

$$\begin{cases} E = h\nu = \hbar\omega \\ \mathbf{p} = \hbar\mathbf{k} \end{cases} \tag{B-2}$$

In other words, the corresponding wavelength is :

$$\lambda = \frac{2\pi}{|\mathbf{k}|} = \frac{h}{|\mathbf{p}|} \qquad \text{(de Broglie relation)} \tag{B-3}$$

COMMENT :

The very small value of the Planck constant h explains why the wavelike nature of matter is very difficult to demonstrate on a macroscopic scale. Complement A_I of this chapter discusses the orders of magnitude of the de Broglie wavelengths associated with various material particles.

2. Wave functions. Schrödinger equation

In accordance with de Broglie's hypothesis, we shall apply the ideas introduced in § A for the case of the photon to all material particles. Recalling the conclusions of this paragraph, we are led to the following formulation :

(*i*) For the classical concept of a trajectory, we must substitute the concept of a time-varying *state*. The quantum state of a particle such as the electron* is characterized by a *wave function* $\psi(\mathbf{r}, t)$, which contains all the information it is possible to obtain about the particle.

(*ii*) $\psi(\mathbf{r}, t)$ is interpreted as a *probability amplitude of the particle's presence*. Since the possible positions of the particle form a continuum, the probability $d\mathscr{P}(\mathbf{r}, t)$ of the particle being, at time t, in a volume element $d^3r = dx\, dy\, dz$ situated at the point $\mathbf{r}$ must be proportional to d^3r and therefore infinitesimal. $|\psi(\mathbf{r}, t)|^2$ is then interpreted as the corresponding *probability density*, with :

$$d\mathscr{P}(\mathbf{r}, t) = C\,|\psi(\mathbf{r}, t)|^2\, d^3r \tag{B-4}$$

where C is a normalization constant [see comment (*i*) at the end of § B-2].

(*iii*) *The principle of spectral decomposition* applies to the measurement of an arbitrary physical quantity :

– The result found must belong to a set of eigen results $\{ a \}$.

– With each eigenvalue a is associated an eigenstate, that is, an eigenfunction $\psi_a(\mathbf{r})$. This function is such that, if $\psi(\mathbf{r}, t_0) = \psi_a(\mathbf{r})$ (where t_0 is the time at which the measurement is performed), the measurement will always yield a.

– For any $\psi(\mathbf{r}, t)$, the probability $\mathscr{P}_a$ of finding the eigenvalue a for a measurement at time t_0 is found by decomposing $\psi(\mathbf{r}, t_0)$ in terms of the functions $\psi_a(\mathbf{r})$:

$$\psi(\mathbf{r}, t_0) = \sum_a c_a\, \psi_a(\mathbf{r}) \tag{B-5}$$

Then :

$$\mathscr{P}_a = \frac{|c_a|^2}{\sum_a |c_a|^2} \tag{B-6}$$

(the presence of the denominator insures that the total probability is equal to 1 : $\sum_a \mathscr{P}_a = 1$).

– If the measurement indeed yields a, the wave function of the particle immediately after the measurement is :

$$\psi'(\mathbf{r}, t_0) = \psi_a(\mathbf{r}) \tag{B-7}$$

(*iv*) The equation describing the evolution of the function $\psi(\mathbf{r}, t)$ remains to be written. It is possible to introduce it in a very natural way, using the

* We shall not take into account here the existence of electron spin (*cf.* chap. IX).

Planck and de Broglie relations. Nevertheless, we have no intention of proving this fundamental equation, which is called the *Schrödinger equation*. We shall simply assume it. Later, we shall discuss some of its consequences (whose experimental verification will prove its validity). Besides, we shall consider this equation in much more detail in chapter III.

When the particle (of mass m) is subjected to the influence of a potential* $V(\mathbf{r}, t)$, the Schrödinger equation takes on the form :

$$\boxed{i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \Delta\psi(\mathbf{r}, t) + V(\mathbf{r}, t)\,\psi(\mathbf{r}, t)} \tag{B-8}$$

where Δ is the Laplacian operator $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

We notice immediately that this equation is linear and homogeneous in ψ. Consequently, for material particles, there exists a superposition principle which, combined with the interpretation of ψ as a probability amplitude, is the source of wavelike effects. Note, moreover, that the differential equation (B-8) is first-order with respect to time. This condition is necessary if the state of the particle at a time t_0, characterized by $\psi(\mathbf{r}, t_0)$, is to determine its subsequent state.

Thus there exists a fundamental analogy between matter and radiation : in both cases, a correct description of the phenomena necessitates the introduction of quantum concepts, and, in particular, the idea of wave-particle duality.

COMMENTS :

(*i*) For a system composed of only one particle, the total probability of finding the particle anywhere in space, at time t, is equal to 1 :

$$\int d\mathscr{P}(\mathbf{r}, t) = 1 \tag{B-9}$$

Since $d\mathscr{P}(\mathbf{r}, t)$ is given by formula (B-4), we conclude that *the wave function* $\psi(\mathbf{r}, t)$ *must be square-integrable* :

$$\int |\psi(\mathbf{r}, t)|^2 \, d^3r \quad \text{is finite} \tag{B-10}$$

The normalization constant C which appears in (B-4) is then given by the relation :

$$\frac{1}{C} = \int |\psi(\mathbf{r}, t)|^2 \, d^3r \tag{B-11}$$

(we shall later see that the form of the Schrödinger equation implies that C is time-independent). One often uses wave functions which are normalized, such that :

$$\int |\psi(\mathbf{r}, t)|^2 \, d^3r = 1 \tag{B-12}$$

* $V(\mathbf{r}, t)$ designates a potential energy here. For example, it may be the product of an electric potential and the particle's charge. In quantum mechanics, $V(\mathbf{r}, t)$ is commonly called a potential.

The constant C is then equal to 1.

(*ii*) Note the important difference between the concepts of classical states and quantum states. The classical state of a particle is determined at time t by the specification of six parameters characterizing its position and its velocity at time t : $x, y, z ; v_x, v_y, v_z$. The quantum state of a particle is determined by an *infinite number* of parameters : the values at the various points in space of the wave function $\psi(\mathbf{r}, t)$ which is associated with it. For the classical idea of a trajectory (the succession in time of the various states of the classical particle), we must substitute the idea of the propagation of the wave associated with the particle. Consider, for example, Young's double-slit experiment, previously described for the case of photons, but which in principle can also be performed with material particles such as electrons. When the interference pattern is observed, it makes no sense to ask through which slit each particle has passed, since the wave associated with it passed through both.

(*iii*) It is worth noting that, unlike photons, which can be emitted or absorbed during an experiment, material particles can neither be created nor destroyed. The electrons emitted by a heated filament for example already existed in the filament. In the same way, an electron absorbed by a counter does not disappear; it becomes part of an atom or an electric current. Actually, the theory of relativity shows that it is possible to create and annihilate material particles : for example, a photon having sufficient energy, passing near an atom, can materialize into an electron-positron pair. Inversely, the positron, when it collides with an electron, annihilates with it, emitting photons. However, we pointed out in the beginning of this chapter that we would limit ourselves here to the non-relativistic quantum domain, and we have indeed treated time and space coordinates asymmetrically. In the framework of non-relativistic quantum mechanics, material particles can neither be created nor annihilated. This conservation law, as we shall see, plays a role of primary importance. The need to abandon it is one of the important difficulties encountered when one tries to construct a relativistic quantum mechanics.

C. QUANTUM DESCRIPTION OF A PARTICLE. WAVE PACKETS

In the preceding paragraph, we introduced the fundamental concepts which are necessary for the quantum description of a particle. In this paragraph, we are going to familiarize ourselves with these concepts and deduce from them several very important properties. Let us begin by studying a very simple special case, that of a free particle.

1. Free particle

Consider a particle whose potential energy is zero (or has a constant value) at every point in space. The particle is thus not subjected to any force; it is said to be free.