

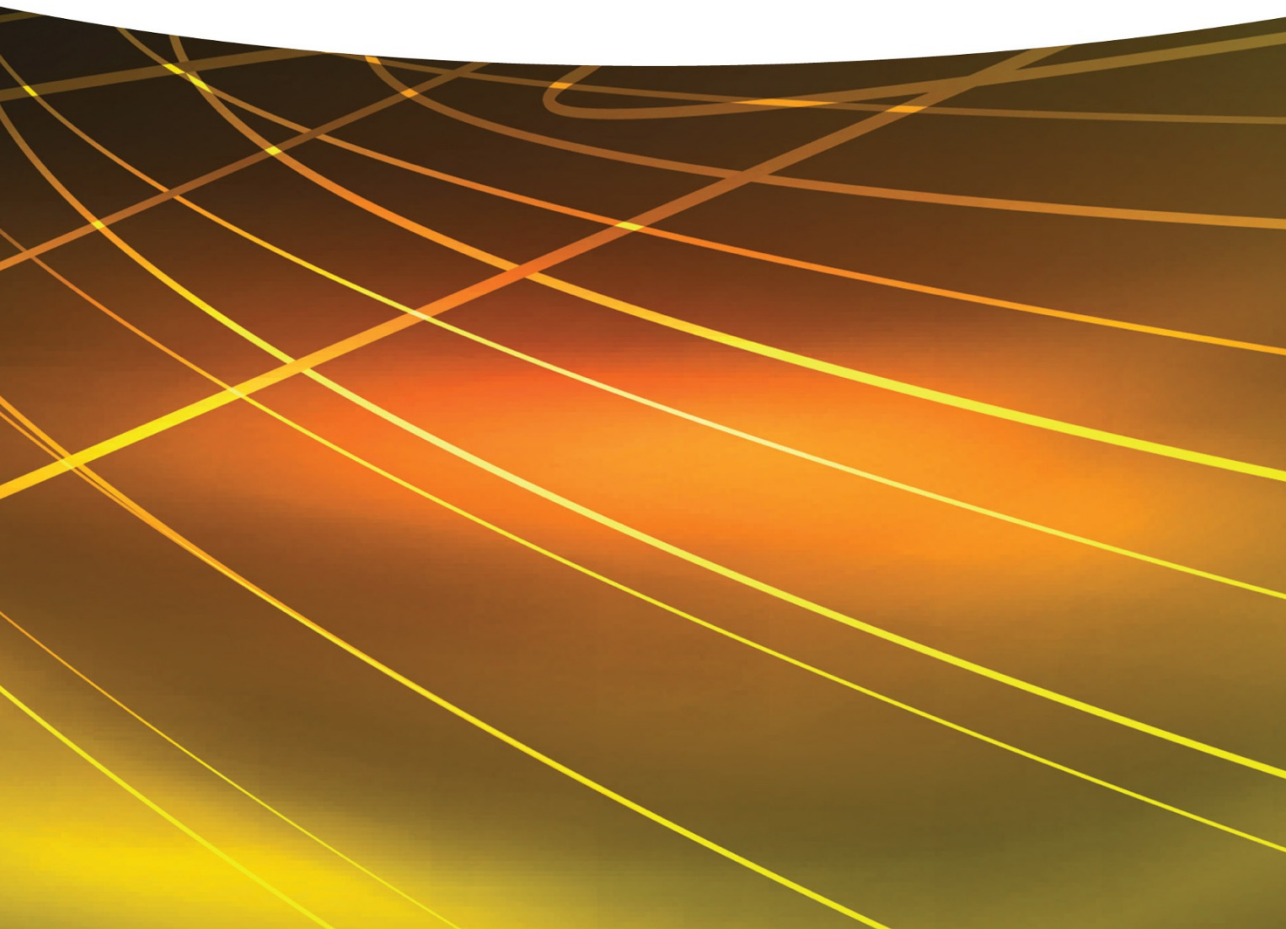
Claude Cohen-Tannoudji, Bernard Diu, and
Franck Laloë



Quantum Mechanics

Volume II: Angular Momentum, Spin,
and Approximation Methods

Second Edition



QUANTUM MECHANICS

Volume II

Angular Momentum, Spin, and Approximation Methods

Claude Cohen-Tannoudji, Bernard Diu,
and Franck Laloë

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Directions for Use

This book is composed of chapters and their complements:

- *The chapters* contain the fundamental concepts. Except for a few additions and variations, they correspond to a course given in the last year of a typical undergraduate physics program (Volume I) or of a graduate program (Volumes II and III). The 21 chapters are *complete in themselves* and can be studied independently of the complements.
- *The complements* follow the corresponding chapter. Each is labelled by a letter followed by a subscript, which gives the number of the chapter (for example, the complements of Chapter V are, in order, A_V, B_V, C_V, etc.). They can be recognized immediately by the symbol ● that appears at the top of each of their pages.

The complements vary in character. Some are intended to expand the treatment of the corresponding chapter or to provide a more detailed discussion of certain points. Others describe concrete examples or introduce various physical concepts. One of the complements (usually the last one) is a collection of exercises.

The *difficulty* of the complements varies. Some are very simple examples or extensions of the chapter. Others are more difficult and at the graduate level or close to current research. In any case, the reader should have studied the material in the chapter before using the complements.

The complements are generally independent of one another. *The student should not try to study all the complements of a chapter at once.* In accordance with his/her aims and interests, he/she should choose a small number of them (two or three, for example), plus a few exercises. The other complements can be left for later study. To help with the choice, the complements are listed at the end of each chapter in a “*reader’s guide*”, which discusses the difficulty and importance of each.

Some passages within the book have been set in small type, and these can be omitted on a first reading.

Foreword

Quantum mechanics is a branch of physics whose importance has continually increased over the last decades. It is essential for understanding the structure and dynamics of microscopic objects such as atoms, molecules and their interactions with electromagnetic radiation. It is also the basis for understanding the functioning of numerous new systems with countless practical applications. This includes lasers (in communications, medicine, milling, etc.), atomic clocks (essential in particular for the GPS), transistors (communications, computers), magnetic resonance imaging, energy production (solar panels, nuclear reactors), etc. Quantum mechanics also permits understanding surprising physical properties such as superfluidity or supraconductivity. There is currently a great interest in entangled quantum states whose non-intuitive properties of nonlocality and nonseparability permit conceiving remarkable applications in the emerging field of quantum information. Our civilization is increasingly impacted by technological applications based on quantum concepts. This why a particular effort should be made in the teaching of quantum mechanics, which is the object of these three volumes.

The first contact with quantum mechanics can be disconcerting. Our work grew out of the authors' experiences while teaching quantum mechanics for many years. It was conceived with the objective of easing a first approach, and then aiding the reader to progress to a more advance level of quantum mechanics. The first two volumes, first published more than forty years ago, have been used throughout the world. They remain however at an intermediate level. They have now been completed with a third volume treating more advanced subjects. Throughout we have used a progressive approach to problems, where no difficulty goes untreated and each aspect of the diverse questions is discussed in detail (often starting with a classical review).

This willingness to go further “without cheating or taking shortcuts” is built into the book structure, using two distinct linked texts: *chapters* and *complements*. As we just outlined in the “Directions for use”, the chapters present the general ideas and basic concepts, whereas the complements illustrate both the methods and concepts just exposed.

Volume I presents a general introduction of the subject, followed by a second chapter describing the basic mathematical tools used in quantum mechanics. While this chapter can appear long and dense, the teaching experience of the authors has shown that such a presentation is the most efficient. In the third chapter the postulates are announced and illustrated in many of the complements. We then go on to certain important applications of quantum mechanics, such as the harmonic oscillator, which lead to numerous applications (molecular vibrations, phonons, etc.). Many of these are the object of specific complements.

Volume II pursues this development, while expanding its scope at a slightly higher level. It treats collision theory, spin, addition of angular momenta, and both time-dependent and time-independent perturbation theory. It also presents a first approach to the study of identical particles. In this volume as in the previous one, each theoretical concept is immediately illustrated by diverse applications presented in the complements. Both volumes I and II have benefited from several recent corrections, but there have also been additions. Chapter XIII now contains two sections §§ D and E that treat random perturbations, and a complement concerning relaxation has been added.

Volume III extends the two volumes at a slightly higher level. It is based on the use of the creation and annihilation operator formalism (second quantization), which is commonly used in quantum field theory. We start with a study of systems of identical particles, fermions or bosons. The properties of ideal gases in thermal equilibrium are presented. For fermions, the Hartree-Fock method is developed in detail. It is the base of many studies in chemistry, atomic physics and solid state physics, etc. For bosons, the Gross-Pitaevskii equation and the Bogolubov theory are discussed. An original presentation that treats the pairing effect of both fermions and bosons permits obtaining the BCS (Bardeen-Cooper-Schrieffer) and Bogolubov theories in a unified framework. The second part of volume III treats quantum electrodynamics, its general introduction, the study of interactions between atoms and photons, and various applications (spontaneous emission, multiphoton transitions, optical pumping, etc.). The dressed atom method is presented and illustrated for concrete cases. A final chapter discusses the notion of quantum entanglement and certain fundamental aspects of quantum mechanics, in particular the Bell inequalities and their violations.

Finally note that we have not treated either the philosophical implications of quantum mechanics, or the diverse interpretations of this theory, despite the great interest of these subjects. We have in fact limited ourselves to presenting what is commonly called the “orthodox point of view”. It is only in Chapter XXI that we touch on certain questions concerning the foundations of quantum mechanics (nonlocality, etc.). We have made this choice because we feel that one can address such questions more efficiently after mastering the manipulation of the quantum mechanical formalism as well as its numerous applications. These subjects are addressed in the book *Do we really understand quantum mechanics?* (F. Laloë, Cambridge University Press, 2019); see also section 5 of the bibliography of volumes I and II.

Acknowledgments:

Volumes I and II:

The teaching experience out of which this text grew were group efforts, pursued over several years. We wish to thank all the members of the various groups and particularly Jacques Dupont-Roc and Serge Haroche, for their friendly collaboration, for the fruitful discussions we have had in our weekly meetings and for the ideas for problems and exercises that they have suggested. Without their enthusiasm and valuable help, we would never have been able to undertake and carry out the writing of this book.

Nor can we forget what we owe to the physicists who introduced us to research, Alfred Kastler and Jean Brossel for two of us and Maurice Levy for the third. It was in the context of their laboratories that we discovered the beauty and power of quantum mechanics. Neither have we forgotten the importance to us of the modern physics taught at the C.E.A. by Albert Messiah, Claude Bloch and Anatole Abragam, at a time when graduate studies were not yet incorporated into French university programs.

We wish to express our gratitude to Ms. Aucher, Baudrit, Boy, Brodschi, Emo, Heywaerts, Lemirre, Touzeau for preparation of the manuscript.

Volume III:

We are very grateful to Nicole and Daniel Ostrowsky, who, as they translated this Volume from French into English, proposed numerous improvements and clarifications. More recently, Carsten Henkel also made many useful suggestions during his translation of the text into German; we are very grateful for the improvements of the text that resulted from this exchange. There are actually many colleagues and friends who greatly contributed, each in his own way, to finalizing this book. All their complementary remarks and suggestions have been very helpful and we are in particular thankful to:

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A. Introduction

A-1. Importance of collision phenomena

Many experiments in physics, especially in high energy physics, consist of directing a beam of particles (1) (produced for example by an accelerator) onto a target composed

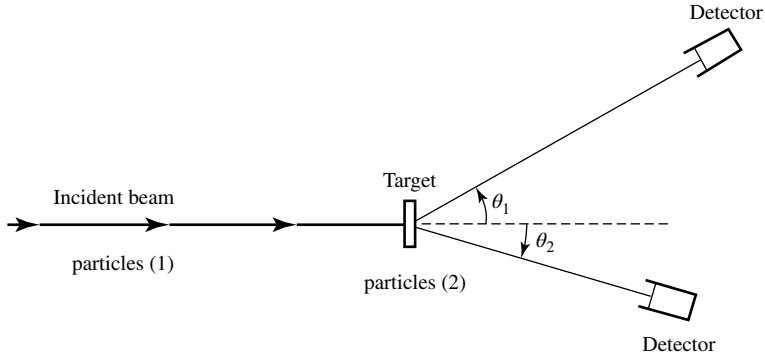


Figure 1: Diagram of a collision experiment involving the particles (1) of an incident beam and the particles (2) of a target. The two detectors represented in the figure measure the number of particles scattered through angles θ_1 and θ_2 with respect to the incident beam.

of particles (2), and studying the resulting collisions: the various particles¹ constituting the final state of the system – that is, the state after the collision (*cf.* Fig. 1) – are detected and their characteristics (direction of emission, energy, etc.) are measured. Obviously, the aim of such a study is to determine the interactions that occur between the various particles entering into the collision.

The phenomena observed are sometimes very complex. For example, if particles (1) and (2) are in fact composed of more elementary components (protons and neutrons in the case of nuclei), the latter can, during the collision, redistribute themselves amongst two or several final composite particles which are different from the initial particles; in this case, one speaks of “rearrangement collisions”. Moreover, at high energies, the relativistic possibility of the “materialization” of part of the energy appears: new particles are then created and the final state can include a great number of them (the higher the energy of the incident beam, the greater the number). Broadly speaking, one says that collisions give rise to *reactions*, which are described most often as in chemistry:



Amongst all the reactions possible² under given conditions, *scattering* reactions are defined as those in which the final state and the initial state are composed of the same particles (1) and (2). In addition, a scattering reaction is said to be elastic when none of the particles’ internal states change during the collision.

¹In practice, it is not always possible to detect all the particles emitted, and one must often be satisfied with partial information about the final system.

²Since the processes studied occur on a quantum level, it is not generally possible to predict with certainty what final state will result from a given collision; one merely attempts to predict the probabilities of the various possible states.

A-2. Scattering by a potential

We shall confine ourselves in this chapter to the study of the elastic scattering of the incident particles (1) by the target particles (2). If the laws of classical mechanics were applicable, solving this problem would involve determining the deviations in the incident particles' trajectories due to the forces exerted by particles (2). For processes occurring on an atomic or nuclear scale, it is clearly out of the question to use classical mechanics to resolve the problem; we must study the evolution of the wave function associated with the incident particles under the influence of their interactions with the target particles [which is why we speak of the “scattering” of particles (1) by particles (2)]. Rather than attack this question in its most general form, we shall introduce the following simplifying hypotheses:

- (i) We shall suppose that particles (1) and (2) have no spin. This simplifies the theory considerably but should not be taken to imply that the spin of particles is unimportant in scattering phenomena.
- (ii) We shall not take into account the possible internal structure of particles (1) and (2). The following arguments are therefore not applicable to “inelastic” scattering phenomena, where part of the kinetic energy of (1) is absorbed in the final state by the internal degrees of freedom of (1) and (2) (*cf.* for example, the experiment of Franck and Hertz). We shall confine ourselves to the case of *elastic scattering*, which does not affect the internal structure of the particles.
- (iii) We shall assume that the target is thin enough to enable us to neglect multiple scattering processes; that is, processes during which a particular incident particle is scattered several times before leaving the target.
- (iv) We shall neglect any possibility of coherence between the waves scattered by the different particles which make up the target. This simplification is justified when the spread of the wave packets associated with particles (1) is small compared to the average distance between particles (2). Therefore we shall concern ourselves only with the elementary process of the scattering of a particle (1) of the beam by a particle (2) of the target. This excludes a certain number of phenomena which are nevertheless very interesting, such as coherent scattering by a crystal (Bragg diffraction) or scattering of slow neutrons by the phonons of a solid, which provide valuable information about the structure and dynamics of crystal lattices. When these coherence effects can be neglected, the flux of particles detected is simply the sum of the fluxes scattered by each of the \mathcal{N} target particles, that is, \mathcal{N} times the flux scattered by any one of them (the exact position of the scattering particle inside the target is unimportant since the target dimensions are much smaller than the distance between the target and the detector).
- (v) We shall assume that the interactions between particles (1) and (2) can be described by a potential energy $V(\mathbf{r}_1 - \mathbf{r}_2)$, which depends only on the relative position $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ of the particles. If we follow the reasoning of § B, Chapter VII, then, in the center-of-mass reference frame³ of the two particles (1) and (2), the problem

³In order to interpret the results obtained in scattering experiments, it is clearly necessary to return to the laboratory reference frame. Going from one frame of reference to another is a simple kinematic problem that we will not consider here. See for example Messiah (1.17), vol. I. Chap. X, § 7.

reduces to the study of *the scattering of a single particle by the potential* $V(\mathbf{r})$. The mass μ of this “relative particle” is related to the masses m_1 and m_2 of (1) and (2) by the formula:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (\text{A-2})$$

A-3. Definition of the scattering cross section

Let Oz be the direction of the incident particles of mass μ (fig. 2). The potential $V(\mathbf{r})$ is localized around the origin O of the coordinate system [which is in fact the center of mass of the two real particles (1) and (2)]. We shall designate by F_i the flux of particles in the incident beam, that is, the number of particles per unit time which traverse a unit surface perpendicular to Oz in the region where z takes on very large negative values. (The flux F_i is assumed to be weak enough to allow us to neglect interactions between different particles of the incident beam.)

We place a detector far from the region under the influence of the potential and in the direction fixed by the polar angles θ and φ , with an opening facing O and subtending the solid angle $d\Omega$ (the detector is situated at a distance from O which is large compared to the linear dimensions of the potential's zone of influence). We can thus count the number dn of particles scattered per unit time into the solid angle $d\Omega$ about the direction (θ, φ) . The differential dn is obviously proportional to $d\Omega$ and to the incident flux F_i . We shall define $\sigma(\theta, \varphi)$ to be the coefficient of proportionality between dn and $F_i d\Omega$:

$$\boxed{dn = F_i \sigma(\theta, \varphi) d\Omega} \quad (\text{A-3})$$

The dimensions of dn and F_i are, respectively, T^{-1} and $(L^2 T)^{-1}$, $\sigma(\theta, \varphi)$ therefore has the dimensions of a surface; it is called the *differential scattering cross section* in the direction (θ, φ) . Cross sections are frequently measured in barns and submultiples of barns:

$$1 \text{ barn} = 10^{-24} \text{ cm}^2 \quad (\text{A-4})$$

The definition (A-3) can be interpreted in the following way: the number of particles per unit time which reach the detector is equal to the number of particles which would cross a surface $\sigma(\theta, \varphi) d\Omega$ placed perpendicular to Oz in the incident beam.

Similarly, the *total scattering cross section* σ is defined by the formula:

$$\sigma = \int \sigma(\theta, \varphi) d\Omega \quad (\text{A-5})$$

Comments:

- (i) Definition (A-3), in which dn is proportional to $d\Omega$, implies that only the scattered particles are taken into consideration. The flux of these particles reaching a given detector D [of fixed surface and placed in the direction

(θ, φ) is inversely proportional to the square of the distance between D and O (this property is characteristic of a scattered flux). In practice, the incident beam is laterally bounded [although its width remains much larger than the extent of the zone of influence of $V(\mathbf{r})$], and the detector is placed outside its trajectory so that it receives only the scattered particles. Of course, such an arrangement does not permit the measurement of the cross section in the direction $\theta = 0$ (the forward direction), which can only be obtained by extrapolation from the values of $\sigma(\theta, \varphi)$ for small θ .

- (ii) The concept of a cross section is not limited to the case of elastic scattering: reaction cross sections are defined in an analogous manner.

A-4. Organization of this chapter

§ B is devoted to a brief study of scattering by an arbitrary potential $V(\mathbf{r})$ (decreasing however faster than $1/r$ as r tends toward infinity). First of all, in § B-1, we introduce the fundamental concepts of a stationary scattering state and a scattering amplitude. We then show, in § B-2, how knowledge of the asymptotic behavior of the wave functions associated with stationary scattering states enables us to obtain scattering cross sections. Afterwards, in § B-3, we discuss in a more precise way, using the integral scattering equation, the existence of these stationary scattering states. Finally (in § B-4), we derive an approximate solution of this equation, valid for weak potentials. This leads us to the Born approximation, in which the cross section is very simply related to the Fourier transform of the potential.

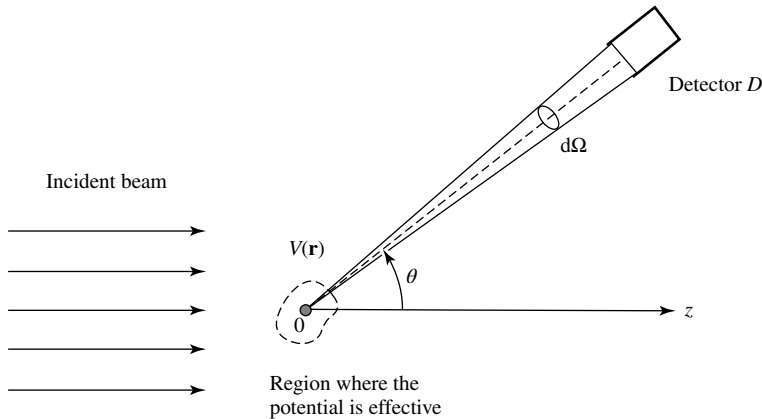


Figure 2: The incident beam, whose flux of particles is F_i , is parallel to the axis Oz ; it is assumed to be much wider than the zone of influence of the potential $V(\mathbf{r})$, which is centered at O . Far from this zone of influence, a detector D measures the number dn of particles scattered per unit time into the solid angle $d\Omega$, centered around the direction defined by the polar angles θ and φ . The number dn is proportional to F_i and to $d\Omega$; the coefficient of proportionality $\sigma(\theta, \varphi)$ is, by definition, the scattering “cross section” in the direction (θ, φ) .

For a central potential $V(\mathbf{r})$, the general methods described in § B clearly remain applicable, but the method of partial waves, set forth in § C, is usually considered preferable. This method is based (§ C-1) on the comparison of the stationary states with well-defined angular momentum in the presence of the potential $V(r)$ (which we shall call “partial waves”) and their analogues in the absence of the potential (“free spherical waves”). Therefore, we begin by studying, in § C-2, the essential properties of the stationary states of a free particle, and more particularly those of free spherical waves. Afterwards (§ C-3), we show that the difference between a partial wave in the potential $V(r)$ and a free spherical wave with the same angular momentum l is characterized by a “phase shift” δ_l . Thus, it is only necessary to know how stationary scattering states can be constructed from partial waves in order to obtain the expression of cross sections in terms of phase shifts (§ C-4).

B. Stationary scattering states. Calculation of the cross section

In order to describe in quantum mechanical terms the scattering of a given incident particle by the potential $V(\mathbf{r})$, it is necessary to study the time evolution of the wave packet representing the state of the particle. The characteristics of this wave packet are assumed to be known for large negative values of the time t , when the particle is in the negative region of the Oz axis, far from and not yet affected by the potential $V(\mathbf{r})$. It is known that the subsequent evolution of the wave packet can be obtained immediately if it is expressed as a superposition of stationary states. This is why we are going to begin by studying the eigenvalue equation of the Hamiltonian:

$$H = H_0 + V(\mathbf{r}) \quad (\text{B-1})$$

where:

$$H_0 = \frac{\mathbf{P}^2}{2\mu} \quad (\text{B-2})$$

describes the particle’s kinetic energy.

Actually, to simplify the calculations, we are going to base our reasoning directly on the stationary states and not on wave packets. We have already used this procedure in Chapter I, in the study of “square” one-dimensional potentials (§ D-2 and complement H_I). It consists of considering a stationary state to represent a “probability fluid” in steady flow, and studying the structure of the corresponding probability currents. Naturally, this simplified reasoning is not rigorous: it remains to be shown that it leads to the same results as the correct treatment of the problem, which is based on wave packets. Assuming this will enable us to develop certain general ideas easily, without burying them in complicated calculations⁴.

⁴The proof was given in complement J_I, for a particular one-dimensional problem; we verified that the same results are obtained by calculating the probability current associated with a stationary scattering state or by studying the evolution of a wave packet describing a particle which undergoes a collision.

B-1. Definition of stationary scattering states

B-1-a. Eigenvalue equation of the Hamiltonian

Schrödinger's equation describing the evolution of the particle in the potential $V(\mathbf{r})$ is satisfied by solutions associated with a well-defined energy E (stationary states):

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r}) e^{-iEt/\hbar} \quad (\text{B-3})$$

where $\varphi(\mathbf{r})$ is a solution of the eigenvalue equation:

$$\left[-\frac{\hbar^2}{2\mu} \Delta + V(\mathbf{r}) \right] \varphi(\mathbf{r}) = E \varphi(\mathbf{r}) \quad (\text{B-4})$$

We are going to assume that the potential $V(\mathbf{r})$ decreases faster than $1/r$ as r approaches infinity. Notice that this hypothesis excludes the Coulomb potential, which demands special treatment; we shall not consider it here.

We shall only be concerned with solutions of (B-4) associated with a positive energy E , equal to the kinetic energy of the incident particle before it reaches the zone of influence of the potential. Defining:

$$E = \frac{\hbar^2 k^2}{2\mu} \quad (\text{B-5})$$

$$V(\mathbf{r}) = \frac{\hbar^2}{2\mu} U(\mathbf{r}) \quad (\text{B-6})$$

enables us to write (B-4) in the form:

$$[\Delta + k^2 - U(\mathbf{r})] \varphi(\mathbf{r}) = 0 \quad (\text{B-7})$$

For each value of k (that is, of the energy E), equation (B-7) can be satisfied by an infinite number of solutions (the positive eigenvalues of the Hamiltonian H are infinitely degenerate). As in "square" one-dimensional potential problems (*cf.* Chap. I, § D-2 and complement H_I), we must choose from amongst these solutions the one that corresponds to the physical problem being studied (for example, when we wanted to determine the probability that a particle with a given energy would cross a one-dimensional potential barrier, we chose the stationary state which, in the region on the other side of the barrier, was composed simply of a transmitted wave). Here, the choice proves to be more complicated, since the particle is moving in three-dimensional space and the potential $V(\mathbf{r})$ has, *a priori*, an arbitrary form. Therefore, we shall specify, using wave packet properties in an intuitive way, the conditions that must be imposed on the solutions of equation (B-7) if they are to be used in the description of a scattering process. We shall call the eigenstates of the Hamiltonian which satisfy these conditions *stationary scattering states*, and we shall designate by $v_k^{(\text{scatt})}(\mathbf{r})$ the associated wave functions.

B-1-b. Asymptotic form of stationary scattering states. Scattering amplitude

For large negative values of t , the incident particle is free [$V(\mathbf{r})$ is practically zero when one is sufficiently far from the point O], and its state is represented by a plane wave packet. Consequently, the stationary wave function that we are looking for must contain a term of the form e^{ikz} , where k is the constant which appears in equation (B-7).

When the wave packet reaches the region which is under the influence of the potential $V(\mathbf{r})$, its structure is profoundly modified and its evolution complicated. Nevertheless, for large positive values of t , it has left this region and once more takes on a simple form: it is now split into a transmitted wave packet which continues to propagate along Oz in the positive direction (hence having the form e^{ikz}) and a scattered wave packet. Consequently, the wave function $v_k^{(\text{scatt})}(\mathbf{r})$, representing the stationary scattering state associated with a given energy $E = \hbar^2 k^2 / 2\mu$, will be obtained from the superposition of the plane wave e^{ikz} and a scattered wave (we are ignoring the problem of normalization).

The structure of the scattered wave obviously depends on the potential $V(\mathbf{r})$. Yet its asymptotic form (valid far from the zone of influence of the potential) is simple; reasoning by analogy with wave optics, we see that the scattered wave must present the following characteristics for large r :

- (i) In a given direction (θ, φ) , its radial dependence is of the form e^{ikr}/r . It is a divergent (or “outgoing”) wave which has the same energy as the incident wave. The factor $1/r$ results from the fact that there are three spatial dimensions: $(\Delta + k^2)e^{ikr}$ is not zero, while:

$$(\Delta + k^2) \frac{e^{ikr}}{r} = 0 \quad \text{for } r \geq r_0 \text{ where } r_0 \text{ is any positive distance} \quad (\text{B-8})$$

(in optics, the factor $1/r$ insures that the total flux of energy passing through a sphere of radius r is independent of r for large r ; in quantum mechanics, it is the probability flux passing through this sphere that does not depend on r).

- (ii) Since scattering is not generally isotropic, the amplitude of the outgoing wave depends on the direction (θ, φ) being considered.

Finally, the wave function $v_k^{(\text{scatt})}(\mathbf{r})$ associated with the stationary scattering state is, by definition, the solution of equation (B-7) whose asymptotic behavior is of the form:

$$\boxed{v_k^{(\text{scatt})}(\mathbf{r}) \underset{r \rightarrow \infty}{\sim} e^{ikz} + f_k(\theta, \varphi) \frac{e^{ikr}}{r}} \quad (\text{B-9})$$

In this expression, only the function $f_k(\theta, \varphi)$, which is called the *scattering amplitude*, depends on the potential $V(\mathbf{r})$. It can be shown (*cf.* § B-3) that equation (B-7) has indeed one and only one solution, for each value of k , that satisfies condition (B-9).

Comments:

- (i) We have already pointed out that in order to obtain simply the time evolution of the wave packet representing the state of the incident particle, it is necessary to expand it in terms of eigenstates of the total Hamiltonian H rather than in terms of plane waves. Therefore, let us consider a wave function of the form⁵:

$$\psi(\mathbf{r}, t) = \int_0^\infty dk g(k) v_k^{(\text{scatt})}(\mathbf{r}) e^{-iE_k t / \hbar} \quad (\text{B-10})$$

⁵ Actually, it is also necessary to superpose the plane waves corresponding to wave vectors \mathbf{k} having slightly different orientations, for the incident wave packet is limited in the directions perpendicular to Oz . For the sake of simplicity, we are concerning ourselves here only with the energy dispersion (which limits the spread of the wave packet along Oz)