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QUANTUM THEORY OF SCATTERING PROCESSES: GENERAL PRINCIPLES and ADVANCED TOPICS

BY

J. E. G. FARINA

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PREFACE

The purpose of this book is to give a systematic account of the general principles and concepts governing the non-relativistic quantum mechanical motion of a set of N elementary particles under their mutual interaction, where by "elementary particle" is meant one which can be neither created nor destroyed. (For most purposes in chemical physics the elementary particles are electrons and atomic nuclei.) The book is not strictly an introduction, but is addressed rather to the reader who, after a study of introductory topics,[†] wishes to see the whole subject treated systematically by deduction from general principles. At the same time, it is largely self-contained and efforts have been made to reduce mathematical sophistication to a minimum. The only essential prerequisite is, in fact, a knowledge and understanding of elementary quantum mechanics as contained in earlier volumes of the present series.[‡]

The book commences with a discussion of the unperturbed and perturbed stationary states of the system in Chapter 1, considers its time evolution in Chapter 2, discusses transition amplitudes and cross-sections in Chapter 3, investigates the complications which arise from the possible identity of elementary particles in Chapter 4, and finally gives some examples of applications in Chapter 5. One or more exercises are set at the end of most sections—these are in the main very simple, and should help the reader in following the arguments in the text. The definition of the scattering operator used is that of Rodberg and Thaler,[§] which seems to be the most suitable for the N-particle system considered here.

Thanks are due to Professor McWeeny and Pergamon Press for their kindness and help with the writing and production of this book; without this, the task would have been much more difficult.

[†] For example J. E. G. Farina, *Quantum Theory of Scattering Processes*, Pergamon Press, Oxford (1973) (Volume 4 of Topic 2 in the present series).

[‡] In particular R. McWeeny, *Quantum Mechanics. Principles and Formalism*, Pergamon Press, Oxford (1972) (Volume 1 of Topic 2).

[§] L. S. Rodberg and R. M. Thaler, *Introduction to the Quantum Theory of Scattering*, Academic Press, New York (1967).

CHAPTER 1

THE CHANNELS OF AN N-PARTICLE SYSTEM

1.1. NATURE OF THE SYSTEM TO BE STUDIED

The purpose of this book will be to describe the quantum mechanical theory of the dynamics of an N-particle system. In atomic and molecular physics and chemistry these particles will almost always be electrons and atomic nuclei, and these will be regarded as our "fundamental" particles. As such, we shall regard them as indestructible, and atoms and molecules will be regarded as composed of these elementary particles. In nuclear physics the elementary particles are neutrons and protons, and atomic nuclei are regarded as made up of these. The field of high-energy physics is very much at the frontiers of knowledge, and the nature of the "elementary" particles in this case is still a matter of controversy.

Our system, therefore, consists of N "elementary" particles. We shall suppose the particles to move with non-relativistic velocities under their mutual interactions, and we shall not consider the effect of external agencies such as the electromagnetic field. There will therefore be no photons in our system, and processes involving the absorption or emission of photons will not be considered. Although this rules out many reactions of interest, it does not rule them all out by a long way. In many reactions in the gaseous state processes of the form $A+B \rightarrow C+D$, where A and B are composite particles such as atoms, molecules, or ions, take place, and such reactions can be considered as distinct from any previous or subsequent emission or absorption of radiation. Also of much interest are processes of the form $A+B \rightarrow C^{*}+D$ where C^{*} is an unstable composite particle which subsequently disintegrates, so that a process of the form $C^{*} \rightarrow D+E$, for example, takes place without the absorption or emission of radiation. It is the fundamental theory of such processes which will be studied in this book.

Let us first consider the configuration coordinates of the system. If we label the particles 1, 2, $\ldots$, N the rth particle is specified by its position vector $\mathbf{R}_r$ and spin s_r. The vectors $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$ and numbers $s_1, s_2, \ldots, s_N$ now specify the configuration of the system.

With the vector $\mathbf{R}_r$ is associated a Laplacian operator ∇_r^2. If the mass of the rth particle is m_r its kinetic energy operator is defined by $\mathsf{K}_r = -\hbar^2\nabla_r^2/2m_r$.

In nonrelativistic quantum mechanics the Hamiltonian H_G of the system takes the form[†]

$$\mathsf{H}_G = \sum_{r=1}^{N} \mathsf{K}_r + V. \tag{1.1.1}$$

The system can be decomposed into m "clusters", the jth cluster A_j containing n_j elementary particles, say, so that $n_1+n_2+\ldots+n_m = N$. We shall assume that the quantity V can be expressed in the form

$$V = \sum_{j=1}^{m} V(A_j)+V_i \tag{1.1.2}$$

where $V(A_j)$ depends only on the coordinates of the particles of the jth cluster, while V_i tends to zero as the clusters are separated from each other. The suffix i denotes the particular decomposition, and V_i represents the interaction potential between the clusters.

We can use (2) to put (1) in the form

$$\mathsf{H}_G = \sum_{j=1}^{m} \sum_{r=1}^{n_j} \mathsf{K}_r(j)+ \sum_{=1}^{m} V(A_j)+V_i \tag{1.1.3}$$

where $\mathsf{K}_r(j)$ is the kinetic energy operator for the rth particle of A_j. If we put

$$\mathsf{h}_{jG} = \sum_{r=1}^{n_j} \mathsf{K}_r(j)+V(A_j), \tag{1.1.4}$$

so that h_{jG} depends only on the coordinate of the jth cluster,[‡] (3) becomes

$$\mathsf{H}_G = \sum_{j=1}^{m} \mathsf{h}_{jG}+V_i. \tag{1.1.5}$$

We shall assume that V and V_i are invariant under translations of the system as a whole, and that $V(A_j)$ is invariant under a translation of the jth cluster as a whole. In other words, we assume that the N-particle system is not affected by its environment.

Example 1. If the elementary particles are electrons and atomic nuclei which interact through their Coulombic interactions V is just the sum of these interactions. In this case $V(A_j)$ is the sum of the Coulombic interactions between particles within the jth cluster, while V_i is the sum of the interactions between particles in different clusters. The decomposition (2) is obvious in this case. Since the Coulomb potential depends only on the distance between the particles the translational invariance is also obvious here.

[†] We use the symbol H_G for the Hamiltonian in the laboratory system as later we shall use H for the Hamiltonian after the motion of the centre of mass has been removed.

[‡] Again the suffix G denotes the Hamiltonian before removal of centre of mass motion.

EXAMPLE 2. The assumption remains valid if translational invariance holds and the effect on any one cluster of the others becomes negligible as the clusters separate. For then

$$\mathsf{H}_G \to \sum_{j=1}^{m} \mathsf{h}_{jG} \tag{1.1.6}$$

where h_{jG} is given by an expression of the form (4). If we define V_i by

$$V_i = \mathsf{H}_G - \sum_{j=1}^{m} \mathsf{h}_{jG} \tag{1.1.7}$$

then (5) is obviously satisfied, and from (6) and (7) $V_i \to 0$ as the clusters separate from each other. If we substitute for h_{jG} from (4) into (5) we obtain (3). Hence H_G is given by (1) where V has the form (2).

1.2. SEPARATION OF THE CENTRE OF MASS MOTION

Let us first consider a system consisting of two elementary particles 1 and 2. We shall denote the position vectors of 1 and 2 by $\mathbf{R}_1$ and $\mathbf{R}_2$, the position vector $\mathbf{R}_1 - \mathbf{R}_2$ of 1 relative to 2 by $\mathbf{R}_{12}$, and the position vector $(m_1\mathbf{R}_1 + m_2\mathbf{R}_2)/(m_1+m_2)$ of the centre of mass by $\mathbf{R}_{1+2}$. Associated with the vectors $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_{1+2}$ and $\mathbf{R}_{12}$ we have Laplacians which we denote by ∇_1^2, ∇_2^2, ∇_{1+2}^2 and ∇_{12}^2 respectively.

We can describe the positions of the two particles by either $\mathbf{R}_1$ and $\mathbf{R}_2$, or by $\mathbf{R}_{1+2}$ and $\mathbf{R}_{12}$. If we denote the components of $\mathbf{R}_1$ relative to a set of Cartesian axes $Oxyz$ by (x_1, y_1, z_1), with a similar notation for the components of the other vectors, we can specify the configuration of the system by either the six coordinates $(x_1, y_1, z_1, x_2, y_2, z_2)$ or by the six coordinates $(x_{1+2}, y_{1+2}, z_{1+2}, x_{12}, y_{12}, z_{12})$. The reader may easily verify that the Jacobean of the transformation between them is unity.

The kinetic energy operators for the motion of 1 and 2 are

$$\mathsf{K}_i = -\frac{\hbar^2}{2m_i} \nabla_i^2 \qquad (i = 1, 2). \tag{1.2.1}$$

Let us denote the reduced mass $m_1m_2/(m_1+m_2)$ of 1 and 2 by μ_{12}, the kinetic energy operator for the motion of the centre of mass by K_{1+2}, and the kinetic energy operator for the motion of 1 relative to 2 by K_{12}. In this notation

$$\mathsf{K}_{1+2} = -\frac{\hbar^2}{2(m_1+m_2)} \nabla_{1+2}^2 \tag{1.2.2}$$

and

$$\mathsf{K}_{12} = -\frac{\hbar^2}{2\mu_{12}} \nabla_{12}^2. \tag{1.2.3}$$

The four Laplacians are, of course, given by

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad (i = 1,\ 2,\ 1+2,\ 12). \qquad (1.2.4)$$

The reader should have no difficulty in verifying from equations (1) to (4) that

$$\mathsf{K}_1 + \mathsf{K}_2 = \mathsf{K}_{1+2} + \mathsf{K}_{12}. \qquad (1.2.5)$$

The state of free motion of a particle in which its momentum is $\hbar\mathbf{k}$ may be represented by a ket $|\mathbf{k}\rangle$ whose wave function $\varphi_{\mathbf{k}}(\mathbf{r})$, or representative in configuration space $\langle\mathbf{r}\mid\mathbf{k}\rangle$ (Dirac, 1958), is given by

$$\varphi_{\mathbf{k}}(\mathbf{R}) = \langle\mathbf{R}\mid\mathbf{k}\rangle = (2\pi)^{-3/2}\exp(i\mathbf{k}\cdot\mathbf{R}). \qquad (1.2.6)$$

It is easily verified that

$$\langle\mathbf{k}\mid\mathbf{k}'\rangle = \int\langle\mathbf{k}\mid\mathbf{r}\rangle\langle\mathbf{r}\mid\mathbf{k}'\rangle\,d\mathbf{r} = \int\varphi_{\mathbf{k}}^*(\mathbf{r})\,\varphi_{\mathbf{k}'}(\mathbf{r})\,d\mathbf{r} = \delta(\mathbf{k}-\mathbf{k}'). \quad (1.2.7)$$

The state of motion of two particles 1 and 2 is now specified by the ket $|\mathbf{k}_1\mathbf{k}_2\rangle$, where the momenta are $\hbar\mathbf{k}_1$ and $\hbar\mathbf{k}_2$. At this stage we shall not consider complications arising from the Pauli principle, and so the wave function for the two particles is the product of the separate wave functions $\langle\mathbf{R}_1|\mathbf{k}_1$ and $\langle\mathbf{R}_2|\mathbf{k}_2\rangle$. Hence

$$\langle\mathbf{R}_1\mathbf{R}_2|\mathbf{k}_1\mathbf{k}_2\rangle = \langle\mathbf{R}_1|\mathbf{k}_1\rangle\langle\mathbf{R}_2|\mathbf{k}_2\rangle, \qquad (1.2.8)$$

and so

$$|\mathbf{k}_1\mathbf{k}_2\rangle = |\mathbf{k}_1\rangle\,|\mathbf{k}_2\rangle. \qquad (1.2.9)$$

It is easy to verify that

$$\langle\mathbf{k}_1'\mathbf{k}_2'|\mathbf{k}_1\mathbf{k}_2\rangle = \delta(\mathbf{k}_1'-\mathbf{k}_1)\,\delta(\mathbf{k}_2'-\mathbf{k}_2). \qquad (1.2.10$$

The state of motion may also be specified by the ket $|\mathbf{k}_{1+2}\mathbf{k}_{12}\rangle = |\mathbf{k}_{1+2}\rangle|\mathbf{k}_{12}\rangle$ in which the centre of mass moves with momentum $\hbar\mathbf{k}_{1+2}$, while 1 moves relative to 2 with wave vector $\mathbf{k}_{12}$. The relative wave vector $\mathbf{k}_{12}$ is defined by

$$\mathbf{k}_{12} = \frac{m_2\mathbf{k}_1 - m_1\mathbf{k}_2}{m_1+m_2}, \qquad (1.2.11)$$

and since the centre of mass moves with the total momentum $\hbar\mathbf{k}_1+\hbar\mathbf{k}_2$ it follows that

$$\mathbf{k}_{1+2} = \mathbf{k}_1 + \mathbf{k}_2. \qquad (1.2.12)$$

Now $\mathbf{R}_{1+2} = (m_1\mathbf{R}_1 + m_2\mathbf{R}_2)/(m_1+m_2)$ and $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ so it is easy to show from (6), (11) and (12) that

$$\langle\mathbf{R}_1|\mathbf{k}_1\rangle\langle\mathbf{R}_2|\mathbf{k}_2\rangle = \langle\mathbf{R}_{1+2}|\mathbf{k}_{1+2}\rangle\langle\mathbf{R}_{12}|\mathbf{k}_{12}\rangle, \qquad (1.2.13)$$

hence

$$|\mathbf{k}_1\rangle\,|\mathbf{k}_2\rangle = |\mathbf{k}_{1+2}\rangle\,|\mathbf{k}_{12}\rangle. \qquad (1.2.14)$$

We can abbreviate (14) to

$$|\mathbf{k}_1\mathbf{k}_2\rangle = |\mathbf{k}_{1+2}\mathbf{k}_{12}\rangle. \tag{1.2.15}$$

It is easy to prove by using (6) that

$$\langle\mathbf{k}'_{1+2}\mathbf{k}'_{12}|\mathbf{k}_{1+2}\mathbf{k}_{12}\rangle = \delta(\mathbf{k}'_{1+2}-\mathbf{k}_{1+2})\,\delta(\mathbf{k}'_{12}-\mathbf{k}_{12}). \tag{1.2.16}$$

The kinetic energy associated with the motion of a particle or the centre of mass is given by

$$E_i = \frac{\hbar^2k_i^2}{2m_i} \qquad (i = 1, 2, 1+2) \tag{1.2.17}$$

and the relative kinetic energy is given by

$$E_{12} = \frac{\hbar^2k_{12}^2}{2\mu_{12}}. \tag{1.2.18}$$

It is clear that

$$(\mathsf{K}_1+\mathsf{K}_2)|\mathbf{k}_1\mathbf{k}_2\rangle = (E_1+E_2)|\mathbf{k}_1\mathbf{k}_2\rangle, \tag{1.2.19}$$

$$\mathsf{K}_{1+2}|\mathbf{k}_{1+2}\rangle = E_{1+2}|\mathbf{k}_{1+2}\rangle, \tag{1.2.20}$$

$$\mathsf{K}_{12}|\mathbf{k}_{12}\rangle = E_{12}|\mathbf{k}_{12}\rangle, \tag{1.2.21}$$

and since $|\mathbf{k}_1\mathbf{k}_2\rangle = |\mathbf{k}_{1+2}\mathbf{k}_{12}\rangle$ it follows from (19) to (21), (5) and (15) that

$$E_1+E_2 = E_{1+2}+E_{12}. \tag{1.2.22}$$

The result (22) may also be verified directly from (17) and (18).

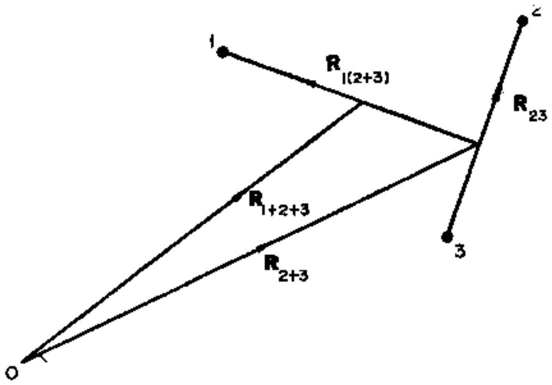

FIG. 1.1. Coordinate vectors for a three-particle system.

We can extend this process to the N-particle case in a systematic way. Firstly, if $N = 3$ we separate out the motion of the centre of mass of 2 and 3. Formally we have (see Fig. 1.1)

$$\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3 \to \mathbf{R}_1, \mathbf{R}_{2+3}, \mathbf{R}_{23}, \tag{1.2.23}$$

$$\mathsf{K}_1+\mathsf{K}_2+\mathsf{K}_3 = \mathsf{K}_1+\mathsf{K}_{2+3}+\mathsf{K}_{23}, \tag{1.2.24}$$

$$|\mathbf{k}_1\rangle|\mathbf{k}_2\rangle|\mathbf{k}_3\rangle = |\mathbf{k}_1\rangle|\mathbf{k}_{2+3}\rangle|\mathbf{k}_{23}\rangle, \tag{1.2.25}$$

$$E_1+E_2+E_3 = E_1+E_{2+3}+E_{23}. \tag{1.2.26}$$

We now separate out the centre of mass motion of 1 and 2+3. This is, of course, the centre of mass of the three particles as a whole, and we can denote it by 1+2+3. The centre of mass of 2 and 3 is denoted hy 2+3 so that, for example, $\mathsf{K}_{1(2+3)}$ denotes the kinetic energy operator for the motion of 1 relative to the centre of mass of 2 and 3. We obtain

$$\mathbf{R}_1,\ \mathbf{R}_{2+3},\ \mathbf{R}_{23} \rightarrow \mathbf{R}_{1+2+3},\ \mathbf{R}_{1(2+3)},\ \mathbf{R}_{23} \qquad (1.2.27)$$

$$\mathsf{K}_1+\mathsf{K}_{2+3}+\mathsf{K}_{23} = \mathsf{K}_{1+2+3}+\mathsf{K}_{1(2+3)}+\mathsf{K}_{23} \qquad (1.2.28)$$

$$|\mathbf{k}_1\rangle|\mathbf{k}_{2+3}\rangle|\mathbf{k}_{23}\rangle = |\mathbf{k}_{1+2+3}\rangle|\mathbf{k}_{1(2+3)}|\mathbf{k}_{23}\rangle \qquad (1.2.29)$$

$$E_1+E_{2+3}+E_{23} = E_{1+2+3}+E_{1(2+3)}+E_{23}. \qquad (1.2.30)$$

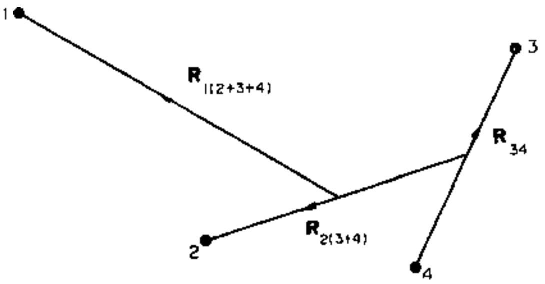

FIG. 1.2. Relative position vectors for a four-particle system.

In the case of four particles we separate out the motion of the centre of mass 2+3+4 of three of them as just described, and finally separate out the overall centre of mass motion from the motion of the remaining particle 1 and that of 2+3+4 (Fig. 1.2). The extension to n particles is straightforward. The configuration of the system is defined by the position vector of the centre of mass of the system, and the vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n-1}$, where $\mathbf{r}_j$ is the position vector of the jth particle relative to the centre of mass of the particles $j+1, j+2, \ldots, n$ $(j = 1, 2, \ldots, n-1)$. The state vector $|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_n\rangle$ is given by

$$|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_n\rangle = |\mathbf{k}_{1+2+\ldots+n}\mathbf{k}_{1(2+3+\ldots+n)}\mathbf{k}_{2(3+4+\ldots+n)}\ldots\mathbf{k}_{(n-1)n}\rangle, \qquad (1.2.31)$$

the total kinetic energy operator is given by

$$\mathsf{K}_1+\mathsf{K}_2+\ldots+\mathsf{K}_n = \mathsf{K}_{1+2+\ldots+n}+\mathsf{K}_{1(2+3+\ldots+n)} + \mathsf{K}_{2(3+4+\ldots+n)}+\ldots+\mathsf{K}_{(n-1)n}, \qquad (1.2.32)$$

and the total kinetic energy is given by

$$E_1+E_2+\ldots+E_n = E_{1+2+\ldots+n}+E_{1(2+3+\ldots+n)} + E_{2(3+4+\ldots+n)}+\ldots+E_{n(n-1)}. \qquad (1.2.33)$$

Relative coordinates other than the ones described here may be used;

however, the simple breakdown of the kinetic energy operator into the sum of the kinetic energy operators associated with each relative coordinate may no longer be possible—cross-terms may appear.

EXERCISES

1. Verify that the Jacobean J of the transformation

$$(x_1, y_1, z_1, x_2, y_2, z_2,) \rightarrow (x_{1+2}, y_{1+2}, z_{1+2}, x_{12}, y_{12}, z_{12})$$

satisfies $|J| = 1$.

2. Verify (5), (10), (13), (16), and (22).

3. Carry out the above separation process in the case of a system of four elementary particles.

4. If the system consists of four elementary particles of equal mass show that

$$E_{1(2+3+4)} : \mathrm{E}_{2(3+4)} : E_{34} = 8k^2_{1(2+3+4)} : 9k^2_{2(3+4)} : 12k^2_{34}.$$

5. Draw the diagram for a system of five elementary particles corresponding to Fig. 1.2 for four elementary particles.

1.3. THE CHANNELS OF A SYSTEM

We saw in Section 1.1 that corresponding to a decomposition of the N particles into m clusters the Hamiltonian H_G of the system can be expressed as

$$\mathsf{H}_G = \sum_{j=1}^{m} \mathsf{h}_{jG} + V_i \tag{1.3.1}$$

where

$$\mathsf{h}_{jG} = \sum_{r=1}^{n_j} \mathsf{K}_r(j) + V(A_j). \tag{1.3.2}$$

h_{jG} is just the Hamiltonian for the cluster A_j in isolation, while V_i is the interaction between the clusters and dies away to zero as the clusters separate to large distances from each other. The kinetic energy operator K_j for the centre of mass motion of each cluster A_j $(j = 1 \ldots m)$ may be separated out as described in the last section so that

$$\mathsf{h}_{jG} = \mathsf{K}_j + \mathsf{h}_j \tag{1.3.3}$$

where h_j describes the internal motion of A_j. If each cluster Hamiltonian h $(j = 1, 2, \ldots, m)$ supports at least one bound state of the particles of the cluster the decomposition is called an *arrangement channel* of the system and denoted by i, say. If the internal states of $A_1, A_2, \ldots, A_m$ are also specified, by a set of quantum numbers labelled n, then we have a *channel*. A channel is therefore denoted by ni. It will be convenient to normally refer to this by the single symbol n, provided this causes no ambiguity. Corresponding to each arrangement channel there is at least one channel. There may be several channels, or indeed an infinite number of channels, corresponding to any arrangement channel.

If we use the procedure of the last section we may specify the configuration of the system by the position vector of the centre of mass, the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\ldots$, $\mathbf{r}_{m-1}$ where $\mathbf{r}_j = \mathbf{R}_{j[(j+1)+(j+2)+\ldots+m]}$ is the position vector of the centre of mass of A_j relative to the centre of mass of A_{j+1}, A_{j+2}, $\ldots$, A_m $(1 \leq j \leq m-1)$, and the internal coordinates of A_1, A_2, $\ldots$, A_m which we collectively denote by $\mathbf{x}$. Now substitution of (3) into (1) yields

$$\mathsf{H}_G = \sum_{j=1}^{m} \mathsf{K}_j + \sum_{j=1}^{m} \mathsf{h}_j + V_i. \tag{1.3.4}$$

If K_G is the kinetic energy for the motion of the centre of mass of the system the procedure of the last section, when applied to the centres of mass of A_1, A_2, $\ldots$, A_m, shows that

$$\sum_{j=1}^{m} \mathsf{K}_j = \mathsf{K}_G + \sum_{j=1}^{m-1} \mathsf{K}_{j[(j+1)+(j+2)+\ldots+m]}. \tag{1.3.5}$$

If we put

$$\mathsf{K} = \sum_{j=1}^{m-1} \mathsf{K}_{j[(j+1)+(j+2)+\ldots+m]}, \tag{1.3.6}$$

so that K is the total relative kinetic energy operator, and

$$\mathsf{h} = \sum_{j=1}^{m} \mathsf{h}_j, \tag{1.3.7}$$

so that h is the total internal Hamiltonian, we see from (4) and (5) that

$$\mathsf{H}_G = \mathsf{K}_G + \mathsf{K} + \mathsf{h} + V_i. \tag{1.3.8}$$

From (8) we get

$$\mathsf{H}_G = \mathsf{K}_G + \mathsf{H} \tag{1.3.9}$$

where

$$\mathsf{H} = \mathsf{K} + \mathsf{h} + V_i \tag{1.3.10}$$

is the Hamiltonian after the centre of mass has been removed.

If we put

$$\mathsf{H}_i = \mathsf{K} + \mathsf{h}, \tag{1.3.11}$$

so that H_i is the unperturbed Hamiltonian of arrangement channel i when the centre of mass motion has been removed, we can rewrite (10) as

$$\mathsf{H} = \mathsf{H}_i + V_i. \tag{1.3.12}$$

The Hamiltonian is therefor the sum of the Hamiltonian H_i for the system when the clusters are far apart, and the interaction V_i between the clusters.

EXAMPLE 1. Suppose we have two electrons a and b, and a proton P. One arrangement channel is that in which electron a is free, while b and P are bound together to form a hydrogen atom. The kinetic energy operator K for the relative motion of the electron and atom is $\mathsf{K}_{a(b+P)}$, the internal Hamiltonian h is $\mathsf{K}_{bP}+V_{bP}$, where V_{bP} is the interaction between b and P, and the interaction V_i is $V_{ab}+V_{aP}$.

EXAMPLE 2. If we have three electrons a, b and c and a proton P, an arrangement channel is that in which a and b are free while c and P form a hydrogen atom. Then the relative kinetic energy operator $\mathsf{K} = \mathsf{K}_{a(b+c+P)}+\mathsf{K}_{b(c+P)}$, while $\mathsf{h} = \mathsf{K}_{cP}+V_{cP}$, $\mathsf{H}_i = \mathsf{K}+\mathsf{h}$, and $V_i = V_{ab}+V_{ac}+V_{aP}+V_{bc}+V_{bP}$ where V_{ij} is the Coulombic interaction between particles i and j; for example, $V_{ab} = -e^2/\varkappa_0 r_{ab}$. If the mass of an electron is negligible compared with that of a proton we can put $\mathsf{K} \simeq \mathsf{K}_{aP}+\mathsf{K}_{bP}$.

EXERCISE

What are the arrangement channels for the four-particle system consisting of three electrons a, b and c, and a proton P? In each case write down expressions for the total relative kinetic energy operator K, total internal Hamiltonian h, and interaction V_i. Which of these expressions simplify if the mass of an electron is regarded as negligible compared with that of a proton?

1.4. UNPERTURBED STATES

Let us denote by H_{iG} the unperturbed Hamiltonian for arrangement channel i in the laboratory system. Then $\mathsf{H}_{iG} = \mathsf{H}_G - V_i$, and so from (1.3.4) and (1.3.7)

$$\mathsf{H}_{iG} = \sum_{j=1}^{m} \mathsf{K}_j + \mathsf{h}. \tag{1.4.1}$$

The internal Hamiltonian h is just the sum of the internal Hamiltonians for the m clusters $A_1, A_2, \ldots, A_m$. An eigenstate of h will therefore be a product of states of $A_1, A_2, \ldots, A_m$. By definition such a state $|n\rangle$ can only belong to the arrangement channel i under consideration if these states of $A_1, A_2, \ldots, A_m$ are all bound states. The energy E_n of the state $|n\rangle$ is the sum of the internal energies of each of the A_j's, and so is negative and satisfies

$$\mathsf{h}\,|n\rangle = E_n\,|n\rangle. \tag{1.4.2}$$

The state of the system as a whole in the laboratory system must be represented by the product of $|n\rangle$ with the kets $|\mathbf{k}_1\rangle, |\mathbf{k}_2\rangle, \ldots, |\mathbf{k}_m\rangle$ representing the free motion of the centres of mass of the A_j's. We denote this by $|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m n\rangle$, and so

$$|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m n\rangle = |\mathbf{k}_1\rangle|\mathbf{k}_2\rangle\ldots|\mathbf{k}_m\rangle|n\rangle = |\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m\rangle|n\rangle. \tag{1.4.3}$$

If the wave vector of the centre of mass is $\mathbf{K} = \mathbf{k}_1+\mathbf{k}_2+\ldots+\mathbf{k}_m$ and $\mathbf{k}_j' = \mathbf{k}_{j[(j+1)+\ldots+m]}$ is the wave vector for the motion of the centre of mass of A_j relative to the centre of mass of $A_{j+1}, A_{j+2}, \ldots, A_m$ it follows, as in

Section 1.2, that

$$|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m n\rangle = |\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m\rangle|n\rangle = |\mathbf{K}\rangle|\mathbf{k}'_1\mathbf{k}'_2\ldots\mathbf{k}'_{m-1}\rangle|n\rangle$$
$$= |\mathbf{K}\rangle|\mathbf{k}'_1\mathbf{k}'_2\ldots\mathbf{k}'_{m-1}n\rangle. \qquad (1.4.4)$$

After the removal of the centre of mass motion the unperturbed state has the wave function

$$\varphi_\nu(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{m-1}, \mathbf{x}) = \langle\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{m-1}, \mathbf{x}|\mathbf{k}'_1\mathbf{k}'_2\ldots\mathbf{k}'_{m-1}n\rangle$$
$$= (2\pi)^{-3(m-1)/2}\exp(i\mathbf{k}'_1\boldsymbol{\cdot}\mathbf{r}_1 + i\mathbf{k}'_2\boldsymbol{\cdot}\mathbf{r}_2 + \ldots + i\mathbf{k}'_{m-1}\boldsymbol{\cdot}\mathbf{r}_{m-1})\,\chi_n(\mathbf{x}) \qquad (1.4.5)$$

where $\chi_n(\mathbf{x}) = \langle\mathbf{x}|n\rangle$ is the internal wave function and $\mathbf{x}$ denotes the internal coordinates of the composite particles $A_1, A_2, \ldots, A_m$ (see Section 1.3). We shall denote the vectors $\mathbf{k}'_1, \mathbf{k}'_2, \ldots, \mathbf{k}'_{m-1}$ by the single $3(m-1)$-dimensional vector $\mathbf{k}$, and the vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{m-1}$ by the single $3(m-1)$-dimensional vector $\mathbf{r}$. Then if

$$\varphi_{\mathbf{k}}(r) = (2\pi)^{-3(m-1)/2}\exp(i\mathbf{k}\boldsymbol{\cdot}\mathbf{r}) \qquad (1.4.6)$$

where $\mathbf{k}\boldsymbol{\cdot}\mathbf{r}$ is the $3(m-1)$-dimensional scalar product $\mathbf{k}_1\boldsymbol{\cdot}\mathbf{r}_1 + \mathbf{k}_2\boldsymbol{\cdot}\mathbf{r}_2 + \ldots + \mathbf{k}_{m-1}\boldsymbol{\cdot}\mathbf{r}_{m-1}$ we can write (5) as

$$\varphi_\nu(\mathbf{r}, \mathbf{x}) = \varphi_{\mathbf{k}}(\mathbf{r})\,\chi_n(\mathbf{x}). \qquad (1.4.7)$$

We shall sometimes denote φ_ν more fully by $\varphi_{\mathbf{k}n}$ or by $\varphi_{\mathbf{k}ni}$. In other words the symbol ν denotes both the arrangement channel i under consideration and the quantum numbers, discrete and continuous, defining a particular state of i. We shall also use Greek letters $\mu, \omega, \alpha, \beta$, etc., instead of ν, to denote the quantum numbers and arrangement channels of unperturbed states of the system.

Since E_n is the internal energy

$$\mathsf{h}\chi_n = E_n\chi_n. \qquad (1.4.8)$$

Let $E_{\mathbf{k}}$ be the sum of the kinetic energies associated with the vectors $\mathbf{k}'_1, \mathbf{k}'_2, \ldots, \mathbf{k}'_{m-1}$. Hence if μ_j is the reduced mass of A_j relative to the centre of mass of the particles $A_{j+1}, A_{j+2}, \ldots, A_m$, we have

$$E_{\mathbf{k}} = \sum_{j=1}^{m-1}\frac{\hbar^2 k_j'^2}{2\mu_j}. \qquad (1.4.9)$$

Then it follows from (1.3.6) and (5) that

$$\mathsf{K}\varphi_{\mathbf{k}} = E_{\mathbf{k}}\varphi_{\mathbf{k}}. \qquad (1.4.10)$$

If we define E_ν by

$$E_\nu = E_{\mathbf{k}} + E_n \qquad (1.4.11)$$

and remember that, by (1.3.11), $\mathsf{H}_i = \mathsf{K}+\mathsf{h}$, while $\varphi_\nu = \varphi_{\mathbf{k}}\chi_n$, we see that (8), (10) and (11) imply

$$\mathsf{H}_i\varphi_\nu = E_\nu\varphi_\nu. \tag{1.4.12}$$

The energy E_ν of the state φ_ν is therefore the sum of the kinetic energies of the particles after the subtraction of the energy associated with the motion of the centre of mass of the system as a whole, viz. $E_{\mathbf{k}}$, and the internal energy E_n.

Suppose the system has a total energy E apart from that of the centre of mass. If it can exist in some channel n, so that its state is given by an expression of the form (3), then $E = E_{\mathbf{k}}+E_n$. Since $E_{\mathbf{k}} \geqslant 0$ it follows that $E \geqslant E_n$. Consequently if the system has energy E it can only exist in those channels for which $E \geqslant E_n$. If $E \geqslant E_n$ we say that the channel n is open, otherwise we say that it is closed.

If we assume that the internal state χ_n is normalized it follows that $\langle\varphi_\mu|\varphi_\nu\rangle = \delta_{\mu\nu}$ if φ_μ and φ_ν belong to the same arrangement channel. If φ_μ and φ_ν belong to different arrangement channels this may not be so.

The states of the arrangement channel F in which all elementary particles move freely are just products of plane waves and spin functions, and hence form a complete orthonormal set for the system. Hence the set of all possible φ_ν is, in general, overcomplete and therefore necessarily not orthogonal. If the system as a whole can have bound states m can take the value one. For completeness we shall regard this case, where obviously $\mathsf{H} = \mathsf{H}_i$, as an arrangement channel. In the literature the bound states are usually not referred to as channels, since their time evolution is a trivial change of phase factor.

EXAMPLE 1. *Two electrons and a proton.* We shall denote the electrons by e and a, the proton by P, and regard the electrons as distinguishable. The possible decompositions are:

0. e, a, P.
1. e, (aP).
2. a, (eP).
3. (eaP).
4. (ea), P.

0 is the arrangement channel in which all the particles are free. To simplify matters let us regard the proton P as infinitely massive. The position vector $\mathbf{r}_e$ of e relative to P is then also the position vector of e relative to the centre of mass of the atom aP. Further, the position vector $\mathbf{r}_a$ of a relative to P is also the position vector of a relative to the atom eP. In a typical state of the system in arrangement channel 0 electron e will have momentum $\hbar\mathbf{k}$ relative to P, while a will have momentum $\hbar\mathbf{l}$ relative to P. It will therefore have a wave function $\varphi_{\mathbf{kl}}$ where

$$\varphi_{\mathbf{kl}}(\mathbf{r}_e, \mathbf{r}_a) = \varphi_{\mathbf{k}}(\mathbf{r}_e)\,\varphi_{\mathbf{l}}(\mathbf{r}_a). \tag{1.4.13}$$

In arrangement channel 1 we can suppose e to be moving freely relative to the centre of mass P of the atom aP with momentum $\hbar\mathbf{k}$, say, while the hydrogen atom aP is in some state $|n\rangle$ with wave function χ_n. The state of the system will therefore have a wave function $\varphi_{\mathbf{k}n1}$ where

$$\varphi_{\mathbf{k}n1}(\mathbf{r}_e, \mathbf{r}_a) = \varphi_{\mathbf{k}}(\mathbf{r}_e)\,\chi_n(\mathbf{r}_a). \qquad (1.4.14$$

In arrangement channel 2 electron a may have momentum $\hbar\mathbf{k}$ relative to the centre of mass P of the atom eP, while the atom is in some state with wave function χ_n. The system now has as its wave function $\varphi_{\mathbf{k}n2}$, say, where

$$\varphi_{\mathbf{k}n2}(\mathbf{r}_e, \mathbf{r}_a) = \varphi_{\mathbf{k}}(\mathbf{r}_a)\,\chi_n(\mathbf{r}_e). \tag{1.4.15}$$

In arrangement channel 3 in which all three particles are bound the possible states are the stable states of the H^- ion. In this case the wave functions are those of the stable states of the H^- ion.

Finally we note that the decomposition 4 is not an arrangement channel, since the electrons e and a cannot form a bound state.

If the mass of the proton is taken into account $\mathbf{r}_e$ must be taken as the position vector of e relative to the centre of mass of a and P in 1, while $\mathbf{r}_a$ must be taken as the position vector of a relative to the centre of mass of e and P in 2; either system can be used for 0 or 3. When spin is taken into account the functions must all be multiplied by the spin functions of e, a and P. We note that the functions of arrangement channel 0 form a complete δ-function normalized set. If P is regarded as infinitely massive it follows from (14) and (15) with $\mathbf{k}$ replaced by $\mathbf{l}$, n replaced by p, that $\langle\varphi_{\mathbf{k}n1} \mid \varphi_{\mathbf{l}p2}\rangle = \langle\varphi_{\mathbf{k}} \mid \chi_p\rangle\langle\chi_n \mid \varphi_{\mathbf{l}}\rangle$. This clearly does not vanish, since it is the product of the Fourier transforms of χ_n and χ_p.

Example 2. *Three electrons.* The forces between the electrons are repulsive, and so the only arrangement channel of the system is that in which all three particles are free. Indeed, this is a system with only one channel whose threshold energy is zero.

Example 3. *Harmonic potentials.* If the potential between two particles i and j has the form $-k_{ij}r_{ij}^2$, where r_{ij} is the distance between i and j and k_{ij} is a positive constant, the particles can never move freely of each other. If we regard the bound states as channels the only arrangement channel is that of the bound states, and the only channels are the bound states. As remarked above, such "channels" are of no interest in scattering theory.

Example 4. As a final example let us consider a system consisting of two electrons a and b, and three protons A, B and C. One arrangement channel is that in which a is bound to A and b is bound to B to form two hydrogen atoms, while C is free. If we take A_1 as C, A_2 as the atom aA, and A_3 as the hydrogen atom bB, we have in the above notation $\mathbf{k}_1' = \mathbf{k}_{1(2+3)} = \mathbf{k}_{C(a+A+b+B)}$, $\mathbf{k}_2' = \mathbf{k}_{23}' = \mathbf{k}_{(a+A)(b+B)}$. A typical unperturbed state in this arrangement channel is $|\,\mathbf{k}_1'\rangle\,|\,\mathbf{k}_2'\rangle\,|\,n_{aA}'\rangle\,|\,n_{bB}''\rangle$ where $|\,n_{aA}'\rangle$ is a state of atom aA with quantum numbers collectively labelled n' and $|\,n_{bB}''\rangle$ is a state of atom bB with quantum numbers collectively labelled n''. If we write $\mathbf{k}$ for $(\mathbf{k}_1', \mathbf{k}_2')$ and n for $n_{aA}'n_{bB}''$ we can further abbreviate this to $|\,\mathbf{k}\rangle\,|\,n\rangle = |\,\mathbf{k}n\rangle$. Thus

$$|\,\mathbf{k}n\rangle = |\,\mathbf{k}_{C(a+A+b+B)}\rangle\,|\,\mathbf{k}_{(a+A)(b+B)}\rangle\,|\,n_{aA}'\rangle\,|\,n_{bB}''\rangle. \tag{1.4.16}$$

If the mass of an electron is negligible compared with that of a proton this simplifies to

$$|\,\mathbf{k}n\rangle \simeq |\,\mathbf{k}_{C(A+B)}\rangle\,|\,\mathbf{k}_{AB}\rangle\,|\,n_{aA}'\rangle\,|\,n_{bB}''\rangle. \tag{1.4.17}$$

The internal Hamiltonian h is given by

$$\mathsf{h} = \mathsf{K}_{aA} + \mathsf{K}_{bB} + V_{aA} + V_{bB} \tag{1.4.18}$$

where V_{ij} is the interaction between particles i and j. The unperturbed Hamiltonian H_i is given by

$$\mathsf{H}_i = \mathsf{K}_{1(2+3)} + \mathsf{K}_{23} + \mathsf{h} = \mathsf{K}_{C(a+A+b+B)} + \mathsf{K}_{(a+A)(b+B)} + \mathsf{h}; \tag{1.4.19}$$

if the mass of an electron is negligible compared with that of a proton this can be replaced by

$$\mathsf{H}_i \simeq \mathsf{K}_{C(A+B)} + \mathsf{K}_{AB} + \mathsf{h}. \tag{1.4.20}$$

EXERCISE

What are the arrangement channels of the five-particle system consisting of two electrons, two protons and an α-particle? Assuming that the interactions between the five particles are Coulombic, write down the internal Hamiltonian h and unperturbed Hamiltonian H_i (after removal of the centre of mass) in each case. Also write down a typical unperturbed state for each arrangement channel when the centre of mass motion has been removed.

[You may assume that the mass of an electron is negligible compared with the nuclear masses.]

1.5. SCATTERING STATES

The scattering states, or Schwinger–Lippmann states, $\psi_\nu^\pm$ corresponding to the unperturbed state φ_ν in the relative coordinate system are defined by

$$\boxed{\psi_\nu^\pm = \varphi_\nu + (E - \mathsf{H} \pm i\varepsilon)^{-1} V_i \varphi_\nu} \tag{1.5.1}$$

where $E = E_\nu$ is the energy of the system. The operators $(E - \mathsf{H} \pm i\varepsilon)^{-1}$ are Green's operators† for the full Hamiltonian H.

If we operate on (1) with $E - \mathsf{H} \pm i\varepsilon$ and rearrange using the fact that $\mathsf{H} = \mathsf{H}_i + V_i$ we obtain

$$(E - \mathsf{H}_i \pm i\varepsilon)(\psi_\nu^\pm - \varphi_\nu) = V_i \psi_\nu^\pm. \tag{1.5.2}$$

Operation on (2) with $(E - \mathsf{H}_i \pm i\varepsilon)^{-1}$ yields

$$\boxed{\psi_\nu^\pm = \varphi_\nu + (E - \mathsf{H}_i \pm i\varepsilon)^{-1} V_i \psi_\nu^\pm.} \tag{1.5.3}$$

It is easy to show from this that, as one of the clusters separates from the others, ψ_ν^+ behaves asymptotically as a sum of φ_ν and outgoing waves.‡

Since $\mathsf{H}_i \varphi_\nu = E_\nu \varphi_\nu = E\varphi_\nu$ and $\mathsf{H} = \mathsf{H}_i + V_i$ we can rewrite (2) as

$$(E - \mathsf{H} \pm i\varepsilon)\,\psi_\nu^\pm = \pm i\varepsilon\varphi_\nu. \tag{1.5.4}$$

It follows from (4) that as $\varepsilon \to 0_+$, $\mathsf{H}\psi_\nu^\pm \to E\psi_\nu^\pm$. In other words, in the limit $\varepsilon \to 0_+$ the functions $\psi_\nu^\pm$ become solutions of the time-independent Schrödinger equation of the system.

If we take the complex conjugate of (1) with the + sign and assume that H and V_i are real, we get

$$(\psi_\nu^+)^* = \varphi_\nu^* + (E - \mathsf{H} - i\varepsilon)^{-1} V_i \varphi_\nu^*. \tag{1.5.5}$$

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† A brief account of Green's operators is given in Appendix C. A fuller account is given in an introductory book on scattering theory by the present author (Farina, 1973, Chapter 5). The positive quantity ε is allowed to tend to zero at the end of any calculation.

‡ This is shown in Appendix C. The development of this book, however, does not need this fact.

Now $\mathsf{H}_i\varphi_\nu = E_\nu\varphi_\nu = E\varphi_\nu$, and $\mathsf{H}_i = \mathsf{H}-V_i$ is real if H and V_i are real, hence $\mathsf{H}_i\varphi_\nu^* = E\varphi_\nu^*$. Thus φ_ν^* is another eigenfunction of H_i with energy E, and so we can write it as φ_μ where μ denotes the quantum numbers defining φ_ν^*. We can therefore write (5) as

$$(\psi_\nu^+)^* = \varphi_\mu+(E-\mathsf{H}-i\varepsilon)^{-1}V_i\varphi_\mu. \qquad (1.5.6)$$

We deduce from (6) that

$$\psi_\mu^- = (\psi_\nu^+)^* \qquad (1.5.7)$$

where $\varphi_\nu = \varphi_\mu^*$.

As one cluster separates from the others

$$\psi_\nu^+ \sim \varphi_\nu + \text{sum of outgoing waves.} \qquad (1.5.8)$$

A corollary of (7) is therefore that, as one cluster separates from the others,

$$\begin{aligned}\psi_\mu^- &\sim \varphi_\nu^* + \text{incoming waves}\\ &= \varphi_\mu + \text{incoming waves.}\end{aligned} \qquad (1.5.9)$$

We can also state these results in the laboratory frame of reference. For if $|\nu\rangle$ is the state vector $|\mathbf{k}_1'\mathbf{k}_2'\ldots\mathbf{k}_{m-1}'n\rangle$ in the relative coordinate system and $|\mathbf{K}\rangle$ describes the motion of the centre of mass it follows from (1.4.4) that the state vector in the laboratory system is given by

$$|\mathbf{k}_1\mathbf{k}_2\ldots\mathbf{k}_m n\rangle = |\mathbf{K}\rangle\,|\nu\rangle = |\mathbf{K}\nu\rangle. \qquad (1.5.10)$$

The energy E_G in the laboratory system is equal to $E+E_K$, where E_K is the energy associated with the motion of the centre of mass. The scattering states $|\mathbf{K}\nu\pm\rangle$ in the laboratory system are defined by

$$\begin{aligned}|\mathbf{K}\nu\pm\rangle &= |\mathbf{K}\nu\rangle+(E_G-\mathsf{H}_G\pm i\varepsilon)^{-1}V_i\,|\mathbf{K}\nu\rangle\\ &= |\mathbf{K}\nu\rangle+(E+E_K-\mathsf{H}-\mathsf{K}_G\pm i\varepsilon)^{-1}V_i\,|\mathbf{K}\nu\rangle.\end{aligned} \qquad (1.5.11)$$

Now $|\mathbf{K}\nu\rangle = |\mathbf{K}\rangle\,|\nu\rangle$ where $|\mathbf{K}\rangle$ involves only the coordinates of the centre of mass, while V_i involves only the remaining coordinates. Also K_G involves only the coordinates of the centre of mass while H involves only the relative coordinates. Since $\mathsf{K}_G\,|\mathbf{K}\rangle = E_K\,|\mathbf{K}\rangle$ it follows from the results of Appendix A, in particular equation (A9), that

$$\begin{aligned}|\mathbf{K}\nu\pm\rangle &= |\mathbf{K}\rangle\,|\nu\rangle+[(E-\mathsf{H}\pm i\varepsilon)^{-1}V_i\,|\nu\rangle]\,|\mathbf{K}\rangle\\ &= |\mathbf{K}\rangle\,[|\nu\rangle+(E-\mathsf{H}\pm i\varepsilon)^{-1}V_i\,|\nu\rangle].\end{aligned} \qquad (1.5.12)$$

The state vector in the square brackets on the right-hand side of (12) is just the state vector $|\nu+\rangle$ represented by the wave function ψ_ν^+. Hence

$$|\mathbf{K}\nu+\rangle = |\mathbf{K}\rangle\,|\nu+\rangle. \qquad (1.5.13)$$

The centre of mass is therefore unperturbed by the potential, as is to be expected from the translational invariance of the system. Equation (13) shows that the ket $| \mathbf{K} \rangle$ for its free motion factorizes out of the scattering state in the laboratory system, leaving the scattering state $| \nu + \rangle$ in the relative coordinate system.

EXAMPLE. In the case of scattering of two elementary particles the unperturbed state in the relative coordinate system is $\varphi_{\mathbf{k}}$, and (1) becomes, in this case,

$$\psi_{\mathbf{k}}^{\pm} = \varphi_{\mathbf{k}} + (E_k - \mathsf{H} \pm i\epsilon)^{-1} V \varphi_{\mathbf{k}}. \tag{1.5.14}$$

Since H and V are real and $\varphi_{\mathbf{k}}^{*} = \varphi_{-\mathbf{k}}$ it follows immediately from (14) that

$$\psi_{\mathbf{k}}^{-} = (\psi_{-\mathbf{k}}^{+})^{*} \tag{1.5.15}$$

REFERENCES

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FARINA, J. E. G. (1973) *Quantum Theory of Scattering Processes*, Pergamon Press. This is Volume 4 in Topic 2 of the *International Encyclopedia of Physical Chemistry and Chemical Physics*, and will be subsequently referred to as simply Volume 4.

CHAPTER 2

THE DYNAMIC STATES OF AN *N*-PARTICLE SYSTEM

2.1. WAVE PACKETS FOR NON-INTERACTING PARTICLES

In the last chapter we considered the stationary states of an N-particle system. However, a chemical or nuclear reaction is a dynamical process which takes place in time; two molecules, for example, collide, interact, and then the products separate. If we want to describe a chemical or nuclear reaction, we must consider the N-particle system as evolving in time, and this we shall do in this chapter.

In this section we shall consider a situation in which the system is in some definite arrangement channel i, consisting of composite particles $A_1, A_2, \ldots, A_m$ $(m \leqslant N)$, which we suppose to be moving freely; we suppose further that $A_1, A_2, \ldots, A_m$ are in definite internal states specified by a collection n of quantum numbers defining the internal state χ_n. As in Chapter 1, we denote by $\mathbf{x}$ the internal coordinates of $A_1, A_2, \ldots, A_m$, by $\mathbf{r}_j$ and $\mathbf{k}_j'$ the position vector and wave vector of the centre of mass of A_j relative to the centre of mass of $A_{j+1}, A_{j+2}, \ldots, A_m$ $(j \leq m-1)$, and by $\mathbf{r}$ and $\mathbf{k}$ the $3(m-1)$-dimensional vectors $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{m-1})$ and $\mathbf{k} = (\mathbf{k}_1', \mathbf{k}_2', \ldots, \mathbf{k}_{m-1}')$. As we saw in Section 1.4, in particular equations (1.4.6) and (1.4.7), a stationary state of the system is given by

$$\varphi_{\mathbf{k}ni}(\mathbf{r}, \mathbf{x}) = (2\pi)^{-3(m-1)/2} \exp(i\mathbf{k}\cdot\mathbf{r})\, \chi_n(\mathbf{x}), \tag{2.1.1}$$

and as usual we can abbreviate $\varphi_{\mathbf{k}ni}$ by $\varphi_{\mathbf{k}n}$ or φ_ν.

Very often the system is prepared in a state where it consists of the particles $A_1, A_2, \ldots, A_m$ in a definite internal state whose wave function is χ_n; that is, the system is in a definite channel. If this is the case the wave function of the system must be the product of $\chi_n \exp(-iE_n t/\hbar)$ and a wave packet describing the free relative motion of the composite particles; we will denote this by $\bar{\varphi}_n(t)$. Such a wave packet must be a superposition of the states $\varphi_{\mathbf{k}} \exp(-iE_{\mathbf{k}}t/\hbar)$ with a weighting function $C(\mathbf{k})$, which must be square integrable; hence

$$\bar{\varphi}(\mathbf{r}, \mathbf{x}, t) = [(\chi_n \exp(-E_n t/\hbar)]\left[\int C(\mathbf{k})\, \varphi_{\mathbf{k}}(\mathbf{r}) \exp(-iE_{\mathbf{k}}t/\hbar)\, d\mathbf{k}\right]. \tag{2.1.2}$$

In (2) the function $\varphi_{\mathbf{k}}$ is given by (1.4.6) while the integration goes over the $3(m-1)$ components of the vector $\mathbf{k}$. The wave packet is, in fact, the most general solution of the Schrödinger equation $i\hbar\partial\psi/\partial t = \mathrm{K}\psi$ for the relative motion of the composite particles, since $\mathrm{K}\varphi_{\mathbf{k}} = E_{\mathbf{k}}\varphi_{\mathbf{k}}$ and the $\varphi_{\mathbf{k}}$ form a complete orthonormal set.

The result (2) may be rewritten as

$$\bar{\varphi}_n(\mathbf{r}, \mathbf{x}, t) = \int C(\mathbf{k})\,\varphi_{\mathbf{k}}(\mathbf{r})\,\chi_n(\mathbf{x})\exp\left[-i(E_{\mathbf{k}}+E_n)t/\hbar\right] d\mathbf{k}. \qquad (2.1.3)$$

We shall often abbreviate $\varphi_{\mathbf{k}}\chi_n$ by $\varphi_{\mathbf{k}n}$, and $E_{\mathbf{k}}+E_n$ by $E_{\mathbf{k}n}$, in which case (3) takes the abbreviated form

$$\bar{\varphi}_n(\mathbf{r}, \mathbf{x}, t) = \int C(\mathbf{k})\,\varphi_{\mathbf{k}n}(\mathbf{r}, \mathbf{x})\;\exp(-iE_{\mathbf{k}n}t/\hbar)\,d\mathbf{k}. \qquad (2.1.4)$$

We have assumed that the χ_n are orthonormal while $\langle\varphi_{\mathbf{k}}\,|\,\varphi_{\mathbf{k}'}\rangle = \delta(\mathbf{k}-\mathbf{k}')$. If these facts are used it is a simple exercise to verify from (2) or (3) that

$$\iint |\bar{\varphi}_n(\mathbf{r}, \mathbf{x}, t)|^2\,d\mathbf{r}\,d\mathbf{x} = \int |C(\mathbf{k})|^2\,d\mathbf{k}. \qquad (2.1.5)$$

The integral on the left-hand side is an integration over the $3(m-1)$ components of $\mathbf{r}$ and the continuous components of $\mathbf{x}$, and a summation over the spin components of $\mathbf{x}$. The integration of the right is over the $3(m-1)$ components of $\mathbf{k}$. We shall always assume that $\bar{\varphi}_n$ is normalized to unity, so that either side of (5) is equal to one.

The probability amplitude for the relative wave vector $\mathbf{k}$ is the scalar product of $\varphi_{\mathbf{k}}\exp(-iE_{\mathbf{k}}t/\hbar)$ with the second term in square brackets on the right-hand side of (2), and this is $C(\mathbf{k})$. It follows that $|C(\mathbf{k})|^2\,d\mathbf{k}$ is the probability that the wave vector $\mathbf{k}$ lies in the $3(m-1)$-dimensional volume element $d\mathbf{k} = d\mathbf{k}'_1\,d\mathbf{k}'_2\ldots d\mathbf{k}'_{m-1}$. The integral on the right-hand side is the probability that the particles $A_1, A_2, \ldots, A_m$ have some relative wave vector $\mathbf{k}$, and so it is natural to normalize this to unity.

EXERCISE

Verify (5).

2.2. THE REMOTE PAST AND FUTURE

If we consider a reaction involving two particles A and B, we can think of times in the remote past before the particles collide, and times in the remote future after the reaction takes place. A may be, for example, a molecule which has been produced in an oven, then accelerated to a certain velocity, while B may be a molecule in a target gas. The "remote past" of the system is the period of time after A has left the oven and accelerator, and before it begins to interact with B. In the case of a reaction in a gas it is the time after

A and B have made their last collisions before meeting each other, but before their own encounter takes place. In either case we may well know the initial state of both A and B, say their ground states; in this case the initial state is in a definite channel as discussed in Section 2.1. On the other hand, if A was produced in an oven, it may well be in an excited state (vibrational or electronic or both) and in this case the initial state will be a superposition of states of the type $\bar{\varphi}_n(t)$ discussed in the last section. If the oven was very hot, A may possibly have dissociated into particles $A'+A''$, in which case the initial state would be a superposition of states from different arrangement channels. In the same way the final state, after the reaction, which we will call the "remote future", may well have possibilities such as $A+B$ (no reaction), $C+D$ (first reaction), or $E+F$ (second reaction), and these will occur with different probabilities. Thus the final state will, in general, be a superposition of states from different arrangement channels; within each possible arrangement channel (possible reaction path) there will occur different possible states. The probability of the reaction $A+B \rightarrow C+D$ taking place will be just the sum of the probabilities of the various states of C and D being produced, the same applying to the other arrangement channels.

We are excluding from our considerations the possibility of the presence of photons, or the creation or destruction of elementary particles. It is therefore possible for us to accept as reasonable, on physical grounds, the following postulate:

> *Postulate*. If a physical system consists of N elementary particles moving under mutual interactions of finite range, and the system is observed in the remote past or remote future, the only observations will be the states of the various arrangement channels of the system. (2.2.1)

We must assume finite range forces, for otherwise the elementary particles can never move freely of each other. In practice it is clear that in the case of electrons and atomic nuclei they must move freely when sufficiently distant from each other, although there are problems which can arise from this (Volume 4, Section 2.5). If we apply the postulate (1) to Example 1 of Section 1.4 we see that, in the case of two electrons and one proton, the only possible observations in the remote past or remote future are either an H^- ion, a hydrogen atom and a free electron, or a free proton and two free electrons. Similar conclusions apply to the other examples of Section 1.4.

The immediate consequence of postulate (1) is that if $\bar{\psi}(t)$ describes the state of the system at time t, then as $t \to \pm\infty$ $\bar{\psi}(t)$ becomes a superposition of wave packets describing the relative motion of the particles in various states and various arrangement channels. Any one such motion was described in Section 2.1. If t_0 is a time in the remote past we must therefore have

$$\bar{\psi}(t_0) = \sum_n B_n \bar{\varphi}_n(t_0) \tag{2.2.2}$$

where the sum $\sum_n$ goes over all possible channels of the system. The summation therefore goes over all possible internal states χ_n of each arrangement channel, and over all arrangement channels. In general the momentum amplitude $C(\mathbf{k})$ will be different for different channels, and so we shall write it as $C_n(\mathbf{k})$.

If we substitute for $\bar{\varphi}_n$ from (2.1.4) into (2) we obtain

$$\bar{\psi}(t_0) = \sum_n \int d\mathbf{k} B_n C_n(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t_0/\hbar) \tag{2.2.3}$$

where, as usual, we write $E_{\mathbf{k}n}$ for $E_{\mathbf{k}}+E_n$ and $\varphi_{\mathbf{k}n}$ for $\varphi_{\mathbf{k}}\chi_n$. The quantity $B_nC_n(\mathbf{k})$ may be abbreviated to A_ν, where $\nu = \mathbf{k}n$ denotes the quantum numbers of the state $\varphi_{\mathbf{k}}\chi_n = \varphi_{\mathbf{k}n} = \varphi_\nu$, and so (3) can be written

$$\boxed{\bar{\psi}(t_0) = \sum_\nu A_\nu \varphi_\nu \exp(-iE_\nu t_0/\hbar).} \tag{2.2.4}$$

Here $\sum_\nu = \sum_n \int d\mathbf{k}$, and goes over all possible unperturbed stationary states $\varphi_\nu = \varphi_{\mathbf{k}n}$ of the system, including the bound states. In the case of the bound states the integration over $\mathbf{k}$ is, of course, omitted.

In the remote future we pick some typical time t_1. $\bar{\psi}(t_1)$ must also be a superposition of wave packets, a wave packet being associated with each channel. The wave packet associated with the nth channel may now be different, so we denote this wave packet by $\bar{\varphi}'_n(t_1)$. The weighting coefficient may also be different – let us call it B'_n. Equation (2) therefore has, as the corresponding result for the remote future,

$$\bar{\psi}(t_1) = \sum_n B'_n \varphi'_n(t_1). \tag{2.2.5}$$

Corresponding to (3) and (4) we have

$$\bar{\psi}(t_1) = \sum_n \int d\mathbf{k} B'_n C'_n(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t_1/\hbar), \tag{2.2.6}$$

$$\boxed{\bar{\psi}(t_1) = \sum_\nu A'_\nu \varphi_\nu \exp(-iE_\nu t_1/\hbar).} \tag{2.2.7}$$

The wave packets $\bar{\varphi}_n(t)$ become mutually orthogonal as $t \rightarrow \pm\infty$. To see this we note that $\langle\bar{\varphi}_p(t)|\bar{\varphi}_n(t)\rangle$ certainly equals zero if $\bar{\varphi}_p$ and $\bar{\varphi}_n$ belong to the same arrangement channel, and $p \neq n$, due to the orthogonality of the internal wave functions χ_p and χ_n; for these are orthonormal eigenfunctions of the same internal Hamiltonian. Suppose now that $\bar{\varphi}_n$ and $\bar{\varphi}_p$ belong to different arrangement channels; it then follows that there is at least one pair of elementary particles, P and Q say, which are bound to the same composite particle in one wave packet and to different composite particles in the other. We can suppose without loss of generality that P and Q are bound to the same composite particle in $\bar{\varphi}_p(t)$, but to different composite particles in $\bar{\varphi}_n(t)$. Now in the remote past or remote future the composite particles must separate, so that there is negligible probability of their being found close to each other. This means that as $t \rightarrow \pm\infty$ the probability of P and Q being found close to each other in the state $\bar{\varphi}_n(t)$ becomes zero. On the other hand, in the state $\bar{\varphi}_p(t)$ the elementary particles P and Q will always be observed close to each other, since they belong to the same composite particle. Now $|\langle\bar{\varphi}_p(t)|\bar{\varphi}_n(t)\rangle|^2$ is the probability of observing the state $\bar{\varphi}_p(t)$ when the system is in the state $\bar{\varphi}_n(t)$, and since in the state $\bar{\varphi}_p$ the particles P and Q must be close this must be negligibly small. In other words $\langle\bar{\varphi}_p(t)|\bar{\varphi}_n(t)\rangle \rightarrow 0$ as $t \rightarrow \pm\infty$, so that the wave functions become orthogonal. Since by definition each $\bar{\varphi}_n(t)$ is normalized to unity we deduce that

$$\langle\bar{\varphi}_p(t)|\bar{\varphi}_n(t)\rangle \underset{t\rightarrow\pm\infty}{\sim} \delta_{pn}. \tag{2.2.8}$$

Similarly the $\bar{\varphi}'_n(t)$ are orthonormal in the remote past or future.

An immediate consequence of (8) is that $|B_n|^2$ is the probability of observing the system to be in the state $\bar{\varphi}_n(t)$ in the remote past; for by (2) the system becomes, when $t = t_0 \sim -\infty$, a superposition of orthonormal states $\bar{\varphi}_n(t_0)$, the coefficient of $\bar{\varphi}_n(t_0)$ being B_n. Similarly in the remote future the probability of observation of the wave packet $\bar{\varphi}'_n(t_1)$ is $|B'_n|^2$. Since the postulate (1) implies that the system must be in some such state both in the remote past and in the remote future we deduce that

$$\sum_n |B_n|^2 = \sum_n |B'_n|^2 = 1. \tag{2.2.9}$$

As we saw in Section 2.1, the probability of the composite particles being in a state of relative motion defined by the $3(m-1)$-dimensional wave vector $\mathbf{k}$ in the $3(m-1)$-dimensional volume element $d\mathbf{k}$ is $|C_n(\mathbf{k})|^2\, d\mathbf{k}$ when the state of the system is $\bar{\varphi}_n(t)$. Hence in the general cases expressed by (3) and (6) the probability of the system being in the arrangement channel i and internal state χ_n with the relative motion of the particles being defined by a wave vector in the volume element $(\mathbf{k}, d\mathbf{k})$ is $|B_n|^2\,|C_n(\mathbf{k})|^2\, d\mathbf{k}$ or $|B'_n|^2\,|C'_n(\mathbf{k})|^2 d\mathbf{k}$. Since $A_\nu = B_n C_n(\mathbf{k})$ and $A'_\nu = B'_n C'_n(\mathbf{k})$ it follows that A_ν and A'_ν are the probability amplitudes for observation of the stationary state φ_ν in the remote past and remote future respectively. It follows immediately that

$$\sum_\nu |A_\nu|^2 = \sum_\nu |A'_\nu|^2 = 1, \tag{2.2.10}$$

which may also be deduced from (9) and the fact that the momentum amplitude functions $C_n(\mathbf{k})$ or $C'_n(\mathbf{k})$ are normalized to unity.

Example. *Two electrons and a proton.* Let us assume that the proton P can be regarded as infinitely massive, and denote by $\mathbf{r}_e$ and $\mathbf{r}_a$ the position vectors of the electrons e and a relative to P. We saw in Example 1 of Section 1.4 that there are four arrangement channels 0, 1, 2, and 3. Typical wave functions in each of these arrangement channels are:

$$\bar\varphi_0(\mathbf{r}_e, \mathbf{r}_a, t) = \left\{\int C(\mathbf{k})\,\varphi_{\mathbf{k}}(\mathbf{r}_e)\exp(-iE_k t/\hbar)\,d\mathbf{k}\right\}\left\{\int D(\mathbf{l})\,\varphi_{\mathbf{l}}(\mathbf{r}_a)\exp(-iE_l t/\hbar)\,d\mathbf{l}\right\}; \tag{2.2.11}$$

$$\begin{aligned}\bar\varphi_1(\mathbf{r}_e, \mathbf{r}_a, t) &= \chi_n(\mathbf{r}_a)\exp(-iE_n t/\hbar)\int C_n(\mathbf{k})\,\varphi_{\mathbf{k}}(\mathbf{r}_e)\exp(-iE_k t/\hbar)\,d\mathbf{k}\\ &= \chi_n(\mathbf{r}_a)\exp(-iE_n t/\hbar)\,\bar\varphi_n(\mathbf{r}_e, t), \quad \text{say};\end{aligned} \tag{2.2.12}$$

$$\begin{aligned}\bar\varphi_2(\mathbf{r}_e, \mathbf{r}_a, t) &= \chi_p(\mathbf{r}_e)\exp(-iE_p t/\hbar)\int C_p(\mathbf{k})\,\varphi_{\mathbf{k}}(\mathbf{r}_a)\exp(-iE_k t/\hbar)\,d\mathbf{k}\\ &= \chi_p(\mathbf{r}_e)\exp(-iE_p t/\hbar)\,\bar\varphi_p(\mathbf{r}_a, t), \quad \text{say};\end{aligned} \tag{2.2.13}$$

$$\bar\varphi_3(\mathbf{r}_e, \mathbf{r}_a, t) = \psi_n(\mathbf{r}_a, \mathbf{r}_e)\exp(-iE_n t/\hbar). \tag{2.2.14}$$

In (14) ψ_n is a wave function of an H^- ion. The expression (11) is a product of two wave packets describing the relative motion of the electrons to the proton when all three elementary particles are free; (12) and (13) define wave functions when one electron is free and the other is bound to the proton to form a hydrogen atom; (14) describes a state of the H^- ion. The wave functions (11) to (14) describe states in the arrangement channels 0 to 3 defined in Example 1 of Section 1.4. The orthogonality of the wave packets is clear enough in this case; for example, the scalar product of $\bar\varphi_1(t)$ and $\bar\varphi_2(t)$ is

$$\langle\bar\varphi_1(t)\,|\,\bar\varphi_2(t)\rangle = \langle\chi_n\,|\,\bar\varphi_p(t)\rangle\langle\bar\varphi_n(t)\,|\,\chi_p\rangle\exp[i(E_n - E_p)\,t/\hbar\}. \tag{2.2.15}$$

The overlaps between χ_n and $\bar\varphi_p(t)$, and between χ_p and $\bar\varphi_n(t)$, both tend to zero by virtue of the expansion of the wave packets.

2.3. THE INTERACTION PICTURE

For the purposes of scattering theory it is useful to define a picture intermediate between those of Schrödinger and Heisenberg, and known as the "Interaction Picture". We transform each wave function $\psi(t)$ of the Schrödinger picture into a wave function $\psi_I(t)$ of the interaction picture according to

$$\psi_I(t) = \exp(i\mathsf{H}_l t/\hbar)\,\psi(t); \tag{2.3.1}$$

hence each arrangement channel gives rise to a specific interaction picture.

If A is an operator in the Schrödinger picture, and $\psi(t)$ is any wave function of that picture, then $\mathsf{A}\psi(t)$ is transformed into $\exp(i\mathsf{H}_l t/\hbar)\mathsf{A}\psi(t) = \exp(i\mathsf{H}_l t/\hbar)\,\mathsf{A}\,\exp(-i\mathsf{H}_l t/\hbar)\psi_I(t)$. This equals $A_I(t)\psi_I(t)$ where $\mathsf{A}_I(t)$ is the operator in the interaction picture corresponding to A in the Schrödinger picture and so

$$\mathrm{A}_I(t) = \exp(i\mathrm{H}_i t/\hbar)\,\mathrm{A}\exp(-i\mathrm{H}_i t/\hbar). \tag{2.3.2}$$

In particular the interaction V_i is transformed into $\mathrm{V}_I(t)$ by

$$\mathrm{V}_I(t) = \exp(i\mathrm{H}_i t/\hbar)\,\mathrm{V}_i\exp(-i\mathrm{H}_i t/\hbar). \tag{2.3.3}$$

From (2) it follows that unitary operators are transformed into unitary operators, and that Hermitian operators are transformed into Hermitian operators.

If the evolution operator in the interaction picture is $\mathrm{U}_i(t, t_0)$ so that†

$$\psi_I(t) = \mathrm{U}_i(t, t_0)\,\psi_I(t_0) \tag{2.3.4}$$

a very similar argument to that above shows that

$$\boxed{\mathrm{U}_i(t, t_0) = \exp(i\mathrm{H}_i t/\hbar)\exp[-i\mathrm{H}(t-t_0)/\hbar]\ \exp(-i\mathrm{H}_i t_0/\hbar).} \tag{2.3.5}$$

From (5) we see immediately that $\mathrm{U}_i(t_0, t_0) = 1$, $\mathrm{U}_i(t, t_1)\,\mathrm{U}_i(t_1, t_0) = \mathrm{U}_i(t, t_0)$, while the Hermitian conjugate $\mathrm{U}_i(t, t_0) = \mathrm{U}_i(t_0, t)$;† hence $\mathrm{U}_i(t, t_0)$ is unitary. Partial differentiation with respect to t yields the operator differential equation

$$(\partial/\partial t)\,\mathrm{U}_i(t, t_0) = (i/\hbar)\exp(i\mathrm{H}_i t/\hbar)(\mathrm{H}_i-\mathrm{H})\exp[-i\mathrm{H}(t-t_0)/\hbar)]\exp(-i\mathrm{H}t_0/\hbar). \tag{2.3.6}$$

Now $\mathrm{H}-\mathrm{H}_i = V_i$ and $\mathrm{V}_I(t)$ is given by (3), hence we deduce from (5) and (6) that

$$\frac{\partial\mathrm{U}_i(t, t_0)}{\partial t} = -\frac{i}{\hbar}\mathrm{V}_I(t)\,\mathrm{U}_i(t, t_0). \tag{2.3.7}$$

This is clearly equivalent to the integral equation

$$\mathrm{U}_i(t, t_0) = 1-\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{V}_I(\tau)\,\mathrm{U}_i(\tau, t_0)\,d\tau \tag{2.3.8}$$

since $\mathrm{U}_i(t_0, t_0) = 1$. If we take the Hermitian conjugate of this and then interchange t and t_0 we obtain

$$\boxed{\mathrm{U}_i(t, t_0) = 1+\frac{i}{\hbar}\int_{t}^{t_0}\mathrm{U}_i(t, \tau)\,\mathrm{V}_I(\tau)\,d\tau.} \tag{2.3.9}$$

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† It is more convenient to use the subscript i rather than I in the symbol $\mathrm{U}_i(t, t_0)$ for the evolution operator in the interaction picture.

EXERCISES

1. Verify that the transformation $\psi \to \psi_I = \exp(i\mathsf{H}_i/\hbar)\psi$ transforms Hermitian operators into Hermitian operators, and unitary operators into unitary operators.
2. Verify (5).

2.4. THE EVOLUTION OF A WAVE PACKET

We are now in a position to describe the evolution of an N-particle wave packet such as that discussed in Section 2.1; in other words, a wave packet initially representing the motion of an N-particle system when the internal states of the particles are defined by the set of quantum numbers n. Before doing this we shall collect together a few results which we shall use in the derivation of the expression for the state into which the system evolves.

The initial wave packet $\bar{\varphi}_n$ is given by (2.1.4); this may be further abbreviated to

$$\bar{\varphi}_n(t) = \int C(\mathbf{k})\,\varphi_{\mathbf{k}n}\exp(-iE_{\mathbf{k}n}t/\hbar)\,d\mathbf{k}. \tag{2.4.1}$$

Now $\varphi_{\mathbf{k}n}$ is an eigenfunction of H_i with energy $E_{\mathbf{k}n}$ and so $\exp(-i\mathsf{H}_it/\hbar)\,\varphi_{\mathbf{k}n} = \exp(-iE_{\mathbf{k}n}t/\hbar)\varphi_{\mathbf{k}n}$. It follows that (1) can be written

$$\bar{\varphi}_n(t) = \exp(-i\mathsf{H}_it/\hbar)\int C(\mathbf{k})\,\varphi_{\mathbf{k}n}\,d\mathbf{k}. \tag{2.4.2}$$

When $t = 0$ equation (1) becomes

$$\bar{\varphi}_n(0) = \int C(\mathbf{k})\,\varphi_{\mathbf{k}n}\,d\mathbf{k}. \tag{2.4.3}$$

Comparison of (2) and (3) yields

$$\bar{\varphi}_n(t) = \exp(-i\mathsf{H}_it/\hbar)\,\bar{\varphi}_n(0), \tag{2.4.4}$$

and so

$$\bar{\varphi}_n(0) = \exp(i\mathsf{H}_it/\hbar)\,\bar{\varphi}_n(t). \tag{2.4.5}$$

Finally we note that if we put $t = 0$ in (2.3.5) we obtain

$$\mathsf{U}_i(0, t_0) = \exp(i\mathsf{H}t_0/\hbar)\exp(-i\mathsf{H}_it_0/\hbar). \tag{2.4.6}$$

We are supposing that in the remote past the system was in the internal state $|n\rangle$. It must therefore be the case that if the wave function of the system is $\bar{\psi}(t)$, then $\bar{\psi}(t) = \bar{\varphi}_n(t)$ for $t \leq t_0$, where t_0 is a time in the remote past. Since $\bar{\varphi}_n(t_0)$ evolves under the full Hamiltonian H into $\bar{\psi}(0)$ we have

$$\bar{\psi}(0) = \exp(i\mathsf{H}t_0/\hbar)\,\bar{\varphi}_n(t_0). \tag{2.4.7}$$

If we put $t = t_0$ in (4) and then substitute the resulting expression for $\bar{\varphi}_n(t_0)$ into (7) we obtain

$$\bar{\psi}(0) = \exp(i\mathsf{H}t_0/\hbar)\exp(-i\mathsf{H}_it_0/\hbar)\,\bar{\varphi}_n(0). \tag{2.4.8}$$

With the aid of (6) we can rewrite (8) as

$$\bar{\psi}(0) = \mathsf{U}_i(0,\, t_0)\,\bar{\varphi}_n(0). \tag{2.4.9}$$

Since this is true for any time in the remote past (8) implies

$$\lim_{t \to -\infty} \exp\,(i\mathsf{H}t/\hbar)\exp\,(-i\mathsf{H}_i t/\hbar)\,\bar{\varphi}_n(0) = \bar{\psi}(0) \tag{2.4.10}$$

and (9) implies

$$\bar{\psi}(0) = \mathsf{U}_i(0,\, -\infty)\,\bar{\varphi}_n(0). \tag{2.4.11}$$

We shall now calculate $\bar{\psi}(0)$, and hence obtain an expression for $\bar{\psi}(t)$. We first substitute for $\mathsf{U}_i(0,\, t_0)$ from (2.3.9) with $t = 0$ into (9); this gives

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{t_0} \mathsf{U}_i(0,\, \tau)\,\mathsf{V}_i(\tau)\,\bar{\varphi}_n(0)\, d\tau. \tag{2.4.12}$$

Now (6) gives $\mathsf{U}_i(0, \tau) = \exp\,(i\mathsf{H}\tau/\hbar)\exp\,(-i\mathsf{H}_i\tau/\hbar)$, (2.3.3) gives $\mathsf{V}_i(\tau) = \exp\,(i\mathsf{H}_i\tau/\hbar)V_i\exp\,(-i\mathsf{H}\tau/\hbar)$, while (5) gives $\bar{\varphi}_n(0) = \exp\,(i\mathsf{H}_i\tau/\hbar)\,\bar{\varphi}_n(\tau)$. Substitution for these three expressions into (12) yields

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{t_0} \exp\,(i\mathsf{H}\tau/\hbar)\,V_i\bar{\varphi}_n(\tau)\, d\tau. \tag{2.4.13}$$

At this stage we introduce a small positive number ε which satisfies the condition $\varepsilon\,|t_0| \ll 1$. Equation (13) can now be replaced by

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{t_0} \exp\,[i(\mathsf{H}-i\varepsilon)\,\tau/\hbar]\,V_i\bar{\varphi}_n(\tau)\, d\tau. \tag{2.4.14}$$

The particles are moving freely when $t \ll t_0$, and so $V_i\bar{\varphi}_n(\tau)$ must be negligible when $\tau < t_0$. We can therefore replace the upper limit t_0 of the integral on the right-hand side of (14) by $-\infty$. If we also put $t = \tau$ in (1) and substitute the resulting expression for $\bar{\varphi}_n(\tau)$ into (14) we find that

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{-\infty} d\tau \int d\mathbf{k}\; C(\mathbf{k})\exp\,[i(\mathsf{H}-i\varepsilon-E_{\mathbf{k}n})\,\tau/\hbar]\,V_i\varphi_{\mathbf{k}n}. \tag{2.4.15}$$

Owing to the presence of the ε term the integrals in (15) may be interchanged and the integration over τ may be carried out by use of the operator identity

$$\int_0^{-\infty} \exp\,[i(\mathsf{H}-i\varepsilon-E_{\mathbf{k}n})\,\tau/\hbar]\, d\tau = (\hbar/i)(E_{\mathbf{k}n}-\mathsf{H}+i\varepsilon)^{-1}; \tag{2.4.16}$$

(16) may be easily verified by an expansion in terms of a complete set of eigenstates of H (see Volume 4, Appendix D). These things done, (15)

becomes

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = \int C(\mathbf{k})(E_{\mathbf{k}n}-\mathsf{H}+i\varepsilon)^{-1}V_i\varphi_{\mathbf{k}n}\,d\mathbf{k}. \tag{2.4.17}$$

If we substitute for $\bar{\varphi}_n(0)$ from (3) into (17) and rearrange we obtain

$$\bar{\psi}(0) = \int C(\mathbf{k})[\varphi_{\mathbf{k}n}+(E_{\mathbf{k}n}-\mathsf{H}+i\varepsilon)^{-1}V_i\varphi_{\mathbf{k}n}]\,d\mathbf{k}. \tag{2.4.18}$$

The definition (1.5.1) shows that, in this case, the term in square brackets under the integral sign in (18) is just $\psi^+_{\mathbf{k}n}$, and so

$$\bar{\psi}(0) = \int C(\mathbf{k})\,\psi^+_{\mathbf{k}n}\,d\mathbf{k}. \tag{2.4.19}$$

Since $\bar{\psi}(t) = \exp(-i\mathsf{H}t/\hbar)\bar{\psi}(0)$ and $\psi^+_{\mathbf{k}n}$ is an eigenstate of H with eigenvalue $E_{\mathbf{k}n}$ it follows from (19) that

$$\bar{\psi}(t) = \int C(\mathbf{k})\,\psi^+_{\mathbf{k}n}\exp(-iE_{\mathbf{k}n}t/\hbar)\,d\mathbf{k}. \tag{2.4.20}$$

The above argument applied to a system which in the remote past was in the state $\bar{\varphi}_n(t)$. We can also consider the case of a system which develops into the state $\bar{\varphi}_n(t)$ in the remote future. In this case $\bar{\psi}(t) = \bar{\varphi}_n(t)$ if $t \gg t_1$, where t_1 is a time sufficiently far in the future. The previous argument which led to (13) is unaltered except that t_0 is replaced throughout by t_1. Hence (13) is replaced by

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{t_1}\exp(i\mathsf{H}\tau/\hbar)\,V_i\bar{\varphi}_n(\tau)\,d\tau. \tag{2.4.21}$$

Now, however, we replace (21) by

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{t_1}\exp[i(\mathsf{H}+i\varepsilon)\tau/\hbar]\,V_i\bar{\varphi}_n(\tau)\,d\tau \tag{2.4.22}$$

where $\varepsilon|t_1| \ll 1$. Since the particles are moving freely in the remote future we have $V_i\varphi_n(\tau) = 0$ if $\tau > t_1$, hence we can replace t_1 in (22) by $+\infty$. If we also substitute for $\bar{\varphi}_n(\tau)$ by means of (1) we see that (22) becomes

$$\bar{\psi}(0)-\bar{\varphi}_n(0) = (i/\hbar)\int_0^{+\infty}d\tau\int d\mathbf{k}\,C(\mathbf{k})\exp[i(\mathsf{H}+i\varepsilon-E_{\mathbf{k}n})\tau/\hbar]V_i\varphi_{\mathbf{k}n}. \tag{2.4.23}$$

Application of the operator integral

$$\int_0^{+\infty}\exp[i(\mathsf{H}+i\varepsilon-E_{\mathbf{k}n})\tau/\hbar]\,d\tau = (\hbar/i)(E_{\mathbf{k}n}-\mathsf{H}-i\varepsilon)^{-1} \tag{2.4.24}$$

and of (3) to (23) gives

$$\bar{\psi}(0) = \int C(\mathbf{k})[\varphi_{\mathbf{k}n}+(E_{\mathbf{k}n}-\mathsf{H}-i\varepsilon)^{-1}V_i\varphi_{\mathbf{k}n}]\,d\mathbf{k}; \tag{2.4.25}$$

the term in square brackets is given by (1.5.1) with $\nu = \mathbf{k}n$ and so (25) becomes

$$\bar{\psi}(0) = \int C(\mathbf{k})\, \psi^-_{\mathbf{k}n}\, d\mathbf{k}. \tag{2.4.26}$$

Since $\bar{\psi}^-_{\mathbf{k}n}$ is an eigenstate of H with eigenvalue $E_{\mathbf{k}n}$ and $\bar{\psi}(t) = \exp(-i\mathsf{H}t/\hbar) \times \bar{\psi}(0)$ we see from (26) that

$$\bar{\psi}(t) = \int C(\mathbf{k})\, \psi^-_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t/\hbar)\, d\mathbf{k}. \tag{2.4.27}$$

We may summarize the results of this section as follows. If the state of the system is represented in the remote past by the expression (1), then its state at any time is represented by (20). *That is to say, in the expression (1) for the wave function in the remote past we replace the unperturbed stationary state* $\varphi_{\mathbf{k}n}$ *by the stationary scattering state* $\psi^+_{\mathbf{k}n}$. On the other hand if (1) represents the state of the system in the remote future the expression for the wave function $\bar{\psi}(t)$ at any time t is now given by (27). In other words *the unperturbed stationary state* $\varphi_{\mathbf{k}n}$ *is replaced by the stationary scattering state* $\psi^-_{\mathbf{k}n}$. These results may be summed up by the formulae

$$\exp[-i\mathsf{H}(t-t_0)/\hbar] \int C(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t_0/\hbar)\, d\mathbf{k} \underset{t_0 \to -\infty}{\sim} \int C(\mathbf{k})\, \psi^+_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t/\hbar)\, d\mathbf{k}, \tag{2.4.28}$$

$$\exp[-i\mathsf{H}(t-t_1)/\hbar] \int C(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t_1/\hbar)\, d\mathbf{k} \underset{t_1 \to +\infty}{\sim} \int C(\mathbf{k})\, \psi^-_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t_1/\hbar)\, d\mathbf{k}. \tag{2.4.29}$$

We can also put these results in another way. Let us define wave functions $\bar{\psi}^\pm_{\mathbf{k}n}(t)$ by

$$\bar{\psi}^\pm_n(t) = \int C(\mathbf{k})\, \psi^\pm_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n}t/\hbar)\, d\mathbf{k}. \tag{2.4.30}$$

Such wave functions may describe the system at all times. The wave function $\bar{\psi}^+_n(t)$ then evolves from $\bar{\varphi}_n(t)$, while $\bar{\psi}^-_n(t)$ evolves into $\bar{\varphi}_n(t)$, where $\bar{\varphi}_n(t)$ is defined by (1). Thus

$$\bar{\psi}^\pm_n(t) \underset{t \to \mp\infty}{\sim} \bar{\varphi}_n(t). \tag{2.4.31}$$

Since $\bar{\psi}^\pm_n(t) = \exp(-i\mathsf{H}t/\hbar)\, \psi^\pm_n(0)$, and $\bar{\varphi}_n(t) = \exp(-i\mathsf{H}_i t/\hbar) \bar{\varphi}_n(0)$, it follows that

$$\exp(-i\mathsf{H}t/\hbar)\, \bar{\psi}^\pm_n(0) \underset{t \to \mp\infty}{\sim} \exp(-i\mathsf{H}_i t/\hbar)\, \bar{\varphi}_n(0), \tag{2.4.32}$$

or equivalently

$$\bar{\psi}^\pm_n(0) \underset{t \to \mp\infty}{\sim} \exp(i\mathsf{H}t/\hbar) \exp(-i\mathsf{H}_i t/\hbar)\, \bar{\varphi}_n(0). \tag{2.4.33}$$

It follows from (6) that (33) can be written

$$\bar{\psi}^\pm_n(0) = \mathsf{U}_i(0, \mp\infty)\, \bar{\varphi}_n(0). \tag{2.4.34}$$

We have not proved (33) in a mathematically rigorous way. We have only shown that such a result is necessary if the physically reasonable postulate (2.2.1) is to be satisfied. To prove equation (33) for particular potentials is a task of great mathematical difficulty, although much progress has been made in this field of recent years. It is not true in the case of Coulomb potentials, for example, due to the long range nature of this potential. If two or more atoms or molecules are ionized they can never be completely out of range of each other, and so (2.2.1) does not hold in such a case. However, for many purposes the potential may be given a cut-off — that is, put equal to zero for $r \neq R$ say, in which case (33) may be proved... (For example, see Taylor 1972.)

2.5. ORTHOGONALITY OF THE SCATTERING STATES

We shall now show that the Schwinger–Lippmann scattering states defined in Section 1.5 are orthogonal. In the case of the arrangement channel in which the system is bound we have $\mathsf{H} = \mathsf{H}_i$, so that $V_i = 0$. In this case case (1.5.1) shows that $\psi_\nu^\pm = \varphi_\nu$, where φ_ν is the bound state—we shall denote this by ψ_b. Let $\psi_{\mathbf{k}n}^+$ be a scattering state in some arrangement channel i, and consider the state represented by

$$\bar{\psi}_n(t) = \int C(\mathbf{k})\,\psi_{\mathbf{k}n}^+ \exp(-iE_{\mathbf{k}n}t/\hbar)\,d\mathbf{k}. \tag{2.5.1}$$

We consider the value of the scalar product $\langle\bar{\psi}_n(t)|\psi_b \exp(-iE_b t/\hbar)\rangle$ as $t \to -\infty$, where E_b is the energy of the bound state. In Section 2.4 we saw that the wave function $\bar{\psi}_n(t)$ given by (1) develops from $\bar{\varphi}_n(t)$ in the remote past, where $\bar{\varphi}_n(t)$ is given by (2.4.1). We therefore have

$$\langle\bar{\psi}_n(t)\,|\,\psi_b \exp(-iE_b t/\hbar)\rangle \underset{t\to-\infty}{\sim} \langle\bar{\varphi}_n(t)\,|\,\psi_b \exp(-iE_b t/\hbar)\rangle. \tag{2.5.2}$$

Now ψ_b is always confined to some finite region of configuration space while $\bar{\varphi}_n(t)$ spreads out as the particles $A_1, A_2, \ldots, A_m$ separate when $t \to -\infty$; hence the right-hand side of (2) tends to zero as $t \to -\infty$. At the same time the left-hand side of (2) equals

$$\langle\exp(-i\mathsf{H}t/\hbar)\,\bar{\psi}_n(0)\,|\,\exp(-i\mathsf{H}t/\hbar)\,\psi_b\rangle \tag{2.5.3}$$

and since $\exp(-i\mathsf{H}t/\hbar)$ is unitary this is

$$\langle\bar{\psi}_n(0)\,|\,\psi_b\rangle; \tag{2.5.4}$$

thus (2) becomes

$$\langle\bar{\psi}_n(0)\,|\,\psi_b\rangle \underset{t\to-\infty}{\sim} 0. \tag{2.5.5}$$

The left-hand side of (5) is independent of t and so equals zero; that is,

$$\langle \bar{\psi}_n(0) \mid \psi_b \rangle = 0. \tag{2.5.6}$$

If we put $t = 0$ in (1) and substitute the resulting expression for $\bar{\psi}_n(0)$ into (6) we obtain

$$\int C^*(\mathbf{k}) \langle \psi^+_{\mathbf{k}n} \mid \psi_b \rangle \, d\mathbf{k} = 0; \tag{2.5.7}$$

but $C^*(\mathbf{k})$ is arbitrary and so

$$\langle \psi^+_{\mathbf{k}n} \mid \psi_b \rangle = 0. \tag{2.5.8}$$

We have now shown that any scattering state $\psi^+_{\mathbf{k}n}$ is orthogonal to any bound state ψ_b. A similar argument applied to (1) with $\psi^+_{\mathbf{k}n}$ replaced by $\psi^-_{\mathbf{k}n}$ and with t allowed to tend to $+\infty$ shows that any scattering state $\psi^-_{\mathbf{k}n}$ is orthogonal to any bound state ψ_b. Since the bound states are orthonormal it follows that all we have remaining to show is that $\langle \psi^\pm_{\mathbf{k}n} \mid \psi^\pm_{\mathbf{l}p} \rangle = \delta(\mathbf{k} - \mathbf{l})\, \delta_{np} \delta_{if}$, where $\varphi_{\mathbf{k}n}$ and $\varphi_{\mathbf{l}p}$ belong to arrangement channels i and f respectively, and this will complete the proof of the orthogonality of the Schwinger–Lippmann states.

In order to complete the proof we consider the wave packet

$$\bar{\psi}_p(t) = \int D(\mathbf{l})\, \psi^+_{\mathbf{l}p} \exp(-iE_{\mathbf{l}p} t/\hbar)\, d\mathbf{l}; \tag{2.5.9}$$

$\psi^+_{\mathbf{l}p}$ is the scattering state with outgoing wave boundary conditions associated with the unperturbed state $\varphi_{\mathbf{l}p}$. The wave function $\varphi_{\mathbf{l}p}$ is assumed to represent a state in some arrangement channel f which may differ from i, the arrangement channel of $\varphi_{\mathbf{k}n}$. As we saw in the last section, as $t \to -\infty$ $\bar{\psi}_p(t) \sim \bar{\varphi}_p(t)$ where

$$\bar{\varphi}_p(t) = \int D(\mathbf{l})\, \varphi_{\mathbf{l}p} \exp(-iE_{\mathbf{l}p} t/\hbar)\, d\mathbf{l}, \tag{2.5.10}$$

and so

$$\langle \bar{\psi}_p(t) \mid \bar{\psi}_n(t) \rangle \underset{t \to -\infty}{\sim} \langle \bar{\varphi}_p(t) \mid \bar{\varphi}_n(t) \rangle. \tag{2.5.11}$$

Now we showed in Section 2.2, in particular equation (2.2.8), that the wave packets $\bar{\varphi}_n(t)$ and $\bar{\varphi}_p(t)$ become orthogonal as $t \to -\infty$ if $p \neq n$. They are therefore orthogonal if the arrangement channels i and f are different, and so

$$\langle \bar{\varphi}_p(t) \mid \bar{\varphi}_n(t) \rangle \underset{t \to -\infty}{\sim} \delta_{fi} \langle \bar{\varphi}_p(t) \mid \bar{\varphi}_n(t) \rangle. \tag{2.5.12}$$

Further,

$$\begin{aligned} \langle \bar{\psi}_p(t) \mid \bar{\psi}_n(t) \rangle &= \langle \exp(-i\mathrm{H}t/\hbar)\, \bar{\psi}_p(0) \mid \exp(-i\mathrm{H}t/\hbar)\, \bar{\psi}_n(0) \rangle \\ &= \langle \bar{\psi}_p(0) \mid \bar{\psi}_n(0) \rangle. \end{aligned} \tag{2.5.13}$$

It follows from (13), (11) and (12) that

$$\langle \bar{\psi}_p(0) \mid \bar{\psi}_n(0) \rangle \underset{t \to -\infty}{\sim} \delta_{fi} \langle \bar{\varphi}_p(t) \mid \bar{\varphi}_n(t) \rangle. \tag{2.5.14}$$

We may write (14) out more fully using (9), (1), (10) and (2.4.1) as

$$\begin{aligned}\int d\mathbf{l}\, D^*(\mathbf{l}) \int d\mathbf{k}\, C(\mathbf{k}) \langle \psi^+_{\mathbf{l}p} \,|\, \psi^+_{\mathbf{k}n} \rangle & \\ \underset{t \to -\infty}{\sim} \delta_{fi} \int d\mathbf{l}\, D^*(\mathbf{l}) \int d\mathbf{k}\, C(\mathbf{k}) \langle \varphi_{\mathbf{l}p} \,|\, \varphi_{\mathbf{k}n} \rangle \exp\,[i(E_{\mathbf{l}p} - E_{\mathbf{k}n})t/\hbar]. & \quad (2.5.15)\end{aligned}$$

Now if $f = i$ we know that $\langle \varphi_{\mathbf{l}p} | \varphi_{\mathbf{k}n} \rangle = \delta(\mathbf{l}-\mathbf{k})\delta_{pn}$, and if $f \neq i$ the right-hand side of (15) is zero. We can therefore put $E_{\mathbf{l}p} = E_{\mathbf{k}n}$ and express (15) as

$$\int d\mathbf{l}\, D^*(\mathbf{l}) \int d\mathbf{k}\, C(\mathbf{k}) \langle \psi^+_{\mathbf{l}p} \,|\, \psi^+_{\mathbf{k}n} \rangle \underset{t \to -\infty}{\sim} \int d\mathbf{l}\, D^*(\mathbf{l}) \int d\mathbf{k}\, C(\mathbf{k})\, \delta_{fi} \delta(\mathbf{l}-\mathbf{k})\, \delta_{pn}. \tag{2.5.16}$$

Both sides of (16) are independent of t, and so they are equal. Since $D^*(\mathbf{l})$ is arbitrary we deduce that

$$\int C(\mathbf{k}) \langle \psi^+_{\mathbf{l}p} \,|\, \psi^+_{\mathbf{k}n} \rangle \, d\mathbf{k} = \int C(\mathbf{k})\, \delta_{fi}\, \delta(\mathbf{l}-\mathbf{k})\, \delta_{pn}\, d\mathbf{k}. \tag{2.5.17}$$

Since $C(\mathbf{k})$ is also arbitrary we infer from (17) that

$$\langle \psi^+_{\mathbf{l}p} \,|\, \psi^+_{\mathbf{k}n} \rangle = \delta_{fi}\, \delta(\mathbf{l}-\mathbf{k})\, \delta_{pn}. \tag{2.5.18}$$

A similar argument which considers the asymptotic behaviour of the system in the remote future rather than the remote past leads to

$$\langle \psi^-_{\mathbf{l}p} \,|\, \psi^-_{\mathbf{k}n} \rangle = \delta_{fi}\, \delta(\mathbf{l}-\mathbf{k})\, \delta_{pn}. \tag{2.5.19}$$

In other words, the scattering states are orthonormal. The bound states of the system are orthonormal, and we have already shown that the bound states are orthogonal to the scattering states. If we denote the general member of the set $\{\psi_b, \psi^+_{\mathbf{k}n}\}$ of eigenfunctions of H by ψ^+_ν, and the general member of the set $\{\psi_b, \psi^-_{\mathbf{k}n}\}$ of eigenfunctions of H by ψ^-_ν, these results may be summarized by the single important formula

$$\boxed{\langle \psi^\pm_\mu \,|\, \psi^\pm_\nu \rangle = \delta_{\mu\nu}.} \tag{2.5.20}$$

In other words, the ψ^+_ν are orthonormal eigenfunctions of the full Hamiltonian H, and so also are the ψ^-_ν. The question of their completeness will be considered in the next section.

EXERCISES

1. Prove that any scattering state $\psi^-_{\mathbf{k}n}$ is orthogonal to any bound state ψ_b.
2. Prove (19).

2.6. THE COMPLETENESS THEOREM

In the last section we saw that the sets ψ_ν^+ and ψ_ν^- are both orthonormal, and in this section we shall show that they are both complete. According to the fundamental postulate (2.2.1), for any time t_0 sufficiently far in the remote past the wave function $\bar{\psi}(t)$ has the form (2.2.3). This may be written

$$\bar{\psi}(t_0) = \sum_b B_b \psi_b \exp(-iE_b t_0/\hbar) + \sum_n B_n \int C_n(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n} t/\hbar)\, d\mathbf{k} \tag{2.6.1}$$

where the summation $\sum_b$ goes over all bound states ψ_b, while $\sum_n$ goes over all internal states of the system when it consists of two or more freely moving composite particles. Similarly for any time t_1 sufficiently far in the future the wave function $\bar{\psi}(t)$ has the form

$$\bar{\psi}(t_1) = \sum_b B_b' \psi_b \exp(-iE_b t_1/\hbar) + \sum_n B_n' \int C_n'(\mathbf{k})\, \varphi_{\mathbf{k}n} \exp(-iE_{\mathbf{k}n} t_1/\hbar)\, d\mathbf{k}. \tag{2.6.2}$$

To evaluate $\bar{\psi}(t)$ we operate on (1) with $\exp[-i\mathsf{H}(t-t_0)/\hbar]$. This is a linear operator and so we can use the fact that

$$\exp[-i\mathsf{H}(t-t_0)/\hbar]\,\psi_b = \exp[-iE_b(t-t_0)/\hbar]\,\psi_b \tag{2.6.3}$$

along with (2.4.28) to obtain

$$\bar{\psi}(t) = \sum_b B_b \psi_b \exp(-iE_b t/\hbar) + \sum_n B_n \int C_n(\mathbf{k})\, \psi_{\mathbf{k}n}^+ \exp(-iE_{\mathbf{k}n} t/\hbar)\, d\mathbf{k}. \tag{2.6.4}$$

Similarly if we operate on (2) with $\exp[-i\mathsf{H}(t-t_1)/\hbar]$ and use (2.4.29) we obtain

$$\bar{\psi}(t) = \sum_b B_b' \psi_b \exp(-iE_b t/\hbar) + \sum_n B_n' \int C_n'(\mathbf{k})\, \psi_{\mathbf{k}n}^- \exp(-iE_{\mathbf{k}n} t/\hbar)\, d\mathbf{k}. \tag{2.6.5}$$

Now $\psi_b = \psi_b^\pm$, B_b or $B_n C_n(\mathbf{k})$ may be written A_ν and B_b' or $B_n' C_n'(\mathbf{k})$ may be written A_ν'. The results (4) and (5) may therefore be written more concisely as

$$\boxed{\begin{aligned} \bar{\psi}(t) &= \sum_\nu A_\nu \psi_\nu^+ \exp(-iE_\nu t/\hbar), \qquad (2.6.6)\\ \bar{\psi}(t) &= \sum_\nu A_\nu' \psi_\nu^- \exp(-iE_\nu t/\hbar). \qquad (2.6.7) \end{aligned}}$$

We discussed the quantities A_ν and A'_ν in Section 2.2 where we saw that they are the probability amplitudes for the unperturbed states φ_ν in the remote past and future.

The expressions (6) and (7) show that any wave function $\bar{\psi}(t)$ may be expanded in terms of either of the orthonormal sets ψ_ν^+ or ψ_ν^-. We have therefore obtained the following theorem:

> *Completeness Theorem.* The Schwinger–Lippmann states ψ_ν^+, including the bound states, form a complete orthonormal set. The Schwinger–Lippmann states ψ_ν^-, including the bound states, form a second complete orthonormal set. (2.6.8)

The theorem (8) enables us to generate sets other than the two explicitly stated there. For we can associate complete sets with every arrangement channel of the system, viz. the product of the plane waves describing the relative motion of the composite particles $A_1, A_2 \ldots, A_m$, together with the complete sets ψ_ν^+ or ψ_ν^- for each of the sub-systems of elementary particles which make up $A_1, A_2, \ldots, A_m$. Such sets of eigenstates of H_i are orthonormal and complete, and there are 2^m of them. Which complete set we choose will depend upon the problem under consideration, as we shall show later by an example.

At this stage we should point out that we have not *proved* the completeness theorem. For the theorem is a statement of a mathematical fact about certain Hamiltonians. It can be proved in a mathematically rigorous way for certain potentials; being a mathematical fact it cannot be deduced from a physical postulate. What we have shown here is that, if a Hamiltonian is to describe a physical system satisfying the *physical* postulate (2.2.1), then it must have the *mathematical* property (8). If, for example, the potential is too singular, particles may spiral into each other and amalgamate, in which case the postulate (2.2.1) is obviously not adhered to. Only potentials which satisfy (8) can be regarded as realistic potentials for the system (Taylor, 1972).

EXAMPLE. Suppose we have a three-particle system consisting of two electrons a and b, and proton A. For simplicity we suppose the mass of A to be effectively infinite compared with that of a or b, and ignore spin. Typical unperturbed states of the four arrangement channels are: $|\, n_{abA}\rangle$, a state of the H^- ion; $|\, \mathbf{k}_{aA} n_{bA}\rangle = |\, \mathbf{k}_{aA}\rangle \,|\, n_{bA}\rangle$, a state in which electron a moves freely with momentum $\hbar\mathbf{k}$ relative to A and b is bound to the proton A to form a hydrogen atom in state $|\, n\rangle$; $|\, \mathbf{k}_{bA} n_{aA}$, obtained from the previous one by interchanging the electrons; $|\mathbf{k}_{aA}\mathbf{l}_{bA}\rangle$, a state in which the electrons a and b move freely with momenta $\hbar\mathbf{k}$ and $\hbar\mathbf{l}$ relative to A respectively. The scattering states corresponding to the last three may be written $|\mathbf{k}_{aA} n_{bA};\, \pm\rangle$, $|\mathbf{k}_{bA} n_{aA};\, \pm\rangle$, and $|\mathbf{k}_{aA}\mathbf{l}_{bA};\, \pm\rangle$ respectively. Two complete sets are therefore

$$\{|n_{abA}\rangle, \quad |\mathbf{k}_{aA}n_{bA};+\rangle, \quad |\mathbf{k}_{bA}n_{aA};+\rangle, \quad |\mathbf{k}_{aA}\mathbf{l}_{bA};+\rangle\}, \qquad (2.6.9)$$

$$\{|n_{abA}\rangle, \quad |\mathbf{k}_{aA}n_{bA};-\rangle, \quad |\mathbf{k}_{bA}n_{aA};-\rangle, \quad |\mathbf{k}_{aA}\mathbf{l}_{bA};-\rangle\}. \qquad (2.6.10)$$

The above set is a complete orthonormal set of eigenstates of the total Hamiltonian H. We can form other complete sets which are eigenstates of the unperturbed Hamiltonians H_i corresponding to the various arrangement channels. For example, consider the arrangement channel in which b is free while a is bound to A to form a hydrogen atom. Since we are assuming that the mass of a proton is effectively infinite compared with that of an electron the centre of mass of the atom is A, and so in this case

$$\mathsf{H}_i = \mathsf{K}_{bA}+\mathsf{K}_{aA}+V_{aA} = \mathsf{K}_{bA}+\mathsf{h}. \qquad (2.6.11)$$

The eigenstates of K_{bA} are $|\mathbf{k}_{bA}\rangle$, representing the free motion of b relative to A with momentum $\hbar\mathbf{k}$. The eigenstates of the internal Hamiltonian h are the bound states $|n_{aA}\rangle$ of the atom aA, and its ionized states $|\boldsymbol{\varkappa}_{aA}\pm\rangle$ representing the scattering of a by A when the unperturbed momentum of a relative to A is $\hbar\boldsymbol{\varkappa}$. Two complete orthonormal sets are therefore

$$\{|\mathbf{k}_{bA}\rangle\,|n_{aA}\rangle, \quad |\mathbf{k}_{bA}\rangle\,|\boldsymbol{\varkappa}_{aA}+\rangle\}, \qquad (2.6.12)$$

and

$$\{|\mathbf{k}_{bA}\rangle\,|n_{aA}\rangle, \quad |\mathbf{k}_{bA}\rangle\,|\boldsymbol{\varkappa}_{aA}-\rangle\}. \qquad (2.6.13)$$

In the problem of scattering of electron b with momentum $\hbar\mathbf{k}$ when the atom is in its ground state $|0_{aA}\rangle$ we may have reason to believe that there is not much likelihood of excitation or ionization of the atom. If this is the case we can truncate the complete set (12) selecting only the set $|\mathbf{k}_{bA}\rangle\,|0_{aA}\rangle$ where $\mathbf{k}$ takes all values. In this case the scattering state has the form

$$|\mathbf{k}_{bA}0_{aA};+\rangle \simeq \int \tilde{F}(\mathbf{k})\,|0_{aA}\rangle\,|\mathbf{k}_{bA}\rangle\,d\mathbf{k} = |0_{aA}\rangle \int \tilde{F}(\mathbf{k})\,|\mathbf{k}_{bA}\rangle\,d\mathbf{k} \qquad (2.6.14)$$

where $\tilde{F}$ is some function of $\mathbf{k}$. The scattering state is therefore the product of the ground atomic state $|0_{aA}\rangle$ and some state $\int \tilde{F}(\mathbf{k})\,|\mathbf{k}_{bA}\rangle d\mathbf{k}$ of motion of b relative to A. Its wave function is now

$$\psi^{+}_{\mathbf{k}0}(\mathbf{r}_{aA}, \mathbf{r}_{bA}) \simeq \chi_0(\mathbf{r}_{aA})\,F(\mathbf{r}_{bA}) \qquad (2.6.'$$

where $F(\mathbf{r}_{bA})$, the Fourier transform of $\tilde{F}(\mathbf{k})$, is some unknown function. Such an approximation forms a basis for a calculation of the electron–hydrogen scattering amplitude (Mott and Massey, 1965, chapter XVII).

EXERCISES

1. Write out the complete sets corresponding to the various arrangement channels of a system of two electrons and a proton. Can you think of any other complete sets?

2. Repeat Exercise 1 in the case of the four-particle system consisting of two electrons and two protons.

2.7. THE SCATTERING MATRIX

Let us summarize the results so far obtained in this chapter. For any time t_0 sufficiently far in the past the system is represented by the wave function

$$\psi(t_0) = \sum_{v} A_v\varphi_v \exp(-iE_v t_0/\hbar) \qquad (2.7.1)$$

where $\sum_\nu$ goes over the unperturbed stationary states φ_ν of the system, including the bound states. For any time t_1 sufficiently far in the future the system is represented by the wave function

$$\psi(t_1) = \sum_\nu A'_\nu \varphi_\nu \exp(-iE_\nu t_1/\hbar). \tag{2.7.2}$$

At any time t, whether in the past, present or future, the wave function is given by either (2.6.6), viz.

$$\psi(t) = \sum_\nu A_\nu \psi_\nu^+ \exp(-iE_\nu t/\hbar) \tag{2.7.3}$$

or by (2.6.7), viz.

$$\psi(t) = \sum_\nu A'_\nu \psi_\nu^- \exp(-iE_\nu t/\hbar). \tag{2.7.4}$$

The quantities A_ν and A'_ν are the probability amplitudes for the state φ in the remote past or future. The ψ_ν^+ and ψ_ν^- form two complete sets of orthonormal eigenstates of H. We can remember these results by noting that in *evolution from* φ_ν is replaced by ψ_ν^+, while in *evolution into* φ_ν is replaced by ψ_ν^-.

The fundamental problem when considering the dynamics of a system is to be able to predict the future of the system when we know its past. Since we are dealing with a quantum mechanical system we cannot predict with certainty how any particular reaction will proceed, but we are concerned, given the initial state of the reactants, with the problem of predicting what reactions may take place and with what probabilities. The key to the solution of this problem is the so-called scattering matrix, and this is the concept which we will introduce in this section. The discussion of practical methods of actually calculating such probabilities will be postponed to subsequent chapters.

If we replace the summation index ν in (3) or (4) by α, then put $t = 0$, we obtain

$$\sum_\alpha A'_\alpha \psi_\alpha^- = \sum_\alpha A_\alpha \psi_\alpha^+, \tag{2.7.5}$$

since both sides equal $\psi(0)$. If we take the scalar product of this on the left with ψ_β^- and use the orthogonality property of the scattering states in the form $\langle \psi_\beta^- \mid \psi_\alpha^- \rangle = \delta_{\beta\alpha}$ we obtain

$$A'_\beta = \sum_\alpha \langle \psi_\beta^- \mid \psi_\alpha^+ \rangle A_\alpha. \tag{2.7.6}$$

Let us define a quantity $S_{\beta\alpha}$ by

$$\boxed{S_{\beta\alpha} = \langle \psi_\beta^- \mid \psi_\alpha^+ \rangle.} \tag{2.7.7}$$

We can now rewrite (6) as

$$\boxed{A'_\beta = \sum_\alpha S_{\beta\alpha} A_\alpha.} \tag{2.7.8}$$

(8) has the form of a matrix equation. The "column vector" of probability amplitudes A_α for the various states of free motion of the particles of the various arrangement channels of the system in the initial state is transformed into the column vector of corresponding probability amplitudes A'_β in the final state by multiplication by the matrix $S_{\beta\alpha}$ whose elements are defined by (7). If the matrix $S_{\beta\alpha}$ is known, the state of the system after the reaction can be, in principle, calculated if the initial state before the reaction is known. For this reason $S_{\beta\alpha}$ is known as the *Scattering Matrix.*

We can define a scattering operator S by the expression

$$\mathsf{S} = \sum_\nu |\psi_\nu^+\rangle\langle\psi_\nu^-|; \tag{2.7.9}$$

for it follows immediately from the orthonormality of the $\psi_\nu^\pm$, (7) and (9) that

$$\begin{aligned}\langle\psi_\beta^- |\mathsf{S}|\psi_\alpha^-\rangle &= \sum_\nu \langle\psi_\beta^-|\psi_\nu^+\rangle\langle\psi_\nu^-|\psi_\alpha^-\rangle = \sum_\nu \langle\psi_\beta^-|\psi_\nu^+\rangle\,\delta_{\nu\alpha}\\ &= \langle\psi_\beta^-|\psi_\alpha^+\rangle = S_{\beta\alpha},\end{aligned} \tag{2.7.10}$$

and similarly

$$\langle\psi_\beta^+|\mathsf{S}|\psi_\alpha^+\rangle = S_{\beta\alpha}. \tag{2.7.11}$$

In other words, the scattering matrix $S_{\beta\alpha}$ is just the matrix of the operator S relative to either the complete orthonormal set of the ψ_ν^+ or relative to the complete orthonormal set of the ψ_ν^-.

The scattering matrix is unitary. For from (7) and the completeness of the ψ_ν^-

$$\begin{aligned}(\mathsf{S}^\dagger\mathsf{S})_{\beta\alpha} &= \sum_\nu \mathsf{S}^\dagger_{\beta\nu}\mathsf{S}_{\nu\alpha} = \sum_\nu \mathsf{S}^*_{\nu\beta}\mathsf{S}_{\nu\alpha} = \sum_\nu \langle\psi_\nu^-|\psi_\beta^+\rangle^*\langle\psi_\nu^-|\psi_\alpha^+\rangle\\ &= \sum_\nu \langle\psi_\beta^+|\psi_\nu^-\rangle\langle\psi_\nu^-|\psi_\alpha^+) = \langle\psi_\beta^+|\psi_\alpha^+\rangle = \delta_{\beta\alpha}.\end{aligned} \tag{2.7.12}$$

Similarly $(\mathsf{SS}^\dagger)_{\beta\alpha} = \delta_{\beta\alpha}$, and so we conclude that

$$\boxed{\mathsf{S}^\dagger\mathsf{S} = \mathsf{SS}^\dagger = 1;} \tag{2.7.13}$$

in other words, S is unitary. The unitarity of S has, in effect, been deduced from the postulate (2.2.1); since this says that any past or future observation will show the system to be in some free state φ_ν we expect probability to be conserved, as expressed by (2.2.10). This is ensured by unitarity, for from (8)

$$\begin{aligned}\sum_{\beta} | A'_{\beta} |^2 &= \sum_{\beta} A'^{*}_{\beta} A'_{\beta} = \sum_{\beta}\sum_{\alpha} S^{*}_{\beta\alpha} A^{*}_{\alpha} \sum_{\gamma} S_{\beta\gamma} A_{\gamma} \\ &= \sum_{\alpha}\sum_{\gamma} A^{*}_{\alpha} A_{\gamma} \sum_{\beta} S^{\dagger}_{\alpha\beta} S_{\beta\gamma} = \sum_{\alpha}\sum_{\gamma} A^{*}_{\alpha} A_{\gamma}\, \delta_{\alpha\gamma} \\ &= \sum_{\alpha} | A_{\alpha} |^2 = 1. \qquad (2.7.14)\end{aligned}$$

Before we proceed to the physical interpretation of the scattering operator S defined by (9) we note two of its properties. Firstly it follows from (9) that

$$\mathsf{S}\psi_{\nu}^{-} = \sum_{\mu} \psi_{\mu}^{+} \langle \psi_{\mu}^{-} | \psi_{\nu}^{-} \rangle = \sum_{\mu} \psi_{\mu}^{+} \delta_{\mu\nu} = \psi_{\nu}^{+}. \qquad (2.7.15)$$

Secondly, if $f(\mathsf{H})$ is any function of H we see from (9) that

$$f(\mathsf{H})\,\mathsf{S} = \sum_{\nu} f(E_{\nu})\,| \psi_{\nu}^{+} \rangle \langle \psi_{\nu}^{-} |, \qquad (2.7.16)$$

$$\mathsf{S} f(\mathsf{H}) = \sum_{\nu} | \psi_{\nu}^{+} \rangle \langle \psi_{\nu}^{-} | f(E_{\nu}), \qquad (2.7.17)$$

and so

$$f(\mathsf{H})\,\mathsf{S} = \mathsf{S} f(\mathsf{H}). \qquad (2.7.18)$$

In other words S commutes with every function of H.

We can now discuss the physical interpretation of the scattering operator. The state $\sum_{\nu} A_{\nu}\psi_{\nu}^{-}$ at time $t = 0$ evolves into the state $\sum_{\nu} A_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar)$ at time t_1, and so

$$\exp(-i\mathsf{H}t_1/\hbar) \sum_{\nu} A_{\nu}\psi_{\nu}^{-} = \sum_{\nu} A_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar). \qquad (2.7.19)$$

If we operate on (19) with S and use the fact that S commutes with any function of H we get

$$\exp(-i\mathsf{H}t_1/\hbar) \sum_{\nu} A_{\nu}\mathsf{S}\psi_{\nu}^{-} = \mathsf{S} \sum_{\nu} A_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar). \qquad (2.7.20)$$

We can substitute for $\mathsf{S}\psi_{\nu}^{-}$ from (15) into (20) to obtain

$$\mathsf{S} \sum_{\nu} A_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar) = \exp(-i\mathsf{H}t_1/\hbar) \sum_{\nu} A_{\nu}\psi_{\nu}^{+}. \qquad (2.7.21)$$

Now $\sum_{\nu} A_{\nu}\psi_{\nu}^{+} = \bar{\varphi}(0)$ develops into $\sum_{\nu} A'_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t/\hbar)$, for A'_{ν} is the final probability amplitude, and since t_1 is a time in the remote future (21) becomes

$$\boxed{\mathsf{S} \sum_{\nu} A_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar) = \sum_{\nu} A'_{\nu}\varphi_{\nu} \exp(-iE_{\nu}t_1/\hbar).} \qquad (2.7.22)$$

The result (22) shows that S *transforms the state that would have emerged if there had been no interaction into that which actually emerges.*

The bound states $\psi_b = \varphi_b$ are orthonormal, and orthogonal to the scattering states, while $\psi_b^- = \psi_b^+ = \psi_b$; hence particular cases of the definition (7) are:

$$S_{b,\,b'} = \langle \psi_b | \psi_{b'} \rangle = \delta_{b,\,b'}, \tag{2.7.23}$$

$$S_{b,\,\mathbf{k}n} = \langle \psi_b | \psi_{\mathbf{k}n}^+ \rangle = 0, \tag{2.7.24}$$

$$S_{\mathbf{k}n,\,b} = \langle \psi_{\mathbf{k}n}^- | \psi_b \rangle = 0. \tag{2.7.25}$$

The results (23) to (25) may be expressed by the single formula

$$S_{b\nu} = S_{\nu b} = \delta_{b\nu}. \tag{2.7.26}$$

It follows from (26) and (8) that

$$A_b' = \sum_\alpha S_{b\alpha} A_\alpha = \sum_\alpha \delta_{b\alpha} A_\alpha = A_b, \tag{2.7.27}$$

so that the probability amplitudes of the bound states are unaltered by the collision. This is not surprising, however, for it means no more than that a bound state is stable, which it certainly must be. A metastable particle which decays into products with time is not, in fact, a bound state, but a superposition of continuum states forming a wave packet which remains localized for an unusually long time. The result (27) is therefore a confirmation of the general theory.

EXERCISES

1. Verify (11).
2. Prove that $(SS^\dagger)_{\beta\alpha} = \delta_{\beta\alpha}$.

REFERENCES

Mott, N. F. and Massey, H. S. W. (1965) *The Theory of Atomic Collisions*, Clarendon Press, Oxford.

Taylor, J. R. (1972) *Scattering Theory: The Quantum Theory on Nonrelativistic Collisions*, J. Wiley & Sons.

CHAPTER 3

TRANSITION RATES

3.1. THE WAVE OPERATORS

We started by discussing the stationary states of a system of N elementary particles in its various arrangement channels, in the first place when the composite particles move freely, and in the second place when their mutual interactions are taken into account. Having done this we considered the evolution in time of such a system, and this led to the concepts of the scattering operator and scattering matrix. The definitions (2.7.7) and (2.7.9) of the scattering matrix and scattering operator arise naturally from a study of the dynamics of the system, but are not in a form useful for actually calculating the probabilities of various collision and reaction processes taking place. It will be the object of this chapter to derive expressions which will enable us to perform actual calculations.

Let us define operators $\Omega_i^{\pm}(E)$ by the expression

$$\Omega_i^{\pm}(E) = 1+(E-\mathsf{H}\pm i\varepsilon)^{-1}V_i. \tag{3.1.1}$$

where ε is a small positive number which is usually allowed to tend to zero at the end of any calculation. (1) defines an *operator-valued function* of the energy; given the arrangement channel i, the operator is specified once the variable parameter E (which has the dimensions of energy) is defined. It follows immediately from (1) and (1.5.1) that

$$\psi_\nu^{\pm} = \Omega_i^{\pm}(E_\nu)\,\varphi_\nu \qquad (\nu \text{ in } i), \tag{3.1.2}$$

where ν in i means that φ_ν is an unperturbed stationary state of arrangement channel i. In other words the operators $\Omega_i^{\pm}(E)$ transform any unperturbed state φ_ν of arrangement channel i into the scattering states $\psi_\nu^{\pm}$ provided $E = E_\nu$. The operators $\Omega_i^{\pm}(E)$ are known as the "Möller operators" or "Wave operators".[†]

Energy-independent operators $\Omega_i^{\pm}$ may be defined as follows:

$$\Omega_i^{\pm} = \sum_{\nu \text{ in } i} |\psi_\nu^{\pm}\rangle\langle\varphi_\nu| \tag{3.1.3}$$

[†] The wave operators are discussed in the simpler context of potential scattering in Volume 4, p. 88.

where the summation goes over those unperturbed states φ_ν which belong to arrangement channel i. From (2) and (3) and the orthonormality of the φ_ν's belonging to the same arrangement channel we see that

$$\Omega_i^\pm \varphi_\nu = \psi_\nu^\pm = \Omega_i^\pm(E_\nu)\,\varphi_\nu \qquad (\nu \text{ in } i); \tag{3.1.4}$$

that is, $\Omega_i^\pm$ and $\Omega_i^\pm(E_\nu)$ coincide when operating upon the unperturbed state φ_ν of arrangement channel i. In time-independent theory this is normally the important case and we then often do not distinguish between them. The $\Omega_i^\pm$ defined by (3) are also referred to as Möller operators or wave operators. In the remainder of this section we will be concerned with wave packets. These have a spread in energy, and so we shall concentrate on the energy-independent operators defined by (3).

The Möller operators are closely connected with the time development of the system considered in Section 2.4. Firstly we note that

$$\mathsf{U}_i(0,\, t)(\lambda\bar{\psi}+\mu\bar{\varphi}) = \lambda\mathsf{U}_i(0,\, t)\,\bar{\psi}+\mu\mathsf{U}_i(0,\, t)\,\bar{\varphi} \tag{3.1.5}$$

where $\bar{\psi}$, $\bar{\varphi}$ are any elements of Hilbert space. It follows from (5) that if $\mathsf{U}_i(0,\, t)\bar{\psi}$ and $\mathsf{U}_i(0,\, t)\bar{\varphi}$ have limits as $t \to \mp\infty$ then

$$\mathsf{U}_i(0,\, \mp\infty)(\lambda\bar{\psi}+\mu\bar{\varphi}) = \lambda\mathsf{U}_i(0,\, \mp\infty)\,\psi+\mu\mathsf{U}_i(0,\, \mp\infty)\,\bar{\varphi}, \tag{3.1.6}$$

and so $\mathsf{U}_i(0,\, \mp\infty)$ is also a linear operator. It therefore follows from (2.4.34) that

$$\sum_{n \text{ in } i} B_n\bar{\psi}_n^\pm(0) = \mathsf{U}_i(0,\, \mp\infty)\sum_{n \text{ in } i} B_n\bar{\varphi}_n(0) \tag{3.1.7}$$

provided the summation is confined to internal states χ_n of arrangement channel i, as indicated. If we substitute for $\bar{\psi}_n^\pm(0)$ and $\bar{\varphi}_n(0)$ from (2.4.30) and (2.4.3) we obtain

$$\sum_{n \text{ in } i} \int d\mathbf{k}\, B_n C_n(\mathbf{k})\,\psi_{\mathbf{k}n}^\pm = \mathsf{U}_i(0,\, \mp\infty)\sum_{n \text{ in } i} \int d\mathbf{k}\, B_n C_n(\mathbf{k})\,\varphi_{\mathbf{k}n}; \tag{3.1.8}$$

(8) can be abbreviated to

$$\sum_{\nu \text{ in } i} A_\nu\psi_\nu = \mathsf{U}_i(0,\, \mp\infty)\sum_{\nu \text{ in } i} A_\nu\varphi_\nu. \tag{3.1.9}$$

Since $\psi_\nu^\pm = \Omega_i\varphi_\nu$ when ν in i it follows from (9) that

$$\Omega_i^\pm \sum_{\nu \text{ in } i} A_\nu\varphi_\nu = \mathsf{U}_i(0,\, \mp\infty)\sum_{\nu \text{ in } i} A_\nu\varphi_\nu. \tag{3.1.10}$$

We cannot conclude from (10) that $\mathsf{U}_i(0,\, \mp\infty) = \Omega_i^\pm$, for in general the φ_ν for a given arrangement channel are not complete—they do not include the ionized states of the composite particles $A_1, A_2, \ldots, A_m$. The exception to this is when $i = F$, the arrangement channel in which all the elementary particles are free. In this case the φ_ν form a complete set, and so

$$\Omega_F^{\pm} = \mathsf{U}_F(0, \mp\infty). \tag{3.1.11}$$

If we make use of (2.3.5) we see that (11) can be written

$$\Omega_F^{\pm} = \lim_{t\to\mp\infty} \exp(i\mathsf{H}t/\hbar)\exp(-i\mathsf{H}_F t/\hbar). \tag{3.1.12}$$

By use of (2.3.5) we can write the result (10) as

$$\Omega_i^{\pm} \sum_{\nu \text{ in } i} A_\nu \varphi_\nu = \lim_{t\to\mp\infty} \exp(i\mathsf{H}t/\hbar)\exp(-i\mathsf{H}_i t/\hbar) \sum_{\nu \text{ in } i} A_\nu \varphi_\nu. \tag{3.1.13}$$

This result forms the basis of a mathematically rigorous treatment of the subject. It becomes a matter of showing that if $\bar{\varphi}_i$ describes a state of free motion governed by the Hamiltonian H_i, and $\mathsf{H} = \mathsf{H}_i + V_i$ is the full Hamiltonian, then $\exp(i\mathsf{H}t/\hbar)\exp(-i\mathsf{H}_i t/\hbar)\bar{\varphi}_i$ has a limit as $t \to \mp\infty$ in the sense that there are states $\bar{\psi}^{\pm}$ for which $\| \bar{\psi}^{\pm} - \exp(i\mathsf{H}t/\hbar)\exp(i\mathsf{H}_i t/\hbar)\bar{\varphi}_i \| \to 0$ as $t \to \mp\infty$ (Taylor, 1972, chapter 16). In the case when $i = F$, H_F is just the kinetic energy operator, and we obtained the result (12). The precise sense in which this is true is that $\exp(i\mathsf{H}t/\hbar)\exp(-i\mathsf{H}_F t/\hbar)\,\bar{\psi}$ has a well-defined limit for every $\bar{\psi}$ in Hilbert space.

EXERCISES

1. Prove that, for any arrangement channel i,

$$\Omega_i^{\pm\dagger}\Omega_i^{\pm} = \sum_{\nu \text{ in } i} |\varphi_\nu\rangle\langle\varphi_\nu|.$$

$$\Omega_i^{\pm}\Omega_i^{\pm\dagger} = \sum_{\nu \text{ in } i} |\psi_\nu^{\pm}\rangle\langle\psi_\nu^{\pm}|.$$

2. Prove that, for the arrangement channel F in which all elementary particles are free,

$$\Omega_F^{\pm\dagger}\Omega_F^{\pm} = 1,$$

$$\Omega_F^{\pm}\Omega_F^{\pm\dagger} = \sum_{\nu \text{ in } F} |\psi_\nu^{\pm}\rangle\langle\psi_\nu^{\pm}|.$$

Deduce that $\Omega_F^{\pm}$ preserves scalar products.

3. Prove that if the forces between the elementary particles are all repulsive then the wave operators are unitary.

3.2. CALCULATION OF THE SCATTERING MATRIX

In Section 2.7 we defined the scattering matrix $S_{\beta\alpha}$ and calculated its elements when one or both of φ_β, φ_α are bound states of the whole system. As we saw the result, viz. (2.7.26), is not the physically interesting one (although it provides a useful check on the consistency of the theory). In this section we shall obtain an expression for the elements $S_{\mathbf{l}p,\mathbf{k}n}$ of the scattering matrix between two scattering states specified by the quantum numbers $\mathbf{k}n$ (channel i) and $\mathbf{l}p$ (channel f).

The scattering matrix $S_{\beta\alpha}$ is defined by (2.7.7). We can rewrite this, using the orthonormality of the Schwinger–Lippmann states, as

$$S_{\beta\alpha} = \langle\psi_\beta^+ \mid \psi_\alpha^+\rangle + \langle\psi_\beta^- - \psi_\beta^+ \mid \psi_\alpha^+\rangle = \delta_{\beta\alpha} + \langle\psi_\beta^- - \psi_\beta^+ \mid \psi_\alpha^+\rangle, \tag{3.2.1}$$

or as

$$S_{\beta\alpha} = \langle\psi_\beta^- \mid \psi_\alpha^-\rangle + \langle\psi_\beta^- \mid \psi_\alpha^+ - \psi_\alpha^-\rangle = \delta_{\beta\alpha} + \langle\psi_\beta^- \mid \psi_\alpha^+ - \psi_\alpha^-\rangle. \tag{3.2.2}$$

Let us calculate $\langle\psi_\beta^- - \psi_\beta^+ \mid \psi_\alpha^+\rangle$ when $\beta = \mathbf{l}p, \alpha = \mathbf{k}n$. We do this by putting

$$\bar{\varphi} = \int C(\mathbf{k})\, \psi_{\mathbf{k}n}^+\, d\mathbf{k} \tag{3.2.3}$$

and considering $\langle\psi_{\mathbf{l}p}^- - \psi_{\mathbf{l}p}^+ \mid \bar{\varphi}\rangle$. From (1.5.1) with $E = E_\nu = E_{\mathbf{l}p}$ we have

$$\begin{aligned} \langle\psi_{\mathbf{l}p}^- - \psi_{\mathbf{l}p}^+ \mid \bar{\varphi}\rangle &= \langle[(E_{\mathbf{l}p} - \mathsf{H} - i\varepsilon)^{-1} - (E_{\mathbf{l}p} - \mathsf{H} + i\varepsilon)^{-1}]\, V_f \varphi_{\mathbf{l}p} \mid \bar{\varphi}\rangle \\ &= \langle\varphi_{\mathbf{l}p} \mid V_f[(E_{\mathbf{l}p} - \mathsf{H} + i\varepsilon)^{-1} - (E_{\mathbf{l}p} - \mathsf{H} - i\varepsilon)^{-1}] \mid \bar{\varphi}\rangle \\ &= \int C(\mathbf{k})\langle\varphi_{\mathbf{l}p} \mid V_f[(E_{\mathbf{l}p} - E_{\mathbf{k}n} + i\varepsilon)^{-1} - (E_{\mathbf{l}p} - E_{\mathbf{k}n} - i\varepsilon)^{-1}] \mid \psi_{\mathbf{k}n}^+\rangle\, d\mathbf{k} \end{aligned} \tag{3.2.4}$$

on use of (3). From (3) and (4) we see that

$$\int C(\mathbf{k})\langle\psi_{\mathbf{l}p}^- - \psi_{\mathbf{l}p}^+ \mid \psi_{\mathbf{k}n}^+\rangle\, d\mathbf{k} = \int C(\mathbf{k})\, \frac{-2i\varepsilon}{(E_{\mathbf{l}p} - E_{\mathbf{k}n})^2 + \varepsilon^2}\, \langle\varphi_{\mathbf{l}p} \mid V_f \mid \psi_{\mathbf{k}n}^+\rangle\, d\mathbf{k}. \tag{3.2.5}$$

It is easy to see that as $\varepsilon \to 0+$ an expression of the form

$$\frac{\varepsilon}{x^2 + \varepsilon^2} \tag{3.2.6}$$

must tend to $\pi\delta(x)$; for if $x \neq 0$ the limit is zero, and the integral of the expression from $x = -\infty$ to $x = +\infty$ is π. If we insert this in (5) with $x = E_{\mathbf{l}p} - E_{\mathbf{k}p}$ we find that

$$\int C(\mathbf{k})\langle\psi_{\mathbf{l}p}^- - \psi_{\mathbf{l}p}^+ \mid \psi_{\mathbf{k}n}^+\rangle\, d\mathbf{k} = \int C(\mathbf{k})(-2\pi i)\, \delta(E_{\mathbf{l}p} - E_{\mathbf{k}n})\langle\varphi_{\mathbf{l}p} \mid V_f \mid \psi_{\mathbf{k}n}^+\rangle\, d\mathbf{k}, \tag{3.2.7}$$

and since $C(\mathbf{k})$ is arbitrary (7) implies

$$\langle\psi_{\mathbf{l}p}^- - \psi_{\mathbf{l}p}^+ \mid \psi_{\mathbf{k}n}^+\rangle = -2\pi i\delta(E_{\mathbf{l}p} - E_{\mathbf{k}n})\langle\varphi_{\mathbf{l}p} \mid V_f \mid \psi_{\mathbf{k}n}^+\rangle. \tag{3.2.8}$$

Insertion of this last result into (1) with $\beta = \mathbf{l}p$, $\alpha = \mathbf{k}n$, yields

$$S_{\mathbf{l}p,\,\mathbf{k}n} = \delta_{fi}\delta(\mathbf{l} - \mathbf{k})\, \delta_{pn} - 2\pi i\delta(E_{\mathbf{l}p} - E_{\mathbf{k}n})\langle\varphi_{\mathbf{l}p} \mid V_f \mid \psi_{\mathbf{k}n}^+\rangle. \tag{3.2.9}$$

When either φ_β or φ_α is a bound state of the system the quantity $\delta(E_\beta - E_\alpha)\times\langle\varphi_\beta| V_f | \psi_\alpha^+\rangle$ must vanish. For if φ_β is a bound state $V_f = 0$ and the result is obvious, while if φ_α is a bound state, $\psi_\alpha^+ = \varphi_\alpha$. Since $V_f = \mathsf{H} - \mathsf{H}_f$ we have in the latter case $\langle\varphi_\beta| V_f |\psi_\alpha^+\rangle = \langle\varphi_\beta | \mathsf{H} - \mathsf{H}_f | \varphi_\alpha\rangle$. Now φ_α is a bound state, so is negligible outside some finite volume of configuration space, and hence H, H_f must be Hermitian between φ_β and φ_α. Since $\mathsf{H}_f\varphi_\beta = E_\beta\varphi_\beta$ and $\mathsf{H}\varphi_\alpha = E_\alpha\varphi_\alpha$ it follows that

$$\langle\varphi_\beta | V_f | \psi_\alpha^+\rangle = \langle\varphi_\beta | \mathsf{H} - \mathsf{H}_f | \varphi_\alpha\rangle = (E_\beta - E_\alpha)\langle\varphi_\beta | \varphi_\alpha\rangle \tag{3.2.10}$$

and so

$$\delta(E_\beta - E_\alpha)\langle\varphi_\beta | V_f | \psi_\alpha^+\rangle = \delta(E_\beta - E_\alpha)(E_\beta - E_\alpha)\langle\varphi_\beta | \varphi_\alpha\rangle = 0. \tag{3.2.11}$$

Also $S_{\beta\alpha} = \delta_{\beta\alpha}$ if either either φ_β or φ_α is a bound state. Hence

$$S_{\beta\alpha} = \delta_{\beta\alpha} - 2\pi i\delta(E_\beta - E_\alpha)\langle\varphi_\beta | V_f | \psi_\alpha^+\rangle; \tag{3.2.12}$$

for if either φ_β or φ_α is a bound state (12) states that $S_{\beta\alpha} = \delta_{\beta\alpha}$, and if neither φ_β nor φ_α is a bound state (12) is equivalent to (9).

If the same type of argument is followed, but beginning with (2) rather than (1), the result

$$S_{\beta\alpha} = \delta_{\beta\alpha} - 2\pi i\delta(E_\beta - E_\alpha)\langle\psi_\beta^- | V_i | \varphi_\alpha\rangle \tag{3.2.13}$$

is obtained. The expressions (12) and (13) for the elements of the scattering matrix will form the starting point for our derivation of expressions for the differential cross-sections.

EXERCISE

Prove equation (13).

3.3. TRANSITION AMPLITUDES

In a scattering experiment the system is usually prepared in some definite state φ_α of arrangement channel i, say. φ_α will usually represent two composite particles, one at rest (the target), and the other moving towards it (the bombarding particle). Our problem is to discuss the likelihood of a transition from φ_α to some final state φ_β of arrangement channel f (consisting of two or more composite particles). To do this we have to introduce a quantity $T(\alpha \to \beta)$, known as the "transition amplitude" from the state φ_α to the state φ_β; we shall do this in this section.

We first introduce transition operators $\mathsf{T}_{fi}^{\pm}(E)$ according to

$$\mathsf{T}_{fi}^{+}(E) = V_f\Omega_i^{+}(E), \tag{3.3.1}$$

$$\mathsf{T}_{fi}^{-}(E) = \Omega_f^{-\dagger}(E)\, V_i. \tag{3.3.2}$$

It follows from (3.1.1) that

$$\mathsf{T}^{+}_{fi}(E) = V_f + V_f(E - \mathsf{H} + i\varepsilon)^{-1} V_i, \tag{3.3.3}$$

$$\mathsf{T}^{-}_{fi}(E) = V_i + V_f(E - \mathsf{H} + i\varepsilon)^{-1} V_i. \tag{3.3.4}$$

$\mathsf{T}^{\pm}_{fi}(E)$ are known as the transition operators for transitions from arrangement channel i to arrangement channel f at energy E.

As defined above the transition operators depend upon a variable parameter E having the dimensions of energy. They may be defined in an energy-independent way by the expressions

$$\mathsf{T}^{+}_{fi} = V_f \Omega_i^{+}, \tag{3.3.5}$$

$$\mathsf{T}^{-}_{fi} = \Omega_f^{-\dagger} V_i, \tag{3.3.6}$$

where Ω_i^{+} is given by (3.1.3) while, analogously,

$$\Omega_f^{-} = \sum_{\nu \text{ in } f} |\psi_\nu^{-}\rangle\langle\varphi_\nu|. \tag{3.3.7}$$

The quantities $T^{\pm}(\alpha \to \beta)$ are defined as the matrix elements

$$T^{+}(\alpha \to \beta) = \langle\varphi_\beta|\,\mathsf{T}^{+}_{fi}(E_\alpha)\,|\varphi_\alpha\rangle \qquad (\alpha \text{ in } i,\ \beta \text{ in } f), \tag{3.3.8}$$

$$T^{-}(\alpha \to \beta) = \langle\varphi_\beta|\,\mathsf{T}^{-}_{fi}(E_\beta)\,|\varphi_\alpha\rangle \qquad (\alpha \text{ in } i,\ \beta \text{ in } f). \tag{3.3.9}$$

We saw in Section 3.1 that $\Omega_i^{+}(E_\alpha)\varphi_\alpha = \psi_\alpha^{+}$ and so (1) and (8) imply that

$$T^{+}(\alpha \to \beta) = \langle\varphi_\beta|\,V_f\,|\psi_\alpha^{+}\rangle. \tag{3.3.10}$$

We also saw in Section 3.1 that $\psi_\alpha^{+} = \Omega_i^{+}\varphi_\alpha$; if we substitute this for ψ_α^{+} into (10), then use (5), we obtain

$$T^{+}(\alpha \to \beta) = \langle\varphi_\beta|\,T^{+}_{fi}\,|\varphi_\alpha\rangle. \tag{3.3.11}$$

Similarly (2) and (9) show that

$$T^{-}(\alpha \to \beta) = \langle\varphi_\beta|\,\Omega_f^{-\dagger}(E_\beta)\,V_i\,|\varphi_\alpha\rangle = \langle\Omega_f^{-}(E_\beta)\,\varphi_\beta\,|\,V_i\,|\,\varphi_\alpha\rangle \tag{3.3.12}$$

so that

$$T^{-}(\alpha \to \beta) = \langle\psi_\beta^{-}\,|\,V_i\,|\,\varphi_\alpha\rangle. \tag{3.3.13}$$

Since $\psi_\beta^{-} = \Omega_f^{-}\varphi_\beta$, (13) and (6) give

$$T^{-}(\alpha \to \beta) = \langle\varphi_\beta|\,\mathsf{T}^{-}_{fi}\,|\varphi_\alpha\rangle. \tag{3.3.14}$$

From (8) and (11) we see that

$$\langle\varphi_\beta|\,\mathsf{T}^{+}_{fi}(E_\alpha)\,|\varphi_\alpha\rangle = \langle\varphi_\beta|\,\mathsf{T}^{+}_{fi}\,|\varphi_\alpha\rangle, \tag{3.3.15}$$

while from (9) and (14)

$$\langle\varphi_\beta|\,\mathsf{T}^{-}_{fi}(E_\beta)\,|\varphi_\alpha\rangle = \langle\varphi_\beta|\,\mathsf{T}^{-}_{fi}\,|\varphi_\alpha\rangle; \tag{3.3.16}$$

that is to say, $T^+_{fi}(E_\alpha)$ and T^+_{fi} have the same matrix elements between φ_β and φ_α, and so do $T^-_{fi}(E_\beta)$ and T^-_{fi}. As we shall now show, these are in fact, the physically important matrix elements.

If we compare (3.2.12) and (3.2.13) we see that

$$\langle\varphi_\beta\,|V_f|\,\psi^+_\alpha\rangle = \langle\psi^-_\beta\,|V_i|\,\varphi_\alpha\rangle \qquad \text{when} \qquad E_\beta = E_\alpha. \qquad (3.3.17)$$

It therefore follows from (10) and (13) that

$$\boxed{\begin{aligned} T^+(\alpha\to\beta) &= \langle\varphi_\beta\,|V_f|\,\psi^+_\alpha\rangle = \langle\psi^-_\beta\,|V_i|\,\varphi_\alpha\rangle \\ &= T^-(\alpha\to\beta) \qquad \text{when} \qquad E_\beta = E_\alpha. \end{aligned}} \qquad (3.3.18)$$

If we denote the common value of the four terms in (18) by $T(\alpha\to\beta)$ we see that (3.2.12) and (3.2.13) may be replaced by

$$\boxed{S_{\beta\alpha} = \delta_{\beta\alpha} - 2\pi i\,\delta(E_\beta - E_\alpha)\,T(\alpha\to\beta)} \qquad (3.3.19)$$

since the second term on the right-hand side is only non-zero when $E_\beta = E_\alpha$.

The quantity $T(\alpha\to\beta)$ which appears in (19) is known as the "transition amplitude". When $S_{\beta\alpha} = \delta_{\beta\alpha}$ (2.7.8) implies that $A'_\beta = A_\beta$ and so in such a case the interaction is ineffective. The quantity $T(\alpha\to\beta)$ measures the effectiveness of the interaction, and this is the reason for its name.

We saw in Section 3.2 that the quantities $\langle\varphi_\beta|\,V_f\,|\psi^+_\alpha\rangle$ and $\langle\psi^-_\beta|\,V_i\,|\varphi_\alpha\rangle$ must vanish if either φ_β or φ_α is a bound state. It follows from (18) that $T(\alpha\to\beta)$ must vanish if either φ_α or φ_β is a bound state, and since the work of Section 2.7 showed that $S_{\beta\alpha} = \delta_{\beta\alpha}$ if either φ_α or φ_β is a bound state, it follows that (19) is true for all α and β.

The results of this section lead to a very useful corollary. If we take matrix elements of (3) and (4) between φ_β and φ_α and subtract we get

$$\begin{aligned} &\langle\varphi_\beta\,|\,\mathsf{T}^+_{fi}(E)\,|\,\varphi_\alpha\rangle - \langle\varphi_\beta\,|\,\mathsf{T}^-_{fi}(E)\,|\,\varphi_\alpha\rangle \\ &= \langle\varphi_\beta\,|V_f|\,\varphi_\alpha\rangle - \langle\varphi_\beta\,|V_i|\,\varphi_\alpha\rangle. \end{aligned} \qquad (3.3.20)$$

We have seen that the left-hand side of this equation vanishes when $E_\beta = E_\alpha = E$, and so therefore must the right-hand side; in other words:

$$\boxed{\text{If} \qquad E_\beta = E_\alpha, \qquad \langle\varphi_\beta\,|V_f|\,\varphi_\alpha\rangle = \langle\varphi_\beta\,|V_i|\,\varphi_\alpha\rangle.} \qquad (3.3.21)$$

This result will be very useful, for example, in our discussion of the Born approximation (Section 5.3).

EXERCISE

Verify equation (21) in the case of exchange scattering of electrons and hydrogen atoms. (You may assume that the mass of the proton is effectively infinite.)

3.4. CROSS-SECTIONS FOR TWO-PARTICLE COLLISIONS

Let us confine our attention for the time being to collisions of the form

$$A+B \to C+D. \tag{3.4.1}$$

"Direct collisions" are of the form

$$A+B \to A+B; \tag{3.4.2}$$

(2) is a special case of (1). If A and B have the same states as initially the collision is "elastic"; if the states of one or both are changed, the collision is called "inelastic". When the final pair of particles is different from the initial pair we have a "rearrangement collision". More generally, we can define elastic collisions as those in which the channel is unchanged, inelastic collisions as those in which a transition takes place between channels in the same arrangement channel, and rearrangement collisions as those in which a transition takes place between different arrangement channels.

The initial state of the system has the form

$$\varphi_{\mathbf{k}n}(\mathbf{r}_i, \mathbf{x}_i) = \varphi_{\mathbf{k}}(\mathbf{r}_i)\, \chi_n(\mathbf{x}_i) = (2\pi)^{-3/2} \exp(i\mathbf{k}\cdot\mathbf{r}_i)\, \chi_n(\mathbf{x}_i) \tag{3.4.3}$$

where $\mathbf{r}_i$ is the displacement of the centre of mass of A relative to the centre of mass of B (Fig. 3.1a), $\mathbf{x}_i$ denotes the internal coordinates of A and B, χ_n the initial internal state, $\hbar\mathbf{k}$ the initial momentum of A relative to B, and i labels the arrangement channel of A and B. The final state of the system has a corresponding form

$$\varphi_{\mathbf{l}p}(\mathbf{r}_f, \mathbf{x}_f) = \varphi_{\mathbf{l}}(\mathbf{r}_f)\, \chi_p(\mathbf{x}_f) = (2\pi)^{-3/2} \exp(i\mathbf{l}\cdot\mathbf{r}_f)\, \chi_p(\mathbf{x}_f). \tag{3.4.4}$$

We must now consider how we can define an experimentally determinable quantity which measures the rate at which the reaction (1) proceeds. In many collision experiments a uniform beam of the particles A is aimed at a target containing N_t particles in the path of the beam. The number of particles C emerging per unit time in the solid angle $d\hat{\mathbf{r}}_f$ in the direction of the unit vector $\hat{\mathbf{r}}_f$ relative to the recoil particle D when the internal state of the product particles is χ_p is measured (Fig. 3.1b). Under suitable experimental conditions this is found to be proportional to N_t, $d\hat{\mathbf{r}}_f$ and the "incident flux" I; the incident flux I is the number of particles per unit time crossing a unit area placed transverse to the beam. Since we suppose the incident beam to be uniform, I must be independent of the position of the unit area. The number $N(\mathbf{k}n \to \hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f$ of pairs C, D emerging per unit time in $d\hat{\mathbf{r}}_f$ with displacement $\hat{\mathbf{r}}_f$ of C relative to D, the internal state being χ_p, is therefore of the form

$$N(\mathbf{k}n \to \hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f = \sigma(\mathbf{k}n \to \mathbf{r}_f p)\, I N_t\, d\hat{\mathbf{r}}_f \tag{3.4.5}$$

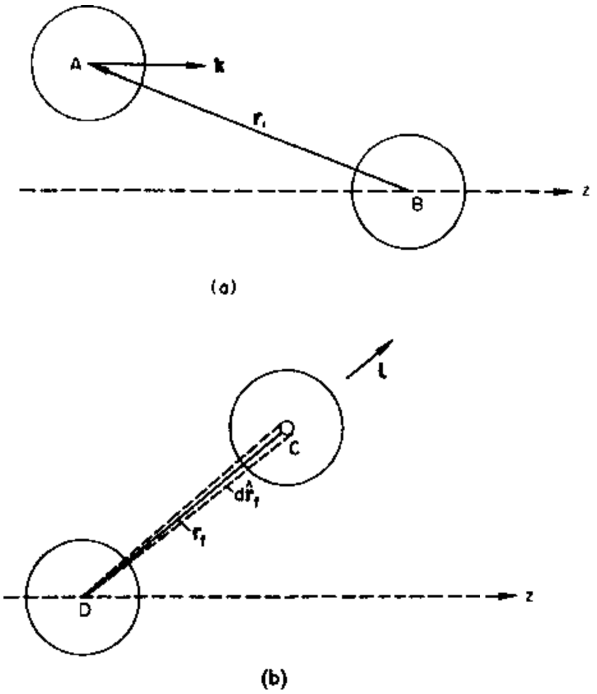

FIG. 3.1. Configuration of the system (a) before the collision, (b) after the collision.

where $\sigma(\mathbf{k}n \to \hat{\mathbf{r}}_f p)$ is a quantity known as the *differential cross-section* rof the process. The fact that $N(\mathbf{k}n \to \hat{\mathbf{r}}_f p)$ is proportional to both I and N_t means that the collisions are independent; there are no multiple collisions, nor do the particles of the incident beam or of the target interfere with each other. It is therefore possible for us to evaluate the probability of the process $\varphi_{\mathbf{k}n} \to \varphi_{\mathbf{l}p}$ for a single collision, and hence evaluate $\sigma(\mathbf{k}n \to \hat{\mathbf{r}}_f p)$ from (5).

The cross-section for the process $\chi_n \to \chi_p$ is given by

$$\sigma(\mathbf{k}n \to p) = \int \sigma(\mathbf{k}n \to \hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f \tag{3.4.6}$$

where the integral is taken over the unit sphere. From (5) and (6) we can see that $IN_t\sigma(\mathbf{k}n \to p)$ is just the number of pairs of particles C and D produced in the internal state χ_p. If we sum this over all energetically possible final states χ_p we obtain the cross-section $\sigma(\mathbf{k}n \to f)$ where

$$\sigma(\mathbf{k}n \to f) = \sum_{p \text{ in } f}{}' \sigma(\mathbf{k}n \to p) = \sum_{p \text{ in } f}{}' \int d\hat{\mathbf{r}}_f \sigma(\mathbf{k}n \to \hat{\mathbf{r}}_f p). \tag{3.4.7}$$

In (7) $\sum'_{p \text{ in } f}$ means summation over the energetically allowed channels of f. From (5) and (7) we see that $IN_t\sigma(\mathbf{k}n \to f)$ is just the number of pairs C and D produced per unit time, and is consequently closely related to the rate constant for the reaction (Bunker, 1966).

3.5. EVALUATION OF TWO-PARTICLE CROSS-SECTIONS

We shall now obtain the relationship between the cross-sections defined in Section 3.4 and the transition amplitudes defined in Section 3.3. To do this we will first consider the initial state of the system, which must have the form

$$\bar{\varphi}_n(\mathbf{r}_i, \mathbf{x}_i, t) = \bar{\varphi}(\mathbf{r}_i, t)\,\chi_n(\mathbf{x}_i)\exp(-iE_n t/\hbar) \tag{3.5.1}$$

where

$$\varphi(\mathbf{r}_i, t) = (2\pi)^{-3/2}\int C(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}_i)\exp(-iE_k t/\hbar)\,d\mathbf{k}. \tag{3.5.2}$$

Certain experimental conditions which must be satisfied in a properly performed experiment will enable us to calculate the flux I. The work of Sections 3.1 to 3.3 will then enable us to calculate $N(\mathbf{k}_0 n \rightarrow \hat{\mathbf{r}}_f p)$, and hence the differential cross-section $\sigma(\mathbf{k}n \rightarrow \hat{\mathbf{r}}_f p)$, where $\mathbf{k}_0$ is the mean relative wave vector of the incident beam.

The initial wave packet is normalized to unity, and since this holds for all times we have

$$\int |\bar{\varphi}(\mathbf{r}_i, 0)|^2\,d\mathbf{r}_i = 1. \tag{3.5.3}$$

We suppose that the incident beam is parallel to the axis Oz of Cartesian coordinates $Oxyz$; the wave packet $\bar{\varphi}$ must therefore have a cross-section A perpendicular to Oz and possessing the shape of the diaphragm through which the incident beam is emitted (Fig. 3.2). It is thus possible to replace (3) by the equivalent expression

$$\iint_A dx\,dy\int_{-\infty}^{+\infty} dz\,|\bar{\varphi}(x, y, z, 0)|^2 = 1 \tag{3.5.4}$$

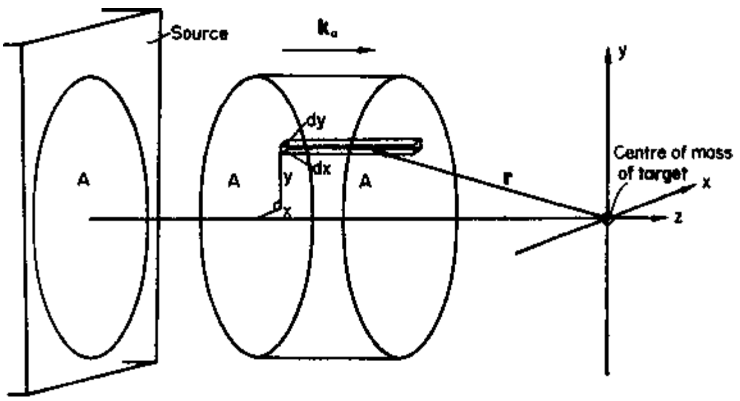

FIG. 3.2. The incident wave packet for motion relative to the target 0. The probability that $\mathbf{r}_i$ lies in the cylinder of cross-section $dxdy$ is independent of x and y.

where $\mathbf{r}_i$ has components (x, y, z) relative to $Oxyz$. Now the integral with respect to z is a function of x and y which, when multiplied by $dxdy$, gives the probability of the relative displacement $\mathbf{r}_i$ being in a cylinder of cross-section $dxdy$ and axis parallel to Oz (Fig. 3.2). In a properly performed scattering experiment the incident beam is uniform, and so this probability must be independent of x and y. We can therefore put $x = y = 0$ so that (4) becomes

$$\iint_{\mathrm{A}} dx\, dy \int_{-\infty}^{+\infty} dz\, |\bar{\varphi}(0, 0, z, 0)|^2 = 1. \tag{3.5.5}$$

The integrand of the double integral in (5) is independent of x and y, and so if we denote the area of A by A we obtain

$$A \int_{-\infty}^{+\infty} dz\, |\bar{\varphi}(0, 0, z, 0)|^2 = 1. \tag{3.5.6}$$

If we substitute for $\bar{\varphi}(0, 0, z, 0)$ in (6) from (2) we obtain

$$1 = A(2\pi)^{-3} \int_{-\infty}^{+\infty} dz \int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{+\infty} dk_y \int_{-\infty}^{+\infty} dk_z\, C^*(k_x, k_y, k_z) \exp(-ik_z z) \times$$
$$\times \int_{-\infty}^{+\infty} dk'_x \int_{-\infty}^{+\infty} dk'_y \int_{-\infty}^{+\infty} dk'_z\, C(k'_x, k'_y, k'_z) \exp(ik'_z z).$$

Integration over z and then over k'_z yields

$$1 = A(2\pi)^{-2} \int_{-\infty}^{+\infty} dk_z \left| \int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{+\infty} dk_y\, C(k_x, k_y, k_z) \right|^2. \tag{3.5.7}$$

Let us suppose that N_b bombarding particles are emitted per unit time. The incident flux is then $I = N_b A^{-1}$, and so from (7) with the dummy variable of integration k_z replaced by k

$$I = N_b(2\pi)^{-2} \int_{-\infty}^{+\infty} dk \left| \int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{+\infty} dk_y\, C(k_x, k_y, k) \right|^2. \tag{3.5.8}$$

We have now calculated the incident flux; the next task is to calculate the probability $P(\hat{\mathbf{r}}_f p)$ of a particle C emerging in the direction relative to the recoil particle D specified by the unit vector $\hat{\mathbf{r}}_f$, the internal state of C and D being represented by χ_p. In order to do this we must first calculate the probability amplitude $A'_{\mathbf{l}p}$ of observing the final state $\varphi_{\mathbf{l}p}$. According to (2.7.8) this is given by

$$A'_{\mathbf{l}p} = \sum_n \int d\mathbf{k}\, S_{\mathbf{l}p,\, \mathbf{k}n} A_{\mathbf{k}n}, \tag{3.5.9}$$

where $\sum_n$ goes over all channels. By hypothesis we have only the initial internal state χ_n, and so the probability amplitude $A_{\mathbf{k}n}$ is just the momentum amplitude $C(\mathbf{k})$; hence (9) becomes

$$A'_{\mathbf{l}p} = \int S_{\mathbf{l}p,\,\mathbf{k}n}\, C(\mathbf{k})\, d\mathbf{k}. \tag{3.5.10}$$

The scattering matrix is given by (3.3.19) which in this case becomes

$$S_{\mathbf{l}p,\,\mathbf{k}n} = \delta_{fi}\delta_{pn}\delta(\mathbf{l}-\mathbf{k}) - 2\pi i\delta(E_{\mathbf{l}p}-E_{\mathbf{k}n})\, T(\mathbf{k}n \to \mathbf{l}p). \tag{3.5.11}$$

If we substitute (11) into (10) we obtain

$$A'_{\mathbf{l}p} = \delta_{fi}\delta_{pn}C(\mathbf{l}) - 2\pi i \int C(\mathbf{k})\,\delta(E_{\mathbf{l}p}-E_{\mathbf{k}n})\, T(\mathbf{k}n \to \mathbf{l}p)\, d\mathbf{k}. \tag{3.5.12}$$

In practice we need only consider cases when $C(\mathbf{l}) = 0$; for we will only observe elastic collisions ($f = i$, $p = n$) when the final velocity of C relative to D is not parallel to the incident beam. This implies that there is no probability of observation of the momentum $\hbar\mathbf{l}$ in the initial wave packet describing the state of motion of A relative to B in the incident beam, and so $|C(\mathbf{l})|^2 = 0$, whence $C(\mathbf{l}) = 0$. If $C(\mathbf{l})$ did not vanish the detector would, in fact, be swamped by the incident beam. We can therefore replace (12) by

$$A'_{\mathbf{l}p} = -2\pi i \int C(\mathbf{k})\,\delta(E_{\mathbf{l}p}-E_{\mathbf{k}n})\, T(\mathbf{k}n \to \mathbf{l}p)\, d\mathbf{k}, \tag{3.5.13}$$

which may also be written

$$A'_{\mathbf{l}p} = -2\pi i \int_0^\infty k^2\, dk \int d\hat{\mathbf{k}}\, C(k\hat{\mathbf{k}})\,\delta(E_{\mathbf{l}p}-E_{\mathbf{k}n})\, T(k\hat{\mathbf{k}}n \to \mathbf{l}p). \tag{3.5.14}$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$.

If we carry out the integration over k, and remember that $E_{\mathbf{k}n} = \hbar^2k^2/2\mu_i + E_n$, where μ_i is the reduced mass of A and B, this becomes

$$A'_{\mathbf{l}p} = -2\pi i\mu_i k\hbar^{-2} \int C(k\hat{\mathbf{k}})\, T(k\hat{\mathbf{k}}n \to \mathbf{l}p)\, d\hat{\mathbf{k}}. \tag{3.5.15}$$

In (15) k is determined by the condition $E_{\mathbf{k}n} = E_{\mathbf{l}p}$, which expresses the conservation of energy.[†] In a well-performed experiment collimation is sufficiently good to ensure that there is no variation in the transition amplitude $T(k\hat{\mathbf{k}}n \to \mathbf{l}p)$ as $\hat{\mathbf{k}}$ varies over the directions of the incident beam; in other words, as $\hat{\mathbf{k}}$ takes values for which $C(k\hat{\mathbf{k}}) \neq 0$. We can therefore replace $T(k\hat{\mathbf{k}}n \to \mathbf{l}p)$ in (15) by $T(k\hat{\mathbf{k}}_0 n \to \mathbf{l}p)$ where $\hat{\mathbf{k}}_0$ is the unit vector in the direction of Oz. T can then be taken outside the integral in (15), and so

$$A'_{\mathbf{l}p} = -2\pi i\mu_i k\hbar^{-2}\, T(k\hat{\mathbf{k}}_0 n \to \mathbf{l}p) \int C(k\hat{\mathbf{k}})\, d\hat{\mathbf{k}} \tag{3.5.16}$$

where $E_{\mathbf{k}n} = E_{\mathbf{l}p}$.

[†] It may happen that there is no k for which $E_{\mathbf{l}p} = E_{\mathbf{k}n}$, in which case $A'_{\mathbf{l}p} = 0$. Such a case would arise if the internal energy of the final particles C and D were less than the internal energy of the initial particles A and B. Then if $E_{\mathbf{l}} < E_n - E_p$, $E_{\mathbf{l}p} < E_{\mathbf{k}n}$ for all k. We shall assume that this is not the case here.

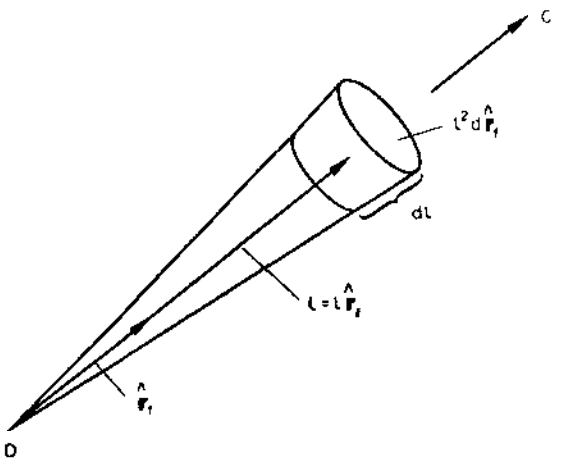

FIG. 3.3. The final relative wave vector $\mathbf{l}$ of C and D is defined by its magnitude l and direction, viz. that of the unit vector $\hat{\mathbf{r}}_f$. As $\mathbf{l}$ takes magnitudes between l and dl and directions in the solid angle $d\mathbf{r}_f$ it fills a volume element $d\mathbf{l}$ of cross-section $l^2\, d\mathbf{r}_f$ and length dl. The probability of observing $\mathbf{l}$ in the volume element $d\mathbf{l}$ is $|A'_{\mathbf{l}p}|^2\, d\mathbf{l}$, and so equals $|A'_{\mathbf{l}p}|^2\, l^2\, dl\, d\mathbf{r}_f$.

In order to calculate $P(\hat{\mathbf{r}}_f p)$ we note that the probability of observing the final wave vector $\mathbf{l}$ in the volume element $l^2 dl d\hat{\mathbf{r}}_f$ at the point $\mathbf{l} = l\hat{\mathbf{r}}_f$ of $\mathbf{l}$-space is $|A'_{\mathbf{l}p}|^2 l^2 dl d\hat{\mathbf{r}}_f$ (Fig. 3.3). It follows that the probability $P(\hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f$ of observing the final relative displacement being in the solid angle $d\hat{\mathbf{r}}_f$ along $\hat{\mathbf{r}}_f$ is

$$P(\hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f = d\hat{\mathbf{r}}_f \int_0^\infty l^2\, dl\, |A'_{\mathbf{l}p}|^2,$$

and so by (16), if we remember that $\mathbf{l} = l\hat{\mathbf{r}}_f$,

$$P(\hat{\mathbf{r}}_f p) = \int_0^\infty dl\, 4\pi^2 k^2 l^2 \mu_i^2 \hbar^{-4}\, |T(k\hat{\mathbf{k}}_0 n \to l\hat{\mathbf{r}}_f p)|^2\, \Big|\int C(k\hat{\mathbf{k}})\, d\hat{\mathbf{k}}\Big|^2. \quad (3.5.17)$$

Now $C(k\hat{\mathbf{k}}) \neq 0$ only if $k \simeq k_0$, and in a properly performed scattering experiment the energy resolution is sufficiently good to ensure that the modulus of the transition amplitude does not vary much for different energies in the incident beam. We can therefore replace $|T(k\hat{\mathbf{k}}_0 n \to \mathbf{l}\hat{\mathbf{r}}_f p)|$ in (17) by $|T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f p)$ where $\mathbf{k}_0 = k_0\hat{\mathbf{k}}_0$ and l_0 is obtained from k_0 by the energy conservation condition; $|T|^2$ can now be taken outside the integral sign in (17), which becomes

$$P(\hat{\mathbf{r}}_f p) = |2\pi\mu_i \hbar^{-2}\, T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f p)|^2 \int_0^\infty dl\, l^2 k^2 \Big|\int C(k\hat{\mathbf{k}})\, d\hat{\mathbf{k}}\Big|^2. \quad (3.5.18)$$

The unit vector $\hat{\mathbf{k}}$ is almost parallel to $\hat{\mathbf{k}}_0$ if $C(k\hat{\mathbf{k}}) \neq 0$ so we can put $d\hat{\mathbf{k}} = k_0^{-2}\, dk_x\, dk_y$ where (k_x, k_y, k_z) are the components of $k\hat{\mathbf{k}} = \mathbf{k}$ (Fig. 3.4).

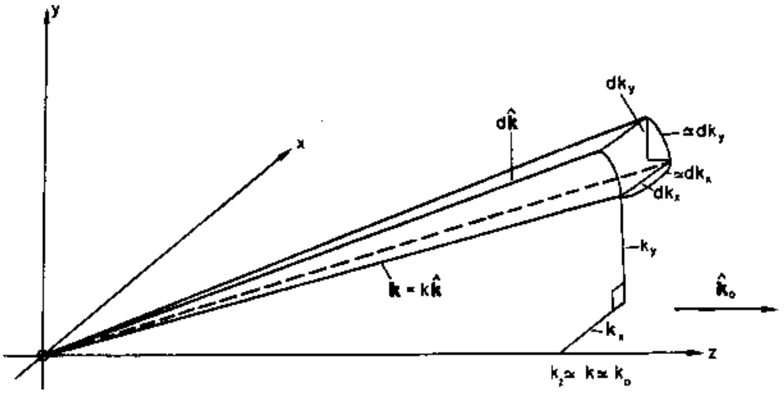

FIG. 3.4. The solid angle $d\mathbf{k}$ is generated by vectors $\mathbf{k}$ whose x and y components lie between k_x and k_x+dk_x, k_y and k_y+dk_y, respectively. Since the magnitudes of such vectors approximately equal k_0, while their directions are nearly parallel to $\hat{\mathbf{k}}_0$, the intercept that $d\hat{\mathbf{k}}$ makes with a sphere of radius k is approximately a rectangle perpendicular to Oz, and with sides of lengths dk_x and dk_y. It follows that $d\mathbf{k} \simeq dk_x\, dk_y/k_0$.

Hence

$$\int_0^\infty dl\, l^2k^2 \left| \int C(k\hat{\mathbf{k}})\, d\hat{\mathbf{k}} \right|^2 = \int_0^\infty dl\, l^2k^2k_0^{-4} \left| \iint dk_x\, dk_y\, C(k_x, k_y, k_z) \right|^2 \quad (3.5.19)$$

where the double integral inside the modulus signs on the right-hand side of (19) may be taken over all values of k_x and k_y, since C vanishes unless both k_x and k_y are very much less than k_0. The energy equation $E_{lp} = E_{kn}$ can be written more fully as

$$\frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2\mu_i}+E_n = \frac{\hbar^2l^2}{2\mu_f}+E_p \quad (3.5.20)$$

where μ_f is the reduced mass of C and D, and for fixed l this determines k_z as a function of k_x and k_y. If we differentiate (20) partially and implicitly with respect to k_x we see that $\partial k_z/\partial k_x = -(k_x/k_z)$, and this is obviously small if $C(k\hat{\mathbf{k}}) \neq 0$, since then $k_x \ll k_0$ and $k_z \simeq k_0$. Similarly $\partial k_z/\partial k_y$ is small, and so k_z may be regarded as independent of k_x and k_y, and given by (20) with $k_x = k_y = 0$; then $k_z = k$ where

$$\frac{\hbar^2k^2}{2\mu_i}+E_n = \frac{\hbar^2l^2}{2\mu_f}+E_p. \quad (3.5.21)$$

We can therefore replace k_z in (19) by k to obtain

$$\int_0^\infty dl\, l^2k^2 \left| \int d\hat{\mathbf{k}}\, C(k\hat{\mathbf{k}}) \right|^2 = \int_0^\infty dl\, l^2k^2k_0^{-4} \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2, \quad (3.5.22)$$

and from (21) we can replace l as the variable of integration by k. Now $C(k_x, k_y, k) = 0$ if k is less then the threshold value $[2\mu_i(E_p-E_n)/\hbar^2]^{1/2}$, otherwise the collision energy would be too close to zero for resolution. This threshold is the lower limit on k corresponding to $l = 0$. We can therefore extend the lower limit on the integration over k to $-\infty$ to obtain from (21) and (22)

$$\int_0^\infty dl\, l^2k^2 \left| \int d\hat{\mathbf{k}}\, C(k\hat{\mathbf{k}}) \right|^2 = \int_{-\infty}^{+\infty} dk\, \mu_f\mu_i^{-1} l k^3 k_0^{-4} \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2. \tag{3.5.23}$$

The momentum amplitude C vanishes unless $k \simeq k_0$, in which case by (21) $l = l_0$ where

$$\frac{\hbar^2 k_0^2}{2\mu_i} + E_n = \frac{\hbar^2 l_0^2}{2\mu_f} + E_p. \tag{3.5.24}$$

We can therefore replace (23) by

$$\int_0^\infty dl\, l^2k^2 \left| \int d\hat{\mathbf{k}}\, C(k\hat{\mathbf{k}}) \right|^2 = \mu_f\mu_i^{-1} l_0 k_0^{-1} \int_{-\infty}^{+\infty} dk \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2 \tag{3.5.25}$$

and hence from (18)

$$P(\hat{\mathbf{r}}_f p) = \mu_f\mu_i^{-1} l_0 k_0^{-1} \left| 2\pi\mu_i\hbar^{-2} T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f p) \right|^2 \times \\ \times \int_{-\infty}^{+\infty} dk \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2. \tag{3.5.26}$$

The number $N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p)\, d\hat{\mathbf{r}}_f$ of particles C emerging per unit time in the solid angle $(\hat{\mathbf{r}}_f, d\hat{\mathbf{r}}_f)$ with C and D in the internal state χ_p is given by

$$N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p) = N_b N_t P(\hat{\mathbf{r}}_f p) \tag{3.5.27}$$

since N_t is the number of target particles and N_b the number of bombarding particles per unit time, and so by (26)

$$N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p) = \mu_f\mu_i l_0 k_0^{-1} \left| 2\pi\hbar^{-2} T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f p) \right|^2 N_b N_t \times \\ \times \int_{-\infty}^{+\infty} dk \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2. \tag{3.5.28}$$

We have now obtained $N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p)$. The differential cross-section is given by (3.4.5), hence

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p) = I^{-1} N_t^{-1} N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p). \tag{3.5.29}$$

If we substitute for I and $N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p)$ in (29) from (8) and (28) we obtain

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p) = \mu_f\mu_i l_0 k_0^{-1} \left| 4\pi^2\hbar^{-2} T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f P) \right|^2. \tag{3.5.30}$$

(30) is the required relation between the differential cross-section and the transition amplitude.

The *scattering amplitude* $f(\mathbf{k}_0 n \to \mathbf{l}p)$ is defined by

$$\boxed{f(\mathbf{k}_0 n \to \mathbf{l}p) = (-4\pi^2\mu_f/\hbar^2)\,T(\mathbf{k}_0 n \to \mathbf{l}p).} \tag{3.5.31}$$

Since $\hbar k_0/\mu_i$ is the initial speed v_0 and $\hbar l_0/\mu_f$ is the final speed v_0' (31) enables us to rewrite (30) as

$$\boxed{\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_f p) = (v_0'/v_0)\,|f(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_f p)|^2.} \tag{3.5.32}$$

EXERCISES

1. If θ is the angle which the direction of the scattered particle makes with the direction of the incident particle, $\mathbf{k}$ and $\mathbf{l}$ are the initial and final relative wave vectors, and $\mathbf{q} = \mathbf{k}-\mathbf{l}$, show that

$$q^2 = k^2+l^2-2kl\cos\theta.$$

Explain why the scattering amplitude can only depend upon k and q if the problem has axial symmetry about the direction of the incident particle.

2. Use the results of Exercise 1 and (3.4.6) to show that if the collision is direct, and has axial symmetry about the direction of the incident particle, then the total cross-section $\sigma(\mathbf{k}n \to p)$ is given by

$$\sigma(\mathbf{k}n \to p) = \frac{2\pi}{k^2}\int\limits_{|l-k|}^{l+k} |f(q, k)|^2\, q\, dq,$$

where $f(q, k)$ is the scattering amplitude.

3.6. GENERAL PROCESSES

In the last section we obtained the expression (3.5.32) for the differential cross-section $\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}} p_f)$ for the two-particle process $A+B \to C+D$. Although in most reactions the initial state of the system consists of two particles, it is quite often the case that after the reaction there are more than two particles; for example, collisions in which one or both of the colliding particles are ionized. We can reduce these examples to that of Section 3.5 by choosing one of the resulting particles as the "recoil" particle. If we label it as C, the remaining particles may be grouped together and collectively labelled as D. We can denote by $\mathbf{r}_1$ the position vector of the centre of mass of C relative to the centre of mass of D, and by $\mathbf{l}$ the corresponding relative wave vector. The final state now takes the form

$$\varphi_{\mathbf{l}\kappa p}(\mathbf{r}_1, \mathbf{q}) = \varphi_{\mathbf{l}}(\mathbf{r}_1)\,\xi_{\kappa p}(\mathbf{q}) \tag{3.6.1}$$

where $\xi_{\varkappa p}$ is a product of δ-function normalized plane waves which describe the relative motion of the particles of D, $\boldsymbol{\varkappa} = (\boldsymbol{\varkappa}_2, \ldots, \boldsymbol{\varkappa}_{m-1})$ denoting the collection of wave vectors specifying the relative momenta of these particles, with the wave function χ_p representing the internal state. Here $\mathbf{q}$ denotes collectively the internal coordinates $\mathbf{x}_f$ and the relative displacements $\mathbf{r}_2, \ldots, \mathbf{r}_{m-1}$ of the particles of D.

The probability that the wave vector $\mathbf{l}$ for the motion of C relative to D lies in the volume element $d\mathbf{l} = l^2\, dl\, d\mathbf{r}_1$ while the relative wave vectors $\boldsymbol{\varkappa} = (\boldsymbol{\varkappa}_2, \ldots, \boldsymbol{\varkappa}_{m-1})$ lie in the volume elements $d\boldsymbol{\varkappa}_2, \ldots, d\boldsymbol{\varkappa}_{m-1}$, the internal state being represented by χ_p, is given by $|A'_{\mathbf{l}\varkappa p}|^2\, l^2\, dl\, d\hat{\mathbf{r}}_1\, d\boldsymbol{\varkappa}_2 \ldots d\boldsymbol{\varkappa}_{m-1}$ where $A'_{\mathbf{l}\varkappa p}$ is the amplitude for the final state $\varphi_{\mathbf{l}\varkappa p}$. We can therefore calculate the probability $P(\hat{\mathbf{r}}_1\varkappa p)\, d\hat{\mathbf{r}}_1\, d\boldsymbol{\varkappa}_2 \ldots d\boldsymbol{\varkappa}_{m-1}$ that the motion of C relative to D lies in the solid angle $d\hat{\mathbf{r}}_1$ along $\hat{\mathbf{r}}_1$ while the relative wave vectors $\boldsymbol{\varkappa}_2, \ldots, \boldsymbol{\varkappa}_{m-1}$ of the recoil particles lie in the volume elements $d\boldsymbol{\varkappa}_2$ at $\boldsymbol{\varkappa}_2, \ldots, d\boldsymbol{\varkappa}_{m-1}$ at $\boldsymbol{\varkappa}_{m-1}$, by integrating $|A'_{\mathbf{l}\varkappa p}|^2\, l^2\, dl$ from $l = 0$ to $l = \infty$. The calculation follows that of Section 3.5 with p replaced by $\varkappa p$, $\hat{\mathbf{r}}_f$ replaced by $\hat{\mathbf{r}}_1$, the product $d\boldsymbol{\varkappa}_2, \ldots, d\boldsymbol{\varkappa}_{m-1}$ inserted where appropriate, and so $P(\hat{\mathbf{r}}_1\varkappa p)$ will be given by (3.5.18) modified in the same way. Following the reasoning of Section 3.5 we find that the number $N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p)\, d\boldsymbol{\varkappa}_2 \ldots d\boldsymbol{\varkappa}_{m-1}$ of particles appearing in the solid angle $d\hat{\mathbf{r}}_1$ along $\hat{\mathbf{r}}_1$ per unit time is given by (3.5.28) modified as described; that is, by

$$\begin{aligned} N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p) = {} & \mu_f\mu_i l_0 k_0^{-1}\,|2\pi\hbar^{-2}\,T(\mathbf{k}_0 n \to \mathbf{l}_0\hat{\mathbf{r}}_1\varkappa p)|^2 \times \\ & \times N_b N_t \int_{-\infty}^{+\infty} dk\, \left| \iint dk_x\, dk_y\, C(k_x, k_y, k) \right|^2. \end{aligned} \tag{3.6.2}$$

In (2) l_0 is given by the energy conservation equation

$$\frac{\hbar^2 l_0^2}{2\mu_f} + E_{\varkappa p} = \frac{\hbar^2 l_0^2}{2\mu_f} + E_\varkappa + E_p = \frac{\hbar^2 k_0^2}{2\mu_i} + E_n \tag{3.6.3}$$

where $E_\varkappa$ is the total relative kinetic energy of the recoil particles, E_p the final internal energy of the particles, and μ_f the reduced mass of C relative to the recoil particles.

The differential cross-section $\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p)$ for the final state $\varphi_{\mathbf{l}\varkappa p}$ where $\mathbf{l} = l_0\hat{\mathbf{r}}_1$ is now naturally defined by

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p) = I^{-1} N_t^{-1} N(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p), \tag{3.6.4}$$

so that $IN_t\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p)\, d\hat{\mathbf{r}}_1\, d\boldsymbol{\varkappa}_2 \ldots d\boldsymbol{\varkappa}_{m-1}$ is the number of particles C appearing in the solid angle $d\hat{\mathbf{r}}_1$ per unit time along $\hat{\mathbf{r}}_1$ when the relative wave vectors lie in the volume elements $d\boldsymbol{\varkappa}_2$ at $\boldsymbol{\varkappa}_2, \ldots, d\boldsymbol{\varkappa}_{m-1}$ at $\boldsymbol{\varkappa}_{m-1}$. The expression (3.5.8) for I remains valid, and so we deduce from (2) and (4) that

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1\varkappa p) = \mu_f\mu_i l_0 k_0^{-1}\,|4\pi^2\hbar^{-2}\,T(\mathbf{k}_0 n \to l_0\hat{\mathbf{r}}_1\varkappa p)|^2. \tag{3.6.5}$$

The scattering amplitude is defined by (3.5.31) with p replaced by $\varkappa p$, that is by

$$f(\mathbf{k}_0 n \to \mathbf{l}\varkappa p) = (-4\pi^2\mu_f/\hbar^2)\,T(\mathbf{k}_0 n \to \mathbf{l}\varkappa p), \tag{3.6.6}$$

where μ_f is the reduced mass of C and D. As before we obtain the result

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1 \varkappa p) = (v_0'/v_0)\,|f(\mathbf{k}_0 n \to l_0 \hat{\mathbf{r}}_1 \varkappa p)|^2 \tag{3.6.7}$$

where v_0' is the speed of the scattered particle relative to the centre of mass of the recoil particles.

The flux into the solid angle $d\hat{\mathbf{r}}_1$ when the particle of arrangement channel f are in the internal state χ_p is clearly obtained by integrating over all energetically possible sets of values of $\varkappa_2, \ldots, \varkappa_{m-1}$, and so the differential cross-section $\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1 p)$ for the final internal state χ_p is given by

$$\sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1 p) = \int' d\varkappa_2 \ldots \int' d\varkappa_{m-1}\, \sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1 \varkappa p), \tag{3.6.8}$$

the primes signifying that the region of integration is that allowed by energy conservation; that is, the region for which $E_{\varkappa p}$ is less than or equal to $E - E_p$, where E is the total energy. The cross-section $\sigma(\mathbf{k}_0 n \to f)$ for production of particles in arrangement channel f is obviously obtained by forming the sum and integral

$$\sigma(\mathbf{k}_0 n \to f) = \sum_{p \text{ in } f}' \int d\hat{\mathbf{r}}_1\, \sigma(\mathbf{k}_0 n \to \hat{\mathbf{r}}_1 p) \tag{3.6.9}$$

where the primed sum goes over all energetically possible final internal states χ_p of arrangement channel f; that is, all states χ_p of f satisfying $E_p \leq E$.

EXERCISE

Hydrogen atoms in their ground state are ionized by electron impact. The initial wave vector of the incident electron is $\mathbf{k}$, and its final wave vector is $\mathbf{l}$, while $\mathbf{q} = \mathbf{k} - \mathbf{l}$. The momentum of the atomic electron relative to the proton after ionization is $\hbar\boldsymbol{\varkappa}$. Relative to spherical polar coordinates with $\mathbf{q}$ as polar axis $\boldsymbol{\varkappa}$ has coordinates $\varkappa$, χ, ψ. Explain why the scattering amplitude for the process can be expected to depend only upon k, q, $\varkappa$, χ and ψ at most.

Deduce that the ionization cross-section σ is given by

$$\sigma = \frac{2\pi}{k^2} \int_0^{\varkappa_0} \varkappa^2\, d\varkappa \int_{|k-k_\varkappa|}^{k+k_\varkappa} q\, dq \int_0^{2\pi} d\chi \int_0^{\pi} \sin\psi\, d\psi\, |f|^2$$

where

$$k_\varkappa^2 = k^2 - \varkappa^2 - 2mI/\hbar^2,$$

I being the ionization energy of the hydrogen atom, while

$$\varkappa_0 = (k^2 - 2mI/\hbar^2)^{1/2}.$$

(The mass of the proton may be taken as effectively infinite, and the mass of the electron is m.)

3.7. MIXED STATES

In many experiments the target beam consists of particles in different states; for example, in the case of ionized molecules produced in a furnace various vibrational levels may be populated. It is always assumed that such a mixture of states forms a statistical mixture, so that the differential cross-section measured in the laboratory is obtained by averaging over the initial states. Thus if the incident beam and target system consists of various initial states φ_α, and p_α is the probability of the occurrence of the state φ_α, the differential cross-section $\sigma(\rightarrow\beta)$ for transition to the final state φ_β is given by

$$\sigma(\rightarrow\beta) = \sum_\alpha p_\alpha \sigma(\alpha\rightarrow\beta) \qquad (3.7.1)$$

where Σ_α runs over all initial states.

It is worth pausing to consider the physical conditions which must be satisfied if (1) is to be accepted as a valid rule of calculation. Suppose for the sake of argument that there are only two internal states, χ_1 and χ_2 say. At some time t_0 in the past a particle A of the incident beam and a particle B of the target system will be in a state $\bar{\varphi}(t_0)$ where

$$\bar{\varphi}(t_0) = c_1\bar{\varphi}_1(t_0)+c_2\bar{\varphi}_2(t_0), \qquad (3.7.2)$$

c_1 and c_2 are complex numbers, and $\bar{\varphi}_1(t_0)$, $\bar{\varphi}_2(t_0)$ are each products of a wave packet describing the relative motion of A and B and the internal state χ_1 or χ_2 respectively (see Section 2.1). If each particle is produced under the same experimental conditions the functions $\bar{\varphi}_1$ and $\bar{\varphi}_2$ and positive numbers $|c_1|$ and $|c_2|$ will always be the same, but the phases θ_1 and θ_2 of c_1 and c_2 may possibly vary. If p_1 and p_2 are the probabilities of observing the states represented by χ_1 and χ_2 in the incident beam we have $|c_1| = p_1^{1/2}$, $|c_2| = p_2^{1/2}$, and so (2) can be written

$$\bar{\varphi}(t_0) = p_1^{1/2}\exp(i\theta_1)\,\bar{\varphi}_1(t_0)+p_2^{1/2}\exp(i\theta_2)\,\bar{\varphi}_2(t_0). \qquad (3.7.3)$$

Let $|m\rangle$ be a state of the system in which a complete set of commuting observables (such as the relative momenta of the elementary particles of the system) have definite values. The probability of observing the system to have such a set of values at time t_0 is $|\langle m|\bar{\varphi}(t_0)\rangle|^2 = P(m)$ say, and so from (3) we find

$$\begin{aligned} P(m) &= p_1\,|\langle m|\,\bar{\varphi}_1(t_0)\rangle|^2+p_2\,|\langle m|\,\bar{\varphi}_2(t_0)\rangle|^2 \\ &\quad +2(p_1p_2)^{1/2}\,\mathrm{Re}\,\exp[i(\theta_1-\theta_2)]\langle m|\,\bar{\varphi}_1(t_0)\rangle\langle m|\,\bar{\varphi}_2(t_0)\rangle.^{*} \qquad (3.7.4) \end{aligned}$$

Now $|\langle m|\bar{\varphi}_s(t_0)\rangle|^2$ $(s = 1, 2)$ is just the probability $P_s(m)$ of observing the values m in the state $\bar{\varphi}_s(t_0)$, and so (4) is equivalent to

$$P(m) = p_1P_1(m)+p_2P_2(m)+2(p_1p_2)^{1/2}\,\mathrm{Re}\,\exp[i(\theta_1-\theta_2)]\times \\ \times\langle m\,|\,\bar{\varphi}_1(t_0)\rangle\langle m\,|\,\bar{\varphi}_2(t_0)\rangle^*. \tag{3.7.5}$$

In any beam produced, for example, by a furnace it is found that the classical statistical formula

$$P(m) = p_1P_1(m)+p_2P_2(m) \tag{3.7.6}$$

holds. The probability (6) is obtained from (5) by averaging over a large number of observations of such initial states. The third term on the right-hand side of (5) therefore always disappears, and this can only be the case if the arbitrary phase relationship $\theta_1-\theta_2$ between $\bar{\varphi}_1$ and $\bar{\varphi}_2$ is assumed to vary in a random way.

Let us now consider what happens after the collision. The state $\bar{\varphi}(t_0)$ now develops under the full Hamiltonian H into the state $\bar{\psi}(t) = \exp[-i\mathrm{H}(t-t_0)/\hbar]\bar{\varphi}(t_0)$, and similarly $\bar{\varphi}_1(t_0)$ and $\bar{\varphi}_2(t_0)$ develop into $\bar{\psi}_1(t)$, $\bar{\psi}_2(t)$ say. If we operate on (3) with the evolution operator $\exp[-i\mathrm{H}(t-t_0)/\hbar]$ we obtain

$$\bar{\psi}(t) = p_1^{1/2}\exp(i\theta_1)\,\bar{\psi}_1(t)+p_2^{1/2}\exp(i\theta_2)\,\bar{\psi}_2(t). \tag{3.7.7}$$

As we saw in the last chapter the probability amplitude A'_β for observation of the state φ_β after the collision is given by $\langle\psi_\beta^-\,|\,\bar{\psi}(0)\rangle$[†] and so by (7)

$$A'_\beta = p_1^{1/2}\exp(i\theta_1))\,\langle\psi_\beta^-\,|\,\bar{\psi}_1(0)\rangle+p_2^{1/2}\exp(i\theta_2)\,\langle\psi_\beta^-\,|\,\bar{\psi}_2(0)\rangle \tag{3.7.8}$$

It follows that the probability $P(\beta) = |\,A'_\beta|^2$ of observing the state φ_β after the collision is given by

$$P(\beta) = p_1P_1(\beta)+p_2P_2(\beta)+2(p_1p_2)^{1/2}\,\mathrm{Re}\,\exp[i(\theta_1-\theta_2)]\times \\ \times\langle\psi_\beta^-\,|\,\bar{\psi}_1(0)\rangle\langle\psi_\beta^-\,|\,\bar{\psi}_2(0)\rangle^* \tag{3.7.9}$$

where $P_s(\beta) = |\langle\psi_\beta^-\,|\,\bar{\psi}_s(0)\rangle|^2$ $(s = 1, 2)$ is the probability of observing the state φ_β after the collision in which the initial state is $\bar{\varphi}_s(t_0)$. To find the experimentally measured probability we must average (9) over a large number of observations. Since the phase relationship $\theta_1-\theta_2$ has been seen to vary in a random way it follows that the phase $\theta_1-\theta_2$ of the third term on the right-hand side of (7) will also vary in a random way, and so

$$P(\beta) = p_1P_1(\beta)+p_2P_2(\beta); \tag{3.7.10}$$

in other words, the probability of observing the final state φ_β is obtained by averaging over the initial states. A similar argument will apply if there are more than two states in the initial beam, and so it is easy to see that (1) follows.

[†] To see this, put $t = 0$ in (2.6.7) and then take the inner product on the left with ψ_β^-, using the orthonormality of the ψ_ν^-.

The addition of cross-sections for different final states is also worthy of some further comment. In order to find the differential cross-section for scattering into the direction of the unit vector $\hat{\mathbf{r}}_f$ for collisions of the form $A+B \to C+D$ we can observe the different differential cross-sections when various final internal states χ_p are produced; the summation of the differential cross-sections over the states χ_p is then obvious. In an experiment when only the differential cross-section is observed, and not the final internal states, we must expect to get the same result; for it is a fundamental assumption that the transition probabilities (and hence differential cross-sections) are determined by the history of the system *before* the measurement, and are not dependent upon the nature of the measurement. The same arguments obviously apply to more complicated processes.

We may sum up the conclusions of this section by the following rule:

> In order to calculate cross-sections for various initial and final states, given the cross-sections for individual initial and final states, we average over initial states and sum over final states.

(3.7.11)

A related problem is that of spin. For simplicity, let us suppose that the problem is one of scattering of two elementary spin $\frac{1}{2}$ particles. Normally beams and target particles are "unpolarized", so that there is equal probability of either colliding partner having "spin up" or "spin down". The spin state of the incident particle is therefore $a_\alpha|\alpha\rangle + a_\beta|\beta\rangle$, where $|\alpha\rangle$ and $|\beta\rangle$ are the "spin up" and "spin down" states respectively, and $|a_\alpha| = |a_\beta| = \frac{1}{2}$. Similarly the spin state of the target particle is $b_\alpha|\alpha\rangle + b_\beta|\beta\rangle$ where $|b_\alpha| = |b_\beta| = \frac{1}{2}$. The initial spin state of the system is therefore $(a_\alpha|\alpha\rangle + a_\beta|\beta\rangle) \times (b_\alpha|\alpha\rangle + b_\beta|\beta\rangle)$. If we put $|\alpha\rangle|\alpha\rangle = |\alpha\alpha\rangle$, so that $|\alpha\alpha\rangle$ is the spin state when both particles have spin up, $|\alpha\rangle|\beta\rangle = |\alpha\beta\rangle$, so that $|\alpha\beta\rangle$ is the spin state when the incident particle has spin up and the target particle has spin down, etcetera, we see that the overall initial state has the form

$$\bar{\varphi}(t_0)[c_1|\alpha\alpha\rangle + c_2|\alpha\beta\rangle + c_3|\beta\beta\rangle + c_4|\beta\alpha\rangle]; \qquad (3.7.12)$$

in (12) $c_1 = a_\alpha b_\alpha$, $c_2 = a_\alpha b_\beta$, $c_3 = a_\beta b_\beta$, and $c_4 = a_\beta b_\alpha$. Thus $|c_1| = |c_2| = |c_3| = |c_4| = \frac{1}{4}$. The wave packet $\bar{\varphi}(t_0)$ will be the same for all identical experiments apart from a phase factor which can be incorporated into the coefficients c_1, c_2, c_3 and c_4.

As before the phase relationship between c_1, c_2, c_3 and c_4 must vary in a random way; for the expectation value of any spin-dependent operator A is

$$\sum_{r=1}^{4} \sum_{s=1}^{4} c_r^* c_s \langle \bar{\varphi}(t_0)\eta_r | A | \bar{\varphi}(t_0)\eta_s \rangle \qquad (3.7.13)$$

where $\eta_1 \ldots \eta_4$ are the four spin states $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\beta\rangle$ and $|\beta\alpha\rangle$. In any unpolarized beam this will always be observed to have the value

$$\sum_{r=1}^{4} |c_r|^2 \langle \bar{\varphi}(t_0)\eta_r | A | \bar{\varphi}(t_0)\eta_r \rangle = \tfrac{1}{4} \sum_{r=1}^{4} \langle \bar{\varphi}(t_0)\eta_r | A | \bar{\varphi}(t_0)\eta_r \rangle; \quad (3.7.14)$$

this is the average of the expectation values in the four states. Again this can only be the case if the phase relationships between c_1, c_2, c_3 and c_4 vary in a random way, so that the cross terms in (13) vanish on averaging over a large number of observations.

The spin space of the particle is spanned by the four orthonormal spin states $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\beta\rangle$ and $|\beta\alpha\rangle$. It is also spanned by the four orthonormal spin states

$$|0\rangle = 2^{-1/2}[|\alpha\beta\rangle - |\beta\alpha\rangle], \quad (3.7.15)$$

$$|1\rangle = |\alpha\alpha\rangle \quad (3.7.16)$$

$$|2\rangle = 2^{-1/2}[|\alpha\beta\rangle + |\beta\alpha\rangle], \quad (3.7.17)$$

$$|3\rangle = |\beta\beta\rangle \quad (3.7.18)$$

$|0\rangle$ is the singlet state, $|1\rangle$, $|2\rangle$ and $|3\rangle$ are the three triplet states. We can express (12) in terms of these states—we get

$$\begin{aligned} &\bar{\varphi}(t_0)[c_1|1\rangle + 2^{-1/2}(c_2+c_4)|2\rangle + c_3|3\rangle + 2^{-1/2}(c_2-c_4)|0\rangle] \\ &\qquad = \bar{\varphi}(t_0)[d_1|1\rangle + d_2|2\rangle + d_3|3\rangle + d_0|0\rangle], \quad \text{say.} \quad (3.7.19) \end{aligned}$$

If we take the average of the values of $|d_1|^2$ and $|d_3|^2$ we get $\frac{1}{4}$, since $d_1 = c_1$ and $d_3 = c_3$. Also $|d_2|^2 = \frac{1}{2}(|c_2|^2 + |c_4|^2) + \mathrm{Re}\, c_2^* c_4 = \frac{1}{4} + \mathrm{Re}\, c_2^* c_4$, and averaged over a large number of observations this is $\frac{1}{4}$. Similarly $|d_0|^2$ has average value $\frac{1}{4}$. On the other hand $d_r^* d_s$ averages to zero if $r \neq s$; for example $d_1^* d_3 = c_1^* c_3$ which we already know averages to zero, while again $d_2^* d_0 = \frac{1}{2}(c_2^* + c_4^*)(c_2 - c_4) = \mathrm{Im}\, c_4^* c_2$, and this averages to zero. This means that we can select as our initial states the four states $|0\rangle$, $|1\rangle$, $|2\rangle$ and $|3\rangle$ rather than $|\alpha\alpha\rangle$, $|\alpha\beta\rangle$, $|\beta\alpha\rangle$ and $|\beta\beta\rangle$; in later examples we shall find this more convenient. We can calculate the transition probability for each of the initial states $|0\rangle$, $|1\rangle$, $|2\rangle$ and $|3\rangle$, and average over these for our final result.

We can also take the final states to be the singlet and triplet states, rather than the ones in which each particle has a definite spin, for the reason given above. If we do not observe the spin states the probability of observing the final momentum to be $\hbar\mathbf{l}$ is the sum of the probabilities of observing the four spin states, and must obviously be the same whichever final set of spin states we choose.

3.8. EXPRESSION FOR THE TOTAL CROSS-SECTION

We saw in Section 3.6 that the differential cross-section for the process $\chi_n \to \chi_p$ is given by (3.6.7). Let us denote the initial speed of the bombarding particle relative to the target particle by v and the final speed of the scattered particle relative to the centre of mass of the recoil particles by $v_{\varkappa p}$. The latter quantity is given by the energy conservation condition

$$\tfrac{1}{2}\mu_i v^2 + E_n = \tfrac{1}{2}\mu_f v_{\varkappa p}^2 + E_{\varkappa p} \tag{3.8.1}$$

where μ_f is the final reduced mass, and the initial and final wave numbers k and $l_{\varkappa p}$ are given by $\hbar k = \mu_i v$, $\hbar l_{\varkappa p} = \mu_f v_{\varkappa p}$. We can therefore rewrite (3.6.7) as

$$\sigma(\mathbf{k}n \to \hat{\mathbf{r}}_1 \varkappa p) = (v_{\varkappa p}/v)\,|f(\mathbf{k}n \to l_{\varkappa p}\hat{\mathbf{r}}_1 \varkappa p)|^2. \tag{3.8.2}$$

We can now use the addition of final states rule to obtain the cross-section for transitions $\chi_n \to \chi_p$ by integrating (2) over all energetically allowed values of the final relative wave vectors $\varkappa = (\varkappa_2, \ldots, \varkappa_{m-1})$ of the recoil particles and over all values of the unit vector $\hat{\mathbf{r}}_1$ in the direction of the scattered particle. This gives

$$\sigma(\mathbf{k}n \to p) = \int' d\varkappa (v_{\varkappa p}/v) \int d\hat{\mathbf{r}}_1\, |f(\mathbf{k}n \to l_{\varkappa p}\hat{\mathbf{r}}_1 \varkappa p)|^2 \tag{3.8.3}$$

where the region of integration over $\varkappa$ is determined by energy considerations If the final state consists of only two particles we omit the integration over $\varkappa$ Since $l_{\varkappa p}\hat{\mathbf{r}}_1$ is the final wave vector $\mathbf{l}$ for the motion of the scattered particle relative to the recoil particles and $E_{\mathbf{l}\varkappa p} = \hbar^2 l^2/2\mu_f + E_{\varkappa p}$ while $v_{\varkappa p}/v = \mu_i l_{\varkappa p}/\mu_f k$ the expression (3) is equivalent to

$$\sigma(\mathbf{k}n \to p) = \int d\varkappa \int_0^\infty dl \int d\hat{\mathbf{r}}_1 \frac{\mu_i l_{\varkappa p}}{\mu_f k} \frac{\hbar^2 l_{\varkappa p}}{\mu_f}\, \delta(E_{\mathbf{l}\varkappa p} - E_{\mathbf{k}n})\, |f(\mathbf{k}n \to \mathbf{l}\varkappa p)|^2; \tag{3.8.4}$$

the integral over $\varkappa$ may now be taken over all $\varkappa$-space, since the integral over l automatically vanishes if $\xi_{\varkappa p}$ is energetically unattainable. Now $l_{\varkappa p}$ can be replaced by l in the integrand of (4) due to the presence of the δ-function in energy; since $d\mathbf{l} = l^2\, dl\, d\hat{\mathbf{r}}_1$ we see that (4) is equivalent to

$$\sigma(\mathbf{k}n \to p) = \int d\varkappa \int d\mathbf{l}\, \frac{\hbar^2 \mu_i}{\mu_f^2 k}\, \delta(E_{\mathbf{l}\varkappa p} - E_{\mathbf{k}n})\, |f(\mathbf{k}n \to \mathbf{l}\varkappa p)|^2. \tag{3.8.5}$$

If we substitute for $f(\mathbf{k}n \to \mathbf{l}\varkappa p)$ from (3.6.6) we obtain

$$\sigma(\mathbf{k}n \to p) = \frac{16\pi^4 \mu_i}{\hbar^2 k} \int d\varkappa \int d\mathbf{l}\, \delta(E_{\mathbf{l}\varkappa p} - E_{\mathbf{k}n})\, |T(\mathbf{k}n \to \mathbf{l}\varkappa p)|^2. \tag{3.8.6}$$

In order to obtain the total cross-section σ we must first sum (6) over all states χ_p of arrangement channel f; we can include the energetically unattainable states since the δ-function then vanishes for all $\varkappa$ and $\mathbf{l}$. Having done this we sum over all final arrangement channels apart from the bound states and so we obtain

$$\sigma = \frac{16\pi^4\mu_i}{\hbar^2 k} \sum_{f \neq b} \sum_{p \text{ in } f} \int d\varkappa \int d\mathbf{l}\, \delta(E_{\mathbf{l}\varkappa p} - E_{\mathbf{k}n}) \,|\, T(\mathbf{k}n \to \mathbf{l}\varkappa p) \,|^2. \qquad (3.8.7)$$

If we put $\alpha = \mathbf{k}n$, $\beta = \mathbf{l}\varkappa p$ we see that (7) may be abbreviated to

$$\sigma = \frac{16\pi^4\mu_i}{\hbar^2 k} \sum_{f \neq b} \sum_{\beta \text{ in } f} \delta(E_\beta - E_\alpha) \,|\, T(\alpha \to \beta) \,|^2. \qquad (3.8.8)$$

In Section 3.3 we noticed that $T(\alpha \to \beta)$ vanishes if either φ_α or φ_β is a bound state, and hence $T(\alpha \to \beta) = 0$ for all φ_β which are bound; we can therefore further abbreviate (8) to

$$\sigma = (16\pi^4\mu_i/\hbar^2 k) \sum_{\beta} \delta(E_\beta - E_\alpha) \,|\, T(\alpha \to \beta) \,|^2. \qquad (3.8.9)$$

We can generalize the definitions (3.5.31) and (3.6.6). The *scattering amplitude* for the process $\varphi_\alpha \to \varphi_\beta$ is defined by

$$\boxed{f(\alpha \to \beta) = (-4\pi^2\mu_f \hbar^{-2})\, T(\alpha \to \beta).} \qquad (3.8.10)$$

With this defintion (9) can be rewritten

$$\sigma = \hbar^2\mu_i\mu_f^{-2}k^{-1} \sum_{\beta} \delta(E_\beta - E_\alpha) \,|\, f(\alpha \to \beta) \,|^2. \qquad (3.8.11)$$

3.9. THE LABORATORY SYSTEM

It is sometimes useful to work in the laboratory system. In the laboratory system the initial state is represented by the product of the m kets $|\,\mathbf{k}_1\rangle$, $|\,\mathbf{k}_2\rangle$, $\ldots$, $|\,\mathbf{k}_m\rangle$ which represent the free motion of the centres of mass of the m composite particles with momenta $\hbar\mathbf{k}_1$, $\hbar\mathbf{k}_2$, $\ldots$, $\hbar\mathbf{k}_m$, and the ket $|\,n\rangle$ which represents the internal state of the particles. We can separate out the centre of mass motion for the whole system in the way described in Section 1.2. If $\mathbf{K} = \mathbf{k}_1 + \mathbf{k}_2 + \ldots + \mathbf{k}_m$ is the wave vector for the motion of the centre of mass G of the system, and $|\,\mathbf{k}\rangle$ represents the relative motion of the composite particles, we obtain

$$|\,\mathbf{k}_1\rangle\,|\,\mathbf{k}_2\rangle \ldots |\,\mathbf{k}_m\rangle\,|\,n\rangle = |\,\mathbf{K}\rangle\,|\,\mathbf{k}\rangle\,|\,n\rangle. \qquad (3.9.1)$$

The product $|\,\mathbf{k}\rangle\,|\,n\rangle$ describes the state of the system after removal of the centre of mass motion, and can be replaced by the single ket $|\,\alpha\rangle$. Thus (1) gives

$$|\,\mathbf{k}_1\rangle\,|\,\mathbf{k}_2\rangle\ldots|\,\mathbf{k}_m\rangle\,|\,n\rangle = |\,\mathbf{K}\rangle\,|\,\alpha\rangle = |\,\mathbf{K},\alpha\rangle, \quad \text{say.} \tag{3.9.2}$$

In exactly the same way the final state is represented by the ket $|\,\mathbf{L},\beta\rangle = |\,\mathbf{L}\rangle\,|\,\beta\rangle$, where $\mathbf{L}$ is the wave vector of the centre of mass and $|\,\beta\rangle$ the state of the system in the relative coordinate system.

The full Hamiltonian H_G in the laboratory system consists of the sum of the kinetic energy operators for the motion of the centres of mass of the composite particles, the sum of their internal Hamiltonians, and the interaction V_i. We may express the sum of the kinetic energy operators as the sum of the kinetic energy operator K_G associated with the motion of G and the sum K of the relative kinetic energy operators (see Section 1.2). The full Hamiltonian H_G in the laboratory system therefore has the form

$$\mathsf{H}_G = \mathsf{K}_G + \mathsf{H} \tag{3.9.3}$$

where H is the full Hamiltonian in the relative coordinate system.

The transition operator $\mathsf{T}^+_{fi}(E)$ in the relative coordinate system is defined by (3.3.3), viz.

$$\mathsf{T}^+_{fi}(E) = V_f + V_f(E-\mathsf{H}+i\varepsilon)^{-1}V_i. \tag{3.9.4}$$

We define a corresponding transition operator in the laboratory system by

$$\mathsf{T}^+_{fiG}(E) = V_f + V_f(E-\mathsf{H}_G+i\varepsilon)^{-1}V_i. \tag{3.9.5}$$

We saw in Section 1.2 that if E_α is the energy of the state $|\,\alpha\rangle$, and so the energy of the initial state in the relative coordinate system, the energy $E_{\alpha K}$ of the initial state in the laboratory system is $E_\alpha + E_K$ where E_K is the kinetic energy associated with the motion of G. It follows from (5) that

$$\mathsf{T}^+_{fiG}(E_{\alpha K})\,|\,\mathbf{K},\alpha\rangle = [V_f + V_f(E_{\alpha K}-\mathsf{H}_G+i\varepsilon)^{-1}V_i]\,|\,\mathbf{K},\alpha\rangle, \tag{3.9.6}$$

and so by (2) and (3)

$$\mathsf{T}^+_{fiG}(E_{\alpha K})\,|\,\mathbf{K},\alpha\rangle = V_f\,|\,\mathbf{K}\rangle\,|\,\alpha\rangle + V_f(E_\alpha+E_K-\mathsf{H}-\mathsf{K}_G+i\varepsilon)^{-1}V_i\,|\,\mathbf{K}\rangle\,|\,\alpha\rangle. \tag{3.9.7}$$

Now H, V_i and $|\,\alpha\rangle$ are independent of the coordinates of the centre of mass G, K_G and $|\,\mathbf{K}\rangle$ depend only on the coordinates of G, and $\mathsf{K}_G\,|\,\mathbf{K}\rangle = E_K|\,\mathbf{K}\rangle$. We can therefore apply the results of Appendix A to obtain

$$(E_\alpha+E_K-\mathsf{H}-\mathsf{K}_G+i\varepsilon)^{-1}V_i\,|\,\mathbf{K}\rangle\,|\,\alpha\rangle = \{(E_\alpha-\mathsf{H}+i\varepsilon)^{-1}V_i\,|\,\alpha\rangle\}\,|\,\mathbf{K}\rangle. \tag{3.9.8}$$

Since V_f is also independent of the coordinates of G we deduce from (7) and

(8) that

$$\mathsf{T}^{+}_{fiG}(E_{\alpha K})\,|\,\mathbf{K},\alpha\rangle = \{[V_f+V_f(E_\alpha-\mathsf{H}+i\varepsilon)^{-1}V_i]\,|\alpha\rangle\}\,|\,\mathbf{K}\rangle, \tag{3.9.9}$$

and so by (3.3.3)

$$\mathsf{T}^{+}_{fiG}(E_{\alpha K})\,|\,\mathbf{K},\alpha\rangle = \{\mathsf{T}^{+}_{fi}(E_\alpha)\,|\,\alpha\rangle\}\,|\,\mathbf{K}\rangle. \tag{3.9.10}$$

The final state is $|\,\mathbf{L},\beta\rangle = |\,\mathbf{L}\rangle\,|\,\beta\rangle$, where $|\,\mathbf{L}\rangle$ depends on the coordinates of G and $|\,\beta\rangle$ is independent of these. If we take the inner product of (10) on the left with $|\,\mathbf{L},\beta\rangle = |\,\mathbf{L}\rangle\,|\,\beta\rangle$ we therefore obtain

$$\langle\mathbf{L},\beta\,|\,\mathsf{T}^{+}_{fiG}(E_{\alpha K})\,|\,\mathbf{K},\alpha\rangle = \delta(\mathbf{L}-\mathbf{K})\langle\beta\,|\,\mathsf{T}^{+}_{fi}(E_\alpha)\,|\,\alpha\rangle. \tag{3.9.11}$$

The δ-function in (11) expresses the conservation of total momentum. For by (3.1.2) we have $\psi^{+}_{\alpha} = \Omega^{+}_{i}(E_\alpha)\varphi_\alpha$, and hence by (3.3.1)

$$\langle\varphi_\beta\,|\,V_f\,|\,\psi^{+}_{\alpha}\rangle = \langle\varphi_\beta\,|\,V_f\Omega^{+}_{i}(E_\alpha)\,|\,\varphi_\alpha\rangle = \langle\varphi_\beta\,|\,T^{+}_{fi}(E_\alpha)\,|\,\varphi_\alpha\rangle. \tag{3.9.12}$$

We can therefore rewrite (3.2.12) as

$$S_{\beta\alpha} = \delta_{\beta\alpha}-2\pi i\delta(E_\beta-E_\alpha)\langle\varphi_\beta\,|\,T^{+}_{fi}(E_\alpha)\,|\,\varphi_\alpha\rangle. \tag{3.9.13}$$

If we had worked in the laboratory system, rather than in the centre of mass system, we should have obtained a scattering matrix $S_{\beta\mathbf{L},\,\alpha\mathbf{K}}$ where, instead of (13),

$$S_{\beta\mathbf{L},\,\alpha\mathbf{K}} = \delta_{\beta\alpha}\delta(\mathbf{L}-\mathbf{K})-2\pi i\delta(E_{L\beta}-E_{K\alpha})\langle\varphi_{\mathbf{L}\beta}\,|\,T^{+}_{fiG}(E_{\alpha K})\,|\,\varphi_{\mathbf{K}\alpha}\rangle \tag{3.9.14}$$

where $\varphi_{\mathbf{K}\alpha}$ and $\varphi_{\mathbf{L}\beta}$ are the wave functions corresponding to the states $|\,\mathbf{K}\alpha\rangle$ and $|\,\mathbf{L}\beta\rangle$ respectively, while $E_{K\alpha}$ and $E_{L\beta}$ are their respective energies. Insertion of (11) into (14) shows that $S_{\beta L,\,\alpha K}$ has a factor $\delta(\mathbf{L}-\mathbf{K})$, ensuring the conservation of the total momentum which is associated with the motion of the centre of mass G.

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CHAPTER 4

IDENTICAL PARTICLES

4.1. INTRODUCTION

So far we have developed our theory without taking into account the fact that some or all of the "elementary particles" involved in the collision may be identical. In the initial state the internal wave functions for the composite particles will be automatically symmetric (or antisymmetric) in the internal coordinates of identical particles. As a result of a collision identical elementary particles may be exchanged between composite particles. If an observation of the system after the collision is made there will be no means of telling whether exchange has taken place or not—in fact this is an unanswerable question. All we shall be able to observe after the process will be the distribution of identical elementary particles among the composite particles produced by the reaction—there is no means of relating this to the distribution of elementary particles before the collision. In this chapter we shall turn our attention to the task of investigating the modifications which must be made in order to take account of the possibility of the (unobservable) exchange of identical particles.

We shall now discuss the approach which will be given in this chapter. Before the collision the wave function of the system is $\bar{\varphi}(t_0)$, say. We operate upon this state with an operator $\mathcal{S}$, called the "symmetrizer", so that the resulting state $\mathcal{S}\varphi(t_0)$ is invariant under the interchange of two identical bosons, but changes sign under the interchange of two identical fermions. If there is only one species of identical particle the symmetrizer $\mathcal{S}$ is defined by the expression

$$\mathcal{S} = \frac{1}{M!}\sum_{\mathsf{P}} \delta_{\mathsf{P}}\mathsf{P} \tag{4.1.1}$$

where M is the number of identical particles, $\sum_{\mathsf{P}}$ is a summation of all permutations P of the identical particles; in the case of bosons $\delta_{\mathsf{P}} = 1$, but in the case of fermions δ_{P} is the parity (± 1) of the permutation P. It is easy to show that $\mathcal{S} = \mathcal{S}^{\dagger}$ (Hermiticity), $\mathcal{S}^2 = \mathcal{S}$ (idempotency), and that $\mathcal{S}$ is linear.

The state represented by $\bar{\varphi}(t_0)$ is normalized, but the state $\mathcal{S}\bar{\varphi}(t_0)$ may no longer be normalized.[†] We saw in Section 3.7 that the initial state may usually be regarded as in some definite channel, and therefore in some arrangement channel i. The state $\mathcal{S}\bar{\varphi}(t_0)$ may be normalized by multiplication by a normalization constant which, as we shall see, may depend upon the initial arrangement channel i. We shall therefore denote this constant by a_i. The symmetrized and normalized initial state therefore takes the form

$$\bar{\varphi}_{\mathcal{S}}(t_0) = a_i\mathcal{S}\bar{\varphi}(t_0). \tag{4.1.2}$$

In the remote future the state $(\bar{\varphi}_{\mathcal{S}}t_0)$ evolves into the state $\bar{\varphi}'_{\mathcal{S}}(t_1)$ where

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = \exp\left[-i\mathsf{H}(t_1-t_0)/\hbar\right]\bar{\varphi}_{\mathcal{S}}(t_0) = \exp\left[-i\mathsf{H}(t_1-t_0)/\hbar\right]a_i\mathcal{S}\bar{\varphi}(t_0). \tag{4.1.3}$$

Now the total Hamiltonian H must be invariant under permutations of the identical particles, and so $\mathcal{S}$ commutes with the evolution operator $\exp\left[-i\mathsf{H}(t_1-t_0)/\hbar\right]$. Since the unsymmetrized function $\bar{\varphi}(t_0)$ evolves into $\bar{\varphi}'(t_1)$ we see that (3) becomes

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = a_i\mathcal{S}\exp\left[-i\mathsf{H}(t_1-t_0)/\hbar\right]\bar{\varphi}(t_0) = a_i\mathcal{S}\bar{\varphi}'(t_1). \tag{4.1.4}$$

The expression (4) enables us to see how to proceed. Initially identical particles belonging to different colliding partners will be distinguishable, since they will be confined to different regions of space. If we did not have to take account of the Pauli principle we could let this evolve into the state $\bar{\varphi}'(t_1)$. The probability of observing some state φ_β after the collision is then the square of the modulus of the coefficient A'_β of $\varphi_\beta \exp(-iE_\beta t_1/\hbar)$ in $\bar{\varphi}'(t_1)$. The experimental arrangements do not allow us to distinguish this observation from that of a state φ_γ, say, where φ_γ can be obtained from φ_β by a permutation of identical particles. We will only be able to observe whether, after the collision, the system is in the state φ_β or a state obtainable from φ_β by a permutation of identical particles. If we write $\gamma \approx \beta$ to mean that the state represented by φ_γ may be obtained from the state φ_β by a permutation of identical particles the probability we shall actually observe is

$$\sum_{\gamma\approx\beta} |A'_\gamma|^2 \tag{4.1.5}$$

where the summation goes over all distinct states φ_γ obtainable from φ_β by a permutation of identical particles, including φ_β itself.

The result (5) will not, in general, agree with experiment, for it fails to take

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[†] Strictly speaking, operators such as P or $\mathcal{S}$ operate on vectors representing states. In the coordinate representation they operate on the wave functions representing the vectors, and hence the states. If an operation carries a wave function $\bar{\varphi}$ into $\lambda\bar{\varphi}$, $\lambda \neq 1$, a distinct vector or wave function is produced, but the state is unchanged. For example, if $\bar{\varphi}$ is antisymmetric then $\mathsf{P}\bar{\varphi} = -\bar{\varphi}$, a distinct wave function, but the state is unchanged—thus, in this case, the operator P does not produce a distinct state.

account of the Pauli principle. To do this we operate upon $\bar{\varphi}'(t)$ with $\mathcal{S}$ and then multiply by a_i. As we have seen this gives us a final wave function with the correct symmetry, and also normalized to unity since the evolution operator in (3) conserves norm. It follows that if the coefficient of $\varphi_\beta \exp(-iE_\beta t_1/\hbar)$ in $\bar{\varphi}'_{\mathcal{S}}(t_1)$ is $A'_\beta(\mathcal{S})$ then the probability of observing φ_β is $|A'(\mathcal{S})|^2$. As before the experimental apparatus will not distinguish between φ_β and any state φ_γ obtainable from it by a permutation of identical elementary particles; the probability which we shall be able to observe is therefore

$$\sum_{\gamma \approx \beta} |A'_\gamma(\mathcal{S})|^2. \tag{4.1.6}$$

Now the symmetry of the final state will naturally lead to the equality of the terms in the sum (6). This will therefore be replaceable by

$$M_f |A'_\beta(\mathcal{S})|^2 \tag{4.1.7}$$

where M_f is the number of distinct states obtainable from φ_β by a permutation of identical particles—this number clearly depends only on the arrangement channel f to which φ_β belongs. The result (7) will enable us to write down a formula for the cross-section in terms of the correctly symmetrized scattering amplitudes.

In Section 4.2 we will follow this argument through in the simplest possible case, namely the collision of two spinless bosons. Section 4.3 will then consider the more complicated case of electron–helium scattering, while Section 4.4 will deal with the more general case when M of the N elementary particles are identical, but the remaining ones are distinct. The remaining sections will deal with some further results and generalizations.

EXERCISES

1. Prove that if P is a permutation of identical particles then P is linear, and $\mathsf{P}^\dagger = \mathsf{P}^{-1}$. Deduce that the norm of a wave function is invariant under permutations of identical particles.
2. Prove that the operator $\mathcal{S}$ defined by (1) is linear, Hermitian and idempotent.

4.2. THE COLLISION OF TWO IDENTICAL SPINLESS BOSONS

Initially the system is described by the wave packet

$$\bar{\varphi}(\mathbf{r}, t_0) = \int A_\mathbf{k} \varphi_\mathbf{k} \exp(-iE_\mathbf{k} t/\hbar)\, d\mathbf{k}. \tag{4.2.1}$$

In this case $M = 2$, and since we are dealing with bosons $\delta_\mathsf{P} = 1$; hence the definition (4.1.1) particularizes to

$$\mathcal{S} = \tfrac{1}{2}(1+\mathsf{P}) \tag{4.2.2}$$

where P interchanges the two particles. It follows that $\mathsf{P}\bar{\varphi}(\mathbf{r}, t_0) = \bar{\varphi}(-\mathbf{r}, t_0)$ and so from (1) and (2)

$$\bar{\varphi}_{\mathcal{S}}(\mathbf{r}, t_0) = a_i\mathcal{S}\bar{\varphi}(\mathbf{r}, t_0) = \tfrac{1}{2}\, a_i[\bar{\varphi}(\mathbf{r}, t_0)+\bar{\varphi}(-\mathbf{r}, t_0)]. \tag{4.2.3}$$

To obtain $\|\bar{\varphi}_{\mathcal{S}}(t_0)\|$ we take the square of the modulus of the right-hand side of (3) and integrate over all space. Now initially the wave packet moves in the direction of positive z towards the origin (Fig. 3.2), and so in the remote past $\bar{\varphi}(\mathbf{r}, t_0)$ will only be non-vanishing for negative values of z. It follows that $\bar{\varphi}(\mathbf{r}, t_0)$ is non-vanishing if, and only if, $\bar{\varphi}(-\mathbf{r}, t_0) = 0$. This implies that the cross-term in the expression for $|\bar{\varphi}_{\mathcal{S}}(\mathbf{r}, t_0)|^2$ vanishes, and so

$$\begin{aligned} \|\bar{\varphi}_{\mathcal{S}}(t_0)\|^2 &= \tfrac{1}{4}\, a_i^2[\textstyle\int |\bar{\varphi}(\mathbf{r}, t_0)|^2\, d\mathbf{r} + \int |\bar{\varphi}(-\mathbf{r}, t_0)|^2\, d\mathbf{r}] \\ &= \tfrac{1}{4}\, a_i^2[\textstyle\int |\bar{\varphi}(\mathbf{r}, t_0)|^2\, d\mathbf{r} + \int |\bar{\varphi}(\mathbf{r}, t_0)|^2\, d\mathbf{r}] \\ &= \tfrac{1}{2}\, a_i^2 \end{aligned} \tag{4.2.4}$$

since $\bar{\varphi}(t_0)$ is normalized to unity. Now $\|\bar{\varphi}_{\mathcal{S}}(t_0)\| = 1$, and hence (4) implies $a_i = 2^{1/2}$. Expression (3) can now be rewritten

$$\bar{\varphi}_{\mathcal{S}}(t_0) = 2^{-1/2}[\bar{\varphi}(\mathbf{r}, t_0)+\bar{\varphi}(-\mathbf{r}, t_0)]. \tag{4.2.5}$$

The unsymmetrized state in the far future has the form

$$\bar{\varphi}'(t_1) = \int A'_{\mathbf{l}}\varphi_{\mathbf{l}} \exp(-iE_l t/\hbar)\, d\mathbf{l}. \tag{4.2.6}$$

Equation (6) can be rewritten

$$\bar{\varphi}'(t_1) = \int'' (A'_{\mathbf{l}}\varphi_{\mathbf{l}}+A'_{-\mathbf{l}}\varphi_{-\mathbf{l}}) \exp(-iE_l t/\hbar)\, d\mathbf{l} \tag{4.2.7}$$

where $\int''$ is an integration over all $\mathbf{l}$ for which $l_z > 0$, say. In (7) we have taken advantage of the fact that E_l is unaltered when $\mathbf{l}$ becomes $-\mathbf{l}$. Equation (7) expresses $\bar{\varphi}'(t_1)$ as a linear combination of the states $\varphi_{\mathbf{l}}$ and the states $\varphi_{-\mathbf{l}}$ obtained from them by interchange of the two particles, and an integration over all states $\varphi_{\mathbf{l}}$ which cannot be transformed into each other by an exchange of the particles.

Since $a_i = 2^{1/2}$ we see from (2) that $a_i\mathcal{S} = 2^{-1/2}(1+\mathsf{P})$. The normalized and symmetrized final state $\bar{\varphi}'_{\mathcal{S}}(t_1)$ is obtained from (7) by operation with $a_i\mathcal{S}$; since $\mathsf{P}\varphi_{\mathbf{l}} = \varphi_{-\mathbf{l}}$ we obtain

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = 2^{-1/2} \int'' [(A'_{\mathbf{l}}\varphi_{\mathbf{l}}+A'_{-\mathbf{l}}\varphi_{-\mathbf{l}})+(A'_{\mathbf{l}}\varphi_{-\mathbf{l}}+A'_{-\mathbf{l}}\varphi_{\mathbf{l}})]\, d\mathbf{l}. \tag{4.2.8}$$

The coefficient of $\varphi_{\mathbf{l}}$ is therefore

$$A'_{\mathcal{S}}(\mathbf{l}) = 2^{-1/2}(A'_{\mathbf{l}}+A'_{-\mathbf{l}}) \tag{4.2.9}$$

while the coefficient of $\varphi_{-\mathbf{l}}$ is

$$A'_{\mathcal{S}}(-\mathbf{l}) = 2^{-1/2}(A'_{-\mathbf{l}}+A'_{\mathbf{l}}). \tag{4.2.10}$$

The probability of observing the final relative momentum to be $\hbar\mathbf{l}$ or $-\hbar\mathbf{l}$ is therefore

$$\sum_{\lambda=\pm\mathbf{l}} |A'_{\mathscr{S}}(\boldsymbol{\lambda})|^2 = |A'_{\mathscr{S}}(\mathbf{l})|^2+|A'_{\mathscr{S}}(-\mathbf{l})|^2 = 2|A'_{\mathscr{S}}(\mathbf{l})|^2 = |A'_{\mathbf{l}}+A'_{-\mathbf{l}}|^2. \qquad (4.2.11)$$

In this case M_f, the number of distinct states which can be obtained from $\varphi_{\mathbf{l}}$ by a permutation of the two particles, is two.

We deduce from (11) that the probability amplitude for observation of the final relative momentum being $\hbar\mathbf{l}$ or $-\hbar\mathbf{l}$ is $A'_{\mathbf{l}}+A'_{-\mathbf{l}}$. This must therefore replace $A'_{\mathbf{l}}$ in the derivations of the last chapter concerning the differential cross-section. The differential cross-section now refers to a final observation in which the relative momentum is $\hbar\mathbf{l}$ or $-\hbar\mathbf{l}$. The result (3.5.32) becomes

$$\sigma_{\mathscr{S}}(\mathbf{k} \to \mathbf{l} \text{ or } -\mathbf{l}) = |f_{\mathscr{S}}(\mathbf{k} \to \mathbf{l} \text{ or } -\mathbf{l})|^2, \qquad (4.2.12)$$

since the initial and final velocities v and v' must obviously be the same, where the symmetrized scattering amplitude is defined by

$$f_{\mathscr{S}}(\mathbf{k} \to \mathbf{l} \text{ or } -\mathbf{l}) = f(\mathbf{k} \to \mathbf{l})+f(\mathbf{k} \to -\mathbf{l}). \qquad (4.2.13)$$

If the spherical polar angles defining $\mathbf{l}$ relative to $\mathbf{k}$ are (θ, φ) the result (13) may be rewritten

$$f_{\mathscr{S}}(\theta, \varphi) = f(\theta, \varphi)+f(\pi-\theta, \varphi+\pi), \qquad (4.2.14)$$

while (12) may be rewritten

$$\sigma_{\mathscr{S}}(\theta, \varphi) = |f_{\mathscr{S}}(\theta, \varphi)|^2. \qquad (4.2.15)$$

In calculating the total cross-section $\sigma_{\mathscr{S}}$ we must be careful not to count the same event twice. We must therefore integrate $\sigma_{\mathscr{S}}(\mathbf{k} \to \mathbf{l} \text{ or } -\mathbf{l})$ only over values of $\hat{\mathbf{l}}$ for which $l_z > 0$, say, thereby counting all possible final outcomes precisely once; hence

$$\sigma_{\mathscr{S}} = \int'' \sigma_{\mathscr{S}}(\mathbf{k} \to \mathbf{l} \text{ or } -\mathbf{l})\, d\hat{\mathbf{l}} \qquad (4.2.16)$$

where the integration goes over all $\hat{\mathbf{l}}$ with positive z-component. Equivalently to (16) we have

$$\sigma_{\mathscr{S}} = \int_0^{\frac{1}{2}\pi} d\theta \int_0^{2\pi} d\varphi\, \sigma_{\mathscr{S}}(\theta, \varphi). \qquad (4.2.17)$$

The application of this result to the scattering of α-particles is discussed elsewhere (Volume 4, Chapter 3).

EXERCISE

In the case of the collision of two electrons the initial wave function in the centre of mass system may be written

$$\bar{\varphi}(t_0) = \sum_{n=0}^{3} \int d\mathbf{k} A_{\mathbf{k}n} \varphi_{\mathbf{k}} \chi_n(1, 2) \exp(-iE_k t_0/\hbar)$$

where χ_0 is the singlet spin wave function of the two electrons 1 and 2, while χ_1, χ_2 and χ_3 are the three triplet wave functions. If $A'_{1p}(\mathcal{S})$ $(p = 0, 1, 2, 3)$ is the coefficient of $\varphi_1\chi_p \exp(-iE_l t_1/\hbar)$ in the antisymmetrized and normalized final state while A'_{1p} is the coefficient of $\varphi_1\chi_p \exp(-iE_l t_1/\hbar)$ in the final state before antisymmetrization prove that

$$A'_{10}(\mathcal{S}) = 2^{-1/2}(A'_{10} + A'_{-10}),$$
$$A'_{1p}(\mathcal{S}) = 2^{-1/2}(A'_{1p} - A'_{1p}) \qquad (p = 1, 2, 3).$$

Deduce that the differential cross-section for scattering of two electrons is

$$\sigma_{\mathcal{S}}(\theta, \varphi) = \tfrac{1}{4}\,|f(\theta, \varphi) + f(\pi-\theta, \varphi+\pi)|^2 + \tfrac{3}{4}\,|f(\theta, \varphi) - f(\pi-\theta, \varphi+\pi)|^2$$

where $f(\theta, \varphi)$ is the amplitude for direct scattering.

4.3. ELECTRON–HELIUM SCATTERING

We will now follow through the argument of Section 4.1 in the more complicated case of electron–helium scattering. In the initial state $\bar{\varphi}(t_0)$ we suppose an electron 1 impinges upon a helium atom with electrons 2 and 3. If the momentum of 1 relative to the centre of mass of the atom is $\hbar\mathbf{k}$ the relative motion is described by a plane wave $\varphi_{\mathbf{k}}(1, 23)$. Let the "spin up" and "spin down" wave functions be α_1 and α_2, so that $\alpha_m(1)$ is the spin function of electron 1 when in the spin state α_m, and let $\chi_n(23)$ denote the internal wave function of the helium atom. The initial unsymmetrized wave function $\bar{\varphi}(t_0)$ is then

$$\bar{\varphi}(t_0) = \int A_{\mathbf{k}nm}(1, 23)\, \varphi_{\mathbf{k}}(1, 23)\, \alpha_m(1)\, \chi_n(23) \exp(-iE_{kn}t_0/\hbar)\, d\mathbf{k} \qquad (4.3.1)$$

where $A_{\mathbf{k}nm}(1, 23)$ is the initial probability amplitude for the stationary state in which 1 has spin α_m and momentum $\hbar\mathbf{k}$ relative to the centre of mass of the helium atom, while $\chi_n(23)$ is the atomic wave function.

In this case we are dealing with three identical fermions, viz. the electrons, and so (4.1.1) particularizes to

$$\mathcal{S} = \frac{1}{3!}(\mathsf{P}_{123} - \mathsf{P}_{132} + \mathsf{P}_{231} - \mathsf{P}_{213} + \mathsf{P}_{312} - \mathsf{P}_{321}) \qquad (4.3.2)$$

where P_{ijk} is the permutation which takes 123 into ijk. To form the antisymmetrized initial state we must operate on (1) with $a_i\mathcal{S}$. The resulting expression is simplified if we note that the resulting terms are equal in pairs. For P_{123} leaves $\bar{\varphi}(t_0)$ unaltered, whereas

$$\begin{aligned} -\mathsf{P}_{132}[A_{\mathbf{k}nm}(1, 23)\, \varphi_{\mathbf{k}}(1, 23)\alpha_m(1)\, \chi_n(23) \exp(-iE_{kn}t_0/\hbar)] \\ = -[A_{\mathbf{k}nm}(1, 23)\, \varphi_{\mathbf{k}}(1, 32)\alpha_m(1)\, \chi_n(32) \exp(-iE_{kn}t_0/\hbar)]. \qquad (4.3.3) \end{aligned}$$

The plane wave is unaffected by interchange of electrons 2 and 3, since this cannot change the centre of mass of the atom. Since electrons are fermions χ_n must be antisymmetric in its electron coordinates, and so (3) becomes

$$\begin{aligned} -\mathsf{P}_{132}[A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23)\exp(-iE_{kn}t_0/\hbar)] \\ = A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23)\exp(\ \ iE_{kn}t_0/\hbar) \\ = \mathsf{P}_{123}[A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23)\exp(-iE_{kn}t_0/\hbar)], \end{aligned} \tag{4.3.4}$$

and so the first two terms in $\bar{\varphi}_{\mathcal{S}}(t_0) = a_i\mathcal{S}\bar{\varphi}(t_0)$ are equal.

Similarly

$$\begin{aligned} -\mathsf{P}_{213}[A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23)\exp(-iE_{kn}t_0/\hbar)] \\ = -[A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(2, 13)\,\alpha_m(2)\,\chi_n(13)\exp(-iE_{kn}t_0/\hbar)] \\ = A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(2, 31)\,\alpha_m(2)\,\chi_n(31)\exp(-iE_{kn}t_0/\hbar) \\ = \mathsf{P}_{231}[A_{\mathbf{k}nm}(1, 23)\,\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23)\exp(-iE_{kn}t_0/\hbar)], \end{aligned} \tag{4.3.5}$$

and so the fourth term equals the third term. Likewise the last two terms ara equal. Indeed the resulting states in each of these pairs differ only by e permutation of identical particles in the same composite particle, viz. the helium atom, and this is the reason for their equality.

If we use these results we obtain, after operation on (1) with $a_i\mathcal{S}$, the result

$$\begin{aligned} \bar{\varphi}_{\mathcal{S}}(t_0) = \tfrac{1}{3}a_i \int A_{\mathbf{k}nm}(1, 23)\exp(-iE_{kn}t_0/\hbar)[\varphi_{\mathbf{k}}(1, 23)\,\alpha_m(1)\,\chi_n(23) \\ +\varphi_{\mathbf{k}}(2, 31)\,\alpha_m(2)\,\chi_n(31)+\varphi_{\mathbf{k}}(3, 12)\,\alpha_m(3)\,\chi_n(12)]\,d\mathbf{k}. \end{aligned} \tag{4.3.6}$$

The sum under the integral sign in (6) is a sum over the three distinct states which can be obtained by permuting the electrons. The factor 1/3! has been multiplied by 2, the number of states which differ by a permutation of electrons within the atom.

Let us denote the unsymmetrized wave function $\varphi(t_0)$ by $\bar{\varphi}(1, 23, t_0)$ to emphasize that it represents the state when 1 is the incident electron. With this notation (6) may be written

$$\bar{\varphi}_{\mathcal{S}}(t_0) = \tfrac{1}{3}a_i[\bar{\varphi}(1, 23, t_0)+\bar{\varphi}(2, 31, t_0)+\bar{\varphi}(3, 12, t_0). \tag{4.3.7}$$

Since $||\bar{\varphi}_{\mathcal{S}}(t_0)|| = 1$ we deduce from (7) that

$$9 = a_i^2||\bar{\varphi}(1, 23, t_0)+\bar{\varphi}(2, 31, t_0)+\bar{\varphi}(3, 12, t_0)||^2. \tag{4.3.8}$$

Now $||\bar{\varphi}(1, 23, t_0)|| = 1$, and it is easy to prove that the norm of a function is invariant under permutations of identical particles; hence

$$||\bar{\varphi}(1, 23, t_0)|| = ||\bar{\varphi}(2, 31, t_0)|| = ||\bar{\varphi}(3, 12, t_0)|| = 1. \tag{4.3.9}$$

The three terms inside the norm signs in (8) represent the states in which 1, 2 and 3 are free respectively, the other two electrons being bound to the atom. It follows that the cross-terms in the expansion of the square of the norm, which are overlap integrals, must vanish. For example, since t_0 is a time in the remote past $\bar{\varphi}(1, 23, t_0)$ can only be non-vanishing if 1 is far from the nucleus of the atom, but $\bar{\varphi}(2, 31, t_0)$ can only be non-vanishing if 1 is close to the nucleus. A similar argument applies to the other cross-terms. The vanishing of the cross-terms together with (9) enables us to infer from (8) that $9 = 3a_i^2$, and hence that $a_i = 3^{1/2}$.

In the remote future the state $\bar{\varphi}(t_0)$ evolves into the state $\bar{\varphi}'(t_1)$ where

$$\begin{aligned}\bar{\varphi}'(t_1) = \sum_{pq} \int d\mathbf{l} \exp(-iE_{lp}t_1/\hbar)[&A'_{\mathbf{l}pq}(1, 23)\,\varphi_{\mathbf{l}}(1, 23)\,\alpha_q(1)\,\chi_p(23)\\ &+A'_{\mathbf{l}pq}(2, 31)\,\varphi_{\mathbf{l}}(2, 31)\,\alpha_q(2)\,\chi_p(31)\\ &+A'_{\mathbf{l}pq}(3, 12)\,\varphi_{\mathbf{l}}(3, 12)\,\alpha_q(3)\,\chi_p(12)]\\ &+\text{terms in which the helium atom is singly ionized}\\ &+\text{terms in which the helium atom is doubly ionized.}\end{aligned} \qquad (4.3.10)$$

$A'_{\mathbf{l}pq}(1, 23)$ is the final probability amplitude for the state in which electron 1 has wave vector $\mathbf{l}$ relative to the centre of mass of the atom and spin function α_q, the atom having wave function χ_p, while $A'_{\mathbf{l}pq}(2, 31)$ and $A'_{\mathbf{l}pq}(3, 21)$ are the final probability amplitudes for the two distinct states obtained from this by the corresponding permutations of the electrons. No bound states can occur in (10) since there are no such states initially. The first terms on the right-hand side of (10) are a sum and integration over those states in which one electron is finally free and the others are bound to the nucleus to form a helium atom.

To normalize and symmetrize $\bar{\varphi}'(t_1)$ we must operate upon (10) with $a_i\mathcal{S}$. Since $a_i = 3^{1/2}$ and $\mathcal{S}$ is given by (2) we have

$$a_i\mathcal{S} = \frac{1}{2\sqrt{3}}(\mathsf{P}_{123}-\mathsf{P}_{132}+\mathsf{P}_{231}-\mathsf{P}_{213}+\mathsf{P}_{312}-\mathsf{P}_{321}). \qquad (4.3.11)$$

Let us concentrate for the time being on those final states in which only one electron is free, and determine the coefficient $A'_{\mathbf{l}pq}(2, 31, \mathcal{S})$ of the state $\varphi_{\mathbf{l}}(2, 31)\alpha_q(2)\chi_p(31)$ in $\bar{\varphi}'_{\mathcal{S}}(t)$. If we operate with $a_i\mathcal{S}$ on (10) the term in square brackets becomes

$$\begin{aligned}&\frac{1}{2\sqrt{3}}A'_{\mathbf{l}pq}(1, 23)[\varphi_{\mathbf{l}}(2, 31)\,\alpha_q(2)\,\chi_p(31)-\varphi_{\mathbf{l}}(2, 13)\,\alpha_q(2)\,\chi_p(13)]\\ +&\frac{1}{2\sqrt{3}}A'_{\mathbf{l}pq}(2, 31)[\varphi_{\mathbf{l}}(2, 31)\,\alpha_q(2)\,\chi_p(31)-\varphi_{\mathbf{l}}(2, 13)\,\alpha_q(2)\,\chi_p(13)]\\ +&\frac{1}{2\sqrt{3}}A'_{\mathbf{l}pq}(3, 12)[-\varphi_{\mathbf{l}}(2, 13)\,\alpha_q(2)\,\chi_p(13)+\varphi_{\mathbf{l}}(2, 31)\,\alpha_q(2)\,\chi_p(31)]\\ &\qquad\qquad+\text{terms in which 2 is bound.}\end{aligned} \qquad (4.3.12)$$

The two terms in each of the square brackets differ by only a permutation of the electrons of the atom, and so differ from each other in sign only. Accordingly, (12) equals

$$3^{-1/2}[A'_{\mathbf{l}pq}(1,\,23)+A'_{\mathbf{l}pq}(2,\,31)+A'_{\mathbf{l}pq}(3,\,12)]\,\varphi_{\mathbf{l}}(2,\,31)\,\alpha_q(2)\,\chi_p(31)$$
$$+\text{terms in which 2 is bound.} \qquad (4.3.13)$$

It follows from (13) that

$$A'_{\mathbf{l}pq}(2,\,31\,|\,\mathcal{S}) = 3^{-1/2}[A'_{\mathbf{l}pq}(1,\,23)+A'_{\mathbf{l}pq}(2,\,31)+A'_{\mathbf{l}pq}(3,\,12)]. \qquad (4.3.14)$$

If we had calculated $A'_{\mathbf{l}pq}(2,\,13|\,\mathcal{S})$ we would have obtained (14) with a negative sign.

The reader may verify similarly that

$$A'_{\mathbf{l}pq}(1,\,23\,|\,\mathcal{S}) = A'_{\mathbf{l}pq}(2,\,31\,|\,\mathcal{S}) = A'_{\mathbf{l}pq}(3,\,12\,|\,\mathcal{S}) = -A'_{\mathbf{l}pq}(1,\,32\,|\,\mathcal{S})$$
$$= -A'_{\mathbf{l}pq}(2,\,13\,|\,\mathcal{S}) = -A'_{\mathbf{l}pq}(3,\,21\,|\,\mathcal{S}). \qquad (4.3.15)$$

The probability of observing 1 free in the final state is therefore the same as that of observing 2 or 3 free. The probability of observing *an* electron with wave vector **l** relative to the centre of mass of the atom and spin function α_q, while the atom is in the state χ_p, is therefore

$$3\,|\,A'_{\mathbf{l}pq}(1,\,23\,|\,\mathcal{S})\,|^2 = 3\,|\,A'_{\mathbf{l}pq}(2,\,31\,|\,\mathcal{S})|^2 = 3\,|\,A'_{\mathbf{l}pq}(3,12)\,|^2$$
$$= |\,A'_{\mathbf{l}pq}(1,\,23)+A'_{\mathbf{l}pq}(2,\,31)+A'_{\mathbf{l}pq}(3,\,12)\,|^2 \qquad (4.3.16)$$

by (14). The probability amplitude for observing *an* electron free with momentum $\hbar\mathbf{l}$ relative to the atomic centre of mass and spin function α_q, the atomic wave function being χ_p, is therefore

$$A'_{\mathbf{l}pq}(1,\,23)+A'_{\mathbf{l}pq}(2,\,31)+A'_{\mathbf{l}pq}(3,\,12). \qquad (4.3.17)$$

Let $f(\nu_1\nu_2\nu_3\mathbf{k}nm \to \nu'_1\nu'_2\nu'_3\mathbf{l}pq)$ denote the scattering amplitude for the process in which initially electron ν_1 has momentum $\hbar\mathbf{k}$ relative to the atomic centre of mass, and spin function α_m, the atomic wave function being $\chi_n(\nu_2\nu_3)$, while finally electron ν'_1 has momentum $\hbar\mathbf{l}$ relative to the atomic centre of mass and spin function α_q, the atomic wave function being χ_p. Let us further denote by $f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq)$ the scattering amplitude for the process when initially the incident electron has momentum $\hbar\mathbf{k}$ relative to the centre of mass of the atom and spin function α_m, the atomic wave function being χ_n, while finally *an* electron has momentum $\hbar\mathbf{l}$ relative to the atomic centre of mass and spin function α_q, the atomic wave function being $\chi_p(\nu'_2\nu'_3)$. It follows then from (17) that

$$f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq) = f(123\mathbf{k}nm \to 123\mathbf{l}pq)+f(123\mathbf{k}nm \to 231\mathbf{l}pq)$$
$$+f(123\mathbf{k}nm \to 312\mathbf{l}pq). \qquad (4.3.18)$$

The differential cross-section for the process is given by

$$\sigma(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq) = (v'/v)\,|f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq)|^2, \tag{4.3.19}$$

and the total cross-section for the process is

$$\sigma(\mathbf{k}nm \to \mathcal{S}pq) = (v'/v)\int |f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq)|^2\, d\hat{\mathbf{l}}. \tag{4.3.20}$$

The correct amplitude which takes into account the Pauli principle is given by (18). It is a sum of two terms; the first term represents direct scattering, while the remaining two terms represent exchange scattering. At high energies the exchange terms are small, and so (18) becomes

$$f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq) \simeq f(\mathbf{k}nm \to \mathbf{l}pq), \tag{4.3.21}$$

where $f(\mathbf{k}lm \to \mathbf{l}pq)$ is the scattering amplitude for direct scattering. In other words, at high energies exchange effects may be ignored. At low and intermediate energies, however, they become important.

EXERCISE

Verify (15).

4.4. IONIZATION OF HELIUM ATOMS BY ELECTRON IMPACT

We shall now consider the process whereby a helium atom is doubly ionized by electron impact. In other words, we shall discuss collisions of the form

$$\mathrm{He}+\mathrm{e} \to \mathrm{He}^{++}+\mathrm{e}+\mathrm{e}+\mathrm{e}. \tag{4.4.1}$$

The initial state has been described in the last section. The final unsymmetrized state is given by (4.3.10), which is now more conveniently written

$$\begin{aligned}\ddot{\varphi}'(t_1) = \sum_{qrs}\int d\mathbf{l}\int d\boldsymbol{\varkappa}\int d\boldsymbol{\lambda}\exp\left(-iE_{l\varkappa\lambda}t_1/\hbar\right) A'_{\mathbf{l}\varkappa\lambda qrs}(1,\,2,\,3)\times \\ \times\varphi_{\mathbf{l}}(1,\,23)\,\varphi_{\varkappa}(2,\,3)\,\varphi_{\lambda}(3)\,\alpha_q(1)\,\alpha_r(2)\,\alpha_s(3) \\ +\text{terms in which the helium atom is neutral} \\ \text{or singly ionized.}\end{aligned} \tag{4.4.2}$$

In (2) the plane wave $\varphi_{\mathbf{l}}(1, 23)$ represents the free motion of electron 1 relative to the centre of mass of the nucleus and electrons 2 and 3, $\varphi_{\varkappa}(2, 3)$ represents the free motion of electron 2 relative to the centre of mass of the nucleus and electron 3, while $\varphi_{\lambda}(3)$ represents the free motion of electron 3 relative to the nucleus. The terms α_q, α_r and α_s are spin functions, while $E_{l\varkappa\lambda} = E_l + E_\varkappa + E_\lambda$ is the total relative energy in the final state. The quantity $A_{\mathbf{l}\varkappa\lambda qrs}(1, 23)$ is the final probability amplitude for this state.

Let us now introduce an ordering of the three electrons according to the following scheme. We shall take as first electron that one whose speed relative to the centre of mass of the other particles is greatest. It is natural to treat this as the "scattered electron". As second electron we take that one of the remaining two electrons whose speed relative to the centre of mass of the nucleus and other electron is the greater. The remaining electron we take as third. We shall also denote by $\int'' d\mathbf{l} \int'' d\boldsymbol{\varkappa} \int'' d\boldsymbol{\lambda}$ an integration restricted to values of $\mathbf{l}$, $\boldsymbol{\varkappa}$ and $\boldsymbol{\lambda}$ which satisfy the above ordering. Any state in the integrand of such an integral cannot be transformed into another such state by a permutation of the electrons. On the other hand any state of the arrangement channel in which all three electrons are free can be transformed into a state with such an ordering by a permutation of the three electrons.

These considerations enable us to rewrite (2) in the form

$$\begin{aligned}\bar{\varphi}'(t_1) = \sum_{qrs} \int'' d\mathbf{l} \int'' d\boldsymbol{\varkappa} \int'' d\boldsymbol{\lambda} \exp\left(-iE_{l\varkappa\lambda}t_1/\hbar\right) \times \\ \times [A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3)\, \varphi_{\mathbf{l}}(1, 23)\, \varphi_{\boldsymbol{\varkappa}}(2, 3)\, \varphi_{\boldsymbol{\lambda}}(3)\, \alpha_q(1)\, \alpha_r(2)\, \alpha_s(3) \\ + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 3, 2)\, \varphi_{\mathbf{l}}(1, 32)\, \varphi_{\boldsymbol{\varkappa}}(3, 2)\, \varphi_{\boldsymbol{\lambda}}(2)\, \alpha_q(1)\, \alpha_r(3)\, \alpha_s(2) \\ + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 3, 1)\, \varphi_{\mathbf{l}}(2, 31)\, \varphi_{\boldsymbol{\varkappa}}(3, 1)\, \varphi_{\boldsymbol{\lambda}}(1)\, \alpha_q(2)\, \alpha_r(3)\, \alpha_s(1) \\ + \text{remaining permutations of 1, 2 and 3}] \\ + \text{terms in which the helium atom is neutral or singly ionized.} \end{aligned} \tag{4.4.3}$$

The first term represents a sum and integral over all states in which 1 separates more quickly from the centre of mass of 2, 3 and the nucleus than 2 separates from the centre of mass of 1, 3 and the nucleus or 3 separates from the centre of mass of 1, 2 and the nucleus, while 2 separates more quickly from the centre of mass of 3 and the nucleus than 3 moves from the centre of mass of 2 and the nucleus. The second term is a sum and integral over all states in which the role of electrons 2 and 3 is interchanged. In states of the third sum electron 2 moves more rapidly from its partners than 3 or 1, while 3 moves more rapidly from 1 and the nucleus than 1 moves from 3 and the nucleus. The remaining terms make up the remaining states in which all electrons are free. $E_{l\varkappa\lambda} = E_l + E_\varkappa + E_\lambda$ is the total energy in the centre of mass system, and is obviously invariant under permutations of the electrons.

The normalized and antisymmetrized final state $\bar{\varphi}'_{\mathcal{S}}(t_1)$ is obtained by operating upon (3) with $a_l\mathcal{S}$, which is given by (4.3.11) in this case. If we do this we find for the coefficient $A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3 \mid \mathcal{S})$ of the state $\varphi_{\mathbf{l}}(1, 23)\, \varphi_{\boldsymbol{\varkappa}}(2, 3) \times \varphi_{\boldsymbol{\lambda}}(3)\, \alpha_q(1)\, \alpha_r(2)\, \alpha_s(3)$ in the consequent expression for $\varphi'_{\mathcal{S}}(t_1)$ the result

$$\begin{aligned}A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3 \mid \mathcal{S}) = \frac{1}{2\sqrt{3}} [A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3) - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 3, 2) + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 3, 1) \\ - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 1, 3) + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 1, 2) - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 2, 1)].\end{aligned} \tag{4.4.4}$$

The result for $A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 3, 2 \mid \mathcal{S})$ is the negative of this. It is easy to see that this is a consequence of the fact that the permutation P_{132} has negative parity. In fact the reader may easily verify that

$$\begin{aligned} &A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3 \mid \mathcal{S}) = A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 3, 1 \mid \mathcal{S}) = A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 1, 2 \mid \mathcal{S}) \\ &= -A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 3, 2 \mid \mathcal{S}) = -A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 1, 3 \mid \mathcal{S}) = -A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 2, 1 \mid \mathcal{S}). \end{aligned} \tag{4.4.5}$$

The signs arise from the fact that the permutations P_{123}, P_{231}, and P_{312} all have parity $+1$, while the permutations P_{132}, P_{213} and P_{321} all have parity -1. More briefly we may write

$$\delta_{123} = \delta_{231} = \delta_{312} = 1, \tag{4.4.6}$$

$$\delta_{132} = \delta_{213} = \delta_{321} = -1. \tag{4.4.7}$$

The probability that after the collision *an* electron has momentum $\hbar\mathbf{l}$ relative to the centre of mass of the remaining particles, *one of the remaining* electrons has momentum $\hbar\boldsymbol{\varkappa}$ relative to the centre of mass of the remaining electron and the nucleus, and *the remaining* electron has momentum $\hbar\boldsymbol{\lambda}$ relative to the nucleus is the sum of the squares of the moduli of the six probability amplitudes in (5), and therefore six times the square of the modulus of any one of them. This probability thus equals, for example, on using (4)

$$\begin{aligned} &6 \mid A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3 \mid \mathcal{S})|^2 \\ &\quad = \tfrac{1}{2} \mid A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 2, 3) - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(1, 3, 2) + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 3, 1) \\ &\qquad - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(2, 1, 3) + A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 1, 2) - A'_{\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs}(3, 2, 1) \mid^2. \end{aligned} \tag{4.4.8}$$

Let us denote the scattering amplitude when the final state is $\varphi_{\mathbf{l}}(\nu_1, \nu_2\nu_3)\varphi_{\boldsymbol{\varkappa}}(\nu_2, \nu_3)\varphi_{\boldsymbol{\lambda}}(\nu_3)\alpha_q(\nu_1)\alpha_r(\nu_2)\alpha_s(\nu_3)$ by $f(123\mathbf{k}nm \rightarrow \nu_1\nu_2\nu_3\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs)$, and the symmetrized scattering amplitude by $f(\mathbf{k}nm \rightarrow \mathcal{S}\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs)$. The expression (8) gives

$$\begin{aligned} f(\mathbf{k}nm \rightarrow \mathcal{S}\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) = 2^{-1/2}[&f(123\mathbf{k}nm \rightarrow 123\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) \\ &-f(123\mathbf{k}nm \rightarrow 132\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) + f(123\mathbf{k}nm \rightarrow 231\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) \\ &-f(123\mathbf{k}nm \rightarrow 213\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) + f(123\mathbf{k}nm \rightarrow 312\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) \\ &-f(123\mathbf{k}nm \rightarrow 321\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs)]. \end{aligned} \tag{4.4.9}$$

The total cross-section for the double ionization process, which we can denote by σ_d^{++}, is given by

$$\sigma_d^{++} = \sum_{qrs} \int d_{\mathbf{l}} \int''' d\boldsymbol{\varkappa} \int''' d\boldsymbol{\lambda}(v'/v) \mid f(\mathbf{k}nm \rightarrow \mathcal{S}\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs)|^2. \tag{4.4.10}$$

In (10) $\hbar\mathbf{l}$ is the momentum of the electron which recedes fastest from the centre of mass of the others relative to that centre of mass, $\hbar\boldsymbol{\varkappa}$ is the momentum of the electron which recedes fastest from the centre of mass of the remaining two particles relative to that centre of mass, $\hbar\boldsymbol{\lambda}$ is the momentum of the remaining electron relative to the nucleus; α_q, α_r and α_s are the spin functions of the three electrons in order. The magnitude l of $\mathbf{l}$ is determined by energy conservation, and the triple primes denote that the region of integration goes over values of $\boldsymbol{\varkappa}$ and $\boldsymbol{\lambda}$ which obey the given ordering relation and are also energetically attainable.

In fact only three of the six terms in (9) are distinct. According to (3.3.18) the transition amplitude for the process $\varphi_\alpha \to \varphi_\beta$ is given by

$$T(\alpha \to \beta) = \langle \varphi_\beta | V_f | \psi_\alpha^+ \rangle \tag{4.4.11}$$

where φ_β belongs to arrangement channel f. By the definition (1.5.1), if φ_α belongs to arrangement channel i,

$$T(\alpha \to \beta) = \langle \varphi_\beta | V_f [1 + (E - \mathsf{H} + i\varepsilon)^{-1} V_i] | \varphi_\alpha \rangle \tag{4.4.12}$$

where $E_\alpha = E_\beta = E$. Let P be the permutation which interchanges electrons 2 and 3. Since 2 and 3 are the atomic electrons in the initial state $\mathsf{P}\varphi_\alpha = -\varphi_\alpha$, and so (11) can be written

$$T(\alpha \to \beta) = \langle \varphi_\beta | V_f [1 + (E - \mathsf{H} + i\varepsilon)^{-1} V_i] | -\mathsf{P}\varphi_\alpha \rangle. \tag{4.4.13}$$

The potential V_i refers to the incident channel in which 2 and 3 belong to the helium atom, and so is invariant under P. Further H must also be invariant under interchange of 2 and 3, and since V_f is Hermitian and $\mathsf{P}^\dagger = \mathsf{P}^{-1} = \mathsf{P}$ equation (13) can be replaced by

$$T(\alpha \to \beta) = -\langle P(V_f \varphi_\beta) | 1 + (E - \mathsf{H} + i\varepsilon)^{-1} V_i | \varphi_\alpha \rangle. \tag{4.4.14}$$

If P transforms the final state φ_β in arrangement channel f into the state φ_γ of arrangement channel g, it also transforms V_f into V_g, and so

$$\begin{aligned} T(\alpha \to \beta) &= -\langle V_g \varphi_\gamma | 1 + (E - \mathsf{H} + i\varepsilon)^{-1} V_i | \varphi_\alpha \rangle \\ &= -\langle \varphi_\gamma | V_g [1 + (E - \mathsf{H} + i\varepsilon)^{-1} V_i] | \varphi_\alpha \rangle = -T(\alpha \to \gamma). \end{aligned} \tag{4.4.15}$$

If we denote γ by $\mathsf{P}\beta$ we can write (15) as

$$T(\alpha \to \mathsf{P}\beta) = -T(\alpha \to \beta). \tag{4.4.16}$$

In other words, if two final states differ by an interchange of electrons 2 and 3 the scattering amplitude for these final states differ by a sign.

It follows from (16) that the first and second, third and sixth, and fourth and fifth amplitudes on the right-hand side of (9) are opposite in sign. Equation (9) therefore simplifies to

$$\begin{aligned} f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) = 2^{1/2}[&f(123\mathbf{k}nm \to 123\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) \\ &+ f(123\mathbf{k}nm \to 231\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs) + f(123\mathbf{k}nm \to 312\mathbf{l}\boldsymbol{\varkappa}\boldsymbol{\lambda}qrs)]. \end{aligned} \tag{4.4.17}$$

EXERCISES

1. Verify (5).

2. Repeat the above discussion in the case when helium atoms are singly ionized under electron impact.

3. Prove that in the case of exchange scattering of electrons by helium atoms interchange of the atomic electrons of the final state changes the sign of the scattering amplitude.

Deduce that (4.3.18) can be simplified to

$$f(\mathbf{k}nm \to \mathcal{S}\mathbf{l}pq) = f(123\mathbf{k}nm \to 123\mathbf{l}pq) - 2f(123\mathbf{k}nm \to 213\mathbf{l}pq).$$

4.5. THE *N*-PARTICLE SYSTEM WITH ONE SPECIES OF IDENTICAL PARTICLES

We shall now consider an N-particle system in which M elementary particles are identical, but the remaining $N-M$ particles are distinct from the first M, and from each other. For example, our system may consist of M electrons and $N-M$ atomic nuclei, where the nuclei are all different. The approach is a straightforward generalization of the particular cases studied in the previous sections of this chapter.

In the remote past the system has a wave function $\bar{\varphi}(t_0)$ given by an expression of the form

$$\bar{\varphi}(t_0) = \sum_n B_n \bar{\varphi}_n(t_0) \tag{4.5.1}$$

where $\bar{\varphi}_n(t_0)$ is a wave packet in channel n, when the internal state of the m composite particles $A_1, A_2, \ldots, A_m$ is represented by χ_n. Since we sum over final states and average over initial states we can assume that only one channel is present, so that (1) can be replaced by

$$\bar{\varphi}(t_0) = \bar{\varphi}_n(t_0). \tag{4.5.2}$$

To obtain the symmetrized initial state $\bar{\varphi}_{\mathcal{S}}(t_0)$ we operate on $\bar{\varphi}(t_0)$ with the symmetrizer $\mathcal{S}$ defined by (4.1.1). This gives

$$\bar{\varphi}_{\mathcal{S}}(t_0) = a_i(M!)^{-1} \sum_{\mathsf{P}} \delta_{\mathsf{P}} P\bar{\varphi}(t_0) \tag{4.5.3}$$

where $\sum_{\mathsf{P}}$ goes over all permutations of identical particles.

Suppose P and R are two permutations which have the property that the wave function $\mathsf{P}\bar{\varphi}(t_0)$ differs from the wave function $\mathsf{R}\bar{\varphi}(t_0)$ by a permutation Q which permutes the identical particles of $\mathsf{R}\bar{\varphi}(t_0)$ within each of the composite particles $A_1, A_2, \ldots, A_m$ but does not interchange identical particles between composite particles; thus

$$\mathsf{P}\bar{\varphi}(t_0) = \mathsf{QR}\bar{\varphi}(t_0). \tag{4.5.4}$$

Since Q permutes identical particles of $\mathsf{R}\bar{\varphi}(t_0)$ within the same composite particle without interchange between composite particles its effect is to leave the wave function unaltered if the particles are bosons, but to multiply it by the parity of Q if the identical particles are fermions. In other words

$$\mathsf{QR}\bar{\varphi}(t_0) = \delta_{\mathsf{Q}}\mathsf{R}\bar{\varphi}(t_0) \tag{4.5.5}$$

where $\delta_{\mathsf{Q}} = 1$ for bosons, and equals the parity of Q for fermions. Now (4) implies that $\mathsf{P} = \mathsf{QR}$, and so $\delta_{\mathsf{P}} = \delta_{\mathsf{Q}}\delta_{\mathsf{R}}$. Since $\delta_{\mathsf{Q}}^2 = 1$ we see on multiplication by δ_{Q} that $\delta_{\mathsf{P}}\delta_{\mathsf{Q}} = \delta_{\mathsf{Q}}^2\delta_{\mathsf{R}} = \delta_{\mathsf{R}}$, and so from (4) and (5)

$$\delta_{\mathsf{P}}\mathsf{P}\bar{\varphi}(t_0) = \delta_{\mathsf{P}}\mathsf{QR}\bar{\varphi}(t_0) = \delta_{\mathsf{P}}\delta_{\mathsf{Q}}\mathsf{R}\bar{\varphi}(t_0) = \delta_{\mathsf{R}}\mathsf{R}\bar{\varphi}(t_0). \tag{4.5.6}$$

The result (6) shows that terms in (3) which differ from each other by a permutation of identical particles within the same composite particles are identical.

Let the number of permutations of identical particles which permute particles within the same composite particles without exchange of identical particles between composite particles be M_i. The integer M_i obviously depends only on the arrangement channel i to which the initial channel n belongs. If M_{ir} is the number of identical particles in the composite particle A_r of arrangement channel i we have

$$M_i = \prod_{r=1}^{m} (M_{ir}!). \tag{4.5.7}$$

If two arrangement channels, i and g say, can be transformed into each other by a permutation of identical particles then obviously $M_i = M_g$.

The number of terms in (3) which are equal to $\delta_{\mathsf{P}}\mathsf{P}\bar{\varphi}(t_0)$ for any given permutation P is M_i. We can therefore replace (3) by

$$\bar{\varphi}_{\mathscr{S}}(t_0) = a_i(M!)^{-1}M_i \sum_{\mathsf{P}}{}' \delta_{\mathsf{P}}\mathsf{P}\bar{\varphi}(t_0) \tag{4.5.8}$$

where $\sum_{\mathsf{P}}'$ goes over all functions $\mathsf{P}\bar{\varphi}(t_0)$ which cannot be transformed into each other by permutations of identical particles within the same composite particles. That is to say, any two terms under the sum on the right-hand side of (8) differ by an interchange of identical particles between composite particles. Such states are therefore initially distinguishable from each other.

We shall now determine the value of a_i from the condition that $\bar{\varphi}_{\mathscr{S}}(t_0)$ is normalized to unity. We have seen that if $\mathsf{P}\bar{\varphi}(t_0)$ and $\mathsf{R}\bar{\varphi}(t_0)$ are two states on the right-hand side of (8) there is at least one elementary particle e which will be attached to different composite particles in these states; different, that is, in the sense that they are localized in different regions of space, for some composite particles may be identical in composition and structure. For example, e may be attached to a particle of the incident beam in $\mathsf{P}\bar{\varphi}(t_0)$ but to a target particle in $\mathsf{R}\bar{\varphi}(t_0)$. It follows that $\mathsf{P}\bar{\varphi}(t_0)$ and $\mathsf{R}\bar{\varphi}(t_0)$ are only non-vanishing when e is close to the centres of mass of different composite particles which at time t_0 must be well separated. The product $[\mathsf{P}\bar{\varphi}(t_0)]^* \times \times [\mathsf{R}\bar{\varphi}(t_0)]$ must therefore vanish, and so must therefore the inner product of $\mathsf{P}\bar{\varphi}(t_0)$ and $\mathsf{R}\bar{\varphi}(t_0)$. If we take the inner product of $\bar{\varphi}_{\mathcal{S}}(t_0)$ with itself with the aid of (8) we consequently obtain

$$\|\bar{\varphi}_{\mathcal{S}}(t_0)\|^2 = a_i^2(M!)^{-2}M_i^2 \sum_{\mathsf{P}}{}' \, \|\mathsf{P}\bar{\varphi}(t_0)\|^2. \tag{4.5.9}$$

We have already pointed out that $\|\bar{\varphi}(t_0)\| = 1$, and since the norm of a wave function is invariant under a permutation of identical particles we have $\|\mathsf{P}\bar{\varphi}(t_0)\| = \|\bar{\varphi}(t_0)\| = 1$. The number of terms in the sum $\sum'_{\mathsf{P}}$ is $M!/M_i$, since it was obtained from the sum $\sum_{\mathsf{P}}$ of $M!$ terms by collecting together groups of M_i equal terms. Equation (9) now gives us $1 = a_i^2(M!)^{-1}M_i$, and so

$$a_i = (M!/M_i)^{1/2}. \tag{4.5.10}$$

We saw in Section 4.1 that the normalized and symmetrized final state is $a_i\mathcal{S}\bar{\varphi}'(t_1)$, where $\bar{\varphi}'(t_1)$ evolves from $\bar{\varphi}(t_0)$ under the action of the total Hamiltonian H. We shall now pick out the coefficient $A'_\beta(\mathcal{S})$ of the final state φ_β in $\bar{\varphi}'_{\mathcal{S}}(t_1)$. We shall assume that the final wave function can be written

$$\bar{\varphi}'(t_1) = \sum_{\beta}{}'' \sum_{\gamma \approx \beta} A'_\gamma \varphi_\gamma \exp(-iE_\gamma t_1/\hbar) \tag{4.5.11}$$

where $\sum_{\gamma \approx \beta}$ goes over all distinct states φ_γ which can be transformed into φ_β by a permutation of identical particles, including φ_β itself, while $\sum''_\beta$ goes over all states φ_β which cannot be so transformed into each other. We have seen examples of the way in which this can be done in previous sections. The interchange of identical particles between composite particles cannot alter the energy of a state, and so $\beta \approx \gamma$ implies $E_\beta = E_\gamma$; hence (11) can be replaced by

$$\bar{\varphi}'(t_1) = \sum_{\beta}{}'' \exp(-iE_\beta t_1/\hbar) \sum_{\gamma \approx \beta} A'_\gamma \varphi_\gamma. \tag{4.5.12}$$

We now operate on (12) with $a_i\mathcal{S}$ to obtain $\bar{\varphi}'_{\mathcal{S}}(t_1)$. Since $\mathcal{S}$ is given by (4.1.1) we get

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = a_i(M!)^{-1} \sum_{\beta}{}'' \exp(-iE_\beta t_1/\hbar) \sum_{\gamma \approx \beta} A'_\gamma \sum_{\mathsf{P}} \delta_{\mathsf{P}}\mathsf{P}\varphi_\gamma. \tag{4.5.13}$$

As we have seen, not all terms in the sum $\sum_{\mathsf{P}}$ are distinct. In fact $\delta_{\mathsf{P}}\mathsf{P}\varphi_\gamma = \delta_{\mathsf{R}}\mathsf{R}\varphi_\gamma$ if, and only if, $\mathsf{P}\varphi_\gamma$ can be transformed into $\mathsf{R}\varphi_\gamma$ by a permutation of identical particles within composite particles. Let M_f be the number of permutations of identical particles within composite particles in arrangement channel f, to which φ_β belongs. Since every $\mathsf{P}\varphi_\gamma$ differs from φ_β only by a permutation of identical particles, it follows that M_f is also the number of permutations of identical particles within composite particles in the arrangement channel to which $\mathsf{P}\varphi_\gamma$ belongs. The $M!$ terms in the sum $\sum_{\mathsf{P}}$ divide into $M!/M_f$ classes — the M_f terms in each class can be transformed into each other by permutations of identical particles within composite particles, and so are all equal. Terms in different classes differ by an interchange of identical particles between composite particles, and are distinct. It follows that (13) can be replaced by

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = a_i(M!)^{-1} \sum_{\beta}'' \exp(-iE_\beta t_1/\hbar)\, M_f \sum_{\gamma\approx\beta} A'_\gamma \sum_{\mathsf{P}}' \delta_{\mathsf{P}} \mathsf{P}\varphi_\gamma \qquad (4.5.14)$$

where $\sum_{\mathsf{P}}'$ goes over distinct states $\mathsf{P}\varphi_\gamma$.

Let $\mathsf{P}_{\gamma\to\delta}$ be the permutation which transforms the state φ_γ into the state φ_δ, and let $\delta_{\gamma\to\delta}$ be the corresponding value of δ_{P}. With this notation (14) can be rewritten

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = a_i(M!)^{-1} \sum_{\beta}'' \exp(-iE_\beta t_1/\hbar)\, M_f \sum_{\gamma\approx\beta} A'_\gamma \sum_{\delta\approx\gamma} \delta_{\gamma\to\delta}\varphi_\delta. \qquad (4.5.15)$$

Now $\sum_{\delta\approx\gamma}$ is a sum over distinct states φ_δ which can be transformed into φ_γ by a permutation of identical particles. Since φ_γ can itself be transformed into φ_β by a permutation of identical particles it follows that the sum $\sum_{\delta\approx\gamma}$ is the same as the sum $\sum_{\delta\approx\beta}$ of distinct states φ_δ which can be transformed into φ_β by a permutation of identical particles. We deduce that (15) can be written

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = a_i(M!)^{-1} \sum_{\beta}'' \exp(-iE_\beta t_1/\hbar)\, M_f \sum_{\gamma\approx\beta} A'_\gamma \sum_{\delta\approx\beta} \delta_{\gamma\to\delta}\varphi_\delta. \qquad (4.5.16)$$

Since $\delta \approx \beta$ implies $E_\delta = E_\beta$ we can rewrite (16) as

$$\bar{\varphi}'_{\mathcal{S}}(t_1) = \sum_{\beta}'' \sum_{\delta\approx\beta} \varphi_\delta \exp(-iE_\delta t_1/\hbar) \left[a_i(M!)^{-1} M_f \sum_{\gamma\approx\beta} \delta_{\gamma\to\delta} A'_\gamma\right]. \qquad (4.5.17)$$

The coefficient $A'_\delta(\mathcal{S})$ of $\varphi_\delta \exp(-iE_\delta t_1/\hbar)$ in the final state $\bar{\varphi}'_{\mathcal{S}}(t_1)$ is therefore

$$A'_\delta(\mathcal{S}) = a_i(M!)^{-1} M_f \sum_{\gamma\approx\beta} \delta_{\gamma\to\delta} A'_\gamma. \qquad (4.5.18)$$

In particular

$$A'_\beta(\mathcal{S}) = a_i(M!)^{-1} M_f \sum_{\gamma\approx\beta} \delta_{\gamma\to\delta} A'_\gamma. \qquad (4.5.19)$$

Now $P_{\gamma\to\delta} = P_{\beta\to\delta} P_{\gamma\to\beta}$, hence $\delta_{\gamma\to\delta} = \delta_{\beta\to\delta}\delta_{\gamma\to\beta}$, so if we substitute for $\delta_{\gamma\to\delta}$ in (18) we obtain

$$A'_\delta(\mathcal{S}) = a_i(M!)^{-1} M_f \delta_{\beta\to\delta} \sum_{\gamma\approx\beta} \delta_{\gamma\to\beta} A'_\gamma. \qquad (4.5.20)$$

Comparison of (19) and (20) shows that

$$A'_\delta(\mathcal{S}) = \delta_{\beta\to\delta} A'_\beta(\mathcal{S}). \tag{4.5.21}$$

The probability of observing the final state φ_β, or any other final state φ_δ which can be obtained from it by a permutation of identical particles, which we shall denote by $P(\alpha \to \mathcal{S}\beta)$, is given by

$$P(\alpha \to \mathcal{S}\beta) = \sum_{\delta \approx \beta} |A'_\beta(\mathcal{S})|^2. \tag{4.5.22}$$

From (21) we see that $|A'_\delta(\mathcal{S})|^2 = |A'_\beta(\mathcal{S})|^2$, and there are $M!M_f^{-1}$ distinct states, including φ_β, which can be obtained from φ_β by a permutation of identical particles. The observable probability (22) therefore becomes

$$P(\alpha \to \mathcal{S}\beta) = M!M_i^{-1}|A'_\beta(\mathcal{S})|^2. \qquad (4.5.23$$

Now by (10) $a_i = (M!/M_i)^{1/2}$, and so if we substitute for $A'_\beta(\mathcal{S})$ from (19) into (23) we obtain

$$P(\alpha \to \mathcal{S}\beta) = M_f M_i^{-1} \,|\sum_{\gamma \approx \beta} \delta_{\gamma\to\beta}\, A'_\gamma|^2. \tag{4.5.24}$$

We can therefore take as the probability amplitude for observation of the final state φ_β, or any final state φ_γ obtainable from it by a permutation of identical particles, the quantity

$$A'(\alpha \to \mathcal{S}\beta) = (M_f/M_i)^{1/2} \sum_{\gamma \approx \beta} \delta_{\gamma\to\beta} A'_\gamma. \tag{4.5.25}$$

This quantity replaces the final probability amplitude A'_β in derivations of expressions for the observed differential cross-section. If we define the symmetrized scattering amplitude $f(\alpha \to \mathcal{S}\beta)$ by

$$\boxed{f(\alpha \to \mathcal{S}\beta) = (M_f/M_i)^{1/2} \sum_{\gamma \approx \beta} \delta_{\gamma\to\beta} f(\alpha \to \gamma),} \tag{4.5.26}$$

the observed differential cross-section for the process which takes φ_α into φ_β or any other state obtainable from it by a permutation of identical particles is

$$\boxed{\sigma(\alpha \to \mathcal{S}\beta) = (v_\beta/v_\alpha)\,|f(\alpha \to \mathcal{S}\beta)|^2;} \tag{4.5.27}$$

in (27) v_α is the speed of the centre of mass of the incident composite particle relative to the centre of mass of the target composite particle, while v_β is the speed of the scattered composite particle relative to the centre of mass of the recoil composite particle or recoil particles.

The total cross-section σ is given by

$$\boxed{\sigma = \sum_{\beta}''' \sigma(\alpha \to \mathscr{S}\beta)} \tag{4.5.28}$$

where $\sum_{\beta}'''$ goes over all energetically allowed final states φ_β which cannot be transformed into each other by a permutation of identical particles.

Example 1. In the case of scattering of two identical spinless bosons the only permutations are the identity and the exchange operator which takes the plane wave $\varphi_{\mathbf{l}}$ into $\varphi_{-\mathbf{l}}$, while $M_i = M_f = 1$. In this case (26) yields

$$f(\mathbf{k} \to \mathscr{S}\mathbf{l}) = \delta_{\mathbf{l}\to\mathbf{l}} f(\mathbf{k} \to \mathbf{l}) + \delta_{-\mathbf{l}\to\mathbf{l}} f(\mathbf{k} \to -\mathbf{l}) = f(\mathbf{k} \to \mathbf{l}) - f(\mathbf{k} \to -\mathbf{l}) \tag{4.5.29}$$

in agreement with (4.2.13).

Example 2. Let us consider the collision of two spin $\frac{1}{2}$ fermions, such as two electrons or two protons. The initial state is $\varphi_{\mathbf{k}}\alpha_m\,(1, 2)$ $(m = 0, 1, 2, 3)$ where α_0 is the singlet spin function while α_1, α_2 and α_3 are the three triplet spin functions. One final state is $\varphi_{\mathbf{l}}\alpha_q(1, 2)$, and the distinct state obtainable from this by permutation of the particles is $\varphi_{-\mathbf{l}}\alpha_q(2, 1)$. If we denote the scattering amplitudes for these two processes by $f(\mathbf{k}m \to \mathbf{l}q)$ and $f(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q)$ respectively we see that (26) gives

$$f(\mathbf{k}m \to \mathscr{S}\mathbf{l}q) = f(\mathbf{k}m \to \mathbf{l}q) - f(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q). \tag{4.5.30}$$

Now by (3.5.31)

$$f(\mathbf{k}m \to \mathbf{l}q) = -4\pi^2\mu\hbar^{-2}\,T(\mathbf{k}m \to \mathbf{l}q), \tag{4.5.31}$$

$$f(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) = -4\pi^2\mu\hbar^{-2}\,T(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) \tag{4.5.32}$$

where μ is the reduced mass and, by (3.3.18) and (1.5.1), if V is the interaction potential,

$$T(\mathbf{k}m \to \mathbf{l}q) = \langle \varphi_{\mathbf{l}}\alpha_q(1, 2) \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\alpha_m(1, 2)\rangle, \tag{4.5.33}$$

$$T(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) = \langle \varphi_{-\mathbf{l}}\alpha_q(2, 1) \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\alpha_m(1, 2)\rangle. \tag{4.5.34}$$

Also $\alpha_q\,(2, 1) = \delta_q\alpha_q\,(1, 2)$ where $\delta_0 = -1$, $\delta_1 = \delta_2 = \delta_3 = 1$, and so (34) becomes

$$T(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) = \delta_q\langle \varphi_{-\mathbf{l}}\alpha_q(1, 2) \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\alpha_m(1, 2)\rangle. \tag{4.5.35}$$

If the interaction potential V is spin-independent, then so is H, and (33) factorizes into

$$\begin{aligned} T(\mathbf{k}m \to \mathbf{l}q) &= \langle \varphi_{\mathbf{l}} \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\rangle \langle \alpha_q(1, 2) \,|\, \alpha_m(1, 2)\rangle \\ &= \langle \varphi_{\mathbf{l}} \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\rangle\, \delta_{qm} \end{aligned} \tag{4.5.36}$$

by the orthonormality of the spin states. If we define the transition amplitude $T(\mathbf{k} \to \mathbf{l})$ by

$$T(\mathbf{k} \to \mathbf{l}) = \langle \varphi_{\mathbf{l}} \,|\, V + V(E - \mathsf{H} + i\varepsilon)^{-1} V \,|\, \varphi_{\mathbf{k}}\rangle \tag{4.5.37}$$

we can rewrite (36) as

$$T(\mathbf{k}m \to \mathbf{l}q) = T(\mathbf{k} \to \mathbf{l})\,\delta_{mq}. \tag{4.5.38}$$

In a similar way we can infer from (35) that

$$T(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) = \delta_q T(\mathbf{k} \to -\mathbf{l})\,\delta_{mq}. \tag{4.5.39}$$

Let us define a scattering amplitude $f(\mathbf{k} \to \mathbf{l})$ by

$$f(\mathbf{k} \to \mathbf{l}) = -4\pi^2\mu\hbar^{-2}\,T(\mathbf{k} \to \mathbf{l}). \tag{4.5.40}$$

It follows then from (31), (38) and (40) that

$$f(\mathbf{k}m \to \mathbf{l}q) = \delta_{mq} f(\mathbf{k} \to \mathbf{l}), \tag{4.5.41}$$

and from (32), (39) and (40) that

$$f(\mathbf{k}m \to -\mathbf{l}\mathsf{P}q) = \delta_q \delta_{mq} f(\mathbf{k} \to -\mathbf{l}). \tag{4.5.42}$$

Hence (30) gives

$$f(\mathbf{k}m \to \mathcal{S}\mathbf{l}q) = \delta_{mq}[f(\mathbf{k} \to \mathbf{l}) - \delta_q f(\mathbf{k} \to -\mathbf{l})]. \tag{4.5.43}$$

The result (43) implies that if the system is initially in a singlet state, it remains in a singlet state, and the corresponding scattering amplitude $f_s(\mathbf{k} \to \mathcal{S}\mathbf{l})$ is given by

$$f_s(\mathbf{k} \to \mathcal{S}\mathbf{l}) = f(\mathbf{k} \to \mathbf{l}) + f(\mathbf{k} \to -\mathbf{l}), \tag{4.5.44}$$

while if it is initially in a triplet state it remains in it, and the corresponding scattering amplitude $f_t(\mathbf{k} \to \mathcal{S}\mathbf{l})$ is given by

$$f_t(\mathbf{k} \to \mathcal{S}\mathbf{l}) = f(\mathbf{k} \to \mathbf{l}) - f(\mathbf{k} \to -\mathbf{l}). \tag{4.5.45}$$

The differential cross-section $\sigma(\mathbf{k} \to \mathcal{S}\mathbf{l})$ is obtained by averaging over the one singlet state and three triplet states; this yields

$$f(\mathbf{k} \to \mathcal{S}\mathbf{l}) = \tfrac{1}{4}\,|f_s(\mathbf{k} \to \mathcal{S}\mathbf{l})|^2 + \tfrac{3}{4}\,|f_t(\mathbf{k} \to \mathcal{S}\mathbf{l})|^2. \tag{4.5.46}$$

If the interaction depends upon spin the calculation is correspondingly more complicated

Example 3. As a final example we shall discuss the scattering of an electron by an atom. We shall label the incident electron by 0 and the atomic electrons by 1, 2, . . . , n. In the case of direct scattering electron 0 is the scattered electron; the initial state here has wave function $\varphi_\alpha = \varphi_{\mathbf{k}}(0)\alpha_m(0)\chi_n(1, 2, \ldots, n)$, say, while the final state has wave function $\varphi_\beta = \varphi_{\mathbf{l}}(0)\alpha_q(0)\chi_p(1, 2, \ldots, n)$, say. We can denote the scattering amplitude for this process by $f_d(\mathbf{k}n \to \mathbf{l}p)$. There are also n exchange collisions, when electron 0 is exchanged with electron j of the atom. The final state here has wave function $\varphi_\gamma = \varphi_{\mathbf{l}}(j)\alpha_q(j)\chi_p(1, 2, \ldots, j-1, 0, j+1, \ldots, n)$. As j varies from 1 to n we obtain the n distinct states obtainable from φ_α by a permutation of the electrons. In this case, therefore, $M_i = M_f = n+1$. Let us denote the scattering amplitude for the process in which electron 0 is exchanged with electron j by $f_j(\mathbf{k}n \to \mathbf{l}p)$. Each of the n final states for exchange scattering is obtained from the final state φ_β for direct scattering by an interchange of two electrons only, which is a permutation with odd parity. In this case, therefore, (26) becomes

$$f(\mathbf{k}n \to \mathcal{S}\mathbf{l}p) = f_d(\mathbf{k}n \to \mathbf{l}p) - \sum_{j=1}^{n} f_j(\mathbf{k}n \to \mathbf{l}p). \tag{4.5.47}$$

EXERCISES

1. Verify (4.4.9), the expression for the scattering amplitude for the process $\mathrm{He} + \mathrm{e} \to \mathrm{He}^{++} + \mathrm{e} + \mathrm{e} + \mathrm{e}$, by direct application of (26).

2. Use (26) to write down the scattering amplitude for the following processes:

(a) $\mathrm{H} + \mathrm{He} \to \mathrm{H}^- + \mathrm{He}^+$.

(b) $\mathrm{H} + \mathrm{He} \to \mathrm{H}^+ + \mathrm{He}^+ + \mathrm{e} + \mathrm{e}$.

4.6. SIMPLIFICATIONS DUE TO INITIAL OR FINAL SYMMETRY

In the last section we obtained the expression (4.5.26) for the symmetrized scattering amplitude $f(\alpha \to \mathcal{S}\beta)$. Some of the terms in this expression may be equal. In this section we shall obtain conditions on the stationary states φ_α, φ_γ and φ_δ which imply the equality of the terms $\delta_{\gamma\to\beta} f(\alpha \to \gamma)$ and $\delta_{\delta\to\beta}$ $f(\alpha \to \delta)$.

From (1.5.1) and (3.3.18) we obtain

$$T(\alpha \to \beta) = \langle \varphi_\beta | V_f[1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i] | \varphi_\alpha \rangle, \tag{4.6.1}$$

$$\begin{aligned} T(\alpha \to \beta) &= \langle [1+(E-\mathsf{H}-i\varepsilon)^{-1}V_f]\varphi_\beta | V_i | \varphi_\alpha \rangle \\ &= \langle \varphi_\beta | [1+V_f(E-\mathsf{H}+i\varepsilon)^{-1}] V_i | \varphi_\alpha \rangle \end{aligned} \tag{4.6.2}$$

where $E = E_\alpha = E_\beta$. According to (3.6.6) the unsymmetrized scattering amplitude is defined by

$$f(\alpha \to \beta) = -4\pi^2 \mu_f \hbar^{-2} T(\alpha \to \beta) \tag{4.6.3}$$

where μ_f is the reduced mass of the scattered particle relative to the centre of mass of the recoil particles in the final state φ_β. We deduce from (1) and (3) that

$$f(\alpha \to \beta) = -4\pi^2 \mu_f \hbar^{-2} \langle \varphi_\beta | V_f[1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i] | \varphi_\alpha \rangle, \tag{4.6.4}$$

and from (2) and (3) that

$$f(\alpha \to \beta) = -4\pi^2 \mu_f \hbar^{-2} \langle \varphi_\beta | [1+V_f(E-\mathsf{H}+i\varepsilon)^{-1}] V_i | \varphi_\alpha \rangle. \tag{4.6.5}$$

We shall prove the following:

> If P is a permutation which permutes identical particles within the same composite particles of the final state φ_β, then
>
> $$f(\alpha \to \mathsf{P}\beta) = \delta_{\mathsf{P}} f(\alpha \to \beta). \tag{4.6.6}$$

The proof follows immediately from (5), for $\mathsf{P}\varphi_\beta = \delta_{\mathsf{P}}\varphi_\beta$, and so φ_β and $\mathsf{P}\varphi_\beta$ belong to the same arrangement channel f.

As it stands, the result (6) does not help us to simplify (4.5.26), for the sum $\sum_{\gamma\approx\beta}$ goes only over *distinct* final states φ_γ, and φ_β represents the same final state as $\mathsf{P}\varphi_\beta = \delta_{\mathsf{P}}\varphi_\beta$. However, we can use (6) in conjunction with the following result:

> If P is a permutation which permutes identical particles within the same composite particles of the initial state φ_α, and $\mathsf{P}\varphi_\beta$ is denoted by $\varphi_{\mathsf{P}\beta}$, then
>
> $$f(\alpha \to \mathsf{P}\beta) = \delta_{\mathsf{P}} f(\alpha \to \beta). \tag{4.6.7}$$

We prove this by use of (1). Firstly we note that $\mathsf{P}\varphi_\alpha = \delta_\mathsf{P}\varphi_\alpha$, since P permutes identical particles within the same composite particles of φ_α. Hence $\mathsf{P}^2\varphi_\alpha = \delta_\mathsf{P}^2\varphi_\alpha = \varphi_\alpha$, and so $\delta_\mathsf{P}\mathsf{P}^{-1}\varphi_\alpha = \delta_\mathsf{P}\mathsf{P}^{-1}\mathsf{P}^2\varphi_\alpha = \delta_\mathsf{P}\mathsf{P}\varphi_\alpha = \delta_\mathsf{P}^2\varphi_\alpha = \varphi_\alpha$. We can therefore write (1) as

$$T(\alpha \to \beta) = \delta_\mathsf{P}\langle V_f\varphi_\beta \,|\, 1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i \,|\, \mathsf{P}^{-1}\varphi_\alpha\rangle. \tag{4.6.8}$$

Since P permutes identical particles within composite particles of φ_α, P^{-1} does the same, and hence leaves the initial potential V_i invariant. It must also leave H invariant, and so we can replace (8) by

$$T(\alpha \to \beta) = \delta_\mathsf{P}\langle V_f\varphi_\beta \,|\, \mathsf{P}^{-1}[1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i] \,|\, \varphi_\alpha\rangle. \tag{4.6.9}$$

Now $\mathsf{P}^\dagger = \mathsf{P}^{-1}$, hence $(\mathsf{P}^{-1})^\dagger = \mathsf{P}$, whence (9) yields

$$T(\alpha \to \beta) = \delta_\mathsf{P}\langle \mathsf{P}(V_f\varphi_\beta) \,|\, 1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i \,|\, \varphi_\alpha\rangle. \tag{4.6.10}$$

If we denote the arrangement channel to which $\varphi_{\mathsf{P}\beta} = \mathsf{P}\varphi_\beta$ belongs by $\mathsf{P}f$ we see that P transforms V_f into $V_{\mathsf{P}f}$. We can therefore infer from (10) that

$$\begin{aligned} T(\alpha \to \beta) &= \delta_\mathsf{P}\langle V_{\mathsf{P}f}\varphi_{\mathsf{P}\beta} \,|\, 1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i \,|\, \varphi_\alpha\rangle \\ &= \delta_\mathsf{P}\langle \varphi_{\mathsf{P}\beta} \,|\, V_{\mathsf{P}f}[1+(E-\mathsf{H}+i\varepsilon)^{-1}V_i] \,|\, \varphi_\alpha\rangle = \delta_\mathsf{P}T(\alpha \to \mathsf{P}\beta) \end{aligned} \tag{4.6.11}$$

by (1). The result (7) now follows from (3), since the reduced mass μ_f is not changed by a permutation of identical particles.

Example. We shall use the results (6) and (7) to effect a considerable simplification in the expression (4.5.47) for the symmetrized scattering amplitude $f(\mathbf{k} \to \mathcal{S}\mathbf{l}p)$ for electron–atom collisions. The exchange amplitude f_j refers to the final state obtained by exchanging the incident electron 0 with the atomic electron j, where we are using the notation of Example 3 of Section 4.5. Similar considerations apply to the exchange amplitude f_k. Without loss of generality we can assume that $j < k$, in which case the initial state may be denoted schematically by

$$0;\ 1,\ \ldots,\ j,\ \ldots,\ k,\ \ldots,\ n. \tag{4.6.12}$$

The final states in f_j and f_k may be correspondingly denoted by

$$j;\ 1,\ \ldots,\ 0,\ \ldots,\ k,\ \ldots,\ n \tag{4.6.13}$$

$$k;\ 1,\ \ldots,\ j,\ \ldots,\ 0,\ \ldots,\ n. \tag{4.6.14}$$

We can obtain the final state (14) from the final state (13) in two steps. Firstly we interchange 0 and k in (13) to obtain

$$j;\ 1,\ \ldots,\ k,\ \ldots,\ 0,\ \ldots,\ n. \tag{4.6.15}$$

This is an odd permutation of the electrons of the atom in the final state, and so by (6) changes the sign of f_j. If we interchange j and k in (15) we obtain (14), the final state of f_k; but this is an odd permutation of the electrons of the initial state, and so changes the sign of f_j a second time. In other words, $f_j = f_k$. The n exchange amplitudes in (4.5.47) are therefore all equal. If we denote their common value by f_{ex} we see that (4.5.47) simplifies to

$$f(\mathbf{k}n \to \mathcal{S}\mathbf{l}p) = f_d(\mathbf{k}n \to \mathbf{l}p) - nf_{ex}(\mathbf{k}n \to \mathbf{l}p). \tag{4.6.16}$$

EXERCISE

Simplify the symmetrized scattering amplitudes of Exercise 2 of Section 4.5 as far as possible.

4.7. THE N-PARTICLE SYSTEM WITH SEVERAL SPECIES OF IDENTICAL PARTICLES

Hitherto we have assumed that only one species of identical particles has two or more representatives in our N-particle system. We shall now remove this assumption. The arguments and results of Sections 4.1, 4.5 and 4.6 go over to the most general case with a few minor modifications, which we shall now consider.

Suppose there are L species of identical particles, each with two or more representatives in the N-particle system. Let P be an operator in the Hilbert space of states (or wave functions) which permutes the identical particles of each species among themselves. If there are $M^{(l)}$ members of the lth species there are C^{-1} such operators P, where C is defined by

$$\mathrm{C} = \left[\prod_{l=1}^{L} M^{(l)}!\right]^{-1}. \tag{4.7.1}$$

The operator P may be regarded as the product of L permutations. Let δ_{P} be the product of the $L\delta$'s corresponding to these L permutations. In fact $\delta_{\mathsf{P}} = -1$ if P consists of an odd number of odd permutations of fermions, otherwise $\delta_{\mathsf{P}} = 1$; thus $\delta_{\mathsf{P}}^2 = 1$. It is also easy to see that $\delta_{\mathsf{PQ}} = \delta_{\mathsf{P}}\delta_{\mathsf{Q}}$ if Q is a second operator of the same type. Analogously to (4.1.1) we now define a symmetrizer $\mathcal{S}$ by

$$\mathcal{S} = \mathrm{C}\sum_{\mathsf{P}} \delta_{\mathsf{P}}\mathsf{P} \tag{4.7.2}$$

where the summation goes over all C^{-1} operators P. In the special case when $L = 1$ we see from (1) that $\mathrm{C} = (M!)^{-1}$, and (2) reduces to (4.1.1). It is easy to show that $\mathcal{S}$ is linear, Hermitian and idempotent.

The argument of Section 4.1 remains valid in the more general case if $M!$ is replaced throughout by C^{-1}. If $M_f^{(l)}$ is the number of permutations of identical particles of species l which do not interchange particles between composite particles of arrangement channel f the quantity M_f is now given by

$$M_f = \prod_{l=1}^{L} M_f^{(l)}!. \tag{4.7.3}$$

As before, M_f remains the number of ways identical particles may be permuted in arrangement channel f without interchange of particles between composite particles taking place.

Throughout Section 4.5 we must again replace $M!$ by C^{-1}. Exactly similar arguments to those of Section 4.5 show that the C^{-1} terms $\delta_{\mathsf{P}}\mathsf{P}\bar{\varphi}(t_0)$ in $a_i\mathcal{S}\bar{\varphi}(t_0)$

divide into $C^{-1}M_i^{-1}$ groups each containing M_i equal terms, where M_i is the number of ways of permuting identical particles of each species without interchange of particles between composite particles taking place. Corresponding to (3) we have

$$M_i = \prod_{l=1}^{L} M_i^{(l)}!. \tag{4.7.4}$$

The calculation of the value of the normalization constant a_i in Section 4.5 goes over provided $M!$ is replaced by C^{-1}. Instead of (4.5.10) we obtain

$$a_i = (CM_i)^{-1/2}. \tag{4.7.5}$$

The remaining arguments of Section 4.5 also go over. The expression $\gamma \approx \beta$ means that the state φ_γ can be obtained from φ_β by permutation of the identical particles of each species. The operator $\mathsf{P}_{\gamma\to\delta}$ is now that product of permutations of identical particles of each species which takes φ_γ into φ_δ, and $\delta_{\gamma\to\delta}$ the corresponding δ_{P}. Instead of (4.5.20) and (4.5.21) we obtain

$$A_\delta'(\mathcal{S}) = a_i C M_f \delta_{\beta\to\delta} \sum_{\gamma\approx\beta} \delta_{\gamma\to\beta} A_\gamma' = \delta_{\beta\to\delta} A_\beta'(\mathcal{S}) \tag{4.7.6}$$

for the coefficients of φ_δ and φ_β in $\bar{\varphi}_{\mathcal{S}}'(t_1)$.

Since there are $C^{-1}M_f^{-1}$ distinct final states obtainable from φ_β by permutations of identical particles the probability of observation of the state represented by φ_β, or any other state obtainable from it by permutation of identical particles, is

$$\begin{aligned} P(\alpha \to \mathcal{S}\beta) &= C^{-1}M_f^{-1}|A_\beta'(\mathcal{S})|^2 = a_i^2 C M_f \Big|\sum_{\gamma\approx\beta} \delta_{\gamma\to\beta} A_\gamma'\Big|^2 \quad \text{by (6)} \\ &= M_f M_i^{-1} \Big|\sum_{\gamma\approx\beta} \delta_{\gamma\to\beta} A_\gamma'\Big|^2 \end{aligned} \tag{4.7.7}$$

where the last step follows from (5). We conclude therefore that (4.5.26) remains valid provided M_i and M_f are the number of products of permutations of identical particles of each species which do not interchange particles between composite particles in the arrangement channels i and f containing φ_α and φ_β respectively, and the sum goes over all distinct states obtainable from φ_β by permutations of identical particles within each species.

Finally we note that the results (4.6.6) and (4.6.7) remain valid if P is a product of permutations of identical particles of different species.

EXAMPLE 1. Let us apply the above results to the case of scattering of an electron by an n-electron molecule in which two of the nuclei are identical, the remaining nuclei being distinct from the first two, and from each other. Interchange of the identical nuclei does not change the final state, and so the sum (4.5.26) need be taken only over the direct amplitude and the n exchange amplitudes. This means that (4.5.47) remains valid in this case. The argument leading to the simplified result (4.6.16) also remains valid here.

Example 2. As a second example let us consider the dissociative collision

$$\mathrm{He}+\mathrm{H}_2^+ \rightarrow \mathrm{He}+\mathrm{H}+\mathrm{H}^+. \tag{4.7.8}$$

Let us denote the electrons by 1, 2 and 3, and the protons of the H_2^+ by A and B. Let $f(12,\ 3AB \rightarrow 12,\ 3A,\ B)$ denote the scattering amplitude when initially electrons 1 and 2 belong to the helium atom, electron 3 belongs to the H_2^+ ion, while finally 1 and 2 belong to the helium atom, 3 is attached to proton A to form a hydrogen atom, and B is the free proton. For simplicity we omit the initial and final wave vectors and quantum numbers of bound states—these are, of course, unaltered by permutations. In this case $M_i^{(1)} = 2!\times 1! = 2$ (electrons), $M_i^{(2)} = 2! = 2$ (protons), so $M_i = 4$, while $M_f^{(1)} = 2!\times 1! = 2$, $M_f^{(2)} = 1!\times 1! = 1$, hence $M_f = 2$. Application of (4.5.26) gives the following expression for the symmetrized scattering amplitude:

$$\begin{aligned} f(\mathcal{S}) = 2^{-1/2}[&f(12,3AB \rightarrow 12,3A,\ B)-f(12,3AB \rightarrow 12,3B,\ A)\\ &+f(12,3AB \rightarrow 23,1A,\ B)-f(12,3AB \rightarrow 23,1B,\ A)\\ &+f(12,3AB \rightarrow 31,2A,\ B)-f(12,3AB \rightarrow 31,2B,\ A). \end{aligned} \tag{4.7.9}$$

In this case $\mathrm{C}^{-1} = 3!2!$, hence $\mathrm{C}^{-1}M_f^{-1} = 6$, the number of distinct final states in this case. A and B belong to the same initial state, and so terms which differ from each other by their exchange must be equal; (9) therefore becomes

$$\begin{aligned} f(\mathcal{S}) = 2^{+1/2}[&f(12,3AB \rightarrow 12,3A,\ B)+f(12,3AB \rightarrow 23,1A,\ B)\\ &+f(12,3AB \rightarrow 31,2A,\ B)]. \end{aligned} \tag{4.7.10}$$

Electrons 1 and 2 are bound in the initial state, hence

$$f(12,3AB \rightarrow 23,1A,\ B) = -f(12,3AB \rightarrow 13,2A,\ B) = f(12,3AB \rightarrow 31,2A,\ B). \tag{4.7.11}$$

Insertion of (11) into (10) gives

$$f(\mathcal{S}) = 2^{+1/2}[f(12,3AB \rightarrow 12,3A,\ B)+2f(12,3AB \rightarrow 23,1A,\ B)]. \tag{4.7.12}$$

EXERCISES

1. Show that the operator P is linear, and $\mathrm{P}^\dagger = \mathrm{P}^{-1}$.

2. Show that the operator $\mathcal{S}$ defined by (2) is linear, Hermitian and idempotent.

3. Prove (5).

4. Write down and simplify the scattering amplitudes for the following processes:

(a) $\mathrm{He}+\mathrm{H}_2^+ \rightarrow \mathrm{He}^+ + \mathrm{H}_2$.

(b) $\mathrm{He}+\mathrm{H}_2^+ \rightarrow \mathrm{He}^+ + \mathrm{H}+\mathrm{H}$.

CHAPTER 5

SOME APPLICATIONS OF THE THEORY

5.1. SCATTERING BY TWO POTENTIALS

We have now the main principles and results of the non-relativistic quantum theory of radiationless reactions in which "elementary particles" are neither created nor destroyed, but move under their mutual interactions. We have seen that in order to calculate the experimentally interesting cross-section $\sigma(\alpha \to \beta)$ we must, in principle, first calculate either the scattering state ψ_α^+ or the scattering state ψ_β^- corresponding to the initial and final states φ_α and φ_β. Having done this we calculate the scattering amplitude $f(\alpha \to \beta)$ from either the formula

$$\boxed{f(\alpha \to \beta) = (-4\pi^2\mu_f/\hbar^2)\,T(\alpha \to \beta) = (-4\pi^2\mu_f/\hbar^2)\langle\varphi_\beta\,|\,V_f\,|\,\psi_\alpha^+\rangle} \qquad (5.1.1)$$

or from the formula

$$\boxed{f(\alpha \to \beta) = (-4\pi^2\mu_f/\hbar^2)\,T(\alpha \to \beta) = (-4\pi^2\mu_f/\hbar^2)\langle\psi_\beta^-\,|\,V_i\,|\,\varphi_\alpha\rangle.} \qquad (5.1.2)$$

The differential cross-section is then calculated from

$$\sigma(\alpha \to \beta) = (v_\beta/v_\alpha)\,|\,f(\alpha \to \beta)\,|^2 \qquad (5.1.3)$$

where v_α is the initial velocity of the centre of mass of the bombarding particle A relative to the centre of mass of the target particle B, while v_β is the velocity of the centre of mass of the scattered particle C relative to the centre of mass of the recoil particle (or particles) D. We have seen that energy is conserved, so that $E_\alpha = E_\beta$, and v_β is calculated from v_α by this condition.

Now in practice we usually cannot carry out the algorithm just described. Even in the case of the scattering of two elementary particles the calculation of ψ^+ or ψ^- involves the solution of Schrödinger's time-independent equation subject to outgoing or incoming wave boundary conditions followed by the evaluation of the three-dimensional integrals $\langle\varphi_\beta|\,V_f\,|\psi_\alpha^+\rangle$ or $\langle\psi_\beta^-\,|\,V_i\,|\varphi_\alpha\rangle$. In the case of a system of N elementary particles this is a $3(N-1)$-dimensional problem, and so quite beyond the scope of such direct calculations. This means that in practice we have to take advantage of any features of a specific reaction which enable us to make the approximations necessary to render the problem of calculating cross-sections tractable. In this chapter we shall discuss some of the approximate methods of calculation which have been developed in the course of the growth of the subject.

In this section we shall discuss the case when the initial and final interaction potentials V_i and V_f can each be decomposed into sums of two potentials so that

$$V_i = U_i + W_i, \tag{5.1.4}$$

$$V_f = U_f + W_f. \tag{5.1.5}$$

We may know, for example, the solution of the problem when the initial and final potentials are U_i and U_f, and it may be possible to treat W_i and W_f as small perturbations. In such a case we can apply a perturbation technique to find an approximate solution to the whole problem. The actual technique will be discussed in a later section of this chapter, but in order to do this we must first develop a formula known as the "Two-potential Formula".

Corresponding to the unperturbed state φ_α and potential U_i we can define Schwinger–Lippmann states $\theta_\alpha^\pm$ by

$$\theta_\alpha^\pm = \varphi_\alpha + (E - \mathsf{H}_i - U_i \pm i\varepsilon)^{-1} U_i \varphi_\alpha \tag{5.1.6}$$

where $E = E_\alpha$, and reasoning as in Section 1.5, in particular just before equation (1.5.3), we see that these will satisfy the corresponding integral equations

$$\theta_\alpha^\pm = \varphi_\alpha + (E - \mathsf{H}_i \pm i\varepsilon)^{-1} U_i \theta_\alpha^\pm. \tag{5.1.7}$$

Since $\mathsf{H}_i \varphi_\alpha = E\varphi_\alpha$ operation on (7) to the left with $E - \mathsf{H}_i \pm i\varepsilon$ yields

$$(E - \mathsf{H}_i - U_i)\,\theta_\alpha^\pm = \pm i\varepsilon(\varphi_\alpha - \theta_\alpha^\pm) \tag{5.1.8}$$

and so as $\varepsilon \to 0+$ we get $(\mathsf{H}_i + U_i)\,\theta_\alpha^\pm = E\theta_\alpha^\pm$. Thus $\theta_\alpha^\pm$ are eigenstates of the Hamiltonian $\mathsf{H}_i + U_i$ obtained by ignoring W_i.

We shall now show that it is possible to express $\psi_\alpha^\pm$ in terms of $\theta_\alpha^\pm$. The Schwinger–Lippmann equations for $\psi_\alpha^\pm$ are

$$\psi_\alpha^\pm = \varphi_\alpha + (E - \mathsf{H}_i \pm i\varepsilon)^{-1} V_i \psi_\alpha^\pm, \tag{5.1.9}$$

and if we substitute for V_i from (4) into (9) we get

$$\psi_\alpha^\pm = \varphi_\alpha + (E - \mathsf{H} \pm i\varepsilon)^{-1} (U_i + W_i)\, \psi_\alpha^\pm. \tag{5.1.10}$$

By subtracting (7) from (10) we obtain

$$\psi_\alpha^\pm - \theta_\alpha^\pm = (E - \mathsf{H}_i \pm i\varepsilon)^{-1} U_i(\psi_\alpha^\pm - \theta_\alpha^\pm) + (E - \mathsf{H}_i \pm i\varepsilon)^{-1} W_i \psi_\alpha^\pm. \tag{5.1.11}$$

Operation on (11) to the left with $E-\mathsf{H}_i\pm i\varepsilon$ yields

$$(E-\mathsf{H}_i\pm i\varepsilon)\,(\psi_\alpha^\pm-\theta_\alpha^\pm) = (U_i+W_i)\,\psi_\alpha^\pm-U_i\theta_\alpha^\pm, \tag{5.1.12}$$

and this may be rearranged to give

$$(E-\mathsf{H}_i-U_i-W_i\pm i\varepsilon)\,\psi_\alpha^\pm = (E-\mathsf{H}_i-U_i-W_i\pm i\varepsilon)\,\theta_\alpha^\pm+W_i\theta_\alpha^\pm. \tag{5.1.13}$$

If we operate on this to the left with $(E-\mathsf{H}_i-U_i-W_i\pm i\varepsilon)^{-1}$ we find that

$$\psi_\alpha^\pm = \theta_\alpha^\pm+(E-\mathsf{H}_i-U_i-W_i\pm i\varepsilon)^{-1}\,W_i\theta_\alpha^\pm, \tag{5.1.14}$$

and since from (4) $\mathsf{H}_i+U_i+W_i = \mathsf{H}_i+V_i = \mathsf{H}$,

$$\psi_\alpha^\pm = \theta_\alpha^\pm+(E-\mathsf{H}\pm i\varepsilon)^{-1}\,W_i\theta_\alpha^\pm. \tag{5.1.15}$$

Equation (15) has an interesting interpretation. Starting off with the unperturbed plane wave state φ_α we can "distort" it by the potential U_i. The result is $\theta_\alpha^\pm$ according to the boundary conditions imposed on the "distorted wave". (15) now shows that $\psi_\alpha^\pm$ may be obtained from the "distorted states" $\theta_\alpha^\pm$ by treating the latter as the unperturbed states and applying the additional potential W_i to them; thus U_i takes us from φ_α to $\theta_\alpha^\pm$, and W_i takes us from $\theta_\alpha^\pm$ to $\psi_\alpha^\pm$. In the latter step we note that, to obtain the overall state ψ_α^+ with outgoing wave conditions we must use the distorted state with outgoing waves, and similarly with the incoming waves state.

We can derive Schwinger–Lippmann equations for $\psi_\alpha^\pm$ treating $\theta_\alpha^\pm$ as the unperturbed states in the same way as before when φ_α was the unperturbed state. If we rearrange (13) we obtain

$$(E-\mathsf{H}_i-U_i\pm i\varepsilon)\,\psi_\alpha^\pm = (E-\mathsf{H}_i-U_i\pm i\varepsilon)\,\theta_\alpha^\pm+W_i\psi_\alpha^\pm, \tag{5.1.16}$$

and operation on (16) to the left with $(E-\mathsf{H}_i-U_i\pm i\varepsilon)^{-1}$ yields

$$\psi_\alpha^\pm = \theta_\alpha^\pm+(E-\mathsf{H}_i-U_i\pm i\varepsilon)^{-1}\,W_i\psi_\alpha^\pm. \tag{5.1.17}$$

Comparison of (17) with the Schwinger–Lippmann equations (9) shows that (17) is also a kind of Schwinger–Lippmann equation, but with the states $\theta_\alpha^\pm$ replacing φ_α as unperturbed states, H_i+U_i replacing H_i as "unperturbed Hamiltonian", and W_i replacing $V_i = U_i+W_i$ as the interaction.

We saw in Section 3.3 that the transition amplitude $T(\alpha\to\beta)$ is given by

$$T(\alpha\to\beta) = \langle\varphi_\beta|\,V_f|\,\psi_\alpha^+\rangle \tag{5.1.18}$$

where $E_\alpha = E_\beta$. According to (5) $V_f = U_f+W_f$, and so (18) becomes

$$T(\alpha\to\beta) = \langle\varphi_\beta\,|\,U_f|\,\psi_\alpha^+\rangle+\langle\varphi_\beta\,|\,W_f|\,\psi_\alpha^+\rangle. \tag{5.1.19}$$

From (6) with α replaced by β and i replaced by f we have

$$\varphi_\beta = \theta_\beta^- -(E-\mathsf{H}_f-U_f-i\varepsilon)^{-1}\,U_f\varphi_\beta \tag{5.1.20}$$

and substitution for φ_β from (20) into the second term on the right-hand side of (19) gives

$$\begin{aligned} T(\alpha \to \beta) &= \langle \varphi_\beta | U_f | \psi_\alpha^+ \rangle + \langle \theta_\beta^- | W_f | \psi_\alpha^+ \rangle \\ &\quad - \langle (E - \mathsf{H}_f - U_f - i\varepsilon)^{-1} U_f \varphi_\beta | W_f | \psi_\beta^+ \rangle; \end{aligned} \tag{5.1.21}$$

hence

$$T(\alpha \to \beta) = \langle \varphi_\beta | U_f - U_f(E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} W_f | \psi_\alpha^+ \rangle + \langle \theta_\beta^- | W_f | \psi_\alpha^+ \rangle. \tag{5.1.22}$$

The second term on the right-hand side of (22) is, by analogy with (18), the amplitude for the transition from the unperturbed initial state φ_α to the "distorted final state" θ_β^- via the "final interaction" W_f. The first term on the right-hand side of (22) appears to require knowledge of the full scattering state ψ_α^+. We shall, however, show that it is capable of calculation if we know the distorted wave θ_β^-; it does not, in fact, require knowledge of ψ_α^+. In order to do this we must obviously eliminate ψ_α^+ from the first term on the right-hand side of (22), and this we shall now do.

Let us put $\mathsf{A} = E - \mathsf{H}_i + i\varepsilon$, $\mathsf{B} = E - \mathsf{H}_f - U_f + i\varepsilon$ in the identity $\mathsf{A}^{-1} = \mathsf{B}^{-1} + \mathsf{B}^{-1}(\mathsf{B} - \mathsf{A})\,\mathsf{A}^{-1}$; we get

$$\begin{aligned} (E - \mathsf{H}_i + i\varepsilon)^{-1} &= (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} \\ &\quad + (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} (\mathsf{H}_i - \mathsf{H}_f - U_f)(E - \mathsf{H}_i + i\varepsilon)^{-1}. \end{aligned} \tag{5.1.23}$$

Now $\qquad \mathsf{H}_i + V_i = \mathsf{H} = \mathsf{H}_f + V_f = \mathsf{H}_f + U_f + W_f,$

so

$$\mathsf{H}_i - \mathsf{H}_f - U_f = \mathsf{H}_i - (\mathsf{H}_f + U_f) = (\mathsf{H} - V_i) - (\mathsf{H} - W_f); \tag{5.1.24}$$

in other words,

$$\mathsf{H}_i - \mathsf{H}_f - U_f = -(V_i - W_f) \tag{5.1.25}$$

and so (23) becomes

$$\begin{aligned} (E - \mathsf{H}_i + i\varepsilon)^{-1} &= (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} \\ &\quad - (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} (V_i - W_f)(E - \mathsf{H}_i + i\varepsilon)^{-1}. \end{aligned} \tag{5.1.26}$$

If we substitute for $(E - \mathsf{H}_i + i\varepsilon)^{-1}$ from (26) into the Schwinger-Lippmann equation (9) we obtain

$$\begin{aligned} \psi_\alpha^+ &= \varphi_\alpha + (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} V_i \psi_\alpha^+ \\ &\quad - (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} (V_i - W_f)(E - \mathsf{H}_i + i\varepsilon)^{-1} V_i \psi_\alpha^+. \end{aligned} \tag{5.1.27}$$

From (9) we have

$$(E - \mathsf{H}_i + i\varepsilon)^{-1} V_i \psi_\alpha^+ = \psi_\alpha^+ - \varphi_\alpha \tag{5.1.28}$$

and so (27) becomes

$$\begin{aligned} \psi_\alpha^+ &= \varphi_\alpha + (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} V_i \psi_\alpha^+ \\ &\quad - (E - \mathsf{H}_f - U_f + i\varepsilon)^{-1} (V_i - W_f)(\psi_\alpha^+ - \varphi_\alpha) \end{aligned} \tag{5.1.29}$$

or equivalently

$$\begin{aligned}&[1-(E-\mathsf{H}_f-U_f+i\varepsilon)^{-1}W_f]\,\psi_\alpha^+\\&=\varphi_\alpha+(E-\mathsf{H}_f-U_f+i\varepsilon)^{-1}(V_i-W_f)\,\varphi_\alpha.\end{aligned}\tag{5.1.30}$$

We can substitute for the left-hand side of (30) in the first term on the right-hand side of (22) to obtain

$$\begin{aligned}T(\alpha\to\beta)=\langle\varphi_\beta|\,U_f+U_f(E-\mathsf{H}_f-U_f+i\varepsilon)^{-1}\times\\\times(V_i-W_f)\,|\varphi_\alpha\rangle+\langle\theta_\beta^-\,|\,W_f\,|\psi_\alpha^+\rangle.\end{aligned}\tag{5.1.31}$$

We can now see that the first term on the right-hand side of (31) requires only a knowledge of the Green's operator $(E-\mathsf{H}_f-U_f+i\varepsilon)^{-1}$, and not a knowledge of the Green's operator $(E-\mathsf{H}_f-U_f-W_f+i\varepsilon)^{-1}$. It is therefore, in principle, possible to calculate the first term by a knowledge of the solution of the "distortion" problem $(\mathsf{H}_f+U_f)\theta_\beta^-=E\theta_\beta^-$; W_f enters the problem only as a multiplicative operator, and not through the Green's function. We can, however, show this in a more transparent way by writing the first term on the right-hand side of (31) in a different form, which we shall now do.

The first term on the right-hand side of (31) can be rewritten as

$$\langle\varphi_\beta|\,U_f\,|\varphi_\alpha\rangle+\langle(E-\mathsf{H}_f-U_f-i\varepsilon)^{-1}U_f\varphi_\beta|\,V_i-W_f\,|\varphi_\alpha\rangle.\tag{5.1.32}$$

Now from (20)

$$(E-\mathsf{H}_f-U_f-i\varepsilon)^{-1}U_f\varphi_\beta=\theta_\beta^--\varphi_\beta\tag{5.1.33}$$

and so (32) becomes

$$\begin{aligned}&\langle\varphi_\beta|\,U_f\,|\varphi_\alpha\rangle+\langle\theta_\beta^--\varphi_\beta|\,V_i-W_f\,|\varphi_\alpha\rangle\\&\quad=\langle\varphi_\beta|\,U_f+W_f-V_i\,|\varphi_\alpha\rangle+\langle\theta_\beta^-\,|\,V_i-W_f\,|\varphi_\alpha\rangle;\end{aligned}\tag{5.1.34}$$

by (5) this is equal to

$$\langle\varphi_\beta|\,V_f\,|\varphi_\alpha\rangle-\langle\varphi_\beta|\,V_i\,|\varphi_\alpha\rangle+\langle\theta_\beta^-\,|\,V_i-W_f\,|\varphi_\alpha\rangle.\tag{5.1.35}$$

Energy conservation implies that $E_\beta=E_\alpha=E$, and so by (3.3.21) the first two terms cancel, leaving us with $\langle\theta_\beta^-|\,V_i-W_f\,|\varphi_\alpha\rangle$ as a simplified expression for the first term on the right-hand side of (31); (31) can therefore be written

$$T(\alpha\to\beta)=\langle\theta_\beta^-\,|\,V_i-W_f\,|\varphi_\alpha\rangle+\langle\theta_\beta^-\,|\,W_f\,|\psi_\alpha^+\rangle.\tag{5.1.36}$$

The expression (36) is the two-potential formula we have been seeking. We have already seen that the second term on the right-hand side may be interpretated as the transition amplitude for the process which takes us from the initial unperturbed state φ_α to the final distorted state θ_β^- under the action of the potential W_f. The first term also has a physical interpretation, for since $\mathsf{H}_i+V_i = \mathsf{H} = \mathsf{H}_f+U_f+W_f$

$$\mathsf{H}_i+(V_i-W_f) = \mathsf{H}_f+U_f. \tag{5.1.37}$$

If we regard the "distorted" Hamiltonian as H_f+U_f we see that the "initial interaction" is V_i-W_f; by analogy with (2) we see that the first term on the right-hand side of (36) is just the transition amplitude for the process $\varphi_\alpha \to \varphi_\beta$ when the unperturbed Hamiltonians remain H_i and H_f but the initial and final interactions are replaced by V_i-W_f and U_f respectively. It involves only the distorted wave θ_β^- and not the full scattering state ψ_α^+; for this reason this term must be supplemented by the second term $\langle\theta_\beta^-|\,W_f\,|\psi_\alpha^+\rangle$ in order to obtain the total transition amplitude $T(\alpha \to \beta)$.

5.2. THE FINAL STATE INTERACTION

In this section we shall consider break-up collisions of the form

$$A+BC \to A+B+C. \tag{5.2.1}$$

As a result of the collision the target particle BC breaks up into two particles B and C. Since the elementary particles of BC are the same as the elementary particles of B and C separately it is clear that the initial interaction V_i between A and BC is just the sum of the interactions V_{AB} and V_{AC} between A and B, and A and C, respectively; thus

$$V_i = V_{AB}+V_{AC}. \tag{5.2.2}$$

At the same time the final interaction V_f is the interaction between the separate particles A, B and C, and so

$$V_f = V_{AB}+V_{AC}+V_{BC}. \tag{5.2.3}$$

For simplicity we shall, for the moment, assume that A is an elementary particle.

Let $\mathbf{r}$ denote the position vector of A relative to the centre of mass of BC (or B and C) and $\mathbf{R}$ be the position vector of the centre of mass of B relative to the centre of mass of C, and let us denote by $\mathsf{K}_\mathbf{r}$ and $\mathsf{K}_\mathbf{R}$ the kinetic energy operators associated with $\mathbf{r}$ and $\mathbf{R}$ respectively. With each of the particles B and C we can associate internal Hamiltonians h_B and h_C, so that after the collision the total internal Hamiltonian is

$$\mathsf{h}_f = \mathsf{h}_B+\mathsf{h}_C. \tag{5.2.4}$$

Before the collision the internal Hamiltonian also includes V_{BC} and $\mathsf{K}_\mathbf{R}$, and so

$$\mathsf{h}_i = \mathsf{h}_B+\mathsf{h}_C+\mathsf{K}_\mathbf{R}+V_{BC} = \mathsf{K}_\mathbf{R}+V_{BC}+\mathsf{h}_f. \tag{5.2.5}$$

The initial and final unperturbed Hamiltonians are given by

$$\mathsf{H}_i = \mathsf{K}_\mathbf{r} + \mathsf{h}_i, \tag{5.2.6}$$

$$\mathsf{H}_f = \mathsf{K}_\mathbf{r} + \mathsf{K}_\mathbf{R} + \mathsf{h}_f, \tag{5.2.7}$$

respectively. If $\mathbf{q}$ denotes the coordinates other than $\mathbf{r}$ and $\mathbf{R}$, the initial and final states are given by

$$\varphi_{\mathbf{k}n}(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_\mathbf{k}(\mathbf{r})\,\chi_n(\mathbf{R}, \mathbf{q}) \tag{5.2.8}$$

(A has momentum $\hbar\mathbf{k}$ relative to BC and χ_n is the internal state)

$$\varphi_{\mathbf{l}\varkappa p}(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_\mathbf{l}(\mathbf{r})\,\varphi_\varkappa(\mathbf{R})\,\xi_p(\mathbf{q}) \tag{5.2.9}$$

(A has momentum $\hbar\mathbf{l}$ relative to $B+C$, B has momentum $\hbar\boldsymbol{\varkappa}$ relative to C, and ξ_p is the internal state).

Let us put $W_f = V_{AB}+V_{AC}$, $U_f = V_{BC}$, so that (3) implies $V_f = U_f+W_f$. This is a particular case of the decomposition of the potential V_f into a sum of two potentials U_f and W_f discussed in the last section, and so we can apply (5.1.36); since by (2) $V_i = W_f$ we find that

$$T(\mathbf{k}n \rightarrow \mathbf{l}\varkappa p) = \langle \theta^-_{\mathbf{l}\varkappa p} | V_{AB}+V_{AC} | \psi^+_{\mathbf{k}n} \rangle. \tag{5.2.10}$$

$\psi^+_{\mathbf{k}n}$ is the total scattering state and $V_{AB}+V_{AC}$ is the interaction between A and the recoil particles B and C, and equals the initial interaction V_i. We shall now investigate the nature of the state $\theta^-_{\mathbf{l}\varkappa p}$.

The θ^- states are defined by (5.1.6). In this particular case $\alpha = \mathbf{l}\varkappa p$, i is replaced by f, and so

$$\theta^-_{\mathbf{l}\varkappa p} = \varphi_{\mathbf{l}\varkappa p} + (E-\mathsf{H}_f-U_f-i\varepsilon)^{-1}U_f\varphi_{\mathbf{l}\varkappa p}. \tag{5.2.11}$$

Now $U_f = V_{BC}$, while H_f is given by (7). Also $\varphi_{\mathbf{l}\varkappa p}$ is given by (9), and so

$$\theta^-_{\mathbf{l}\varkappa p} = \varphi_\mathbf{l}\varphi_\varkappa\xi_p + (E-\mathsf{K}_\mathbf{r}-\mathsf{K}_\mathbf{R}-\mathsf{h}_f-V_{BC}-i\varepsilon)^{-1}V_{BC}\varphi_\mathbf{l}\varphi_\varkappa\xi_p. \tag{5.2.12}$$

$\mathsf{K}_\mathbf{r}$ and $\varphi_\mathbf{l}$ depend only on $\mathbf{r}$ and $\mathsf{K}_\mathbf{r}\varphi_\mathbf{l} = E_l\varphi_\mathbf{l}$, while $\mathsf{K}_\mathbf{R}+\mathsf{h}_f+V_{BC}$ and $\varphi_\varkappa\xi_p$ are independent of $\mathbf{r}$. It follows from Appendix A that

$$\begin{aligned}(E-\mathsf{K}_\mathbf{r}-\mathsf{K}_\mathbf{R}-\mathsf{h}_f-V_{BC}-i\varepsilon)^{-1}&V_{BC}\varphi_\mathbf{l}\varphi_\varkappa\xi_p \\ &= \{(E-E_l-\mathsf{K}_\mathbf{R}-\mathsf{h}_f-V_{BC}-i\varepsilon)^{-1}V_{BC}\varphi_\varkappa\xi_p\}\,\varphi_\mathbf{l}\end{aligned} \tag{5.2.13}$$

and since by energy conservation $E-E_l = E_{\varkappa p}$, (12) becomes

$$\theta^-_{\mathbf{l}\varkappa p} = \{\varphi_\varkappa\xi_p + (E_{\varkappa p}-\mathsf{K}_\mathbf{R}-\mathsf{h}_f-V_{BC}-i\varepsilon)^{-1}V_{BC}\varphi_\varkappa\xi_p\}\,\varphi_\mathbf{l}. \tag{5.2.14}$$

The expression in the curly brackets of (12) is just the Schwinger–Lippmann state for scattering of B by C via the potential V_{BC} when the unperturbed state is $\varphi_\varkappa\xi_p$ and incoming wave boundary conditions are imposed. It is therefore a continuum state of the system $B+C$ and so by analogy to χ_n, which denotes the initial bound state of BC, we may denote it by $\chi_{\kappa p}^-$; thus

$$\theta_{\mathbf{l}\kappa p}^- = \varphi_{\mathbf{l}}\chi_{\kappa p}^-. \tag{5.2.15}$$

We can now summarize the results of this section. A collision $A+BC \to A+B+C$ may be treated as direct, so that the final interaction as well as the initial interaction is $V_{AB}+V_{AC}$, provided the final state is taken as the product of (i) a plane wave $\varphi_{\mathbf{l}}$ representing the motion of A relative to the centre of mass of the two-particle system $B+C$, (ii) a wave function $\chi_{\kappa p}^-$ describing the motion of B relative to C in the presence of the potential V_{BC} which obeys incoming wave boundary conditions at infinity.

In our derivation of this result we have assumed that A is an elementary particle. If this assumption is removed the initial and final internal states of A must be included. The reader should have no difficulty in proving that (10) still holds, where $\theta_{\mathbf{l}\kappa p}^-$ is given by the product of the final state of A with $\varphi_{\mathbf{l}}\chi_{\kappa p}^-$ and $\chi_{\kappa p}^-$ is the continuum state of BC defined above.

EXERCISE

Prove that if A has structure the result (10) becomes

$$T(\mathbf{k}n \to \mathbf{l}\kappa ps) = \langle \varphi_{\mathbf{l}}\eta_s\chi_{\kappa p}^- \,|\, V_{AB}+V_{AC} \,|\, \psi_{\mathbf{k}n}^+\rangle$$

where η_s is the final internal wave function of A and the other quantities have their usual meanings.

5.3. THE BORN APPROXIMATION

We stated at the outset of this chapter that we would describe approximations which enable us to calculate cross-sections in practice. One of the most useful of these is the Born approximation, which is appropriate at high energies when scattering is small.

In the case of direct scattering the transition amplitude $T(\alpha \to \beta)$ is given by

$$T(\alpha \to \beta) = \langle \varphi_\beta | V | \psi_\alpha^+\rangle = \langle \psi_\beta^- | V | \varphi_\alpha\rangle \tag{5.3.1}$$

where we have dropped the arrangement channel indices. If scattering is small, as is the case at high energies, we shall have $\psi_\alpha^+ \simeq \varphi_\alpha$, $\psi_\beta^- \simeq \varphi_\beta$, and substitution for either ψ_β^- or ψ_α^+ in (1) yields the Born approximation

$$\boxed{T(\alpha \to \beta) \simeq \langle \varphi_\beta | V | \varphi_\alpha\rangle.} \tag{5.3.2}$$

The problem of obtaining the transition amplitude is thus reduced to the calculation of a $3(N-1)$-dimensional integral, since in principle the states φ_α and φ_β are known. If N is large this still remains a formidable problem, and in practice further approximations need then to be made (Mott and Massey, 1965).

The scattering state ψ_α^+ satisfies the integral equation $\psi_\alpha^+ = \varphi_\alpha + (E - \mathsf{H}_0 + i\varepsilon)^{-1} V \psi_\alpha^+$ where H_0 is the unperturbed Hamiltonian; if we denote $(E - \mathsf{H}_0 + i\varepsilon)^{-1}$ by G_0^+ this may be written

$$\psi_\alpha^+ = \varphi_\alpha + \mathsf{G}_0^+ V \psi_\alpha^+. \tag{5.3.3}$$

We may solve (3) by iteration to obtain

$$\psi_\alpha^+ = \varphi_\alpha + \mathsf{G}_0^+ V \varphi_\alpha + \mathsf{G}_0^+ V \mathsf{G}_0^+ V \varphi_\alpha + \dots. \tag{5.3.4}$$

The Born approximation, or first Born approximation, is obtained by approximating ψ_α^+ by the first term of the series on the right-hand side; the "second Born approximation" is obtained by taking the first two terms. Corresponding to the "Born series" (4) for ψ_α^+ we have a Born series for the transition amplitude; we obtain this by substitution for ψ_α^+ from (4) into (1), so that

$$T(\alpha \to \beta) = \langle \varphi_\beta | V | \varphi_\alpha \rangle + \langle \varphi_\beta | V \mathsf{G}_0^+ V | \varphi_\alpha \rangle + \langle \varphi_\beta | V \mathsf{G}_0^+ V \mathsf{G}_0^+ V | \varphi_\alpha \rangle + \dots. \tag{5.3.5}$$

In the case of rearrangement collisions the transition amplitude is given by either of the expressions

$$T(\alpha \to \beta) = \langle \varphi_\beta | V_f | \psi_\alpha^+ \rangle, \tag{5.3.6}$$

$$T(\alpha \to \beta) = \langle \psi_\beta^- | V_i | \varphi_\alpha \rangle. \tag{5.3.7}$$

If V_i is treated as a small perturbation we have $\psi_\alpha^+ \simeq \varphi_\alpha$, and (6) gives

$$T(\alpha \to \beta) \simeq \langle \varphi_\beta | V_f | \varphi_\alpha \rangle. \tag{5.3.8}$$

On the other hand if V_f is treated as small we have $\psi_\beta^- \simeq \varphi_\beta$, and so (7) gives

$$T(\alpha \to \beta) \simeq \langle \varphi_\beta | V_i | \varphi_\alpha \rangle. \tag{5.3.9}$$

Now $E_\beta = E_\alpha$ since energy is conserved, and so by (3.3.21) we see that the right-hand sides of (8) and (9) are equal. The derivation of (3.3.21) depended upon the assumption that φ_α and φ_β are the exact wave functions. If approximate functions are used for the unperturbed states the right-hand sides of (8) and (9) may no longer be equal—a phenomenon often referred to as the "post-prior" discrepancy, V_i being the "prior" interaction and V_f being the "post" interaction.

We saw in Chapter 4 that if exchange of identical particles is taken into account the scattering amplitude is given by the expression (4.5.26). Each of the amplitudes $f(\alpha \to \beta)$ on the right-hand side of (4.5.26) may be obtained by the Born approximation—the resultant expression is then known as the Born–Oppenheimer approximation for the exchange amplitude.

In Section 5.2 we saw that, in the case of break-up collisions of the form $A+B \to A+C+D$, the transition amplitude is given by (5.2.10). If we approximate the scattering state $\psi^+_{\mathbf{k}n}$ by the unperturbed state $\varphi_{\mathbf{k}n}$ in this expression we obtain

$$T(\mathbf{k}n \to \mathbf{l}\varkappa p) \simeq \langle \theta^-_{\mathbf{l}\varkappa p} | V_{AB}+V_{AC} | \varphi_{\mathbf{k}n}\rangle, \tag{5.3.10}$$

which is the Born approximation for break-up collisions.

The result (10) may be generalized as follows. The scattering state ψ^-_β is given by

$$\psi^-_\beta = \varphi_\beta+(E-\mathsf{H}_f-V_f-i\varepsilon)^{-1}V_f\varphi_\beta. \tag{5.3.11}$$

Suppose now that after the collision we have a particle C moving quickly relative to the remaining particles which may be collectively labelled by D. Then $V_f = V'_f+V_{CD}$ where V_{CD} is the interaction between C and D, while V'_f is the interaction between the particles of D. Since C is moving rapidly relative to the other particles it is reasonable to suppose that we can neglect V_{CD} in (11), which can therefore be replaced by the approximate expression

$$\psi^-_\beta \simeq \varphi_\beta+(E-\mathsf{H}_f-V'_f-i\varepsilon)^{-1}V'_f\varphi_\beta. \tag{5.3.12}$$

Now $\mathsf{H}_f = \mathsf{K}_{CD}+\mathsf{h}_C+\mathsf{h}_D$ where K_{CD} is the kinetic energy operator for the motion of the centre of mass of C relative to the centre of mass of D, h_C is the internal Hamiltonian of C, and h_D is the Hamiltonian for the particles D after removal of the centre of mass motion. Further $\varphi_\beta = \varphi_{\mathbf{l}}\xi_C\xi_D$ where $\varphi_{\mathbf{l}}$ is a plane wave describing the relative motion of the centres of mass of C and D, while ξ_C and ξ_D are the unperturbed wave functions of C and D. Since $\mathsf{H}_f = \mathsf{K}_{CD}+\mathsf{h}_C+\mathsf{h}_D$ we see that (12) can be written

$$\psi^-_\beta \simeq \varphi_{\mathbf{l}}\xi_C\xi_D+[E-(\mathsf{K}_{CD}+\mathsf{h}_C)-(\mathsf{h}_D+V'_f)-i\varepsilon]^{-1}V'_f\varphi_{\mathbf{l}}\xi_C\xi_D. \tag{5.3.13}$$

Now V'_f, $\mathsf{h}_D+V'_f$ and ξ_D involve only the internal coordinates of the system D, $\mathsf{K}_{CD}+\mathsf{h}_C$, $\varphi_{\mathbf{l}}$ and ξ_C involve only the remaining coordinates, while $(\mathsf{K}_{CD}+\mathsf{h}_C)\varphi_{\mathbf{l}}\xi_C = (E_l+E_C)\varphi_{\mathbf{l}}\xi_C$ where E_C is the internal energy of C. Hence by Appendix A we have

$$\begin{aligned}&[E-(\mathsf{K}_{CD}+\mathsf{h}_C)-(\mathsf{h}_D+V'_f)-i\varepsilon]^{-1}V'_f\varphi_{\mathbf{l}}\xi_C\xi_D\\ &= \{[E-(E_l+E_C)-(\mathsf{h}_D+V'_f)-i\varepsilon]^{-1}V'_f\xi_D\}\,\varphi_{\mathbf{l}}\xi_C.\end{aligned} \tag{5.3.14}$$

Since $E-(E_l+E_C)$ is the internal energy E_D of the system D the right-hand side of (14) becomes

$$\{(E_D-\mathsf{h}_D-V'_f-i\varepsilon)^{-1}V'_f\xi_D\}\,\varphi_{\mathbf{l}}\xi_C \tag{5.3.15}$$

and so (13) yields

$$\psi^-_\beta \simeq \{\xi_D+(E_D-\mathsf{h}_D-V'_f-i\varepsilon)^{-1}V'_f\xi_D\}\,\varphi_{\mathbf{l}}\xi_C. \tag{5.3.16}$$

The expression inside the curly brackets on the right-hand side of (16) is the scattering state produced by the interaction V_f' among the composite particles of D when the unperturbed state is ξ_D and incoming wave boundary conditions are imposed. We can call this ξ_D^-, so that (16) becomes

$$\psi_\beta^- \simeq \varphi_1 \xi_C \xi_D^- . \tag{5.3.17}$$

The expression (7) for the transition amplitude can now be replaced by the approximate expression

$$T(\alpha \to \beta) \simeq \langle \varphi_1 \xi_C \xi_D^- \,|\, V_i \,|\, \varphi_\alpha \rangle . \tag{5.3.18}$$

In this approximation we neglect only the interaction between the fast moving particle C and the recoil particles D. It should therefore be more accurate than the straight approximation $\langle \psi_\beta^- | \, V_i \, | \, \varphi_\alpha \rangle \simeq \langle \varphi_\beta | \, V_i \, | \varphi_\alpha \rangle$, which neglects the interaction between *all* particles in the final state.

The Born approximation is found experimentally to work well for energies of a few hundred eV or more for electron scattering, and a few hundred keV or more for atomic or molecular scattering.

EXERCISES

1. Show that the Born approximation to the direct scattering amplitude for inelastic collisions of fast electrons with hydrogen atoms is given by

$$f_d(\mathbf{k}n \to \mathbf{l}p) = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r} \int d\mathbf{R}\, \chi_p^*(\mathbf{R}) \exp(-i\mathbf{l}\cdot\mathbf{r}) \frac{e^2}{\varkappa_0 |\mathbf{r}-\mathbf{R}|} \chi_n(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{r}),$$

where m is the mass of an electron and $e^2/\varkappa_0|\mathbf{r}-\mathbf{R}|$ is the Coulomb repulsion between the electrons, if the mass of the proton can be taken as effectively infinite.

2. Show that the Born–Oppenheimer approximation for the exchange amplitude for collisions of fast electrons with hydrogen atoms is given by

$$f_{ex}(\mathbf{k}n \to \mathbf{l}p) = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r} \int d\mathbf{R}\, \chi_p^*(\mathbf{r}) \exp(-i\mathbf{l}\cdot\mathbf{R}) \left[\frac{e^2}{\varkappa_0 |\mathbf{r}-\mathbf{R}|} - \frac{e^2}{\varkappa_0 R}\right] \chi_n(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{r}),$$

provided the mass of the proton can be taken as effectively infinite. Hence, or otherwise, show that

$$\begin{aligned} &\int d\mathbf{r} \int d\mathbf{R}\, \chi_p^*(\mathbf{r}) \exp(-i\mathbf{l}\cdot\mathbf{R})\, R^{-1} \chi_n(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{r}) \\ &= \int d\mathbf{r} \int d\mathbf{R}\, \chi_p^*(\mathbf{r}) \exp(-i\mathbf{l}\cdot\mathbf{R})\, r^{-1} \chi_n(\mathbf{R}) \exp(i\mathbf{k}\cdot\mathbf{r}). \end{aligned}$$

3. Show that the differential cross-section for scattering of fast electrons by hydrogen atoms is given by

$$\sigma(\mathbf{k}n \to \mathbf{l}p) = (v_p/v_n)[\tfrac{1}{4}|f_d(\mathbf{k}n \to \mathbf{l}p) + f_{ex}(\mathbf{k}n \to \mathbf{l}p)|^2 + \tfrac{3}{4}|f_d(\mathbf{k}n \to \mathbf{l}p) - f_{ex}(\mathbf{k}n \to \mathbf{l}p)|^2]$$

where f_d, f_{ex} are as given by Exercises 1 and 2, and v_n and v_p are the initial and final speeds of the electron, provided the mass of the nucleus can be taken as infinite.

5.4. THE DISTORTED WAVE APPROXIMATION

In the last section we discussed the Born approximation for the transition amplitude. We also derived the Born series (5.3.5) for the transition amplitude $T(\alpha \to \beta)$ for direct collisions, which offers a systematic way of improving on the first approximation. In practice this is not very useful, since the integrals increase by $3(N-1)$ dimensions at each successive approximation. We shall now consider a more practicable method of improving on the Born approximation, and thus dealing with collisions at lower energies.

We note firstly that if the crude approximations $\theta_\beta^- \simeq \varphi_\beta$, $\psi_\alpha^+ \simeq \varphi_\alpha$ are made in the two-potential formula (5.1.36) the Born approximation (5.3.9) is obtained. A less crude approximation is obtained from (5.1.36) if we make only the approximation $\psi_\alpha^+ \simeq \theta_\alpha^+$. In other words, as we can see from (5.1.15), we regard W_i as a small perturbation, but treat U_i exactly. With this approximation (5.1.36) becomes

$$T(\alpha \to \beta) \simeq \langle \theta_\beta^- \,|\, V_i - W_f \,|\, \varphi_\alpha \rangle + \langle \theta_\beta^- \,|\, W_f \,|\, \theta_\alpha^+ \rangle. \tag{5.4.1}$$

This is known as the "distorted wave Born approximation", or simply as the "distorted wave approximation", since it takes into account the distortion of the initial and final states φ_α and φ_β by the potentials U_i and U_f. In order to see how it may be applied in practice we will consider some examples.

Example 1. Let us consider processes of the form

$$A + B \to C + D. \tag{5.4.2}$$

The particles involved may be elementary or composite. Let us suppose that U_i is a function of the initial relative displacement $\mathbf{r}_i$ only, while U_f is a function of the final relative displacement $\mathbf{r}_f$ only. For example, we could take

$$U_i = \int V_i(\mathbf{r}_i, \mathbf{x}_i) \,|\, \chi_n(\mathbf{x}_i) \,|^2 \, d\mathbf{x}_i = U_i(\mathbf{r}_i), \tag{5.4.3}$$

$$U_f = \int V_f(\mathbf{r}_f, \mathbf{x}_f) \,|\, \chi_p(\mathbf{x}_f) \,|^2 \, d\mathbf{x}_f = U_f(\mathbf{r}_f), \tag{5.4.4}$$

where $\mathbf{x}_i$ and $\mathbf{x}_f$ denote the initial and final internal coordinates. In other words, U_i and U_f could be the static potentials between A and B, and between C and D, obtained by averaging the potentials V_i and V_f over the static charge clouds of A and B or C and D. Any other potentials will do, provided they are functions only of $\mathbf{r}_i$ and $\mathbf{r}_f$. In the present case $\varphi_\alpha = \varphi_\mathbf{k}\chi_n$ where, as usual, $\varphi_\mathbf{k}$ is the plane wave representing the initial relative motion of A and B, while $\mathsf{H}_i = \mathsf{K}_i + \mathsf{h}_i$ where K_i is the initial relative kinetic energy operator and h_i is the initial internal Hamiltonian. Since $\alpha = \mathbf{k}n$ (5.1.6) becomes

$$\theta_{\mathbf{k}n}^\pm = \varphi_\mathbf{k}\chi_n + [E - (\mathsf{K}_i + U_i) - \mathsf{h}_i \pm i\varepsilon]^{-1} U_i \varphi_\mathbf{k}\chi_n . \tag{5.4.5}$$

Now K_i, U_i and $\varphi_\mathbf{k}$ depend only on $\mathbf{r}_i$; also h_i, χ_n depend only on $\mathbf{x}_i$ and $\mathsf{h}_i\chi_n = E_n\chi_n$. Hence by Appendix A

$$\theta_{\mathbf{k}n}^\pm = \{\varphi_\mathbf{k} + [E - (\mathsf{K}_i + U_i) - E_n \pm i\varepsilon]^{-1} U_i \varphi_\mathbf{k}\} \, \chi_n ; \tag{5.4.6}$$

but $E - E_n = E_k$, and so the term in curly brackets is

$$\varphi_{\mathbf{k}} + (E_k - \mathsf{K}_i - U_i \pm i\varepsilon)^{-1} U_i \varphi_{\mathbf{k}}. \tag{5.4.7}$$

These are, however, the Schwinger–Lippmann states $\theta^{\pm}_{\mathbf{k}}$ for the potential U_i when the unperturbed state is $\varphi_{\mathbf{k}}$; thus

$$\theta^{\pm}_{\mathbf{k}n} = \theta^{\pm}_{\mathbf{k}} \chi_p \tag{5.4.8}$$

where

$$\theta^{\pm}_{\mathbf{k}} = \varphi_{\mathbf{k}} + (E_k - \mathsf{K}_i - U_i \pm i\varepsilon)^{-1} U_i \varphi_{\mathbf{k}}. \tag{5.4.9}$$

In exactly the same way we can also show that, for the final state, when $\beta = \mathbf{l}p$,

$$\theta^{\pm}_{\mathbf{l}p} = \theta^{\pm}_{\mathbf{l}} \chi_p \tag{5.4.10}$$

where

$$\theta^{\pm}_{\mathbf{l}} = \varphi_{\mathbf{l}} + (E_l - \mathsf{K}_f - U_f \pm i\varepsilon)^{-1} U_f \varphi_{\mathbf{l}}. \tag{5.4.11}$$

These expressions show that θ^{+}_{α} is the product of the initial internal state χ_n and a "distorted wave" $\theta^{+}_{\mathbf{k}}$ which describes the initial relative motion under the action of the distorting potential U_i, outgoing wave boundary conditions being imposed. Similarly θ^{-}_{β} is the product of the "distorted wave" $\theta^{-}_{\mathbf{l}}$ (which takes account of the effect on the final relative motion of the potential U_f) and the final internal state χ_p. The solution of Schrödinger's equation for $\theta^{+}_{\mathbf{k}}$ or $\theta^{-}_{\mathbf{l}}$ is a 3-dimensional (one-particle) problem only. If this is done (1) shows that the problem of calculating the transition amplitude is reduced to a quadrature; written out using (8) and (10) it is

$$T(\mathbf{k}n \to \mathbf{l}p) \simeq \langle \theta^{-}_{\mathbf{l}} \chi_p \,|\, V_i - W_f \,|\, \varphi_{\mathbf{k}} \chi_n \rangle + \langle \theta^{-}_{\mathbf{l}} \chi_p \,|\, W_f \,|\, \theta^{+}_{\mathbf{k}} \chi_n \rangle. \tag{5.4.12}$$

Example 2. *Elastic collisions.* As a second example we consider direct collisions $A+B \to A+B$ in which the internal state of the colliding particles is unaltered. The arrangement channel labels i and f may now be dropped, and the potential has the form $V = U+W$. Since $V_i - W_f = V - W = U$, (1) simplifies to

$$T(\alpha \to \beta) \simeq \langle \theta^{-}_{\beta} | U | \varphi_{\alpha} \rangle + \langle \theta^{-}_{\beta} | W | \theta^{+}_{\alpha} \rangle. \tag{5.4.13}$$

In this case $\mathsf{H}_i = \mathsf{H}_f = \mathsf{H}_0$, say, and so θ^{+}_{α} and θ^{-}_{β} are given by (cf. (5.1.6))

$$\theta^{+}_{\alpha} = \varphi_{\alpha} + (E - \mathsf{H}_0 - U + i\varepsilon)^{-1}\, U \varphi_{\alpha}, \tag{5.4.14}$$

$$\theta^{-}_{\beta} = \varphi_{\beta} + (E - \mathsf{H}_0 - U - i\varepsilon)^{-1}\, U \varphi_{\beta}. \tag{5.4.15}$$

In (13) the first term on the right-hand side is obviously the transition amplitude for scattering by the potential U, and the second term is obviously the Born approximation for scattering of the distorted states by the potential W.

In the special case discussed in Example 1, U is a function only of the relative displacement $\mathbf{r}_i = \mathbf{r}_f = \mathbf{r}$, say, and since the internal states of A and B are unchanged (13) becomes

$$T(\mathbf{k}n \to \mathbf{l}n) \simeq \langle \theta^{-}_{\mathbf{l}} \chi_n \,|\, U \,|\, \varphi_{\mathbf{k}} \chi_n \rangle + \langle \theta^{-}_{\mathbf{l}} \chi_n \,|\, W \,|\, \theta^{-}_{\mathbf{k}} \chi_n \rangle \tag{5.4.16}$$

where by (9) and (11)

$$\theta^{+}_{\mathbf{k}} = \varphi_{\mathbf{k}} + (E_{\mathbf{k}} - \mathsf{K} - U + i\varepsilon)^{-1}\, U \varphi_{\mathbf{k}}, \tag{5.4.17}$$

$$\theta^{-}_{\mathbf{l}} = \varphi_{l} + (E_l - \mathsf{K} - U - i\varepsilon)^{-1}\, U \varphi_{\mathbf{l}}. \tag{5.4.18}$$

In (17) and (18) K is the relative kinetic energy operator of A and B. Now U is a function of $\mathbf{r}$ only, while χ_n depends on the internal coordinates only, and $\langle \chi_n | \chi_n \rangle = 1$, hence

$$\langle \theta^{-}_{\mathbf{l}} \chi^{-}_{n} \,|\, U \,|\, \varphi_{\mathbf{k}} \chi_n \rangle = \langle \theta^{-}_{\mathbf{l}} \,|\, U \,|\, \varphi_{\mathbf{k}} \rangle \langle \chi_n | \chi_n \rangle = \langle \theta^{-}_{\mathbf{l}} \,|\, U \,|\, \varphi_{\mathbf{k}} \rangle. \tag{5.4.19}$$

The expression (16) for the transition amplitude therefore simplifies to

$$T(\mathbf{k}n \to \mathbf{l}n) = \langle \theta_{\mathbf{l}}^{-} \mid U \mid \varphi_{\mathbf{k}} \rangle + \langle \theta_{\mathbf{l}}^{-} \chi_n \mid W \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle. \tag{5.4.20}$$

The first term is the exact amplitude for scattering by the potential U; the second term is a first order correction term which takes account of the remainder of the potential W. If we make the further approximations $\theta_{\mathbf{l}}^{-} \simeq \varphi_{\mathbf{l}}$ and $\theta_{\mathbf{k}}^{+} \simeq \varphi_{\mathbf{k}}$ in the second term on the right-hand side of (20) this becomes

$$\begin{aligned}\langle \varphi_{\mathbf{l}} \chi_n \mid W \mid \varphi_{\mathbf{k}} \chi_n \rangle &= \langle \varphi_{\mathbf{l}} \chi_n \mid V - U \mid \varphi_{\mathbf{k}} \chi_n \rangle = \langle \varphi_{\mathbf{l}} \chi_n \mid V \mid \varphi_{\mathbf{k}} \chi_n \rangle - \langle \varphi_{\mathbf{l}} \mid U \mid \varphi_{\mathbf{k}} \rangle \langle \chi_n \mid \chi_n \rangle \\ &= \langle \varphi_{\mathbf{l}} \chi_n \mid V \mid \varphi_{\mathbf{k}} \chi_n \rangle - \langle \varphi_{\mathbf{l}} \mid U \mid \varphi_{\mathbf{k}} \rangle. \end{aligned} \tag{5.4.21}$$

Now if U is the static potential the first term on the right-hand side is, since $\mathbf{x}_i = \mathbf{x}_f = \mathbf{x}$ say,

$$\int d\mathbf{r} \int d\mathbf{x}\, \varphi_{\mathbf{l}}^{*}(\mathbf{r})\, \varphi_{\mathbf{k}}(\mathbf{r})\, V(\mathbf{r}, \mathbf{x}) \mid \chi_n(\mathbf{x}) \mid^2 = \int d\mathbf{r}\, \varphi_{\mathbf{l}}^{*}(\mathbf{r})\, U(\mathbf{r})\, \varphi_{\mathbf{k}}(\mathbf{r}) = \langle \varphi_{\mathbf{l}} \mid U \mid \varphi_{\mathbf{k}} \rangle, \tag{5.4.22}$$

and so $\langle \varphi_{\mathbf{l}} \chi_n \mid W \mid \varphi_{\mathbf{k}} \chi_n \rangle = 0$; that is, (20) becomes

$$T(\mathbf{k}n \to \mathbf{l}p) \simeq \langle \theta_{\mathbf{l}}^{-} \mid U \mid \varphi_{\mathbf{k}} \rangle. \tag{5.4.23}$$

(23) is the transition amplitude for the collision if the interaction potential U is taken as the average of V over all positions of the elementary particles of A and B in the state χ_n. If U is a better potential than this which depends only on $\mathbf{r}$, the term $\langle \varphi_{\mathbf{l}} \chi_n \mid W \mid \varphi_{\mathbf{k}} \chi_n \rangle$ may no longer vanish and the expression obtained by putting $\theta_{\mathbf{l}}^{-} \simeq \varphi_{\mathbf{l}}$, $\theta_{\mathbf{k}}^{+} \simeq \varphi_{\mathbf{k}}$ in (20), viz.

$$T(\mathbf{k}n \to \mathbf{l}n) \simeq \langle \theta_{\mathbf{l}}^{-} \mid U \mid \varphi_{\mathbf{k}} \rangle + \langle \varphi_{\mathbf{l}} \chi_n \mid W \mid \varphi_{\mathbf{k}} \chi_n \rangle, \tag{5.4.24}$$

should give an improved result; if we take (20) as our formula for T, we should obtain an even better result.

EXAMPLE 3. *Inelastic collisions.* Let us now consider collisions of the form $A+B \to A+B$, when one at least of the colliding systems changes its internal state. The decomposition of V now becomes

$$U_i + W_i = V = U_f + W_f. \tag{5.4.25}$$

U_i may be the static potential initially when the internal state is χ_n, while U_f may be the static potential when the internal state is χ_p. Since by (25) $V - W_f = U_f$ and $V_i = V_f = V$, $\mathsf{H}_i = \mathsf{H}_f = \mathsf{H}_0$, the expression (1) now becomes

$V,$

$$T(\alpha \to \beta) \simeq \langle \theta_{\beta}^{-} \mid U_f \mid \varphi_{\alpha} \rangle + \langle \theta_{\beta}^{-} \mid W_f \mid \theta_{\alpha}^{+} \rangle \tag{5.4.26}$$

where by (5.1.6)

$$\theta_{\alpha}^{+} = \varphi_{\alpha} + (E - \mathsf{H}_0 - U_i + i\varepsilon)^{-1}\, U_i \varphi_{\alpha}, \tag{5.4.27}$$

$$\theta_{\beta}^{-} = \varphi_{\beta} + (E - \mathsf{H}_0 - U_f - i\varepsilon)^{-1}\, U_f \varphi_{\beta}. \tag{5.4.28}$$

If U_f is a function of $\mathbf{r}$ only the reasoning of Example 1 shows that (26) can be written as

$$T(\mathbf{k}n \to \mathbf{l}p) = \langle \theta_{\mathbf{l}}^{-} \chi_p \mid U_f \mid \varphi_{\mathbf{k}} \chi_n \rangle + \langle \theta_{\mathbf{l}}^{-} \chi_p \mid W_f \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle \tag{5.4.29}$$

where $\theta_{\mathbf{k}}^{+}$, $\theta_{\mathbf{l}}^{-}$ are given by (9) and (11). In this case they become

$$\theta_{\mathbf{k}}^{+} = \varphi_{\mathbf{k}} + (E_k - \mathsf{K} - U_i + i\varepsilon)^{-1}\, U_i \varphi_{\mathbf{k}}, \tag{5.4.30}$$

$$\theta_{\mathbf{l}}^{-} = \varphi_{\mathbf{l}} + (E_l - \mathsf{K} - U_f - i\varepsilon)^{-1}\, U_f \varphi_{\mathbf{l}} \tag{5.4.31}$$

where K is again the relative kinetic energy operator for A and B. Since U_f is a function of $\mathbf{r}$ only

$$\langle \theta_{\mathbf{l}}^{-} \chi_p \mid U_f \mid \varphi_{\mathbf{k}} \chi_n \rangle = \langle \theta_{\mathbf{l}}^{-} \mid U_f \mid \varphi_{\mathbf{k}} \rangle \langle \chi_p \mid \chi_n \rangle = 0 \tag{5.4.32}$$

due to the orthogonality of χ_n and χ_p. Thus (29) becomes

$$T(\mathbf{k}n \rightarrow \mathbf{l}p) \simeq \langle \theta_{\mathbf{l}}^{-} \chi_p \mid W_f \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle \tag{5.4.33}$$

which is the distorted wave approximation for inelastic collisions when the distorting potentials U_i and U_f depend only on the relative position vector $\mathbf{r}$. (If U_i and U_f are the static potentials it treats these exactly, but takes account of polarization effects, for example, by a perturbation treatment.) Since $V = W_f + U_f$ we have

$$\langle \theta_{\mathbf{l}}^{-} \chi_p \mid V \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle = \langle \theta_{\mathbf{l}}^{-} \chi_p \mid W_f \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle + \langle \theta_{\mathbf{l}}^{-} \chi_p \mid U_f \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle; \tag{5.4.34}$$

but U_f depends only on $\mathbf{r}$, hence

$$\langle \theta_{\mathbf{l}}^{-} \chi_p \mid U_f \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle = \langle \theta_{\mathbf{l}}^{-} \mid U_f \mid \theta_{\mathbf{k}}^{+} \rangle \langle \chi_p \mid \chi_n \rangle = 0, \tag{5.4.35}$$

and so (33) can be rewritten as

$$T(\mathbf{k}n \rightarrow \mathbf{l}p) \simeq \langle \theta_{\mathbf{l}}^{-} \chi_p \mid V \mid \theta_{\mathbf{k}}^{+} \chi_n \rangle. \tag{5.4.36}$$

In other words if U_i and U_f depend only on $\mathbf{r}$, the Born approximation

$$T(\mathbf{k}n \rightarrow \mathbf{l}p) \simeq \langle \varphi_{\mathbf{l}} \chi_p \mid V \mid \varphi_{\mathbf{k}} \chi_n \rangle \tag{5.4.37}$$

for inelastic collisions may be improved by replacing the plane waves $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{l}}$ in the expression for the transition amplitude $T(\mathbf{k}n \rightarrow \mathbf{l}p)$ by the waves $\theta_{\mathbf{k}}^{+}$ and $\theta_{\mathbf{l}}^{-}$ distorted by the potentials U_i and U_f from $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{l}}$ respectively.

EXERCISES

1. Assuming that the mass of the proton is effectively infinite, and that the electrons are spinless and distinguishable, show that the distorted wave approximation to the direct amplitude for inelastic scattering of electrons by hydrogen atoms is given by

$$f_d(\mathbf{k}n \rightarrow \mathbf{l}p) = -\frac{4\pi^2 m e^2}{\hbar^2 \varkappa_0} \int d\mathbf{r} \int d\mathbf{R}\, \theta_{-\mathbf{l}}^{\pm}(\mathbf{r})\, \chi_p^*(\mathbf{R})\, \frac{1}{|\mathbf{R}-\mathbf{r}|}\, \theta_{\mathbf{k}}^{+}(\mathbf{r})\, \chi_n(\mathbf{R}),$$

where $e^2/\varkappa_0|\mathbf{r}-\mathbf{R}|$ is the Coulomb repulsion between the electrons and m is the mass of an electron; $\theta_{-\mathbf{l}}^{\pm}$, $\theta_{\mathbf{k}}^{+}$ are the final and initial waves distorted by the static potentials.

2. With the same assumptions as the previous exercise prove that the exchange amplitude for inelastic scattering of electrons by hydrogen atoms is given by

$$f_{ex}(\mathbf{k}n \rightarrow \mathbf{l}p) = -\frac{4\pi^2 m}{\hbar^2} \int d\mathbf{r} \int d\mathbf{R}\, \theta_{-\mathbf{l}}^{\pm}(\mathbf{R})\, \chi_p^*(\mathbf{r}) \left[\frac{e}{\varkappa_0 |\mathbf{r}-\mathbf{R}|} + (E_n - E_l)\right] \theta_{\mathbf{k}}^{+}(\mathbf{r})\, \chi_n(\mathbf{R})$$

where $\theta_{\mathbf{k}}^{+}$ and $\theta_{-\mathbf{l}}^{\pm}$ are the initial and final waves distorted by the initial and final static potentials.

3. Prove that if the spin and indistinguishability of the electrons are taken into account the exact differential cross-section for inelastic scattering of electrons by hydrogen atoms is given by

$$\sigma(\mathbf{k}n \rightarrow \mathbf{l}p) = (v_p/v_n)[\tfrac{1}{4} \mid f_d(\mathbf{k}n \rightarrow \mathbf{l}p) + f_{ex}(\mathbf{k}n \rightarrow \mathbf{l}p)|^2 + \tfrac{3}{4} \mid f_d(\mathbf{k}n \rightarrow \mathbf{l}p) - f_{ex}(\mathbf{k}n \rightarrow \mathbf{l}p)|^2]$$

where f_d and f_{ex} are the exact direct and exchange scattering amplitudes obtained by ignoring spin and the Pauli principle, and v_n and v_p are the initial and final speeds of the free electron.

[*Note*: The amplitudes f_d and f_{ex} of Exercise 3 may be approximated by the expressions given in Exercises 1 and 2. The resultant expression may be further refined if the effect of exchange in the initial and final distorted waves is also taken into account. For an account of this, and references to calculations which have been made by this method, the interested reader is referred to the book of Mott and Massey (1965).]

5.5. THE GENERALIZED OPTICAL THEOREM

In Section 2.7 we showed that the fundamental postulate (2.2.1) led to the unitarity of the scattering matrix as expressed by (2.7.13). We further showed that the unitarity property expresses the conservation of probability. The property (2.7.13) may be expressed in a rather more concrete form as a relation between the total cross-section and the forward scattering amplitude. Such a relation is directly verifiable by experiment.

We shall start the derivation by first noting that the unitarity condition $S^\dagger S = 1$ may be expressed as

$$\sum_\omega S^\dagger_{\nu\omega} S_{\omega\mu} = \delta_{\mu\nu}. \tag{5.5.1}$$

Since $S^\dagger_{\nu\omega} = S^*_{\omega\nu}$ this is equivalent to

$$\sum_\omega S^*_{\omega\nu} S_{\omega\mu} = \delta_{\mu\nu}. \tag{5.5.2}$$

We can express $S_{\omega\nu}$ and $S_{\omega\mu}$ in terms of the transition amplitudes $T(\nu \to \omega)$ and $T(\mu \to \omega)$ by means of (3.3.19); if we do this and substitute for the results in (2) we get

$$\begin{aligned}\sum_\omega [\delta_{\omega\nu} + 2\pi i \delta(E_\omega - E_\nu) T^*(\nu \to \omega)] \times \\ \times [\delta_{\omega\mu} - 2\pi i \delta(E_\omega - E_\mu) T(\mu \to \omega)] = \delta_{\mu\nu}\end{aligned} \tag{5.5.3}$$

which simplifies to

$$\begin{aligned}2\pi i \delta(E_\mu - E_\nu) T^*(\nu \to \mu) - 2\pi i \delta(E_\nu - E_\mu) T(\mu \to \nu) \\ = -(2\pi)^2 \sum_\omega \delta(E_\omega - E_\nu)\, \delta(E_\omega - E_\mu) T(\mu \to \omega) T^*(\nu \to \omega).\end{aligned} \tag{5.5.4}$$

Now $\delta(E_\omega - E_\nu)\, \delta(E_\omega - E_\mu) = \delta(E_\mu - E_\nu)\, \delta(E_\omega - E_\mu)$, and so both sides of (2) contain the factor $\delta(E_\mu - E_\nu) = \delta(E_\nu - E_\mu)$. It follows that the quantities multiplying $\delta(E_\mu - E_\nu)$ must be equal when $E_\mu = E_\nu$; hence if $E_\mu = E_\nu$,

$$\begin{aligned}i[T^*(\nu \to \mu) - T(\mu \to \nu)] \\ = -2\pi \sum_\omega \delta(E_\omega - E_\mu) T(\mu \to \omega) T^*(\nu \to \omega).\end{aligned} \tag{5.5.5}$$

In particular, if $\mu = \nu$,

$$\operatorname{Im} T(\nu \to \nu) = -\pi \sum_\omega \delta(E_\omega - E_\nu) \,|T(\nu \to \omega)|^2. \tag{5.5.6}$$

This is the generalized optical theorem expressed in terms of transition amplitudes.

Let us now express (6) as a relationship between the cross-section and forward scattering amplitude. To do this we note from (5.1.1) that

$$T(\alpha \to \beta) = (-\hbar^2/4\pi^2\mu_f)f(\alpha \to \beta) \tag{5.5.7}$$

and hence in particular

$$T(\alpha \to \alpha) = (-\hbar^2/4\pi^2\mu_i)f(\alpha \to \alpha). \tag{5.5.8}$$

Since when $\nu = \alpha$ (6) can be written

$$\operatorname{Im} T(\alpha \to \alpha) = -\pi \sum_\beta \delta(E_\beta - E_\alpha)\,|T(\alpha \to \beta)|^2 \tag{5.5.9}$$

we obtain

$$(-\hbar^2/4\pi^2\mu_i)\operatorname{Im} f(\alpha \to \alpha) = \pi \sum_\beta \delta(E_\beta - E_\alpha)\,|T(\alpha \to \beta)|^2. \tag{5.5.10}$$

If we multiply this by $16\pi^3\mu_i/\hbar^2 k$ and use (3.8.9) we obtain the important result

$$\boxed{\sigma = \frac{4\pi}{k}\operatorname{Im} f(\alpha \to \alpha)} \tag{5.5.11}$$

which is the promised relation between the total cross-section σ and the imaginary part of the forward scattering amplitude $f(\alpha \to \alpha)$.

EXAMPLE. *The Born approximation.* According to the Born approximation (5.3.9) the forward transition amplitude is given by

$$T(\alpha \to \alpha) \simeq \langle \varphi_\alpha \,|\, V_i \,|\, \varphi_\alpha \rangle. \tag{5.5.12}$$

Written out more fully this is

$$T(\alpha \to \alpha) \simeq \int d\mathbf{r}_i \int d\mathbf{x}_i\, V_i(\mathbf{r}_i, \mathbf{x}_i)\,|\varphi_\alpha(\mathbf{r}_i, \mathbf{x}_i)|^2. \tag{5.5.13}$$

Since V_i is usually real this is real, and hence so is the forward scattering amplitude $f(\alpha \to \alpha)$; hence (11) implies $\sigma = 0$! We must, however, remember that (5.3.9) is an approximation, and (11) has only been proved to hold for the exact cross-section and forward scattering amplitude. Since (11) was deduced from the unitarity of the scattering matrix, which expresses the conservation of probability, this means that the Born approximation does not conserve probability (or particles). Approximations have been developed using the so-called "reactance matrix" which are, in fact, consistent with (11); these approximations are, however, beyond the scope of the present book (Mott and Massey, 1965, p. 371).

5.6. THE FRANCK–CONDON PRINCIPLE

We shall now discuss collisions of the form

$$A + M \to A + M \tag{5.6.1}$$

where A is an elementary particle and M is a diatomic molecule. For the moment we shall neglect any complications which arise if A is identical with any of the elementary particles of M. Since (1) is a direct collision we shall also be able to drop all arrangement channel indices.

Before the collision the state of the system may be described by the wave function $\varphi_{\mathbf{k}nv}$ given by

$$\varphi_{\mathbf{k}nv}(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_{\mathbf{k}}(\mathbf{r})\,\chi_n(\mathbf{q} \mid \mathbf{R})\,\eta_v(\mathbf{R}) \tag{5.6.2}$$

where χ_n is the initial electronic wave function, η_v is the initial vibrational-rotational wave function, $\mathbf{r}$ is the displacement vector of A relative to the centre of mass of M, $\mathbf{R}$ is the relative displacement vector of the nuclei of M, and $\mathbf{q}$ the remaining coordinates (electron position coordinates and spin) The other symbols have their usual meaning. In this notation the quantum numbers n label the electronic state of the molecule, while the quantum numbers v label the vibrational-rotational state. The notation $\chi_n(\mathbf{q} \mid \mathbf{R})$ is used to indicate that χ_n depends parametrically upon $\mathbf{R}$ (Schiff, 1955, chapter XI). In this case the internal coordinates are the combined coordinates ($\mathbf{R}$, $\mathbf{q}$) while the initial internal state χ_n has been replaced by the product $\chi_n\eta_v$.

After the collision we can assume that the quantum numbers $\mathbf{k}nv$ are replaced by the quantum numbers $\mathbf{l}pw$ which describe the new state of relative motion and new state of the diatomic molecule M, so that (2) is replaced by

$$\varphi_{\mathbf{l}pw}(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_{\mathbf{l}}(\mathbf{r})\,\chi_p(\mathbf{q} \mid \mathbf{R})\,\eta_w(\mathbf{R}). \tag{5.6.3}$$

We will now obtain an approximate expression for the scattering amplitude $f(\mathbf{k}nv \rightarrow \mathbf{l}pw)$.

According to (5.1.1) the scattering amplitude is given by

$$f(\mathbf{k}nv \rightarrow \mathbf{l}pw) = (-4\pi^2\mu/h^2)\langle\varphi_{\mathbf{l}pw} \mid V \mid \psi^+_{\mathbf{k}nv}\rangle \tag{5.6.4}$$

where μ is the reduced mass of A and M, and V is the interaction between A and M. The scattering state $\psi^+_{\mathbf{k}nv}$ is defined by

$$\psi^+_{\mathbf{k}nv} = \varphi_{\mathbf{k}nv} + (E - \mathsf{H} + i\varepsilon)^{-1}\,V\varphi_{\mathbf{k}nv} \tag{5.6.5}$$

$$= \varphi_{\mathbf{k}nv} + (E - \mathsf{H}_0 - V + i\varepsilon)^{-1}\,V\varphi_{\mathbf{k}nv} \tag{5.6.6}$$

where the unperturbed Hamiltonian H_0 has the form

$$\mathsf{H}_0 = \mathsf{K}_{\mathbf{r}} + \mathsf{K}_{\mathbf{R}} + \frac{Z_1 Z_2 e^2}{\varkappa_0 R} + \mathsf{h}_e; \tag{5.6.7}$$

in (7) $\mathsf{K}_{\mathbf{r}}$ and $\mathsf{K}_{\mathbf{R}}$ are the kinetic energy operators corresponding to the relative displacements $\mathbf{r}$ and $\mathbf{R}$, Z_1 and Z_2 are the atomic numbers of the nuclei of the molecule, h_e is the Hamiltonian for the motion of the electrons of the molecule relative to the nuclei, and $\varkappa_0$ is the dielectric constant for free space.

We shall now find an approximate expression for the scattering state $\psi^+_{\mathbf{k}nv}$ based on the Born–Oppenheimer separation process (Schiff, 1955, chapter XI). Let us imagine the nuclei of the molecule frozen at the displacement $\mathbf{R}$. The molecule will have an electronic energy $E_n(R)$, and we can consider the scattering of A by the molecule M if M's nuclei are fixed. The unperturbed Hamiltonian for this process is

$$\mathsf{H}'_0 = \mathsf{K}_{\mathbf{r}} + \mathsf{h}_e, \tag{5.6.8}$$

the interaction is still V, while the energy is $E_k + E_n(R)$ where E_k is the energy of A relative to M. The unperturbed state is $\varphi_{\mathbf{k}n}$ where

$$\varphi_{\mathbf{k}n}(\mathbf{r}, \mathbf{q} \mid \mathbf{R}) = \varphi_{\mathbf{k}}(\mathbf{r})\, \chi_n(\mathbf{q} \mid \mathbf{R}), \tag{5.6.9}$$

and depends parametrically upon $\mathbf{R}$. By definition

$$\psi^+_{\mathbf{k}n} = \varphi_{\mathbf{k}n} + [E_k + E_n(\mathbf{R}) - \mathsf{H}'_0 - V + i\varepsilon]^{-1} V \varphi_{\mathbf{k}n}, \tag{5.6.10}$$

and since $\mathsf{H}'_0 \varphi_{\mathbf{k}n} = [E_k + E_n(R)]\, \varphi_{\mathbf{k}n}$ we deduce that

$$[E_k + E_n(R) - \mathsf{H}'_0 - V + i\varepsilon]\, \psi^+_{\mathbf{k}n} = i\varepsilon \varphi_{\mathbf{k}n}. \tag{5.6.11}$$

If we substitute for H'_0 from (8) into (11) we get

$$[E_k + E_n(R) - \mathsf{K}_{\mathbf{r}} - \mathsf{h}_e - V + i\varepsilon]\, \psi^+_{\mathbf{k}n} = i\varepsilon \varphi_{\mathbf{k}n}. \tag{5.6.12}$$

Let us now consider $\psi^+_{\mathbf{k}n}\eta_v$. From (7) we see that

$$(E - \mathsf{H}_0 - V + i\varepsilon)\, \psi^+_{\mathbf{k}n}\eta_v = \left[E - \mathsf{K}_{\mathbf{r}} - \mathsf{K}_{\mathbf{R}} - \frac{Z_1 Z_2 e^2}{\varkappa_0 R} - \mathsf{h}_e - V + i\varepsilon\right] \psi^+_{\mathbf{k}n}\eta_v. \tag{5.6.13}$$

In the Born–Oppenheimer approximation it is always supposed that the electronic wave function varies slowly with the nuclear coordinates $\mathbf{R}$. In the spirit of this approximation we shall assume that this applies to the state $\psi^+_{\mathbf{k}n}$ also; for it is analogous to the molecular electronic state, since it is calculated with M's nuclei fixed, and obviously depends parametrically upon $\mathbf{R}$. If we make this assumption $\mathsf{K}_{\mathbf{R}}\psi^+_{\mathbf{k}n}$ can be neglected, and so (13) becomes

$$\begin{aligned}(E - \mathsf{H}_0 - V + i\varepsilon)\, \psi^+_{\mathbf{k}n}\eta_v \\ = \{[E - \mathsf{K}_{\mathbf{r}} - \mathsf{h}_e - V + i\varepsilon]\, \psi^+_{\mathbf{k}n}\}\, \eta_v - \psi^+_{\mathbf{k}n} \left\{\left[\mathsf{K}_{\mathbf{R}} + \frac{Z_1 Z_2 e^2}{\varkappa_0 R}\right] \eta_v\right\}\end{aligned} \tag{5.6.14}$$

and by (12) equation (14) can be written

$$\begin{aligned}(E - \mathsf{H}_0 - V + i\varepsilon)\, \psi^+_{\mathbf{k}n}\eta_v \\ = \{[E - E_k - E_n(R)]\, \psi^+_{\mathbf{k}n} + i\varepsilon \varphi_{\mathbf{k}n}\}\, \eta_v - \psi^+_{\mathbf{k}n} \left\{\left[\mathsf{K}_{\mathbf{R}} + \frac{Z_1 Z_2 e^2}{\varkappa_0 R}\right] \eta_v\right\}.\end{aligned} \tag{5.6.15}$$

From (2) and (9) we have $\varphi_{\mathbf{k}n}\eta_v = \varphi_{\mathbf{k}nv}$, hence (15) can be rearranged to give

$$\begin{aligned}(E-\mathsf{H}_0-V+i\varepsilon)\,&\psi^+_{\mathbf{k}n}\eta_v \\ &= \psi^+_{\mathbf{k}n}\left\{\left[E-E_k-E_n(R)-\mathsf{K}_{\mathbf{R}}-\frac{Z_1Z_2e^2}{\varkappa_0 R}\right]\eta_v\right\}+i\varepsilon\varphi_{\mathbf{k}nv}.\end{aligned} \tag{5.6.16}$$

Now η_v is the nuclear wave function, and so satisfies the nuclear wave equation

$$\left[\mathsf{K}_{\mathbf{R}}+E_n(R)+\frac{Z_1Z_2e^2}{\varkappa_0 R}\right]\eta_v = E_{nv}\eta_v. \tag{5.6.17}$$

Here E_{nv} is the total energy of the molecule, hence $E = E_k+E_{nv}$, or $E-E_k = E_{nv}$. The first term on the right-hand side of (16) therefore vanishes, and so (16) becomes

$$(E-\mathsf{H}_0-V+i\varepsilon)\,\psi^+_{\mathbf{k}n}\eta_v = i\varepsilon\varphi_{\mathbf{k}nv}. \tag{5.6.18}$$

Since $\mathsf{H}_0\varphi_{\mathbf{k}nv} = E_{knv}\varphi_{\mathbf{k}nv} = E\varphi_{\mathbf{k}nv}$ this can be rewritten

$$(E-\mathsf{H}_0-V+i\varepsilon)\,\psi^+_{\mathbf{k}n}\eta_v = (E-\mathsf{H}_0-V+i\varepsilon)\,\varphi_{\mathbf{k}nv}+V\varphi_{\mathbf{k}nv}, \tag{5.6.19}$$

and if we operate on (19) to the left with $(E-\mathsf{H}_0-V+i\varepsilon)^{-1}$ we obtain

$$\psi^+_{\mathbf{k}n}\eta_v = \varphi_{\mathbf{k}nv}+(E-\mathsf{H}_0-V+i\varepsilon)^{-1}\,V\varphi_{\mathbf{k}nv}. \tag{5.6.20}$$

If we compare (20) with (6) we see that we have obtained the approximation

$$\psi^+_{\mathbf{k}nv} \simeq \psi^+_{\mathbf{k}n}\eta_v. \tag{5.6.21}$$

The scattering amplitude now follows by substitution of (21) into (4); if we do this we get

$$f(\mathbf{k}nv \to \mathbf{l}pw) = (-4\pi^2\mu/\hbar^2)\langle\varphi_{\mathbf{l}pw}\,|\,V\,|\,\psi^+_{\mathbf{k}n}\eta_v\rangle. \tag{5.6.22}$$

If we substitute for $\varphi_{\mathbf{l}pw}$ in (22) from (3) we obtain

$$f(\mathbf{k}nv \to \mathbf{l}pw) = (-4\pi^2\mu/\hbar^2)\langle\varphi_{\mathbf{l}}\chi_p\eta_w\,|\,V\,|\,\psi^{+}{}_{n}\eta_v\rangle. \tag{5.6.23}$$

Now the scattering amplitude $f(\mathbf{k}n \to \mathbf{l}p\,|\,\mathbf{R})$ for the scattering of A by the fixed nuclei of M is given by

$$f(\mathbf{k}n \to \mathbf{l}p\,|\,\mathbf{R}) = (-4\pi^2\mu/\hbar^2)\langle\varphi_{\mathbf{l}}\chi_p\,|\,V\,|\,\psi^+_{\mathbf{k}n}\rangle \tag{5.6.24}$$

and obviously depends parametrically upon $\mathbf{R}$. (24) gives the amplitude when A's relative momentum is changed from $\hbar\mathbf{k}$ to $\hbar\mathbf{l}$ while the electronic state of M is changed from χ_n to χ_p, its nuclei being fixed at relative displacement $\mathbf{R}$. It follows from (23) and (24) that

$$f(\mathbf{k}nv \to \mathbf{l}pw) = \int \eta^*_w(\mathbf{R})\,\eta_v(\mathbf{R})\,f(\mathbf{k}n \to \mathbf{l}p\,|\,\mathbf{R})\,d\mathbf{R}. \tag{5.6.25}$$

An immediate corollary from (25) is that the scattering amplitude depends on the overlap between the initial and final vibrational states—if there is no overlap there is no scattering. In terms of the potential energy diagram of the molecule (Fig. 5.1) it means that transitions between ground vibrational states which take place in nature must be "vertical", not diagonal—a result known as the "Franck–Condon principle". If one or both of η_v and η_w represent excited vibrational states transitions which are not vertical may take place (Fig. 5.1a).

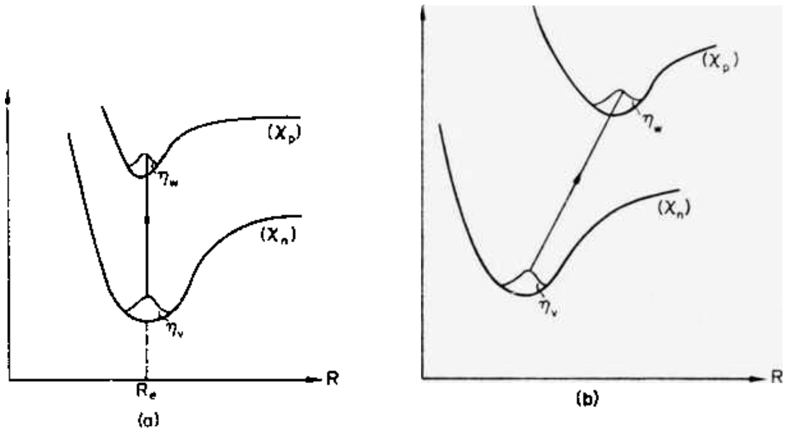

FIG. 5.1. The Franck–Condon principle. In each diagram the lower curve represents the nuclear potential when the electronic state is χ_n, while the upper curve represents the nuclear potential when the electronic state is χ_p. In (a) the transition is vertical, and so there is plenty of overlap between η_v and η_w, giving a high probability of the transition taking place. In (b) the transition is diagonal, giving negligible overlap between η_v and η_w, and so there is negligible probability of a transition taking place. In (a) a transition from η_v to a higher vibrational level is more likely to take place if the upper curve is displaced to the right or left to ensure maximum overlap of the vibrational wave functions.

The energy condition for (24) to be valid is

$$E_k+E_n(R_e) = E_l+E_p(R_e) \tag{5.6.26}$$

when $R = R_e$, the distance of the nuclei from each other in the equilibrium position (Fig. 5.1a). If initially and finally the molecule has low vibrational–rotational quantum numbers, we shall have $E_n(R_e)+Z_1Z_2e^2R_e^{-1}\varkappa_0^{-1} \simeq E_{nv}$ and $E_p(R_e)+Z_1Z_2e^2R_e^{-1}\varkappa_0^{-1} \simeq E_{pw}$. Hence adding $Z_1Z_2e^2R_e^{-1}\varkappa_0^{-1}$ to both of sides (26) we get

$$E_k+E_{nv} = E_l+E_{pw}, \tag{5.6.27}$$

the energy condition for the actual collision. If the difference between the vibrational energies is significant the energy conditions are inconsistent, and the validity of Franck–Condon principle is then in doubt.

EXERCISE

Show that (25) still holds if (i) A is an electron, or (ii) A is identical to one of M's nuclei, or (iii) A is a composite particle some of whose elementary particles may be electrons, or identical with one or other of the nuclei of M, provided the exchange amplitudes for the collision (1) are much smaller than the corresponding direct amplitudes.

5.7. COLLISIONAL DISSOCIATION OF DIATOMIC MOLECULES

We shall now consider collisions of the form

$$A+M \rightarrow A+M_1+M_2 \tag{5.7.1}$$

where A is an elementary particle, M is a diatomic molecule, and M_1, M_2 are two atoms. We shall assume for the moment that A is distinguishable from the elementary particles of M, and that the nuclei of M are distinguishable. If any of these assumptions are not valid—for example, if A has structure—the arguments which we shall present may be easily modified.

The initial state is $\varphi_{\mathbf{k}n v}$ of the last section, given by (5.6.2). After the collision we have an atom M_1, nucleus N_1, whose centre of mass moves with

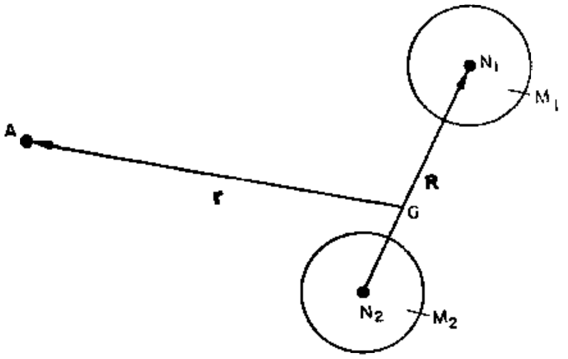

FIG. 5.2. The final state for the collisional dissociation of a diatomic molecule by an elementary particle A. After the collision the molecule M has dissociated into two atoms M_1 and M_2, whose centres of mass approximately coincide with the nuclei N_1 and N_2.

wave vector $\boldsymbol{\varkappa}$ relative to the centre of mass of the second atom M_2, nucleus N_2. We shall take the nuclei N_1 and N_2 as the centres of mass of the two atoms, and denote by $\mathbf{R}$ the displacement vector of N_1 relative to N_2 (Fig. 5.2). The final relative motion of the centres of mass is therefore the final relative motion of the nuclei, and described by the wave function $\varphi_{\varkappa}(\mathbf{R}) = (2\pi)^{-3/2} \exp(i\boldsymbol{\varkappa}\cdot\mathbf{R})$. The motion of A relative to the centre of mass of M_1 and M_2 may be described by $\varphi_{\mathbf{l}}(\mathbf{r}) = (2\pi)^{-3/2} \exp(i\mathbf{l}\cdot\mathbf{r})$, where $\mathbf{r}$ is the displacement vector of A relative to the centre of mass G of N_1 and N_2.

Let us suppose that M possesses n electrons, M_1 possesses m electrons and M_2 possesses $n-m$ electrons; let us further denote the electrons by $1, 2, \ldots, m+1, \ldots, n$. A possible final state is then

$$\varphi_\beta = \varphi_1 \varphi_\varkappa \chi_{p'}^{(1)} \chi_{p''}^{(2)} \tag{5.7.2}$$

where M_1 consists of N_1 and electrons 1 to m with internal wave function $\chi_{p'}^{(1)}$, while M_2 consists of N_2 and electrons $m+1$ to n with internal wave function $\chi_{p''}^{(2)}$. Initially all the electrons are attached to M, and so the number M_i of permutations of electrons which permute electrons within the same composite particles is $n!$ Finally, m electrons are attached to M_1 and $n-m$ electrons belong to M_2, so the number M_f of permutations of electrons which do not interchange electrons between the composite particles M_1 and M_2 is $m!\,(n-m)!$ Consequently it follows from (5.1.1) and (4.5.26) that the dissociation amplitude $f(\mathbf{k}nv \to \mathcal{S}\mathbf{l}p'p'')$ is given by

$$f(\mathbf{k}nv \to \mathcal{S}\mathbf{l}p'p''\varkappa) = \left[\frac{m!(n-m)!}{n!}\right]^{1/2} \left(-\frac{4\pi^2\mu}{\hbar^2}\right) \sum_{\mathsf{P}}/\delta_{\mathsf{P}} \langle \mathsf{P}\varphi_\beta | V_{\mathsf{P}f} | \psi_{\mathbf{k}nv}^+ \rangle \tag{5.7.3}$$

where $\sum_{\mathsf{P}}'$ goes over all distinct final states $\mathsf{P}\varphi_\beta$ obtained from φ_β by permutations P of the electrons, including φ_β itself. In (3) $V_{\mathsf{P}f}$ is the sum of the three interactions between A and the two atoms of the state $\mathsf{P}\varphi_\beta$, δ_{P} is the parity of P, and $\mu = \mu_i$ the reduced mass of A and M (which is also the reduced mass μ_f of M and $M_1 + M_2$).

We saw in Section 5.2 that a dissociative collision of the form (1) may be treated as direct, so that $V_f = V_i = V$ where V is the interaction between A and M, and therefore the interaction of A with M_1 and M_2, provided the final state is taken as the product of φ_1 with a continuum state possessing incoming wave boundary conditions. We therefore have

$$\langle \mathsf{P}\varphi_\beta | V_{\mathsf{P}f} | \psi_{\mathbf{k}nv}^+ \rangle = \langle \varphi_1 \chi_{\mathsf{P}\varkappa p'p''}^- | V | \psi_{\mathbf{k}nv}^+ \rangle \tag{5.7.4}$$

where

$$\chi_{\mathsf{P}\varkappa p'p''}^- \underset{R\to\infty}{\sim} \mathsf{P}[\chi_{p'}^{(1)} \chi_{p''}^{(2)}]\, \varphi_\varkappa + \text{incoming waves.} \tag{5.7.5}$$

If we substitute from (4) into (3) we obtain

$$f(\mathbf{k}nv \to \mathcal{S}\mathbf{l}p'p''\varkappa) = (-4\pi^2\mu\hbar^{-2}) \langle \varphi_1 \chi_{\mathcal{S}\varkappa p'p''}^- | V | \psi_{\mathbf{k}nv}^+ \rangle \tag{5.7.6}$$

where

$$\chi_{\mathcal{S}\varkappa p'p''}^- = \left[\frac{m!(n-m)!}{n!}\right]^{1/2} \sum_{\mathsf{P}}{}' \delta_{\mathsf{P}} \chi_{\mathsf{P}\varkappa p'p''}^- . \tag{5.7.7}$$

From (5) and (7) we see that

$$\chi_{\mathcal{S}\varkappa p'p''}^- \underset{R\to\infty}{\sim} \varphi_\varkappa \left[\frac{m!(n-m)!}{n!}\right]^{1/2} \sum_{\mathsf{P}}{}' \delta_{\mathsf{P}} \mathsf{P}[\chi_{p'}^{(1)} \chi_{p''}^{(2)}] + \text{incoming waves} \tag{5.7.8}$$

Let us assume that the Born–Oppenheimer separation process is applicable when the nuclear states lie in the continuum. It may then be possible to form a linear combination of molecular electronic states χ_p which has the asymptotic form

$$\left[\frac{m!(n-m)!}{n!}\right]^{1/2} \sum_{\mathrm{P}}{}' \delta_{\mathrm{P}} \mathrm{P}[\chi_{p'}^{(1)} \chi_{p''}^{(2)}] \underset{R \to \infty}{\sim} \sum_{\mathrm{P}} a_p \chi_p . \tag{5.7.9}$$

Such a state is obviously normalized. We can then take as the appropriate expression for $\chi_{\mathfrak{s}\varkappa p'p''}^{-}$

$$\chi_{\mathfrak{s}\varkappa p'p''}^{-} = \sum_{\mathrm{P}} a_p \chi_p \eta_{\varkappa}^{(p)-} \tag{5.7.10}$$

where $\eta_{\varkappa}^{(p)-}$ is a continuum nuclear state for the potential curve generated by χ_p which satisfies the asymptotic condition

$$\eta_{\varkappa}^{(p)-} \underset{R \to \infty}{\sim} \varphi_{\varkappa} + \text{incoming wave.} \tag{5.7.11}$$

It then follows from (9) to (11) that the asymptotic condition (8) is satisfied.

The dissociation cross-section for the process $\varphi_{\mathbf{k}} \chi_p \eta_v \to \varphi_{\mathbf{l}} \chi_{p'}^{(1)} \chi_{p''}^{(2)}$ is then obtained by integrating the differential cross-section over all energetically allowed $\varkappa$. With the approximation (5.6.21) and certain other approximations this integration can sometimes be carried out using the closure relation

$$\int d\varkappa\, \eta_{\varkappa}^{(p)-*}(\mathbf{R})\, \eta_{\varkappa}^{(p)-}(\mathbf{R}') + \sum_{v} \eta_v^{(p)*}(\mathbf{R})\, \eta_v^{(p)}(\mathbf{R}') = \delta(\mathbf{R}-\mathbf{R}') \tag{5.7.12}$$

for the complete set of continuum nuclear states $\eta_v^{(p)}$, $\eta_{\varkappa}^{(p)-}$ corresponding to the electronic state χ_p.

5.8. COLLISIONAL DISSOCIATION OF IONIZED HYDROGEN MOLECULES

In this section we suppose that the diatomic molecule M considered in the last section is an ionized hydrogen molecule. In other words we shall consider dissociative collisions of the form

$$A + \mathrm{H}_2^+ \to A + \mathrm{H} + \mathrm{H}^+. \tag{5.8.1}$$

We shall assume initially that the H_2^+ ion is in its $1s\sigma_g$ state, and has vibrational–rotational wave function η_v, while A (which we shall take as elementary) has momentum $\hbar\mathbf{k}$ relative to the centre of mass of the ion. The initial state is therefore represented by the wave function

$$\varphi_\alpha(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_{\mathbf{k}}(\mathbf{r})\, \chi_g(\mathbf{q} \,|\, \mathbf{R})\, \eta_v(\mathbf{R})\, \alpha_r(12) \tag{5.8.2}$$

where $\mathbf{r}$ is the position vector of A relative to the centre of mass of the H_2^+ ion, $\mathbf{R}$ is the relative displacement of proton 1 to proton 2 of the H_2^+ ion (Fig. 5.3), $\mathbf{q}$ denotes the coordinates of the electron, $\chi_g(\mathbf{q} \mid \mathbf{R})$ is the wave function of the $1s\sigma_g$ state of the H_2^+ ion, and $\alpha_r(12)$ is the initial spin function for the protons. A will be assumed to be a spinless atomic nucleus. The spin function of the electron will not be affected by the collision, and may therefore be ignored.

In the final state we shall assume that the hydrogen atom is in its ground state with proton 2 as nucleus, while proton 1 has momentum $\hbar\boldsymbol{\kappa}$ relative to 2 (Fig. 5.3). If A then has momentum $\hbar\mathbf{l}$ relative to the centre of mass of the fragments of the ion while $\chi_0(2)$ is a ground state hydrogenic wave function based on 2 as nucleus the final wave function is

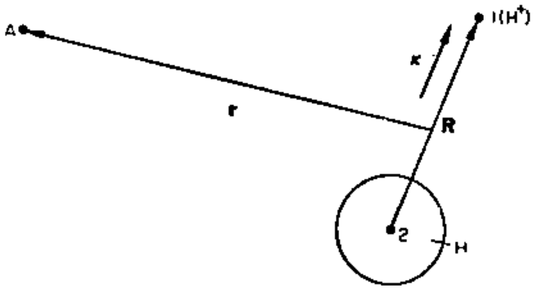

FIG. 5.3. Coordinates of the $A-H_2^+$ system discussed in Section 5.8.

$$\varphi_\beta(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \varphi_l(\mathbf{r})\,\chi_0(\mathbf{q} \mid 2)\varphi_\kappa(\mathbf{R})\,\alpha_s(12) \tag{5.8.3}$$

where α_s is the final spin function of the protons.

The only final state distinct from φ_β, and obtainable from it by permuting the protons, is

$$\begin{aligned}\varphi_{P\beta} &= P\varphi_\beta = \varphi_l(\mathbf{r})\,\chi_0(\mathbf{q} \mid 1)\,\varphi_\kappa(-\mathbf{R})\,\alpha_s(21) \\ &= \varphi_l(\mathbf{r})\,\chi_0(\mathbf{q} \mid 1)\,\varphi_{-\kappa}(\mathbf{R})\,\alpha_s(21).\end{aligned} \tag{5.8.4}$$

In this state 1 is nucleus of the hydrogen atom, and has momentum $-\hbar\boldsymbol{\kappa}$ relative to 2.[†] The number of permutations M_i of protons in the initial state which permute protons within the same composite particle is two, and the corresponding number M_f in the final state is unity. Since protons are fermions (4.5.26) gives

$$f(\alpha \to \mathscr{S}\beta) = 2^{-1/2}[f(\alpha \to \beta) - f(\alpha \to P\beta)]. \tag{5.8.5}$$

Now $\varphi_{P\beta}$ differs from φ_β by an interchange of the protons, which both belong to the same composite particle H_2^+ in the initial state. Hence (4.6.7)

[†] $\varphi_{P\beta}$ is, of course, experimentally indistinguishable from φ_β.

implies $f(\alpha \to \mathsf{P}\beta) = -f(\alpha \to \beta)$, and so (5) simplifies to

$$f(\alpha \to \mathcal{S}\beta) = 2^{1/2} f(\alpha \to \beta). \tag{5.8.6}$$

The amplitude $f(\alpha \to \beta)$ is given by (5.1.1) where $\mu_f = \mu_i = \mu$, the reduced mass of A and the H_2^+ ion or A and the system $H+H^+$. Since $\psi_\alpha^+ = \Omega_i^+(E)\varphi_\alpha$ where $\Omega_i^+(E)$ is the wave operator for the initial arrangement channel we obtain

$$\begin{aligned} f(\alpha \to \beta) &= (-4\pi^2\mu\hbar^{-2})\langle\varphi_\beta \,|\, V_f\Omega_i^+(E) \,|\, \varphi_\alpha\rangle \\ &= (-4\pi^2\mu\hbar^{-2})\langle\varphi_1\chi_0(2)\,\varphi_\kappa\alpha_s(12) \,|\, V_f\Omega_i^+(E) \,|\, \varphi_{\mathbf{k}}\chi_g\eta_v\alpha_r(12)\rangle \end{aligned} \tag{5.8.7}$$

by (2) and (3). Since V_f and $\Omega_i^+(E)$ do not involve spin the spin functions factor out and (7) becomes

$$\begin{aligned} f(\alpha \to \beta) &= (-4\pi^2\mu\hbar^{-2})\,\delta_{rs}\langle\varphi_1\chi_0(2)\,\varphi_\kappa \,|\, V_f\Omega_i^+(E) \,|\, \varphi_{\mathbf{k}}\chi_g\eta_v\rangle \\ &= (-4\pi^2\mu\hbar^{-2})\,\delta_{rs}\langle\varphi_1\chi_0(2)\,\varphi_\kappa \,|\, V_f \,|\, \psi_{\mathbf{k}gv}^+\rangle, \quad \text{say.} \end{aligned} \tag{5.8.8}$$

In (8) the state $\psi_{\mathbf{k}gv}^+ = \Omega_i^+(E)\varphi_{\mathbf{k}}\chi_g\eta_v$ is the initial scattering state with outgoing wave conditions.

As we saw in Section 5.2 the collision (1) may be treated as direct if the final state of the product proton and atom is taken as the scattering state $\chi_{\kappa 0}^-(2)$ which describes the final relative motion of proton 1 and the hydrogen atom based on 2 as nucleus. It is defined by

$$\chi_{\kappa 0}^-(2) = \varphi_\kappa\chi_0(2) + [E - \mathsf{K}_{\mathbf{R}} - \mathsf{h}(2) - U - i\varepsilon]^{-1}\, U\varphi_\kappa\chi_0(2) \tag{5.8.9}$$

where $\mathsf{h}(2)$ is the internal Hamiltonian of the hydrogen atom and U the interaction between H and H^+. As $R \to \infty$ the function $\chi_{\kappa 0}^-(2)$ behaves as $\varphi_\kappa\chi_0(2)$ plus incoming waves. Hence from (8) we obtain

$$f(\alpha \to \beta) = (-4\pi^2\mu\hbar^{-2})\,\delta_{rs}\langle\varphi_1\chi_{\kappa 0}^-(2) \,|\, V \,|\, \psi_{\mathbf{k}gv}^+\rangle \tag{5.8.10}$$

where $V = V_i$ is the interaction between A and the H_2^+ ion, which is also the interaction between A and the system $H+H^+$ in the final state (Fig. 5.3).

The only electronic state of the H_2^+ ion other than the $1s\sigma_g$ state which leads to a hydrogen atom in its ground state in the separated atom position is the $1s\sigma_u$ state. We have denoted the wave function of the $1s\sigma_g$ state by $\chi_g(\mathbf{q} \mid \mathbf{R})$, and so we denote the wave function of the $1s\sigma_u$ state by $\chi_u(\mathbf{q} \mid \mathbf{R})$. The functions χ_g and χ_u have the asymptotic forms

$$\chi_g \underset{R \to \infty}{\sim} 2^{-1/2}[\chi_0(1) + \chi_0(2)], \tag{5.8.11}$$

$$\chi_u \underset{R \to \infty}{\sim} 2^{-1/2}[\chi_0(1) - \chi_0(2)], \tag{5.8.12}$$

and so

$$\chi_g - \chi_u \underset{R \to \infty}{\sim} 2^{1/2}\chi_0(2). \tag{5.8.13}$$

It follows that there is only one linear conbination of molecular states which behaves as $\varphi_\varkappa \chi_0(2)$ + incoming waves as $R \to \infty$, and this can therefore be taken as $\chi_{\varkappa 0}^-(2)$; the expression is

$$\chi_{\varkappa 0}^-(2) = 2^{-1/2}[\chi_g \eta_\varkappa^{g-} - \chi_u \eta_\varkappa^{u-}], \tag{5.8.14}$$

where $\eta_\varkappa^{g-}$, $\eta_\varkappa^{u-}$ are the continuum nuclear states associated with the potential energy curves generated by the $1s\sigma_g$ and $1s\sigma_u$ electronic states respectively (Fig. 5.4), and which behave as $\varphi_\varkappa$ plus an incoming wave when $R \to \infty$.

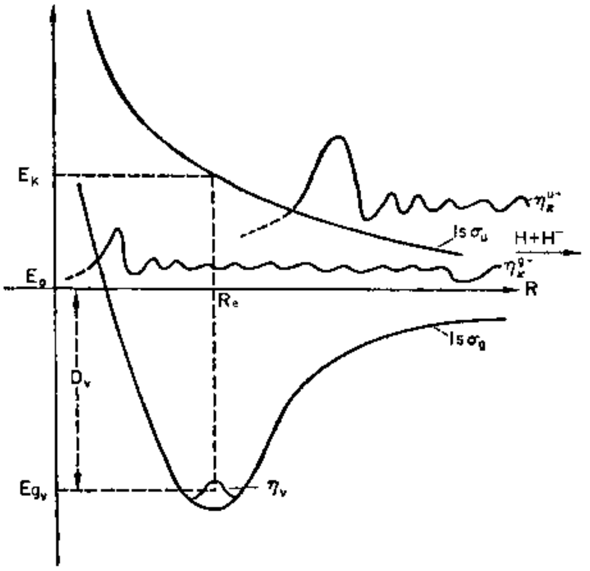

FIG. 5.4. Potential energy curves for the $1s\sigma_g$ and $1s\sigma_u$ states of the H_2^+ ion.

If we insert (14) into (10), and then the resulting expression for $f(\alpha \to \beta)$ into (6), we get

$$f(\alpha \to \mathcal{S}\beta) = -4\pi^2 \mu \hbar^{-2}\, \delta_{rs} \langle \varphi_1 (\chi_g \eta_\varkappa^{g-} - \chi_u \eta_\varkappa^{u-}) \,|\, V \,|\, \psi_{\mathbf{k}gv}^+ \rangle. \tag{5.8.15}$$

Let us define the scattering amplitudes $f(\mathbf{k}gv \to \mathbf{l}g\varkappa)$ and $f(\mathbf{k}gv \to \mathbf{l}u\varkappa)$ by

$$f(\mathbf{k}gv \to \mathbf{l}g\varkappa) = -4\pi^2 \mu \hbar^{-2} \langle \varphi_1 \chi_g \eta_\varkappa^{g-} \,|\, V \,|\, \psi_{\mathbf{k}gv}^+ \rangle, \tag{5.8.16}$$

$$f(\mathbf{k}gv \to \mathbf{l}u\varkappa) = -4\pi^2 \mu \hbar^{-2} \langle \varphi_1 \chi_u \eta_\varkappa^{u-} \,|\, V \,|\, \psi_{\mathbf{k}gv}^+ \rangle. \tag{5.8.17}$$

Equations (2) and (3) show that α and β may be written more fully as $\mathbf{k}gvr$ and $\mathbf{l}o\varkappa s$ respectively; hence, with the aid of (16) and (17), (15) may be written

$$f(\mathbf{k}gvr \to \mathcal{S}\mathbf{l}o\varkappa s) = \delta_{rs}[f(\mathbf{k}gv \to \mathbf{l}g\varkappa) - f(\mathbf{k}gv \to \mathbf{l}u\varkappa)]. \tag{5.8.18}$$

On the left-hand side of (18) we have the scattering amplitude for the process which takes an H_2^+ ion from the electronic $1s\sigma_g$ state, vibrational-rotational state η_v, and spin state α_r, into a state in which a proton has momentum $\hbar\varkappa$ relative to a hydrogen atom in its ground state χ_0, the spin state of the protons being α_s. On the right-hand side of (18) we have a factor δ_{rs}, showing that the spin state of the protons is unaffected by the collision. We also have the scattering amplitudes $f(\mathbf{k}gv \to \mathbf{l}g\varkappa)$ and $f(\mathbf{k}gv \to \mathbf{l}u\varkappa)$. The first amplitude describes a transition to a continuum nuclear state on the $1s\sigma_g$ nuclear potential energy curve (Fig. 5.4); it therefore describes a process by which the diatomic molecule dissociates through nuclear excitation. The amplitude $f(\mathbf{k}gv \to \mathbf{l}u\varkappa)$ represents a process by which the diatomic molecule dissociates via excitation of the repulsive $1s\sigma_u$ electronic state. Equation (18) implies that the differential cross-section $\sigma(\mathbf{k}gvr \to \mathcal{S}\mathbf{l}o\varkappa s)$ for the process is

$$\sigma(\mathbf{k}gvr \to \mathcal{S}\mathbf{l}o\varkappa s) = \delta_{rs}\,|f(\mathbf{k}gv \to \mathbf{l}g\varkappa)-f(\mathbf{k}gv \to \mathbf{l}u\varkappa)|^2. \tag{5.8.19}$$

The observed differential cross-section is obtained from this by summing over the four final spin states and averaging over the four initial ones. The effect of this is to remove the factor δ_{rs}.

Suppose instead of using (14) as final state of the $\mathrm{H}+\mathrm{H}^+$ system we had used

$$2^{-1/2}[\chi_g\eta^{g-}_{-\varkappa}+\chi_u\eta^{u-}_{-\varkappa}]. \tag{5.8.20}$$

Since $\eta^{g-}_{-\varkappa}$ and $\eta^{u-}_{-\varkappa} \sim \varphi_{-\varkappa}$ as $R \to \infty$, while χ_g and χ_u obey the asymptotic conditions (11) and (12), we see that

$$2^{-1/2}[\chi_g\eta^{g-}_{-\varkappa}+\chi_u\eta^{u-}_{-\varkappa}] \underset{R\to\infty}{\sim} \chi_0(1)\,\varphi_{-\varkappa}. \tag{5.8.21}$$

Such a choice of final state describes a situation where, after the collision, the atom on 1 as nucleus is observed to have momentum $-\hbar\varkappa$ relative to the proton 2 (see Fig. 5.3), so that the proton has momentum $\hbar\varkappa$ relative to the atom. This represents the same physical situation as previously, and so an alternative expression for the cross-section is therefore obtained from (19) by replacing the difference of the amplitudes by a sum, and $\varkappa$ by $-\varkappa$; this yields

$$\sigma(\mathbf{k}gvr \to \mathcal{S}\mathbf{l}o\varkappa s) = \delta_{rs}\,|f(\mathbf{k}gv \to \mathbf{l}g-\varkappa)+f(\mathbf{k}gv \to \mathbf{l}u-\varkappa)|^2. \tag{5.8.22}$$

It follows immediately from (19) and (22) that

$$\begin{aligned} &2\,\mathrm{Re}\,[f^*(\mathbf{k}gv \to \mathbf{l}g-\varkappa)\,f(\mathbf{k}gv \to \mathbf{l}u-\varkappa)] \\ &= -2\,\mathrm{Re}\,[f^*(\mathbf{k}gv \to \mathbf{l}g\varkappa)\,f(\mathbf{k}gv \to \mathbf{l}u\varkappa)] \end{aligned} \tag{5.8.23}$$

so that the interference term in (19) or (22) is antisymmetric in $\varkappa$.

The dissociation cross-section $\sigma_d(o)$ for production of a hydrogen atom in its ground state is obtained by inserting (18) into (3.8.11) with the summation over β replaced by a summation over s and integration over all $\mathbf{l}$ and $\varkappa$. Since

$\mu_i = \mu_f = \mu$ we obtain

$$\sigma_d(o) = \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo\varkappa} - E_{kgv})\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa) - f(\mathbf{k}gv \to \mathbf{l}u\varkappa)|^2 \tag{5.8.24}$$

where $E_{kgv} = E_k + E_{gv}$ is the initial energy of the system, and $E_{lo\varkappa} = E_l + E_o + E_\varkappa$ is the final energy. We note that $\sigma_d(o)$ is independent of the spin state of the protons. The quantities E_k and E_l are the initial and final kinetic energies of A relative to the centre of mass of the H_2^+ ion or the $H + H^+$ system, $E_\varkappa$ is the final relative kinetic energy of the proton and atom, and $-E_0$ is the binding energy of a hydrogen atom in its ground state. Since the interference term in (24) is antisymmetric in $\varkappa$ it vanishes on integration over $\varkappa$, and so (24) reduces to

$$\begin{aligned} \sigma_d(o) = {} & \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo\varkappa} - E_{kgv})\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2 \\ & + \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo\varkappa} - E_{kgv})\, |f(\mathbf{k}gv \to \mathbf{l}u\varkappa)|^2. \end{aligned} \tag{5.8.25}$$

We can therefore evaluate the dissociation cross-sections for nuclear and electronic excitation, and add the results to obtain the total dissociation cross-section.

In the spirit of the Born–Oppenheimer separation process we now make the approximation (5.6.21) for $\psi^+_{\mathbf{k}gv}$. On doing this (16) becomes

$$f(\mathbf{k}gv \to \mathbf{l}g\varkappa) \simeq \int \eta_\varkappa^{g-*}(\mathbf{R})\, \eta_v(\mathbf{R}) [-4\pi^2 \mu h^{-2} \langle \varphi_l \chi_g | V | \psi^+{}_g \rangle]\, d\mathbf{R} \tag{5.8.26}$$

where $\psi^+_{\mathbf{k}g}$ is the scattering state with asymptotic boundary condition $\varphi_{\mathbf{k}}\chi_g$ + outgoing waves when the protons are frozen with relative displacement $\mathbf{R}$. The term in square brackets on the right-hand side of (26) is therefore the scattering amplitude $f(\mathbf{k}g \to \mathbf{l}g \mid \mathbf{R})$ for elastic scattering of A by the molecule when in the electronic state χ_g, the protons being frozen with relative displacement $\mathbf{R}$. We can therefore replace (26) by

$$f(\mathbf{k}gv \to \mathbf{l}g\varkappa) = \int \eta_\varkappa^{g-*}(\mathbf{R})\, \eta_v(\mathbf{R})\, f(\mathbf{k}g \to \mathbf{l}g \mid \mathbf{R})\, d\mathbf{R}. \tag{5.8.27}$$

Similarly (17) leads to

$$f(\mathbf{k}gv \to \mathbf{l}u\varkappa) = \int \eta_\varkappa^{u-*}(\mathbf{R})\, \eta_v(\mathbf{R})\, f(\mathbf{k}g \to \mathbf{l}u \mid \mathbf{R})\, d\mathbf{R} \tag{5.8.28}$$

where $f(\mathbf{k}g \to \mathbf{l}u \mid \mathbf{R})$ is the amplitude for inelastic scattering of A by the H_2^+ ion when the electronic transition $1s\sigma_g \to 1s\sigma_u$ takes place, the nuclei being frozen with displacement $\mathbf{R}$.

Let us put

$$\sigma_d(g \to g) = \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo\varkappa} - E_{kgv})\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2, \tag{5.8.29}$$

$$\sigma_d(g \to u) = \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo\varkappa} - E_{kgv})\, |f(\mathbf{k}gv \to \mathbf{l}u\varkappa)|^2. \tag{5.8.30}$$

The quantity $\sigma_d(g \to g)$ is the dissociation cross-section via nuclear excitation only, and $\sigma_d(g \to u)$ is the dissociation cross-section via electronic and nuclear excitation. It follows that (25) can be written more simply as

$$\sigma_d(o) = \sigma_d(g \to g) + \sigma_d(g \to u). \tag{5.8.31}$$

We shall now evaluate $\sigma_d(g \to g)$ by means of the expression (27). Inspection of (27) shows that $f(\mathbf{k}gv \to \mathbf{l}g\varkappa)$ decreases as $\varkappa$ increases due to the increasing oscillation of $\eta_\varkappa^{g-}$ in the integrand. Let us therefore suppose that the main contribution to $\sigma_d(g \to g)$ in (29) comes from the part of the integration where $\varkappa$ is very small. If $\varkappa$ is very small $E_{lo\varkappa} = E_l + E_o + E_\varkappa \simeq E_l + E_o = E_{lo}$, and so from (29)

$$\begin{aligned}\sigma_d(g \to g) &\simeq \hbar^2(\mu k)^{-1} \int d\mathbf{l} \int d\varkappa\, \delta(E_{lo} - E_{kgv}) |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2 \\ &= \hbar^2(\mu k)^{-1} \int d\mathbf{l}\, \delta(E_{lo} - E_{kgv}) \int d\varkappa\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2.\end{aligned} \tag{5.8.32}$$

Now from (27)

$$\begin{aligned}\int d\varkappa\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2 = \int d\varkappa \int d\mathbf{R}\, \eta_\varkappa^{g-*}(\mathbf{R})\, \eta_v(\mathbf{R}) f(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R}) \times \\ \times \int d\mathbf{R}'\, \eta_\varkappa^{g-}(\mathbf{R}')\, \eta_v^*(\mathbf{R}') f^*(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R}').\end{aligned} \tag{5.8.33}$$

The closure relation for the complete set of nuclear states η_w, $\eta_\varkappa^{g-}$ associated with the electronic state χ_g is

$$\int d\varkappa\, \eta_\varkappa^{g-*}(\mathbf{R})\, \eta_\varkappa^{g-}(\mathbf{R}') + \sum_w \eta_w^*(\mathbf{R})\, \eta_w(\mathbf{R}') = \delta(\mathbf{R} - \mathbf{R}') \tag{5.8.34}$$

where $\sum_w$ goes over the bound nuclear states. If we apply (34) to (33) to integrate over $\varkappa$ we obtain

$$\begin{aligned}\int d\varkappa\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2 = \int d\mathbf{R}\, |\eta_v(\mathbf{R})|^2 |f(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R})|^2 \\ - \sum_w \left| \int d\mathbf{R}\, \eta_w^*(\mathbf{R})\, \eta_v(\mathbf{R}) f(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R}) \right|^2.\end{aligned} \tag{5.8.35}$$

By (5.6.25) the general term of the sum $\sum_w$ is the square of the modulus of the scattering amplitude for the nuclear transition $\eta_v \to \eta_w$ without electronic excitation; thus (35) can be written

$$\begin{aligned}&\int d\varkappa\, |f(\mathbf{k}gv \to \mathbf{l}g\varkappa)|^2 \\ &\quad = \int d\mathbf{R}\, |\eta_v(\mathbf{R})|^2 |f(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R})|^2 - \sum_w |f(\mathbf{k}gv \to \mathbf{l}gw)|^2.\end{aligned} \tag{5.8.36}$$

If we insert (36) into (32) we get

$$\begin{aligned}\sigma_d(g \to g) = \hbar^2(\mu k)^{-1} \int d\mathbf{R}\, |\eta_v(\mathbf{R})|^2 \int d\mathbf{l}\, \delta(E_{lo} - E_{kgv}) |f(\mathbf{k}g \to \mathbf{l}g \,|\, \mathbf{R})|^2 \\ - \sum_w \hbar^2(\mu k)^{-1} \int d\mathbf{l}\, \delta(E_{lo} - E_{kgv}) |f(\mathbf{k}gv \to \mathbf{l}gw)|^2.\end{aligned} \tag{5.8.37}$$

Now $E_{lo} - E_{kgv} = E_l + E_o - E_k - E_{gv}$, and $E_o - E_{gv}$ is the dissociation energy

D_v of an H_2^+ ion in the state $\chi_g\eta_v$ (Fig. 5.4). If this is negligible compared with E_k we can put $E_{lo}-E_{kgv} \simeq E_l-E_k$ in the first term. It also follows that $E_l+E_o \simeq E_l+E_{gw} = E_{lgw}$ if E_o-E_{gw}, the dissociation energy of an H_2^+ ion when in the state $\chi_g\eta_w$, is negligible compared with E_l. With these approximations (37) becomes

$$\sigma_d(g \to g) = \hbar^2(\mu k)^{-1} \int d\mathbf{R}\,|\eta_v(\mathbf{R})|^2 \int d\mathbf{l}\,\delta(E_l-E_k)\,|f(\mathbf{k}g \to \mathbf{l}g\,|\,\mathbf{R})|^2$$
$$-\sum_w \hbar^2(\mu k)^{-1} \int d\mathbf{l}\,\delta(E_{lgw}-E_{kgv})\,|f(\mathbf{k}gv \to \mathbf{l}gw)|^2. \tag{5.8.38}$$

In other words the contribution to the dissociation cross-section due to nuclear excitation only is made up of two parts. The first part is the cross-section for elastic scattering of A by the H_2^+ ion, when its nuclei are fixed, averaged over the nuclear probability function $|\eta_v(\mathbf{R})|^2$. The second part is a subtraction of the cross-sections for the process $A+H_2^+ \to A+H_2^+$ when electronic excitation does not take place. It is a subtraction of the terms representing scattering without electronic excitation, and with or without excitation of bound vibrational–rotational states of the molecule.

The expression (30) for the dissociation cross-section $\sigma_d(g \to u)$ via excitation of the $1\sigma g_u$ state may be similarly simplified. From Fig. 5.4 we see that, due to the negligible overlap of $\eta_\varkappa^{u-}$ and η_v, excitation does not take place if $E < E_K$, where E_K is the repulsive potential energy of the protons at the equilibrium separation R_e of the protons. Assuming that the cross-section drops off rapidly as $\varkappa$ increases beyond K, we can replace $E_{l\varkappa o}$ by $E_{lKo} = E_l+E_K+E_0$. Also $E_{kgv} = E_k+E_o-D_v$, where D_v is the dissociation energy of the H_2^+ ion when in the state $\chi_g\eta_v$. Equation (30) now becomes

$$\sigma_d(g \to u) \simeq \hbar^2(\mu k)^{-1} \int d\mathbf{l}\,\delta(E_l+E_K+D_v-E_k) \int d\varkappa\,|f(\mathbf{k}gv \to \mathbf{l}u\varkappa)|^2. \tag{5.8.39}$$

Since the electronic state χ_u is repulsive, there are no bound nuclear states, and so the closure relation (34) is replaced by

$$\int d\varkappa\,\eta_{l\varkappa}^{u-*}(\mathbf{R})\,\eta_\varkappa^{u-}(\mathbf{R}') = \delta(\mathbf{R}-\mathbf{R}'). \tag{5.8.40}$$

Substitution for $f(\mathbf{k}gv \to \mathbf{l}u\varkappa)$ from (28) into (39) and use of (40) now yields

$$\sigma_d(g \to u) \simeq \hbar^2(\mu k)^{-1} \int d\mathbf{l}\,\delta(E_l+E_K+D_v-E_k)\times$$
$$\times \int d\mathbf{R}\,|\eta_v(\mathbf{R})|^2\,|f(\mathbf{k}g \to \mathbf{l}u\,|\,\mathbf{R})|^2. \tag{5.8.41}$$

Hence the cross-section for excitation of the repulsive electronic state must be averaged over all displacements **R** of the fixed nuclei with weight function $|\eta_v(\mathbf{R})|^2$. Equation (31) shows that the dissociation cross-section is just the sum of the cross-sections for dissociation through nuclear excitation and through excitation of the redulsive $1s\sigma_u$ state.

We can also note that, if $E_g(R_e)$ and $E_u(R_e)$ are the values of the electronic energy in the $1s\sigma_g$ and $1s\sigma_u$ states when $R = R_e$, then $E_u(R_e) - E_g(R_e)$ is the difference between the nuclear potential energy curves for the two electronic states at the point $R = R_e$. From Fig. 5.4 this is $E_K + D_v$, and so

$$E_l + E_u(R_e) - E_k - E_g(R_e) = E_l + E_K + D_v - E_k . \qquad (5.8.42)$$

We can therefore rewrite (41) as

$$\sigma_d(g \to u) \simeq \int d\mathbf{R}\,|\eta_v(\mathbf{R})|^2 \hbar^2(\mu k)^{-1} \times \\ \times \int d\mathbf{l}\,\delta[E_l + E_u(R) - E_k - E_g(R)]\,|f(\mathbf{k}g \to \mathbf{l}u\,|\,\mathbf{R})|^2 \qquad (5.8.43)$$

if we use the fact that $\eta_v(\mathbf{R}) \simeq 0$ unless $R \simeq R_e$. In this form we see more clearly that we can obtain the cross-section $\sigma_u(g \to u)$ for dissociation via excitation of the repulsive electronic state $1s\sigma_u$ by fixing the nuclei at relative displacement $\mathbf{R}$, calculating the cross-section for excitation of the $1s\sigma_u$ state, and then averaging the result over all relative displacements $\mathbf{R}$.

EXERCISE

Show that the results of this section remain valid if A is a proton or electron provided exchange between A and the H_2^+ ion can be neglected. Show also that the results remain valid if A has structure provided exchange between any protons or electrons of A and the H_2^+ ion can be neglected.

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APPENDIX A

SUPPOSE $f(\mathsf{H}_a, \mathsf{H}_b)$ is a function of two commuting Hermitian operators H_a and H_b, and $|\,\psi\rangle$ is a state vector such that $\mathsf{H}_a\,|\,\psi\rangle = \alpha\,|\,\psi\rangle$; then

$$f(\mathsf{H}_a, \mathsf{H}_b)\,|\,\psi\rangle = f(\alpha, \mathsf{H}_b)\,|\,\psi\rangle. \tag{A1}$$

Proof. Since H_a and H_b are two commuting Hermitian operators they have a complete set of common eigenvectors $|\,\alpha'\beta'\rangle$ where

$$\mathsf{H}_a\,|\,\alpha'\beta'\rangle = \alpha'\,|\,\alpha'\beta'\rangle, \quad \mathsf{H}_b\,|\,\alpha'\beta'\rangle = \beta'\,|\,\alpha'\beta'\rangle. \tag{A2}$$

By definition

$$f(\mathsf{H}_a, \mathsf{H}_b)\,|\,\psi\rangle = \sum_{\alpha'}\sum_{\beta'} f(\alpha', \beta')\,|\,\alpha'\beta'\rangle\langle\alpha'\beta'\,|\,\psi\rangle. \tag{A3}$$

Since $|\,\alpha'\beta'\rangle$ and $|\,\psi\rangle$ are eigenvectors of the Hermitian operator H_a with eigenvalues α' and α respectively they are orthogonal if $\alpha \neq \alpha'$. Hence $\langle\alpha'\beta'\,|\,\psi\rangle = 0$ if $\alpha' \neq \alpha$, and therefore in (3) $f(\alpha', \beta')$ can be replaced by $f(\alpha, \beta')$; (3) now becomes

$$f(\mathsf{H}_a, \mathsf{H}_b)\,|\,\psi\rangle = \sum_{\beta'} f(\alpha, \beta') \sum_{\alpha'} |\,\alpha'\beta'\rangle\langle\alpha'\beta'\,|\,\psi\rangle. \tag{A4}$$

Since $|\,\alpha'\beta'\rangle = |\,\alpha'\rangle\,|\,\beta'\rangle$ and $\sum_{\alpha'}|\,\alpha'\rangle\langle\alpha'\,| = 1$, we find from (4) that

$$f(\mathsf{H}_a, \mathsf{H}_b)\,|\,\psi\rangle = \sum_{\beta'} f(\alpha, \beta')\,|\,\beta'\rangle\langle\beta'\,|\,\psi\rangle. \tag{A5}$$

By definition the right-hand side of (5) is $f(\alpha, \mathsf{H}_b)\,|\,\psi\rangle$, and so (1) follows.

A particular case of this is when $|\,\psi\rangle = |\,\psi_a\rangle\,|\,\psi_b\rangle = |\,\psi_a\psi_b\rangle$, where $|\,\psi_a\rangle$ involves one set of coordinates $\mathbf{x}_a$ and $|\,\psi_b\rangle$ involves the remainder $\mathbf{x}_b$. Then if H_a depends only on $\mathbf{x}_a$ and H_b depends only on $\mathbf{x}_b$ we see that H_a and H_b commute. Hence if $\mathsf{H}_a\,|\,\psi_a\rangle = \alpha\,|\,\psi_a\rangle$ it follows that $\mathsf{H}_a\,|\,\psi_a\psi_b\,\rangle = [\mathsf{H}_a\,|\,\psi_a\rangle]\,|\,\psi_b\rangle = \alpha\,|\,\psi_a\psi_b\rangle$, and so

$$f(\mathsf{H}_a, \mathsf{H}_b)\,|\,\psi_a\psi_b\rangle = f(\alpha, \mathsf{H}_b)\,|\,\psi_a\psi_b\rangle. \tag{A6}$$

More particularly, if $\mathsf{H}_a\,|\,\psi_a\rangle = \alpha\,|\,\psi_a\rangle$ and V_b is an operator depending only on $\mathbf{x}_b$,

$$\mathsf{H}_a V_b\,|\,\psi_a\rangle\,|\,\psi_b\rangle = [\mathsf{H}_a\,|\,\psi_a\rangle][V_b\,|\,\psi_b\rangle] = \alpha\,|\,\psi_a\rangle[V_b\,|\,\psi_b\rangle] = \alpha V_b\,|\,\psi_a\psi_b\rangle, \tag{A7}$$

hence by (6) with $f(\mathsf{H}_a, \mathsf{H}_b) = (E-\mathsf{H}_a-\mathsf{H}_b \pm i\varepsilon)^{-1}$, and $|\,\psi_a\psi_b\rangle$ replaced by $V_b\,|\,\psi_a\psi_b\rangle$,

$$(E-\mathsf{H}_a-\mathsf{H}_b\pm i\varepsilon)^{-1}V_b\,|\,\psi_a\psi_b\rangle = (E-\alpha-\mathsf{H}_b\pm i\varepsilon)^{-1}V_b\,|\,\psi_a\psi_b\rangle. \quad \text{(A8)}$$

Since $|\,\psi_a\rangle$ is unaffected by V_b and H_b this gives

$$(E-\mathsf{H}_a-\mathsf{H}_b\pm i\varepsilon)^{-1}V_b\,|\,\psi_a\psi_b\rangle = [(E-\alpha-\mathsf{H}_b\pm i\varepsilon)^{-1}V_b\,|\,\psi_b\rangle]\,|\,\psi_a\rangle. \quad \text{(A9)}$$

APPENDIX B

If A and B are two commuting Hermitian operators, and $f(\mathsf{A})$ and $g(\mathsf{B})$ are functions of A and B respectively, then

$$\exp[f(\mathsf{A})+g(\mathsf{B})] = \exp[f(\mathsf{A})]\exp[g(\mathsf{B})] = \exp[g(\mathsf{B})]\exp[f(\mathsf{A})]. \quad \text{(B1)}$$

Proof. Since A and B are Hermitian and commute, they have a complete set of common orthonormal eigenvectors $|A'B'\rangle$ where $\mathsf{A}\,|\,A'B'\rangle = A'\,|\,A'B'\rangle$ and $\mathsf{B}\,|\,A'B'\rangle = B'\,|\,A'B'\rangle$; thus

$$\begin{aligned}[f(\mathsf{A})+g(\mathsf{B})]\,|\,A'B'\rangle &= f(\mathsf{A})\,|\,A'B'\rangle + g(\mathsf{B})\,|\,A'B'\rangle \\ &= [f(A')+g(B')]\,|\,A'B'\rangle. \end{aligned} \quad \text{(B2)}$$

Hence if $|\,\psi\rangle$ is an arbitrary vector

$$\exp[f(\mathsf{A})+g(\mathsf{B})]\,|\,\psi\rangle = \sum_{A'B'} \exp[f(A')+g(B')]\,|\,A'B'\rangle\langle A'B'\,|\,\psi\rangle, \quad \text{(B3)}$$

$$\exp[f(\mathsf{A})]\exp[g(\mathsf{B})]\,|\,\psi\rangle = \sum_{A'B'} \exp[f(A')]\exp[g(B')]\,|\,A'B'\rangle\langle A'B'\,|\,\psi\rangle, \quad \text{(B4)}$$

$$\exp[g(\mathsf{B})]\exp[f(\mathsf{A})]\,|\,\psi\rangle = \sum_{A'B'} \exp[g(B')]\exp[f(A')]\,|\,A'B'\rangle\langle A'B'\,|\,\psi\rangle. \quad \text{(B5)}$$

The right-hand sides of (3) to (5) are obviously equal, and hence so are the left-hand sides; but $|\,\psi\rangle$ is an arbitrary vector, so (1) follows.

A particular case is when $f(\mathsf{A}) = i\mathsf{A}t/\hbar$, $g(\mathsf{B}) = i\mathsf{B}t/\hbar$. Then (1) yields

$$\exp(i\mathsf{A}t/\hbar + i\mathsf{B}t/\hbar) = \exp(i\mathsf{A}t/\hbar)\exp(i\mathsf{B}t/\hbar) = \exp(i\mathsf{B}t/\hbar)\exp(i\mathsf{A}t/\hbar). \quad \text{(B6)}$$

Another case is when $f(\mathsf{B}) = k$, where k is a complex constant; then if C is another Hermitian operator, and $h(\mathsf{C})$ is a function of C,

$$\begin{aligned}\exp[f(\mathsf{A})+k]\exp[h(\mathsf{C})-k] &= \exp[f(\mathsf{A})]\exp(k)\exp(-k)\exp[h(\mathsf{C})] \\ &= \exp[f(\mathsf{A})]\exp[h(\mathsf{C})]. \end{aligned} \quad \text{(B7)}$$

APPENDIX C

GREEN'S OPERATORS AND ASYMPTOTIC SCATTERING STATES

GREEN's operators $(E-\mathsf{H}\pm i\varepsilon)^{-1}$ for a Hermitian operator H are defined by

$$(E-\mathsf{H}\pm i\varepsilon)^{-1}|\psi\rangle = \sum_{\alpha}(E-E_{\alpha}\pm i\varepsilon)^{-1}|\alpha\rangle\langle\alpha|\psi\rangle \tag{C1}$$

where $|\psi\rangle$ is an arbitrary state and H is assumed to have a complete set of orthonormal eigenstates $|\alpha\rangle$ with eigenvalues E_{α}. The quantity ε is an arbitrary positive number and E is real. The Hermiticity of H ensures that the E_{α} are all real, and so the presence of the term $i\varepsilon$ prevents any singularity occurring on the right-hand side of (1). We usually allow ε to tend to zero at the end of any calculation. The operators $(E-\mathsf{H}\pm i\varepsilon)^{-1}$ are obviously the inverses of the operators $E-\mathsf{H}\pm i\varepsilon$.

We can assume that the unperturbed Hamiltonian H_{l} has a complete set of eigenstates $|\mathbf{k}\xi\rangle = |\mathbf{k}\rangle|\xi\rangle$ where $|\mathbf{k}\rangle$ represents the free motion of the centre of mass of a cluster A relative to the centre of mass of the remaining clusters, while $|\xi\rangle$ represents the internal state of all the clusters and the free relative motion of the clusters other than A, if there is more then one of these. Since we shall assume these states to be complete we must include continuum states of the various clusters in the set of $|\mathbf{k}\xi\rangle$'s. The energy associated with the state $|\mathbf{k}\xi\rangle$ is $E_{k\xi} = E_{k}+E_{\xi}$, where E_{ξ} is the internal energy plus the relative energy of the recoil clusters if there are two or more of these.

In this case (1) gives, taking the positive sign,

$$(E-\mathsf{H}_{l}+i\varepsilon)^{-1}|\psi\rangle = \sum_{\xi}\int d\mathbf{k}(E-E_{k\xi}+i\varepsilon)^{-1}|\mathbf{k}\xi\rangle\langle\mathbf{k}\xi|\psi\rangle. \tag{C2}$$

As usual we take $\mathbf{r}$ as the relative position vector of the centre of mass of the recoil cluster and $\mathbf{q}$ to stand for the remaining coordinates. If we take representatives of (2) in configuration space we obtain

$$\begin{aligned}
&\langle\mathbf{rq}|(E-\mathsf{H}_{l}+i\varepsilon)^{-1}|\psi\rangle\\
&= \sum_{\xi}\int d\mathbf{k}(E-E_{k\xi}+i\varepsilon)^{-1}\langle\mathbf{rq}|\mathbf{k}\xi\rangle\int d\mathbf{r}'\int d\mathbf{q}'\langle\mathbf{k}\xi|\mathbf{r}'\mathbf{q}'\rangle\langle\mathbf{r}'\mathbf{q}'|\psi\rangle\\
&= \int d\mathbf{r}'\int d\mathbf{q}'\left\{\sum_{\xi}\left[\int d\mathbf{k}(E-E_{k\xi}+i\varepsilon)^{-1}\langle\mathbf{r}|\mathbf{k}\rangle\langle\mathbf{k}|\mathbf{r}'\rangle\right]\langle\mathbf{q}|\xi\rangle\langle\xi|\mathbf{q}'\rangle\right\}\langle\mathbf{r}'\mathbf{q}'|\psi\rangle.
\end{aligned} \tag{C3}$$

Now the quantity in square brackets in (3), which we can denote by [ ], is

$$[\ ] = 2\mu\hbar^{-2}(2\pi)^{-3}\int d\mathbf{k}[2\mu\hbar^{-2}(E-E_\xi)-k^2+i\eta]^{-1}\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')] \quad \text{(C4)}$$

where $\eta = 2\mu\varepsilon\hbar^{-2}$ while μ is the reduced mass of A and the recoil clusters. If we put $2\mu\hbar^{-2}(E-E_\xi) = \pm k_\xi^2$ according as $E >$ or $< E_\xi$, take spherical polar coordinates for $\mathbf{k}$ relative to $\mathbf{r}-\mathbf{r}'$ as polar axis, and integrate over the angular coordinates of $\mathbf{k}$, we find that (4) yields

$$[\ ] = \frac{\mu}{2\pi^2\hbar^2 i}\int_0^\infty \frac{k\{\exp[ik|\mathbf{r}-\mathbf{r}'|-\exp[-ik|\mathbf{r}-\mathbf{r}'|]\}}{|\mathbf{r}-\mathbf{r}'|(\pm k_\xi^2-k^2+i\eta)}\,dk. \quad \text{(C5)}$$

To evaluate [ ] we replace k by $-k$ in the second integral on the right-hand side of (5); (5) then becomes

$$[\ ] = \frac{\mu}{2\pi^2\hbar^2 i}\int_{-\infty}^{+\infty} \frac{k\exp[ik|\mathbf{r}-\mathbf{r}'|]}{|\mathbf{r}-\mathbf{r}'|(\pm k_\xi^2-k^2+i\eta)}\,dk. \quad \text{(C6)}$$

This may now be evaluated using contour integration. The appropriate contour is a semicircle in the upper half of the complex k-plane, with the origin as centre and the real axis along the base; after using the theorem of residues we then let $\eta \to 0+$. We obtain

$$[\ ] = -\frac{\mu}{2\pi\hbar^2}\frac{\exp(ik_\xi|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}')|} \qquad (E > E_\xi), \quad \text{(C7)}$$

or

$$[\ ] = -\frac{\mu}{2\pi\hbar^2}\frac{\exp(-k_\xi|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \qquad (E < E_\xi). \quad \text{(C8)}$$

(7) and (8) are the two alternative expressions for the square-bracketed term [ ] in (3). If we substitute for [ ] in (3) we can rewrite (3) as

$$\langle\mathbf{rq}|(E-\mathsf{H}_i+i\varepsilon)^{-1}|\psi\rangle = \int d\mathbf{r}'\int d\mathbf{q}'\,G(\mathbf{r},\mathbf{q};\mathbf{r}',\mathbf{q}')\langle\mathbf{r}'\,\mathbf{q}'|\psi\rangle \quad \text{(C9)}$$

where

$$G(\mathbf{r},\mathbf{q};\mathbf{r}',\mathbf{q}') = -\frac{\mu}{2\pi\hbar^2}\sum_\xi{}'\frac{\exp(ik_\xi|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\langle\mathbf{q}|\xi\rangle\langle\xi|q'\rangle$$

$$-\frac{\mu}{2\pi\hbar^2}\sum_\xi{}''\frac{\exp(-ik_\xi|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\langle\mathbf{q}|\xi\rangle\langle\xi|q'\rangle; \quad \text{(C10)}$$

in (10) $\sum_\xi'$ goes over states $|\xi\rangle$ for which $E > E_\xi$, while $\sum_\xi''$ goes over states $|\xi\rangle$ for which $E < E_\xi$. The result (9) shows that Green's operator is an integral operator with kernal $G(\mathbf{r}, \mathbf{q}; \mathbf{r}', \mathbf{q}')$. It also shows that the Schwinger–Lippmann equation (1.5.3) is an integral equation for the scattering wave function ψ_ν^+. 13

To find the asymptotic form of (1.5.3) we note that

$$|\mathbf{r}-\mathbf{r}'| = (r^2-2\mathbf{r}\cdot\mathbf{r}'+r'^2)^{1/2} \underset{r\to\infty}{\sim} r-\frac{\mathbf{r}\cdot\mathbf{r}'}{r} = r-\hat{\mathbf{r}}\cdot\mathbf{r}'. \tag{C11}$$

It follows from (9), (10) and (11) that

$$\langle \mathbf{rq} | (E-\mathsf{H}_i+i\varepsilon)^{-1} | \psi\rangle \underset{r\to\infty}{\sim} \sum_{\xi}{}' f_\xi(\hat{\mathbf{r}}) \frac{\exp(ik_\xi r)}{r} \langle \mathbf{q} | \xi\rangle \tag{C12}$$

where

$$f_\xi(\hat{\mathbf{r}}) = -\frac{\mu}{2\pi\hbar^2}\int d\mathbf{r}' \int d\mathbf{q}' \exp(-ik_\xi \hat{\mathbf{r}}\cdot\mathbf{r}') \langle \xi | q'\rangle \langle \mathbf{r}'\mathbf{q}' | \psi\rangle. \tag{C13}$$

The doubly primed sum does not appear due to the exponential decay of its terms as $r \to \infty$. In the case of the Schwinger–Lippmann equation (1.5.3) we obtain

$$\psi_\nu^+ \underset{r\to\infty}{\sim} \varphi_\nu + \sum_\xi f_\xi(\hat{\mathbf{r}}) \frac{\exp(ik_\xi r)}{r} \langle \mathbf{q} | \xi\rangle \tag{C14}$$

where by (13) $f_\xi(\mathbf{r})$ is now given by

$$f_\xi(\hat{\mathbf{r}}) = -\frac{\mu}{2\pi\hbar^2}\int d\mathbf{r}' \int d\mathbf{q}' \exp(-ik_\xi \mathbf{r}\cdot\mathbf{r}') \langle \xi | \mathbf{q}'\rangle \langle \mathbf{r}'\mathbf{q}' | V_i\psi_\nu^+\rangle. \tag{C15}$$

In the case of a local potential this becomes

$$f_\xi(\hat{\mathbf{r}}) = -\frac{\mu}{2\pi\hbar^2}\int d\mathbf{r}' \int d\mathbf{q}' \exp(-ik_\xi \hat{\mathbf{r}}\cdot\mathbf{r}') \langle \xi | \mathbf{q}'\rangle\, V_i(\mathbf{r}', \mathbf{q}')\, \psi_\nu^+(\mathbf{r}', \mathbf{q}'). \tag{C16}$$

The Schwinger–Lippmann equation with positive sign therefore gives rise to outgoing wave boundary conditions.

Since $k_\xi^2 = 2\mu\hbar^{-2}(E-E_\xi)$ the quantity k_ξ is, by energy conservation, the wave number l of the final state $|\mathbf{l}\xi\rangle = |\mathbf{l}\rangle|\xi\rangle$. The unit vector $\hat{\mathbf{r}}$ is in the direction of the final outgoing wave. We can therefore put $k_\xi\hat{\mathbf{r}} = \mathbf{l}$, and so (15) becomes

$$\begin{aligned} f_\xi(\hat{\mathbf{r}}) &= -\frac{(2\pi)^{1/2}\mu}{\hbar^2}\int d\mathbf{r}' \int d\mathbf{q}' \langle \mathbf{l} | \mathbf{r}'\rangle \langle \xi | \mathbf{q}'\rangle \langle \mathbf{r}'\mathbf{q}' | V_i\psi_\nu^+\rangle \\ &= -(2\pi)^{1/2}\mu\hbar^{-2} \langle \mathbf{l}\xi | V_i | \psi_\nu^+\rangle. \end{aligned} \tag{C17}$$

It is, in fact, $(2\pi)^{-3/2}\times$ the scattering amplitude for the process.

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