# Scattering in Condensed Matter

# Scattering in Condensed Matter

<sup>By</sup> Marian Apostol

**Cambridge Scholars** Publishing



Scattering in Condensed Matter

By Marian Apostol

This book first published 2024

Cambridge Scholars Publishing

Lady Stephenson Library, Newcastle upon Tyne, NE6 2PA, UK

British Library Cataloguing in Publication Data A catalogue record for this book is available from the British Library

Copyright © 2024 by Marian Apostol

All rights for this book reserved. No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the copyright owner.

ISBN (10): 1-5275-5835-5 ISBN (13): 978-1-5275-5835-9

## Contents

1	Pref	ace	1	
2	Scattering, Collisions			
	2.1	Born scattering	9	
	2.2	An exact solution	13	
	2.3	Momentum transfer	15	
	2.4	Beam	17	
	2.5	Quantum transitions	19	
	2.6	Energy transfer	24	
	2.7	Phase factors	26	
3	Elect	tromagnetic Radiation	29	
	3.1	Dipole field	29	
	3.2	Damping force	31	
	3.3	Line breadth	32	
	3.4	Scattering of radiation	33	
	3.5	Absorption of radiation	36	
	3.6	Maxwell equations	37	
	3.7	Energy, force and momentum	40	
	3.8	Longitudinal field	44	
	3.9	Photons	47	
	3.10	Charge in electromagnetic field	49	
	3.11	Scattering off a charge distribution	51	
	3.12	The atom	54	
	3.13	Quantum theory of radiation	59	
	3.14	Emission and absorption: free charges	62	
		Emission and absorption: bound charges	63	
	3.16	Propagation of light, interference	67	
		Doppler effect	70	
		Scattering: first-order perturbation	72	
	3.19	Scattering: second-order perturbation	74	

#### Contents

4	X-Ra	ays Diffraction	79			
	4.1	<i>X</i> -rays	79			
	4.2	Extinction	81			
	4.3	Polarization	82			
	4.4	Elastic scattering of X-rays	87			
	4.5	Diffraction peaks in crystals	88			
	4.6	Form-factor	91			
	4.7	Energy and momentum	97			
	4.8	Average total intensity	100			
	4.9	Diffuse thermal scattering of $X$ -rays $\ldots \ldots \ldots$	102			
	4.10	Lattice distortion and phase defects	103			
	4.11	Temperature dependence: X-rays scattering and phonon	s106			
	4.12	Higher-order effects	109			
F	Nau	tuine Costtoning	113			
5	5.1	trino Scattering	113 113			
	$5.1 \\ 5.2$	Neutrinos	$115 \\ 115$			
	5.2	Scattering parameters	115 116			
	5.4	Classical scattering	110			
	$5.4 \\ 5.5$	Form-factor	120			
	5.6	Temperature dependence	121 126			
		Coherent <i>vs</i> incoherent scattering				
	5.7	Neutrino coherent scattering	127			
	5.8	Coherent-incoherent interplay	129			
	5.9	Quantum scattering	133			
		5.9.1 Introduction	133			
		5.9.2 Center of mass	134			
		5.9.3 Crystal field	138			
		5.9.4 Photon emission (absorption) $\ldots \ldots \ldots$	139			
		5.9.5 Coherent scattering $\ldots$	142			
	F 10	5.9.6 Cross-section	144			
	5.10	Neutrino scattering	146			
	5.11	Coherence domains	151			
6	Neutron Scattering 15					
	6.1	Single-particle scattering	157			
	6.2	Scattering parameters	158			
	6.3	Macroscopic target. Quantum scattering	159			

#### Contents

	6.4	Coherence domains. The principle of maximal cross-			
		section	164		
	6.5	Classical scattering	166		
	6.6	Macroscopic quantum-mechanical scattering	169		
		$6.6.1  Introduction  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $	169		
		6.6.2 Macroscopic quantum-mechanical scattering	171		
		6.6.3 Neutrino scattering	174		
		6.6.4 Other projectiles. Coherence domains	176		
		6.6.5 Classical scattering	177		
7	Moe	essbauer Effect	181		
	7.1	Resonance fluorescence	181		
	7.2	Photon emission	186		
8	Light scattering				
	8.1	Sound	191		
	8.2	Scattering by sound	197		
9	Scattering by laser pulses				
	9.1	Charge scattering by electromagnetic radiation	203		
	9.2	Cross-section	211		
	9.3	Quasi-classical approximation	218		
10	Elec	tron scattering	231		
11	Арр	endix	235		
	11.1	Center of mass	235		
	11.2	$\delta$ -function and the Fourier transform	237		
	11.3	Electromagnetic field and polarization	238		
	11.4	Maxwell equations in matter	239		
Index					

Scattering with one-particle targets is well developed in atomic and nuclear physics, but its counterpart with macroscopic targets still exhibits insufficiencies, in spite of the large amount of spectroscopical techniques employed in condensed matter. This book is devoted to an exploration of scattering in condensed matter. By condensed matter we mean large macroscopic targets, consisting of a large number of scattering centres like atoms, molecules, and unit cells in crystals. Scattering by inhomogeneities in continuous media (*e.g.*, light sound) is briefly treated. Also, we include a recent development of charge scattering by laser pulses. Many other types of condensed matter, like plasmas, soft matter, superfluids, etc, are left aside. As regards the projectiles, we deal with pointlike charges like electrons or ions, light and X- and gamma rays, neutrinos, neutrons. Many other types of scattering in condensed matter are not included. The book focuses on basic problems raised by scattering in condensed matter.

The first problem concerns the classical or quantum-mechanical nature of the interaction of the projectile with a one-particle target. If the range of the interaction is larger than the variation range of the target wavefunction, the collision is classical. For instance, this may happen for radiation scattering, where we can derive the crosssection by classical electromagnetism. On the other hand, the interaction may vary abruptly over the range of the wavefunction, like for neutron contact interaction, where the motion of the target is quantum-mechanical. However, the corresponding energy transfer is thermalized, such that the scattering is classical, as in diffraction.

The scattering process in condensed matter is a local process: a local portion of the incoming wave (radiation, particle wave) interacts with a local portion of the macroscopic target. In this respect, the scattering in condensed matter may have a quantum-mechanical character. We may imagine that an incoming quantum particle is absorbed by

the target and thereafter released, emitted by the target. Therefore, the scattering interaction may carry a quantum phase. If the phase is the same for all scatterers, the scattering is coherent, and the scattering cross-section is proportional to  $N^2$ , where N is the number of scatterers. If the phase varies randomly from scatterer to scatterer, the scattering is incoherent and the cross-section is proportional to N. The difference between coherent and incoherent scattering is well-known for multi-particle targets, but it is not sufficiently exploited in condensed matter.

Although the scattering in condensed matter may be ultimately quantum-mechanical, in some cases a quasi-classical description is valid. However, a phase carried by interaction may also be present in these cases. According to the interpretation of the scattering as an absorption/emission process, this phase has in fact a statistical character.

Another element which receives less attention, in spite of its importance, is the momentum and energy conservation in scattering in condensed matter. This conservation is emphasized throughout this book. together with the force acting upon the target. An estimation of this force, acting in the forward direction, is  $F = \Phi p \sigma$ , where  $\Phi$  is the flux density of the projectile (number of particles per unit time and unit cross-section of the target), p is the momentum of the incident particle and  $\sigma$  is the scattering cross-section. The momentum conservation in coherent scattering may lead to diffraction peaks, infinitesimally extended for macroscopic targets; while the incoherent scattering does not exhibit peaks; it proceeds by the conservation of the momentum of individual scatterers, or elementary excitations like phonons. The infinitesimal extension of the coherent peaks diminishes the scattering cross-section from  $\sim N^2$  to  $\sim N^{4/3}$ . We call this scattering a coherent diffraction. This is the usual point which receives the main attention in scattering in condensed matter. It seems that only the coherent diffraction and the incoherent scattering are known in condensed matter. We call these scatterings classical scatterings.

Here we encounter the first big problem. The cross-section of the coherent diffraction is  $\sigma = N^{4/3}\sigma_0$ , where  $\sigma_0$  is the one-particle cross-section. For all scatterings in condensed matter, with one exception, this cross-section is larger than the cross-section A of the target. The exception is neutrino scattering, which, anyway, raises other problems.

Now, the number of scattered particles (per unit time) cannot exceed the number of incident particles, so the cross-section  $\sigma$  should always be smaller than A. This condition is usually overlooked. It seems that in X-ray diffraction it is implied that this condition would be satisfied by the so-called dynamic X-ray scattering. However, this dynamic scattering brings only small corrections to the cross-section. The way out from this deadlock is provided by the coherence domains

The way out from this deadlock is provided by the coherence domains, which we introduce in this book. Usually, the macroscopic target is at thermal equilibrium. Under the action of the incident particles the macroscopic target is taken out of equilibrium. Consequently, the target tries to regain as much of its thermal equilibrium as possible. This can only be done by developing a disorder, which would increase the entropy. In these circumstances this disorder can only be associated to phase factors. Being still under the action of an external agent, the increase in entropy should be minimal, such that the crosssection is maximal: it is reduced to the target cross-section A. The target cross-section A is a macroscopic quantity in reasonable limits. If the target is very large, then radiation extinction may appear, as well as absorption, multiple scatterings, such that the description of the scattering is not so simple anymore. We assume that a number  $n_d = N/N_d$  of (identical) domains appear in the target, where  $N_d$  is the number of particles in each domain,  $1 < N_d < N$ . In each domain the scattering phase is constant and the domain phases are randomly distributed. It follows that the cross-section becomes

$$\overline{\sigma} = n_d \sigma_d \quad , \tag{1.1}$$

where  $\sigma_d$  is the cross-section of one domain. For a coherent scattering we have  $\sigma_d = N_d^2 \sigma_0$ , for a coherent diffraction we have  $\sigma_d = N_d^{4/3} \sigma_0$ , such that we have  $\overline{\sigma} = N N_d \sigma_0$  for coherent scattering and  $\overline{\sigma} = N N_d^{1/3} \sigma_0$  for coherent diffraction. We note that for an incoherent scattering  $N_d = 1$  and both formulae give the same result  $\overline{\sigma} = N \sigma_0$ . It is convenient to introduce  $f = 1/N_d$ , where 1/N < f < 1. We get

$$\overline{\sigma} = \frac{N\sigma_0}{f} \tag{1.2}$$

for coherent scattering and

$$\overline{\sigma} = \frac{N\sigma_0}{f^{1/3}} \tag{1.3}$$

for coherent diffraction. The condition

$$\overline{\sigma} < A$$
 (1.4)

should be fulfilled for any scattering in condensed matter.

The above inequality should be satisfied for 1/N < f < 1. Now, there is another circumstance which should be included in such an analysis. The domains are regions of continuity of the scattering phase. The phase is associated with the atomic constituents of the macroscopic target. Any macroscopic target has a discrete structure. Therefore, there should exist a critical extension of each continuity domain. We show in this book that the critical number of particles in each (threedimensional) domain is given by  $N_{dc} = (a/a_0)^9$ , where *a* is the mean separation distance between the particles and  $a_0$  is the atomic dimension of each particle. For instance, for  $a = 4a_0$  we can take  $N_{dc}$  of the order  $\simeq 10^6$ . In two dimensions  $N_{dc} = (a/a_0)^4$ , which is of the order  $\simeq 10^3$  for  $a = 4a_0$ . Therefore, *f* should satisfy the condition  $f < 10^{-6}$  $(f < 10^{-3})$ . For  $f > 10^{-6}$   $(f > 10^{-3})$  the domains are not well defined; they are reduced to individual particles and the scattering is incoherent (f = 1).

On the other hand, the principle of maximal cross-section requires  $\overline{\sigma} = A$ , *i.e.*  $f = N\sigma_0/A$  for coherent scattering and  $f = (N\sigma_0/A)^3$  for coherent diffraction. For neutrino scattering, with  $\sigma_0 = 10^{-44} cm^2$  and  $N = 10^{22} (0.1 mol)$  we get  $f = 10^{-22}/A$  for coherent scattering, which is less than 1/N for a macroscopic target. It follows  $N_d = N$ , *i.e.* a coherent scattering in condensed matter, which needs to be accommodated by a theory. For  $\sigma_0 = 10^{-24} cm^2$  (X-, gamma rays, neutrons) we get  $f = 10^{-2}/A$ , which is not acceptable; a tendency exists towards an incoherent scattering  $(f \to 1)$ . Therefore, a coherent diffraction we have  $f = 10^{-6}/A^3$ , which is acceptable, and  $N_d = 10^6A^3$ : a coherent diffraction may appear in this case. The condition  $\overline{\sigma} < A$  ( $\overline{\sigma} = A$ ) is a

necessary condition for scattering. It remains to differentiate between the coherent scattering and the coherent diffraction.

The above hypothesis of coherence domains leads, in certain conditions (neutrino scattering), to a coherent scattering in the whole macroscopic target. That means that the scattering phase is the same in the whole macroscopic target. A constant scattering phase may appear in small targets, with a small number of particles, for incident wavelengths much longer than the dimension of the target; indeed, the phase variation over the dimension of such a target is small, so the phase may be taken constant. In macroscopic targets the scattering phase can only be constant if the incoming particles see the target as a whole. This means that the macroscopic target, namely the constituents of the macroscopic target, should be described in this case by a quantum field (a distributed wavefunction). This is a macroscopic quantum scattering, *i.e.* a scattering which is quantum-mechanical at the macroscopic scale. As long as we introduce phase factors in describing the scattering we deal with a quantum scattering, which requires quantum fields. The coherent diffraction does not employ such fields, although a wavefunction of the whole target (center of mass) is necessary. We may call the coherent diffraction a classical scattering. The macroscopic quantum scattering is introduced in this book. For crystals, a field of the whole target implies the quasi-momentum of the crystal. This is a coherent field (wavefunction). In addition, for all types of targets, there exist fields (wavefunctions) associated with the thermal motion of the atomic constituents. Basically, they are reduced to the one-particle wavefunctions of the target. We call them incoherent fields (wavefunctions). The coherent field has a significant weight in comparison to the incoherent field for stiff crystals with a high Debye temperature. The coherent field leads to a coherent cross-section  $\sim N^2$ , while the incoherent fields give a cross-section  $\sim N$ . In the former case the momentum transfer is taken by the quasi-momentum, *i.e.* by the whole crystal, while in the latter case the momentum is transferred to collective excitations like phonons.

A macroscopic quantum scattering is only possible if the collision time  $\tau$  is longer than the equilibrium time  $\Delta t_{eq}$ ,

$$\tau > \Delta t_{eq}$$
 , (1.5)

such that the incident particle flux sees the target as a whole. The collision time is the mean time between two succesive collisions. It is given by  $\tau = 1/\Phi\overline{\sigma}$ , where  $\Phi$  is the flux density of the incident particles. The equilibrium time is the mean time needed by a target particle to regain its equilibrium. It is given by  $\Delta t_{eq} = \hbar / \Delta E$ , where  $\Delta E$  is the energy transfer to a particle. The energy transfer is estimated as  $\Delta E = (v + p/M)p$ , where v is the thermal velocity of the target particles, M is the mass of the target particles and p is the momentum of the incident particles (of the order of the momentum transfer). It is convenient to introduce a threshold given by p = Mv, such that for p < Mv we may use  $\Delta E = vp$  and for p > Mv we may use  $\Delta E = p^2/M$ . The threshold energy of the incident particles with mass m is  $E = p^2/m = \frac{M}{m}T$ , while for radiation  $E = cp = c\sqrt{MT}$ , where T is the temperature. For instance, for  $M = 10^5 m_e$ , where  $m_e$  is the electron mass, and room temperature T = 300K we get  $E \simeq 1 eV$  for neutrons,  $E \simeq 1 k eV$  for electrons and  $E \simeq 10 k eV$  for radiation (neutrino included).<sup>1</sup> If  $\tau < \Delta t_{eq}$  the incident beam sees the target particles as individual scatterers. This is a coherent diffraction (classical scattering).

Let us apply inequality (1.5) for neutrino coherent scattering. Together with condition (1.4) we have

$$f > \frac{N\sigma_0}{A} , \ f > \frac{\hbar\Phi N\sigma_0}{\Delta E} .$$
 (1.6)

For an incident flux density  $\Phi = 10^{12}/cm^2 \cdot s$  we have  $\Delta E/\hbar\Phi \simeq 10^3 \Delta E(eV)$ ; for E = 1 MeV the energy transfer is  $\simeq 20eV$ , such that  $A \ll \Delta E/\hbar\Phi$ . Consequently, only the first inequality (1.6) needs to be satisfied. This condition has been examined above, so we may conclude that neutrino coherent scattering appears in the whole macroscopic target (for the numerical data used here). The force acting upon the macroscopic target is a measurable force, due to the large cross-section of the sample. This may justify the claims of Weber and others, in spite of many negative opinions, of the possibility of neutrino detection by using a torsion balance with a stiff sapphire crystal.

 $<sup>{}^{1}</sup>m_{e} = 10^{-27}g$ , neutron mass  $m \simeq 2 \times 10^{3}m_{e}$ ,  $c = 10^{10}cm/s$ ,  $1eV = 1.6 \times 10^{-12}erg$ ,  $1K = 1.38 \times 10^{-16}erg$ ,  $\hbar = 10^{-27}$ erg·s.

For a coherent diffraction we need

$$\frac{N\sigma_0}{A} < f^{1/3} < \frac{\hbar\Phi N\sigma_0}{\Delta E} . \tag{1.7}$$

First, we note that these inequalities imply a small energy transfer, such that the energy of the incident neutrons, or radiation is low  $(\Delta E < \hbar \Phi A)$ . Since, according to the principle of maximal crosssection, we have  $\frac{N\sigma_0}{A} = f^{1/3}$ , it follows that this coherent diffraction is possible, with domain dimension as large as that found above  $(N_d = 10^6 A^3)$ . However, the force acting upon the target is small, precisely due to the domain occurrence. For higher energies the energy transfer is larger and we need to apply the inequalities (1.6). Making use of  $\sigma_0 = 10^{-24} cm^2$ , we get  $f = 10^{-2}/A$ , which indicates an incoherent scattering  $(f \to 1)$ . The force acting upon the target is very small.

This book deals with such considerations. Their results depend on the numerical data. Besides a large variety of the known input data, serious uncertainties exist also in some input data. Many types of scattering in condensed matter are not analyzed herein, both for various projectiles and various macroscopic targets. For instance, a special case is the electron scattering, which proceeds on small superficial layers; the coherence domains are two-dimensional. It is an incoherent scattering with a weak coherent diffraction.

## 2.1 Born scattering

A quantum particle with mass m comes from somewhere at minus infinity, where it starts at the moment of time t = 0, and collides with a particle with mass M. The two particles interact with the potential  $U(\mathbf{r})$ , where  $\mathbf{r}$  is the relative position of the two particles. The Mparticle is fixed and structureless. After collision the m-particle goes somewhere at plus infinity, where it arrives at the infinitely long time t. We assume that the potential U falls sufficiently rapidly at infinity, such that the incoming particle at minus infinity and the outgoing particle at plus infinity are free. The motion of the colliding particle obeys the Schroedinger equation

$$-\frac{\hbar^2}{2m}\Delta\psi + U(\boldsymbol{r})\psi = E\psi \quad , \tag{2.1}$$

where  $\psi$  is its wavefunction, E is the particle energy (and  $\hbar$  is Planck's constant). The solution of equation (2.1) is a stationary solution, with a constant energy, which means that the collision is elastic. We write this energy as  $E = \hbar^2 k^2 / 2m$ , where  $\mathbf{k}$  is the wavevector of the incoming particle at minus infinity (and  $\mathbf{p} = \hbar \mathbf{k}$  is its momentum). The particle wavefunction is  $\psi_i = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$ , where V denotes the volume. It satisfies the Schroedinger equation

$$-\frac{\hbar^2}{2m}\Delta\psi_i = E\psi_i \quad , \tag{2.2}$$

written also as

$$\Delta \psi_i + k^2 \psi_i = 0 . \tag{2.3}$$

Let us assume that the potential U is sufficiently small, in a sense which will be shortly specified, such that we seek a perturbationtheory solution of equation (2.1), written as  $\psi = \psi_i + \psi_s$ , where the

small correction  $\psi_s$  satisfies the equation

$$\Delta \psi_s + k^2 \psi_s = \frac{2m}{\hbar^2} U \psi_i + \dots .$$
 (2.4)

The solution is valid as long as  $|\psi_s| \ll |\psi_i|$ .  $\psi_s$  is the scattered wave. This is a Helmholtz equation. Its solution is given by

$$\psi_s(\mathbf{r}) = \frac{2m}{\hbar^2} \int d\mathbf{r}' U(\mathbf{r}') \psi_i(\mathbf{r}') G(\mathbf{r} - \mathbf{r}') \quad , \tag{2.5}$$

where G is the Green function satisfying the equation

$$\Delta G + k^2 G = \delta(\mathbf{r}) \ . \tag{2.6}$$

By using Fourier transformations, we get

$$G(\mathbf{r}) = -\frac{1}{(2\pi)^3} \int d\mathbf{q} \frac{e^{i\mathbf{q}\mathbf{r}}}{q^2 - k^2} = -\frac{1}{4\pi^2 ir} \int_{-\infty}^{+\infty} dq \frac{q e^{iqr}}{q^2 - k^2} \,. \tag{2.7}$$

In order to perform this integration, we need to give a sense to the singularities  $q = \pm k$ . Now, we remember that  $k^2 \sim E/\hbar = \omega$ , and the integration over frequency  $\omega$  of the phase factor  $e^{-i\omega t}$  should be zero for t < 0, in order to satisfy the causality principle. Therefore, the integration should be performed in the upper half-plane (for t < 0) and the  $\omega$ -poles must lie in the lower half plane, *i.e.*  $\omega \to \omega + i\varepsilon$ ,  $\varepsilon \to 0^+$ . Therefore, the integral in equation (2.7) becomes

$$G(\mathbf{r}) = -\frac{1}{4\pi^2 i r} \int_{-\infty}^{+\infty} dq \frac{q e^{i q r}}{q^2 - k^2 - i\varepsilon} = -\frac{1}{4\pi} \frac{e^{i k r}}{r} , \qquad (2.8)$$

and the solution of the Helmholtz equation (2.4) is<sup>1</sup>

$$\psi_s(\mathbf{r}) = -\frac{m}{2\pi\hbar^2\sqrt{V}} \int d\mathbf{r}' U(\mathbf{r}') e^{i\mathbf{k}\mathbf{r}'} \frac{e^{i\mathbf{k}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad .$$
(2.9)

Now, we can estimate the magnitude of  $\psi_s$  for the condition  $|\psi_s| \ll |\psi_i|$ . For a short range potential with magnitude U, extending over a small range a, and low energies  $ka \ll 1$  we get from equation (2.9)

$$\frac{m \mid U \mid a^2}{\hbar^2} \ll 1 ; \qquad (2.10)$$

<sup>&</sup>lt;sup>1</sup>M. Apostol, *Equations of Mathematical Physics*, Cambridge Scholars Publishing, Newcastle upon Tyne (2018).

the potential should be smaller than the localization energy  $\hbar^2/ma^2$  over region of extension a. In the same conditions but for high energies  $ka \gg 1$ , the condition reads, from equation (2.9),

$$\frac{m \mid U \mid a^2}{\hbar^2 k a} \ll 1 \quad , \tag{2.11}$$

or

$$U \mid \ll \frac{\hbar v}{a} \quad , \tag{2.12}$$

where  $v = \hbar k/a$  is the velocity of the incoming particle; for a Coulomb potential  $U = \alpha/r$ , there is no a, and the evaluation of the integral in equation (2.9) leads to  $m \mid \alpha \mid /\hbar^2 k \ll 1$ , or  $\mid \alpha \mid \ll \hbar v$ . These are the validity conditions for the perturbation-theory treatment of this collision problem.<sup>2</sup>

We are interested in the scattered wave at plus infinity. For  $r \gg r'$ ,  $|\mathbf{r} - \mathbf{r}'| \simeq r - \mathbf{r}\mathbf{r}'/r$ , such that  $\mathbf{k}' = k\mathbf{r}/r$  is the wavevector of the scattered particle (Fraunhofer diffraction); the scattered wavefunction given by equation (2.9) becomes

$$\psi_s(\mathbf{r}) \simeq -\frac{m}{2\pi\hbar^2 \sqrt{V}} \frac{e^{ikr}}{r} \int d\mathbf{r}' U(\mathbf{r}') e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}'} ; \qquad (2.13)$$

it is a spherical wave  $e^{ikr}/r$  distorted by the scattering amplitude

$$F(\boldsymbol{k}-\boldsymbol{k}') = -\frac{m}{2\pi\hbar^2} \int d\boldsymbol{r}' U(\boldsymbol{r}') e^{i(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{r}'} ; \qquad (2.14)$$

it is a scattering length. This is Born's formula.<sup>3</sup> The scattering amplitude is proportional to the Fourier transform of the potential. The number of particles scattered in the solid angle at large distances per unit time is

$$v' \mid \psi_s \mid^2 r^2 do = \frac{\hbar k}{mV} \mid F \mid^2 do ,$$
 (2.15)

<sup>&</sup>lt;sup>2</sup>L. Landau and E. Lifshitz, Course of Theoretical Physics, vol. 3, Quantum Mechanics, Butterworth-Heinemann, Oxford (1993).

<sup>&</sup>lt;sup>3</sup>M. Born, "Zur Quantenmechanik der Stossvorgaenge", Z. Phys. **37** 863 (1926); "Quantenmechanik der Stossvorgaenge", Z. Phys. **38** 803 (1926).

where  $\boldsymbol{v}' = \hbar \boldsymbol{k}'/m$ ,  $v' = \hbar k/m$ ; the flux density of the incoming particle is  $v \mid \psi_i \mid^2 = \frac{\hbar k}{mV}$  (current density, number of particles per unit area and unit time). The ratio of these two quantities gives the (differential) cross-section

$$d\sigma = |F|^2 do \tag{2.16}$$

(it has the dimension of an area).

We note that the total number of scattered particles  $\sim |\psi_s|^2 r^3 \sim \sigma/r^2$  in the volume V is much smaller than the total number of incident particles (1), due to the factor 1/r in equation (2.13).

For a screened Coulomb potential  $U = \alpha e^{-\gamma r}/r$  we get  $F = (2m\alpha/\hbar^2)/(q^2 + \gamma^2)$ , where  $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ . The cross-section is much smaller than the characteristic area  $1/\gamma^2 (m\alpha/\hbar^2\gamma \ll 1)$ , precisely due to the condition (2.10).

For the Coulomb potential  $(\gamma \rightarrow 0)$  we get the Rutherford cross-section<sup>4</sup>

$$d\sigma = \frac{\alpha^2}{16E^2 \sin^4 \frac{\theta}{2}} do \quad , \tag{2.17}$$

where  $E = \hbar^2 k^2 / 2m$  is the energy of the projectile and  $\theta$  is the scattering angle (the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ ). The total cross-section is infinite, due to the singularity at  $\theta = 0$ . The Coulomb potential is an unrealistic case (a "pathological" case). The physical electric potentials are screened.

For an atom with the nucleus charge -Ze, where e is the electron charge, the potential is given by the Poisson equation

$$\Delta \varphi = 4\pi Z e \delta(\mathbf{r}) - 4\pi e n(\mathbf{r}) \quad , \tag{2.18}$$

where  $n(\mathbf{r})$  is the electron density. The Fourier transformation gives  $\varphi(\mathbf{q}) = -4\pi e[Z - n(\mathbf{q})]/q^2$ , where  $n(\mathbf{q}) = \int d\mathbf{r}n(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}$  is the atomic form-factor. For an incident charge Q the potential energy is  $U(\mathbf{q}) = -4\pi eQ[Z - n(\mathbf{q})]/q^2$  and the cross-section is  $d\sigma = (2meQ/\hbar^2q^2)^2[Z - n(\mathbf{q})]^2 do.^5$ 

 $<sup>^{4}\</sup>text{E.}$  Rutherford, "The scattering of  $\alpha$  and  $\beta$  particles by matter and the structure of the atom", Phil. Mag. **21** 669 (1911).

<sup>&</sup>lt;sup>5</sup>N. F. Mott, "The scattering of electrons by atoms", Proc. Roy. Soc. A127 658 (1930).

In order to get an estimate of the Coulomb cross-section we assume an electron-electron collision with a screened Coulomb potential. The cross-section is

$$\sigma = \pi \left(\frac{2me^2}{\hbar^2}\right)^2 \frac{1}{k^2 \gamma^2} \frac{4k^2/\gamma^2}{4k^2/\gamma^2 + 1} .$$
 (2.19)

The parameter  $\gamma$  is of the order  $\gamma = 1/a_H$ , where  $a_H = \frac{\hbar^2}{me^2} = 0.53\text{\AA}$  is the Bohr radius ( $\hbar = 10^{-27} erg \cdot s, m = 10^{-27}g, e = -4.8 \times 10^{-10} esu$ ,  $1\text{\AA} = 10^{-8} cm$ ). For  $ka_H \ll 1$  the cross-section is of the order  $a_H^2$ , for  $ka_H \gg 1$  the cross-section is of the order  $\sigma = 4\pi/k^2 \ll a_H^2$  (in both these limiting cases the Born formula is valid).

The atomic structure factor can be written as

$$n(\boldsymbol{q}) = \int d\boldsymbol{r} n(\boldsymbol{r}) e^{-i\boldsymbol{q}\boldsymbol{r}} = \sum_{i} \int d\boldsymbol{r} \delta(\boldsymbol{r} - \boldsymbol{r}_{i}) e^{-i\boldsymbol{q}\boldsymbol{r}} = \sum_{i} e^{i\boldsymbol{q}\boldsymbol{r}_{i}} , \quad (2.20)$$

where the summation is peformed over all the positions  $\mathbf{r}_i$  of the electrons in the atom (these positions are meaningful for heavy atoms, where the Thomas-Fermi theory is valid). At the point  $\mathbf{r}$  the incident wave and the scattered wave interfere, with a phase factor  $e^{-i\mathbf{k}'(\mathbf{r}-\mathbf{r}_i)}e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}_i)} = e^{i\mathbf{q}\mathbf{r}}e^{-i\mathbf{q}\mathbf{r}_i}$ . We can see that the structure factor controls the interference of the two waves. The extension of the heavy atoms is of the order  $a_H$  (with most of the electrons localized around the distance  $a_H/Z^{1/3}$ ). For  $qa_H/Z^{1/3} \ll 1$  the form-factor is  $n(\mathbf{q}) = Z$ ; all the electrons contribute with the same (vanishing) phase to the interference; we say that we have a coherent scattering. For  $qa_H/Z^{1/3} \gg 1$  the form-factor decreases considerably as  $Z^{5/3}/(qa_H)^2$ ; we say that we have an incoherent scattering. The Thomas-Fermi density is  $n(r) = (\kappa^2/4\pi)\frac{Z}{r}e^{-\kappa r}$ , where  $\kappa \simeq 0.85Z^{1/3}/a_H$  is the Thomas-Fermi screening wavevector.<sup>6</sup>

### 2.2 An exact solution

Let us assume a potential U given by a  $\delta$ -function of the form

$$U(\mathbf{r}) = a^3 U_0 \delta(\mathbf{r}) \quad , \tag{2.21}$$

<sup>&</sup>lt;sup>6</sup>M. Apostol, Structure of Matter, Nova, NY (2019).

where a is its range. Equation (2.1) reads

$$\Delta \psi + k^2 \psi = \frac{2ma^3 U_0}{\hbar^2} \delta(\mathbf{r}) \psi \quad , \tag{2.22}$$

with the solution  $\psi = \psi_i + \psi_s$ , where the scattered wave is given by

$$\Delta \psi_s + k^2 \psi_s = \frac{2ma^3 U_0}{\hbar^2} \delta(\mathbf{r}) \left[ \psi_i(0) + \psi_s(0) \right] .$$
 (2.23)

The solution is

$$\psi_s(\mathbf{r}) = -\frac{ma^3 U_0}{2\pi\hbar^2} \left[\psi_i(0) + \psi_s(0)\right] \frac{e^{ikr}}{r} \quad , \tag{2.24}$$

whence

$$\psi_s(0) = -\frac{ma^2 U_0 / 2\pi\hbar^2}{1 + ma^2 U_0 / 2\pi\hbar^2} \psi_i(0)$$
(2.25)

and

$$\psi_s(\mathbf{r}) = -a \frac{ma^2 U_0 / 2\pi\hbar^2}{1 + ma^2 U_0 / 2\pi\hbar^2} \psi_i(0) \frac{e^{ikr}}{r} . \qquad (2.26)$$

The scattering amplitude is

$$F = -a \frac{ma^2 U_0 / 2\pi\hbar^2}{1 + ma^2 U_0 / 2\pi\hbar^2} . \qquad (2.27)$$

We can see that for a  $\delta$ -potential the scattering is isotropic (it does not depend on  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ ). For  $ma^2 |U_0| / 2\pi\hbar^2 \ll 1$  we get the Born amplitude  $F = -ma^3U_0/2\pi\hbar^2$  (equation (2.14)). For  $ma^2 |U_0| / 2\pi\hbar^2 \gg 1$  the scattering amplitude is F = -a. It is worth noting that there exists a singularity in the scattering amplitude for a resonant scattering by attractive potentials.

For resonant scattering it is important to keep the phase factor  $e^{ika}$  in equation (2.25), especially for small values of ka. The scattering amplitude becomes

$$F = \frac{1}{-\frac{1+u}{u}a^{-1} - ik} , \qquad (2.28)$$

where  $u = ma^2 U_0 / 2\pi \hbar^2$ . This is the Wigner formula. au/(1+u) is the scattering length.<sup>7</sup>

<sup>&</sup>lt;sup>7</sup>See M. Apostol, *Theory of Quanta*, Nova, NY (2019) and the References therein.

## 2.3 Momentum transfer

The scattered particle receives an additional momentum  $\hbar(\mathbf{k}' - \mathbf{k})$ . Since the total momentum is conserved the target receives a momentum  $\hbar(\mathbf{k} - \mathbf{k}')$ . This is the momentum transfer to the target.

Let us assume two colliding particles, denoted by 1 and 2, with masses  $m_{1,2}$ , interacting with a potential energy U(1-2). Their wavefunction satisfies the Schroedinger equation

$$\left(-\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2\right)\psi + U(1-2)\psi = E\psi \ . \tag{2.29}$$

The initial wavefunction is the product of two free plane waves  $\psi_{i1,2} = \frac{1}{\sqrt{v}}e^{i\mathbf{k}_{1,2}\mathbf{r}_{1,2}}$ ,

$$\psi_i = \psi_{i1}\psi_{i2} = \frac{1}{V}e^{i\mathbf{k}_1\mathbf{r}_1}e^{i\mathbf{k}_2\mathbf{r}_2} \quad , \tag{2.30}$$

which satisfies the Schroedinger equation

$$\left(-\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2\right)\psi_{i1}\psi_{i2} = = E\psi_{i1}\psi_{i2} = (E_1 + E_2)\psi_{i1}\psi_{i2} , \qquad (2.31)$$

where  $E_{1,2} = \hbar^2 k_{1,2}^2 / 2m_{1,2}$  are the energies of the two particles. We assume that the collision is elastic, *i.e.* each particle preserves its energy. In the first order of the perturbation theory the scattered wave satisfies the Schroedinger equation

$$\left(\frac{\hbar^2}{2m_1}\Delta_1 + \frac{\hbar^2}{2m_2}\Delta_2\right)\psi_s + (E_1 + E_2)\psi_s = U(1-2)\psi_{i1}\psi_{i2} \ . \ (2.32)$$

We are interested in a solution for a large separation distance between the particles, such that the scattered wave is separated, *i.e.*  $\psi_s = \psi_{s1}\psi_{s2}$ , where  $\psi_{s1,2} = \frac{1}{\sqrt{V}}e^{ik'_{1,2}r_{1,2}}$  are two free plane waves. This approximation brings small errors of higher orders in the interaction. Let us assume that we are interested in the scattering of the particle 1 off the particle 2. Equation (2.32) becomes

$$\frac{\hbar^2}{2m_1}\Delta_1\psi_{s1}\cdot\psi_{s2} + E_1\psi_{s1}\cdot\psi_{s2} = U(1-2)\psi_{i1}\psi_{i2} \quad , \tag{2.33}$$

or

$$\Delta_1 \psi_{s1} + k_1^2 \psi_{s1} = \frac{2m_1}{\hbar^2} \int d\mathbf{r}_2 \psi_{2s}^* U(1-2) \psi_{i2} \cdot \psi_{i1} . \qquad (2.34)$$

The solution of this equation is

$$\psi_{s1}(\boldsymbol{r}_{1}) = -\frac{m_{1}}{2\pi\hbar^{2}} \frac{e^{ik_{1}r_{1}}}{r_{1}} \cdot$$

$$\cdot \int d\boldsymbol{r}_{1}^{'} d\boldsymbol{r}_{2} \psi_{2s}^{*} U(\boldsymbol{r}_{1}^{'} - \boldsymbol{r}_{2}) \psi_{i2} \cdot \psi_{i1}(\boldsymbol{r}_{1}^{'}) e^{-i\boldsymbol{k}_{1}^{'}\boldsymbol{r}_{1}^{'}} , \qquad (2.35)$$

or

$$\psi_{s1}(\mathbf{r}_1) = -\frac{m_1}{2\pi\hbar^2 V \sqrt{V}} \frac{e^{ik_1 \mathbf{r}_1}}{r_1} \cdot d\mathbf{r}_2 e^{-i(\mathbf{k}_2' - \mathbf{k}_2)\mathbf{r}_2} U(\mathbf{r}_1' - \mathbf{r}_2) e^{-i(\mathbf{k}_1' - \mathbf{k}_1)\mathbf{r}_1'} , \qquad (2.36)$$

which can also be written as

٠ſ

· |

$$\psi_{s1}(\boldsymbol{r}_{1}) = -\frac{m_{1}}{2\pi\hbar^{2}V\sqrt{V}} \frac{e^{i\boldsymbol{k}_{1}\boldsymbol{r}_{1}}}{r_{1}} \cdot$$

$$\cdot d\boldsymbol{r}_{1}' d\boldsymbol{r}_{2} e^{-i[(\boldsymbol{k}_{2}'-\boldsymbol{k}_{2})+(\boldsymbol{k}_{1}'-\boldsymbol{k}_{1})]\boldsymbol{r}_{2}} U(\boldsymbol{r}_{1}') e^{-i(\boldsymbol{k}_{1}'-\boldsymbol{k}_{1})\boldsymbol{r}_{1}'} .$$
(2.37)

The scattering amplitude is

$$F = -\frac{m_1}{2\pi\hbar^2} \delta_{\mathbf{k}_2' - \mathbf{k}_2, \mathbf{k}_1 - \mathbf{k}_1'} \int d\mathbf{r} U(\mathbf{r}) e^{-i(\mathbf{k}_1' - \mathbf{k}_1)\mathbf{r}'} .$$
(2.38)

We can see that the total momentum is conserved, *i.e.*  $\mathbf{k}'_1 + \mathbf{k}'_2 = \mathbf{k}_1 + \mathbf{k}_2$ . The momentum transferred to the particle 2 (the target) is  $\mathbf{q} = \mathbf{k}'_2 - \mathbf{k}_2 = \mathbf{k}_1 - \mathbf{k}'_1$ . Leaving aside the factor of momentum conservation, equation (2.38) gives the scattering amplitude of the particle 1. The deviation angle  $\theta'$  of the particle 2 with respect to the collision direction, *i.e.* the angle between  $\mathbf{q}$  and  $\mathbf{k}_1$  ( $\theta' = (\mathbf{q}, \mathbf{k}_1)$ ) is given by  $qk_1 \cos \theta' = 2k_1^2 \sin^2(\theta/2)$ , where  $\theta = (\mathbf{k}'_1, \mathbf{k}_1)$  is the deviation angle of the scattered particle. From  $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}'_1$  we get  $q = 2k_1 \sin(\theta/2)$ , such that  $\cos \theta' = \sin(\theta/2)$  and  $\theta' = \frac{1}{2}(\pi - \theta)$ .

The momentum transfer to the target is  $\hbar(\mathbf{k} - \mathbf{k}')$ . The number of collisions per unit time in the solid angle do is  $\frac{\hbar k}{mV} |F|^2 do$ . Therefore, the force acting upon the target is

$$\boldsymbol{f} = \frac{\hbar^2 k}{mV} \int (\boldsymbol{k} - \boldsymbol{k}') \mid F \mid^2 do . \qquad (2.39)$$

If the scattering amplitude depends only on the angle  $\theta$  between k and k' (and k), then the force has only one component along the forward direction, say the z-direction, given by

$$f_z = \frac{\hbar^2 k^2}{mV} \int (1 - \cos\theta) |F|^2 d\sigma , \qquad (2.40)$$

or

$$f_z = \frac{\hbar^2 k^2}{mV} \int (1 - \cos\theta) d\sigma \ . \tag{2.41}$$

The integral in this equation is called the transport cross-section. For a  $\delta$ -potential  $U = a^3 U_0 \delta(\mathbf{r})$  the force is

$$f_z = \frac{\hbar^2 k^2 a^2}{\pi m V} \left(\frac{m a^2 U_0}{\hbar^2}\right)^2 ; \qquad (2.42)$$

 $f_z/a^2$  is the pressure exerted by the projectile upon the target. The volume V in the denominator of this equation arises from the normalization of one particle in the volume V. If we have  $N_i$  incoming particles in the volume V the factor  $n_i = N_i/V$  appears in equation (2.42) instead of 1/V. The flux density of the incoming particles is  $S = vn_i$ , where v is the particle velocity. Usual values of the flux density are of the order  $10^{12}/cm^2 \cdot s$ . For the collision of an electron by an atom the force is  $f_z \simeq 4\pi n_i (\alpha^2/E) \ln(2\hbar v/e^2)$ , where  $\alpha = Ze^2$ , E is the energy of the electron and v is its velocity ( $\hbar v \gg e^2$ ); the screening coefficient is  $\gamma = 1/a_H$ . This is related to the stopping power of charged particles in matter.<sup>8</sup>

### 2.4 Beam

Usually, the particle beams are prepared as a set of identical, independent particles, propagating along the beam direction, with the same velocity for monoenergetic beams. Each particle has an uncertainty along the transverse direction of the order of the atomic distance a, at most, since they are extracted from solid targets. The dispersion

<sup>&</sup>lt;sup>8</sup>H. Bethe, "Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie", Ann. Phys. 5 325 (1930).

angle of the beam is  $\theta \simeq \lambda/a \ll 1$ , at most, where  $\lambda$  is the wavelength along the beam direction. Being localized along the transverse direction the statistics of the beam particles is irrelevant. Indeed, the wavevector k in the wavefunction

$$e^{-i\frac{\hbar k^2}{2m}t + i\mathbf{k}\mathbf{r}} \tag{2.43}$$

has an uncertainty q, such that  $k = k_0 + q$ , where  $k_0$  is the central wavevector of the beam along the beam direction. The wavefunction reads

$$e^{-i\frac{\hbar k_0^2}{2m}t + i\mathbf{k}_0 \mathbf{r}} e^{-i(\mathbf{v}_0 t - \mathbf{r})\mathbf{q} - i\frac{\hbar t}{2m}q^2} , \qquad (2.44)$$

where  $\boldsymbol{v}_0 = \hbar \boldsymbol{k}_0/m$  is the group velocity. For short times we may leave aside the quadratic  $q^2$ -term and integrate with respect to all  $\boldsymbol{q}$ ; the wavefunction is proportional to

$$\delta(\boldsymbol{r} - \boldsymbol{v}_0 t) ; \qquad (2.45)$$

we can see that the particle is localized and propagates with the velocity  $v_0$ . This is a wavepacket. The  $\delta$ -function in equation (2.45) should be read as  $1/a^3$  around the point  $\mathbf{r} = \mathbf{v}_0 t$ , where a is a distance of the order of the atomic distances. Actually, for longer times we cannot neglect the quadratic term, so the integration reads in fact

$$\int d\boldsymbol{q}_{\perp} e^{-i\frac{\hbar t}{2m}q_{\perp}^2} \cdot e^{i\frac{mR^2}{2\hbar t}} \cdot \int dq_{\parallel} e^{-i\frac{\hbar t}{2m}(q_{\parallel} - mR/\hbar t)^2} , \qquad (2.46)$$

where  $\mathbf{R} = \mathbf{r} - \mathbf{v}_0 t$ ,  $q_{\parallel}$  is the longitudinal component of  $\mathbf{q}$  and  $q_{\perp}$  is the transverse component of  $\mathbf{q}$  with respect to  $\mathbf{R}$ . This wavefunction is proportional to

$$(m/\hbar t)^{3/2} e^{i \frac{mR^2}{2\hbar t}}$$
; (2.47)

it goes to zero for long times and has a relevant oscillation for distances of the order  $\Delta R = (\hbar t/m)^{1/2}$ . We can see that the localization is lost, and the particle position exhibits a dispersion. The distance  $\Delta R$  is very small for collision durations. The integration over the whole range of  $\boldsymbol{q}$  in the above equations brings small errors, since the imaginary exponentials with quadratic exponents in  $q_{\perp,\parallel}$  vary very rapidly.

The wavefunction of the beam is a multiparticle wavefunction  $\psi = \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)...$ , with the same  $\varphi$  for each particle (monoenergetic beam) where  $\mathbf{r}_i$ ,  $i = 1, 2, ..., N_i$  are the positions of the  $N_i$  particles in the beam. The potential energy is  $\sum_i U(\mathbf{r}_i)$ . The Schroedinger equation

$$\left(-\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - ...\right)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)...+$$

$$+\sum_i U(\mathbf{r}_i)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)... = N_i E\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)...$$
(2.48)

is reduced to a one-particle Schroedinger equation

$$-\frac{\hbar^2}{2m}\Delta\varphi(\mathbf{r}) + U(\mathbf{r})\varphi(\mathbf{r}) = E\varphi(\mathbf{r}) . \qquad (2.49)$$

Alternatively, instead of multi-particle wavefunctions it is convenient to use the field

$$\psi(\mathbf{r}) = \sqrt{N_i}\varphi(\mathbf{r}) \tag{2.50}$$

normalized to the number of particles in the beam. The incident field is \_\_\_\_\_

$$\psi(\mathbf{r}) = \sqrt{\frac{N_i}{V}} e^{i\mathbf{k}\mathbf{r}} . \qquad (2.51)$$

The field satisfies the Schroedinger equation (2.49). The one-particle operators  $\sum_i O(\mathbf{r}_i)$  are written as  $\int d\mathbf{r}\psi^*(\mathbf{r})O(\mathbf{r})\psi(\mathbf{r})$ . The scattered field acquires a factor  $\sqrt{N_i/V}$ , the scattered current acquires a factor  $n_i = N_i/V$ , which is the density of particles in the beam. The same factor appears in the incident current, such that the cross-section remains unchanged, as expected. The number of collisions per unit time acquires a factor  $n_i$ , which appears, for instance, in equation (2.39) (the momentum transfer and the force).

### 2.5 Quantum transitions

Apart from a momentum transfer there exists also an energy transfer to the target. In order to account for the energy transfer we need the time-dependent Schroedinger equation. Let us assume a target and an

incident beam, described by a field  $\psi_i$  (or a one-particle wavefunction) which satisfies the Schroedinger equation

$$i\hbar \frac{\partial \psi_i}{\partial t} = (H_0 + H_1)\psi_i ; \qquad (2.52)$$

this equation includes the degrees of freedom of both the projectile and the target, including the internal degrees of freedom. If the internal structure of these entities is not changed, the collision is elastic; if their internal structure is changed, the collision is inelastic. The hamiltonian  $H_0$  is the free hamiltonian, while  $H_1$  is the interaction hamiltonian;  $H_1$  may depend on time. The label *i* stands for the initial state. We can check immediately that the solution of this equation is

$$\psi_i = \psi_i^0 - \frac{i}{\hbar} e^{-\frac{i}{\hbar}H_0 t} \int_0^t dt_1 e^{\frac{i}{\hbar}H_0 t_1} H_1 \psi_i \quad , \tag{2.53}$$

where  $\psi_i^0$  is the initial field without interaction, satisfying the equation

$$i\hbar \frac{\partial \psi_i^0}{\partial t} = H_0 \psi_i^0 ; \qquad (2.54)$$

we write this field as

$$\psi_i^0 = e^{-\frac{i}{\hbar}E_i t} \varphi_i^0 \quad , \tag{2.55}$$

where  $E_i$  is the initial energy of the assembly and  $\varphi_i^0$  is the free initial field without time dependence. The lower limit t = 0 in equation (2.53) is misleading, because we still preserve the time dependence in  $\psi_i^0$ . However, for the upper limit going to infinity  $(t \to \infty)$  this is a correct assumption. The second term on the right in equation (2.53) is the scattered wave. We are interested in the content of a final free state  $\psi_f$ , with an energy  $E_f$  at  $t \to \infty$ ,

$$\psi_f = e^{-\frac{i}{\hbar}E_f t} \varphi_f \quad , \tag{2.56}$$

in the scattered state, *i.e.* we are interested in the matrix element

$$c_{fi} = -\frac{i}{\hbar} \left( \psi_f, \, e^{-\frac{i}{\hbar}H_0 t} \int_0^{t \to \infty} dt_1 e^{\frac{i}{\hbar}H_0 t_1} H_1 \psi_i \right) \,. \tag{2.57}$$

This is the scattering matrix.<sup>9</sup> We write iteratively the first two contributions to  $c_{fi} = c_{fi}^{(1)} + c_{fi}^{(2)}$ :

$$c_{fi}^{(1)} = -\frac{i}{\hbar} \left( \psi_f, e^{-\frac{i}{\hbar}H_0 t} \int_0^{t \to \infty} dt_1 e^{\frac{i}{\hbar}H_0 t_1} H_1 \psi_i^0 \right)$$
(2.58)

and

$$c_{fi}^{(2)} = \left(-\frac{i}{\hbar}\right)^2 \left(\psi_f, e^{-\frac{i}{\hbar}H_0 t} \int_0^{t \to \infty} dt_1 e^{\frac{i}{\hbar}H_0 t_1} H_1 e^{-\frac{i}{\hbar}H_0 t_1} \cdot \int_0^{t_1} dt_2 e^{\frac{i}{\hbar}H_0 t_2} H_1 \psi_i^0\right);$$
(2.59)

by introducing the temporal factors we get

$$c_{fi}^{(1)} = -\frac{i}{\hbar} (H_1)_{fi} \int_0^{t \to \infty} dt_1 e^{\frac{i}{\hbar} (E_f - E_i) t_1}$$
(2.60)

and

$$c_{fi}^{(2)} = \left(-\frac{i}{\hbar}\right)^2 \sum_n (H_1)_{fn} (H_1)_{ni} \cdot \\ \cdot \int_0^{t \to \infty} dt_1 e^{\frac{i}{\hbar} (E_f - E_n) t_1} \int_0^{t_1} dt_2 e^{\frac{i}{\hbar} (E_n - E_i) t_2} , \qquad (2.61)$$

where n denotes the intermediate states. The energies include all the contributions of the assembly. If  $H_1$  depends on the time through factors like  $e^{\pm i\omega t}$ , these factors appear in the time exponentials, which read

$$e^{\frac{i}{\hbar}(E_f - E_i \mp \hbar\omega)t_1}$$
,  $e^{\frac{i}{\hbar}(E_f - E_n \mp \hbar\omega)t_1}$ ,  $e^{\frac{i}{\hbar}(E_n - E_i \mp \hbar\omega)t_2}$ . (2.62)

The squared coefficients  $|c_{fi}|^2$  are the number of transitions from the initial state *i* to the final state *f*. The time factor in equation (2.60) is

$$\int_{0}^{t} dt_{1} e^{\frac{i}{\hbar} (E_{f} - E_{i})t_{1}} = \frac{e^{i\Delta\omega t} - 1}{i\Delta\omega} , \qquad (2.63)$$

where  $\Delta \omega = (E_f - E_i)/\hbar$ ; its square is

$$\frac{\sin^2(\Delta\omega t/2)}{(\Delta\omega t/2)^2} \to_{t \to \infty} \pi t \delta(\Delta\omega/2) = 2\pi\hbar t \delta(E_f - E_i) \quad , \qquad (2.64)$$

<sup>&</sup>lt;sup>9</sup>J. A. Wheeler, "On the mathematical description of light nuclei by the method of resonating group structure", Phys. Rev. **52** 1107 (1937); W. Heisenberg, "Die "beobachtbaren Grossen" in der Theorie der Elementarteilchen", Z. Phys. **120** 513 (1943).

which leads to a number of transitions per unit time

$$w_{fi}^{(1)} = \left| c_{fi}^{(1)} \right| / t = \frac{2\pi}{\hbar} \left| (H_1)_{fi} \right|^2 \delta(E_f - E_i) .$$
 (2.65)

This is Fermi's golden rule.

The matrix element  $(H_1)_{fi}$  is of the order  $u\delta E/V$ , where u is the volume over which the perturbation  $\delta E$  is active. For a discrete spectrum  $\delta(E_f - E_i)$  is of the order of the inverse spacing  $1/\Delta E$  of the energy levels. The total number of transitions given by equation (2.65) is of the order  $\frac{u^2}{V^2} \frac{\delta E}{\hbar} \frac{\delta E}{\Delta E} \cdot \frac{l}{v}$ , where  $V = l^3$  and v is the velocity of the scattered particles. The ratio  $\delta E/\Delta E$  is much smaller than unity, because the interaction is a small perturbation; the ratio  $\delta E/\hbar$  is the inverse of the time uncertainty  $1/\delta t$  produced by interaction, which is much smaller than the inverse time v/l, if the measurement of the collision is realized. We can see that the total number of scattered particles is much smaller than the total number of incident particles; mainly, this is due to the very small factor u/V. For a continuous spectrum we need to multiply by  $Vk^2\Delta k$ , such that, instead of  $\frac{\delta E}{\Delta E}$ , we get  $\frac{V}{\lambda^3} (\delta E/E)$ , where  $\lambda$  is the particle wavelength and E is the particle energy; we should have  $\delta E/E \ll 1$ , because the interaction is a small perturbation. The inequality loses a factor 1/V, but still it is fulfilled. If the wavefunctions are normalized to the number of particles N, the above inequality reads  $\frac{N^2 u^2}{V^2} \frac{\delta E}{\hbar} \frac{\delta E}{\Delta E} \cdot \frac{l}{N^{1/3}v} \ll N$ , which is again fulfilled, in the limit  $N, V \to \infty, N/V = const$ .

For the second contribution  $c_{fi}^{(2)}$  the integration with respect to  $t_2$  is over finite times, so the lower limit  $t_2 = 0$  is improper. Actually, the interaction is vanishing at  $t \to -\infty$ , which requires a factor  $e^{\alpha t}$ , where  $\alpha \to 0^+$ . This is the adiabatic hypothesis. Equation (2.63) reads

$$\int_{-\infty}^{t} dt_1 e^{\frac{i}{\hbar}(E_f - E_i)t_1 + \alpha t_1} = \frac{e^{i\Delta\omega t + \alpha t}}{i\Delta\omega + \alpha} , \qquad (2.66)$$

whose square is

$$\frac{e^{2\alpha t}}{\Delta\omega^2 + \alpha^2} \ . \tag{2.67}$$

In order to get the number of transitions per unit time we need to