

# Quantum Physics III

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# Chapter 1

## The semiclassical approximation to quantum mechanics

In this chapter, we will describe the general features of the classical limit of quantum mechanics and present a systematic method of approximation that allows to account in a very simple and efficient way for small quantum effects. This semiclassical approximation allows to find a general approximate form of the wave function describing a quantum system in a quasi classical regime, expressed in terms of quantities describing the classical motion, even in situations where the exact quantum mechanical wave function cannot be found exactly. This is true both in classically allowed regions, where the wave function is an oscillating wave with a sizable amplitude, and in classically forbidden regions, where the wave function is instead an exponentially damped function. The joining of these two kinds of behaviors across classical turning points of the motion requires some care, and the precise gluing prescription must be derived by studying the exact wave function in the vicinity of such a turning point, where the potential can be linearized.

### 1.1 The Hamilton-Jacobi description of classical mechanics

In the Lagrangian formulation of mechanics, a system is described in terms of a Lagrangian functional  $L$  depending on the variables  $q^i(t)$  and the corresponding velocities  $\dot{q}^i(t)$ , besides the time  $t$ :

$$L = L(q^i, \dot{q}^i, t). \quad (1.1.1)$$

In terms of this function, the equations of motions are rewritten as Euler-Lagrange equations, which are  $n$  ordinary differential equations of the second order in time:

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}^i} \right) - \frac{\partial L}{\partial q^i} = 0. \quad (1.1.2)$$

These equations can also be derived from a variational principle: the Hamilton principle. This is based on an action functional obtained by integrating the Lagrangian for an arbitrary path  $q^i(t)$  with the only constraint that its values at some initial and final times  $t_1$

and  $t_2$  are held fixed to some  $q_1^i$  and  $q_2^i$ :

$$I = \int_{t_1}^{t_2} L dt, \quad (1.1.3)$$

The classical trajectory then corresponds to the configuration  $q^i(t)$  that extremizes the above action functional. More precisely, the Euler-Lagrange equations are equivalent to the requirement that the action must be stationary with respect to a generic synchronous variation  $\delta$  of the path  $q^i(t)$  connecting the two fixed end-points:

$$\delta I = 0. \quad (1.1.4)$$

From this variational formulation, it becomes obvious that the Lagrangian function is not uniquely defined, even once a definite parametrization of the problem has been chosen. Indeed, two Lagrangians that differ by the total time-derivative of an arbitrary function  $F$  lead to actions that differ only by the difference of this function at the two end-points, and since at those points the variation  $\delta$  is defined to vanish, these two actions lead to the same equations of motion. Such an ambiguity has however no really interesting consequences in this formulation.

In the Hamiltonian formulation of mechanics, the system is instead described by a Hamiltonian functional  $H$ , which is obtained by performing the Legendre transform of the Lagrangian and depends on the variables  $q^i(t)$  and the canonical momenta  $p^i(t)$  conjugate to the velocities  $\dot{q}^i(t)$ , besides the time  $t$ :

$$H = p_i \dot{q}^i - L = H(q^i, p_i, t), \quad (1.1.5)$$

with

$$p_i = \frac{\partial L}{\partial \dot{q}^i}. \quad (1.1.6)$$

In terms of this function, the equations of motions are rewritten as Hamilton equations, which are  $2n$  ordinary differential equations of the first order in time:

$$\dot{q}^i - \frac{\partial H}{\partial p^i} = 0, \quad (1.1.7)$$

$$\dot{p}^i + \frac{\partial H}{\partial q^i} = 0. \quad (1.1.8)$$

These equations can again be derived from a variational principle: the modified Hamilton principle. This is based on the same action functional as before, but now rewritten by expressing the Lagrangian in terms of the Hamiltonian and interpreting it as a functional of the variables  $q^i(t)$  and the momenta  $p_i(t)$ , which are now to be considered as independent variables:

$$I = \int_{t_1}^{t_2} (p_i \dot{q}^i - H) dt, \quad (1.1.9)$$

The classical trajectory then corresponds to the configuration  $(q^i(t), p_i(t))$  that extremizes the above action functional. More precisely, the Hamilton equations are equivalent to the

requirement that the action must be stationary with respect to generic and independent synchronous variations  $\delta$  of both the path  $q^i(t)$  connecting the two fixed end-points and the momenta  $p_i(t)$ :

$$\delta I = 0. \tag{1.1.10}$$

Again, from this variational formulation, it becomes clear that the canonical momenta and the Hamiltonian function are actually not uniquely defined, even once a definite choice for the coordinates has been made. This is related to the fact that already the Lagrangian was in fact defined modulo the total time-derivative of an arbitrary function  $F$ . In this formulation, it turns out that one can actually exploit this fact in a rather interesting way.

One may at this point consider general reparametrizations of the phase space, which correspond to switching from the variables  $(q^i, p_i)$  to some new variables  $(Q^i, P_i)$ :

$$Q^i = Q^i(q^j, p_j), \tag{1.1.11}$$

$$P_i = P_i(q^j, p_j). \tag{1.1.12}$$

The subset of these transformations that are of interest are the canonical transformations. These are defined by the requirement that the new equations of motion for  $(Q^i, P_i)$  retain the same form as the original Hamilton equations for  $(q^i, p_j)$ , but with some new function  $K(Q^i, P_i)$  replacing the Hamiltonian  $H(q^i, p_i)$ :

$$\dot{Q}^i - \frac{\partial K}{\partial P_i} = 0, \tag{1.1.13}$$

$$\dot{P}^i + \frac{\partial K}{\partial Q_i} = 0. \tag{1.1.14}$$

Recalling the variational formulation, we know that these new equations follow from the stationarity of an action based on the functional  $P_i \dot{Q}^i - K$ , while the original Hamilton equations follow from the stationarity of an action based on the Lagrangian  $p_i \dot{q}^i - H$ . In order for the two sets of equations to coincide, the above two functionals must then differ at most by the total time-derivative of an arbitrary function  $F$ :

$$(K - P_i \dot{Q}^i) - (H - p_i \dot{q}^i) = \dot{F}. \tag{1.1.15}$$

The function  $F$  can depend only on half of all the variables  $q^i, Q^i, p_i, P_i$ , in addition to time, because it should be possible to interpret it both as a function of the old phase space variables and of the new ones, separately. There are then four distinct possibilities, which correspond to chose  $F$  to depend on the variables  $(q^i, Q^i)$ ,  $(q^i, P_i)$ ,  $(p_i, Q^i)$  or  $(p_i, P_i)$ , besides time. For each choice, one may make the form of the total time-derivative  $\dot{F}$  more explicit and plug it back into the constraint (1.1.15). One then finds an equation with two terms that multiply the time derivative of each of the two variables on which  $F$  depends, plus a term that does not depend on time derivatives of these variables. These three terms must then vanish independently, and this fixes the relation between the pair of variables on which  $F$  depends and the other pair, and also the relation between  $K$  and  $H$ . After suitably parametrizing the function  $F$  in terms of some other generating functions  $F_1, F_2$ ,



$F_3$  and  $F_4$ , plus some explicit quadratic functions of the involved variables, one finds that these four types of canonical transformations take the following forms:

$$F_1 = F_1(q^i, Q^i, t) : p_i = +\frac{\partial F_1}{\partial q^i}, \quad P_i = -\frac{\partial F_1}{\partial Q^i}, \quad K = H + \frac{\partial F_1}{\partial t}, \quad (1.1.16)$$

$$F_2 = F_2(q^i, P_i, t) : p_i = +\frac{\partial F_2}{\partial q^i}, \quad Q^i = +\frac{\partial F_2}{\partial P_i}, \quad K = H + \frac{\partial F_2}{\partial t}, \quad (1.1.17)$$

$$F_3 = F_3(p_i, Q^i, t) : q^i = -\frac{\partial F_3}{\partial p_i}, \quad P_i = -\frac{\partial F_3}{\partial Q^i}, \quad K = H + \frac{\partial F_3}{\partial t}, \quad (1.1.18)$$

$$F_4 = F_4(p_i, P_i, t) : q^i = -\frac{\partial F_4}{\partial p_i}, \quad Q^i = -\frac{\partial F_4}{\partial P_i}, \quad K = H + \frac{\partial F_4}{\partial t}. \quad (1.1.19)$$

In the Hamilton-Jacobi formulation, the dynamics of a mechanical system is described in yet a different way, in terms of a principal function  $S$  depending only on the variables and time, and not on the velocities or momenta. This approach proves to be illuminating to understand the classical limit of quantum mechanics. The method to set it up consists in looking for a canonical transformation generated by a function  $F = S$  such that the new variables  $Q^i$  and  $P_i$  are constant:

$$Q^i(q^i, p_i) = Q_0^i, \quad (1.1.20)$$

$$P_i(q^i, p_i) = P_0^i. \quad (1.1.21)$$

This implies that  $\dot{Q}^i = 0$  and  $\dot{P}_i = 0$ , and the new Hamiltonian  $K$  should therefore be a constant. Requiring this to be zero, without loss of generality, one must then have:

$$H(q^i, p_i, t) + \frac{\partial S}{\partial t} = 0. \quad (1.1.22)$$

In this formulation, the dynamics is then entirely contained in the canonical transformation, and solving the problem is equivalent to finding the explicit form of this transformation, that is the generating function  $S$ . To do so, one has to choose one of the four concrete types of canonical transformations listed above. It is convenient to choose the second one, and therefore choose the generating function to depend on the old non-constant coordinates  $q^i$  and the new constant momenta  $P_i$ :  $S = S(q^i, P_i, t)$ . One then finds that:

$$p_i = \frac{\partial S}{\partial q^i}. \quad (1.1.23)$$

Plugging this into eq. (1.1.22), one then deduces that the generating function  $S$  must satisfy the Hamilton-Jacobi equation:

$$H\left(q^i, \frac{\partial S}{\partial q_i}, t\right) + \frac{\partial S}{\partial t} = 0. \quad (1.1.24)$$

This is a single first-order partial differential equation in the  $n$  variables  $q^i$  and time  $t$ , for given values of the variables  $P_i$  which are constants. This fully determines the dependence of  $S$  on the variables  $q^i$  and time, for fixed values of the constant  $P_i$ . Besides an irrelevant additive constant, the general solution then involves  $n$  integration constants

and  $n$  constant values of  $P^i$ , which altogether can be mapped to the  $2n$  initial values  $q_0^i$  and  $p_{0i}$  of the  $q^i$  and the  $p_i$ . One finally verifies that the functional form of  $S$  is formally related to the indefinite action obtained by integrating  $L$  over time, once the trajectory is known. Indeed, one finds:

$$\frac{dS}{dt} = \frac{\partial S}{\partial q^i} \dot{q}^i + \frac{\partial S}{\partial t} = p_i \dot{q}^i - H = L, \quad (1.1.25)$$

The principal function is then given by the following expression, interpreted as a function of  $q^i$  and  $t$  on the trajectory:

$$S = \int_{t_0}^t L dt'. \quad (1.1.26)$$

In the Hamilton-Jacobi approach, the equations of motions are therefore rewritten as a partial differential equation of a single functional  $S$  of the coordinates  $q^i$ , and the momenta  $p_i$  are given by the gradient of this function.

In the cases where the Hamiltonian  $H$  does not depend explicitly on time and corresponds to the conserved energy  $E$  of the system, things further simplify. One then has:

$$H(q^i, p_i) = E. \quad (1.1.27)$$

In this situation, the usual equations of motion can be derived by an alternative variational principle: the Maupertuis or minimal action principle. This is based on a reduced action functional obtained by integrating the function  $p_i \dot{q}^i$  over time between  $t_1$  and  $t_2$  with the constraint that the considered path should correspond to a fixed constant value  $E$  of the Hamiltonian:

$$A = \int_{t_1}^{t_2} p_i \dot{q}^i dt. \quad (1.1.28)$$

The true trajectory with energy  $E$  then corresponds to the configuration that extremizes the above functional for constant  $H = E$ . More precisely, the equations of motions are equivalent to the requirement that the reduced action must be stationary with respect to generic and independent asynchronous variations  $\Delta$  of both  $q^i(t)$  and  $p_i(t)$ :

$$\Delta A = 0. \quad (1.1.29)$$

In this situation, the Hamilton-Jacobi equation also simplifies, and becomes:

$$H\left(q^i, \frac{\partial S}{\partial q_i}\right) + \frac{\partial S}{\partial t} = 0. \quad (1.1.30)$$

The time dependence can then be separated, and the general form of the solution for the principal function  $S$  becomes:

$$S(q^i, t) = W(q^i) - Et. \quad (1.1.31)$$

The function  $W(q^i)$  is called the characteristic function and does not depend explicitly on time. It satisfies the equation

$$H\left(q^i, \frac{\partial W}{\partial q^i}\right) = E. \quad (1.1.32)$$

This is a single first-order partial differential equation in the  $n$  variables  $q^i$ , for given values of the constant  $P_i$ . This entirely determines the dependence of  $S$  on the original variables  $q^i$ . Besides an irrelevant additive constant there are now  $n - 1$  integration constants and  $n$  parameters, which can be mapped to the  $2n - 1$  initial values  $q_0^i$  and  $p_{0i}$  of the  $q^i$  and the  $p_i$  for a trajectory of given energy  $E$ . One finally verifies that the functional form of  $W$  is formally related to the indefinite reduced action obtained by integrating  $p_i \dot{q}^i$  over time, once the trajectory is known. Indeed, one finds:

$$\frac{dW}{dt} = \frac{\partial W}{\partial q^i} \dot{q}^i = p_i \dot{q}^i, \quad (1.1.33)$$

The characteristic function is then given by the following expression, interpreted as a function of  $q^i$  on the trajectory:

$$W = \int_{t_0}^t p_i \dot{q}^i dt'. \quad (1.1.34)$$

To conclude, let us write more explicitly the functions appearing in the various descriptions reviewed in this section for the case of a particle of mass  $m$  moving in a  $d$ -dimensional space with coordinates  $\vec{x}$ , subject to a conservative force  $\vec{F}(\vec{x}) = -\vec{\nabla}V(x)$ . The Lagrangian and the Hamiltonian then take the usual form  $L = T - V$  and  $H = T + V$ , where the kinetic energy has the minimal form  $T = \frac{1}{2}m\dot{\vec{x}}^2 = \vec{p}^2/(2m)$ , while the potential  $V = V(\vec{x})$  is arbitrary. The canonical momentum is given by  $\vec{p} = m\dot{\vec{x}}$ , and the Lagrangian and Hamiltonian equations of motions are just the usual second order and the decomposed first order versions of the Newtonian equations of motions, which read:

$$\dot{\vec{p}} + \vec{\nabla}V = 0. \quad (1.1.35)$$

When the potential is independent of time, the energy is conserved and the corresponding conservation law reads:

$$\frac{\vec{p}^2}{2m} + V = E. \quad (1.1.36)$$

In the Hamilton-Jacobi formulation, the momentum is given by the gradient of the principal function  $S$ , and the dynamics is governed by the Hamilton-Jacobi partial differential equation for this function, which reads:

$$\frac{\partial S}{\partial t} + \frac{1}{2m}(\vec{\nabla}S)^2 + V = 0. \quad (1.1.37)$$

When the potential is independent of time, the energy is conserved and this leads to the reduced Hamilton-Jacobi equation for the characteristic function  $W$ :

$$\frac{1}{2m}(\vec{\nabla}W)^2 + V = E. \quad (1.1.38)$$

In this case, it is possible to verify explicitly that indeed (1.1.37) is equivalent to (1.1.35), and similarly (1.1.38) is equivalent to (1.1.36). To do so, one needs to use the definition of the momentum as the gradient of a field,  $\vec{p} = \vec{\nabla}S$  or  $\vec{p} = \vec{\nabla}W$ , and exploit the fact that one also has  $\vec{p} = m\dot{\vec{x}}$ . Taking the gradient of (1.1.37), one then reproduces (1.1.35). Indeed, the first two terms give  $\partial/\partial t (\vec{\nabla}S) + (\vec{\nabla}S \cdot \vec{\nabla}) (\vec{\nabla}S)/m = [\partial/\partial t + (\dot{\vec{x}} \cdot \vec{\nabla})] \vec{p} = d/dt \vec{p} = \dot{\vec{p}}$ , while the last term simply gives  $\vec{\nabla}V$ . Equation (1.1.38) is instead directly equivalent to (1.1.36). Indeed, the first term on the left-hand side just gives  $(\vec{\nabla}W)^2/(2m) = \vec{p}^2/(2m)$ .

## 1.2 The classical limit of quantum mechanics

The semiclassical expansion of quantum mechanics is based on the idea that in certain situations one may treat  $\hbar$  as a small quantity and perform a formal expansion in powers of it. This will be a good approximation whenever the relevant quantities in the problem with the dimensions of an action are much larger than  $\hbar$ . This is perfectly analogous to the non-relativistic limit of classical mechanics, in which one treats  $c$  as a large quantity and performs an expansion in inverse powers of it. Such an expansion is in that case a good approximation whenever the velocities in the problem are much smaller than  $c$ .

To study the classical limit of quantum mechanics, let us start from the Schrödinger equation for the wave function  $\psi$  in the presence of a generic potential  $V$ , which we rewrite as:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \psi + V \psi. \quad (1.2.39)$$

Clearly we cannot simply take the brutal limit  $\hbar \rightarrow 0$  of this equation, since by doing so it would lose any sense. The physical reason for this is that in the formal limit  $\hbar \rightarrow 0$  the wave function of a quantum system becomes a rapidly oscillating function in classically accessible regions and a strongly damped function in classically forbidden regions, and it is only its squared norm that tends to a simple smooth function representing the density of probability of finding the classical particle at a given position. One then has to proceed in a slightly more sophisticated way, following a method that was developed by Wentzel, Kramers and Brillouin and is often called the WKB approximation. This consists in parametrizing the wave function in the following way:

$$\psi(\vec{x}, t) = A e^{\frac{i}{\hbar} S(\vec{x}, t)}. \quad (1.2.40)$$

Plugging this parametrization back into the Schrödinger equation, one finds that the complex function  $S$  must satisfy the following differential equation:

$$-\frac{\partial S}{\partial t} = \frac{1}{2m} (\vec{\nabla}S)^2 + V - \frac{i\hbar}{2m} \Delta S. \quad (1.2.41)$$

The brutal limit  $\hbar \rightarrow 0$  of this equation makes now sense, and takes the real form

$$-\frac{\partial S}{\partial t} = \frac{1}{2m} (\vec{\nabla}S)^2 + V. \quad (1.2.42)$$

The equation (1.2.42) that we have obtained as the classical limit of Schrödinger's equation governing the evolution of the quantum mechanical wave function is now recognized to be formally identical to the Hamilton-Jacobi equation

$$-\frac{\partial S}{\partial t} = H(\vec{x}, \vec{p}), \quad (1.2.43)$$

where  $S$  is Hamilton's principal function and the momentum  $\vec{p}$  is the gradient of it:

$$\vec{p} = \vec{\nabla} S. \quad (1.2.44)$$

The formal solution for  $S$  is then the indefinite integral of the Lagrangian  $L$  over time, as seen in previous section:

$$S = \int_{t_0}^t L(\vec{x}, \dot{\vec{x}}, t') dt', \quad (1.2.45)$$

We thus discover that in the formal limit  $\hbar \rightarrow 0$ , the phase  $S$  of the quantum-mechanical wave function describing a generic state maps to the indefinite action  $S$  of the classical trajectory. This implies that in this limit the quantum system can be described by classical trajectories, which are orthogonal to the surfaces of constant  $S$ , since the momentum is the gradient of the latter. We can then say that in the classical limit the behavior of the quantum system defined by the wave function  $\psi = Ae^{\frac{i}{\hbar}S}$  is described by a classical trajectory that is orthogonal to the surfaces of constant phase  $S$ .

The situation further simplifies for stationary configurations. Recall that for a stationary state of definite energy  $E$ , the wave function has a fixed time-dependence and can be written as:

$$\psi(\vec{x}, t) = \phi(\vec{x})e^{-\frac{i}{\hbar}Et}. \quad (1.2.46)$$

The stationary wave function  $\phi(\vec{x})$  then satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\Delta\phi + V\phi = E\phi \quad (1.2.47)$$

To discuss the classical limit, we now proceed as before and parameterize the stationary wave function through a stationary phase, as:

$$\phi(\vec{x}) = Ae^{\frac{i}{\hbar}W(\vec{x})}. \quad (1.2.48)$$

Comparing (1.2.48) with (1.2.40), we see that

$$S(\vec{x}, t) = W(\vec{x}) - Et. \quad (1.2.49)$$

Plugging now the parametrization (1.2.46) into (1.2.47), one finds the complex equation:

$$\frac{1}{2m}(\nabla W)^2 + V - \frac{i\hbar}{2m}\Delta W = E. \quad (1.2.50)$$

The brutal limit  $\hbar \rightarrow 0$  then leads to the real equation

$$\frac{1}{2m}(\nabla W)^2 + V = E. \quad (1.2.51)$$

The equation (1.2.51) corresponds to the reduced Hamilton-Jacobi equation for motions with a given energy  $E$ , that is

$$H(\vec{x}, \vec{p}) = E, \quad (1.2.52)$$

where  $W$  is Hamilton's characteristic function and the momentum  $\vec{p}$  is the gradient of it:

$$\vec{p} = \vec{\nabla} W. \quad (1.2.53)$$

The formal solution for  $W$  is then given by the integral of the phase-space differential, as reviewed in previous section:

$$W = \int_{t_0}^t \vec{p} \cdot \dot{\vec{x}} dt'. \quad (1.2.54)$$

We thus see that in the formal limit  $\hbar \rightarrow 0$ , the phase  $W$  of the quantum-mechanical wave function of a stationary state maps to the indefinite reduced action  $W$  of the classical trajectory. As before, in this limit the quantum system can be described by classical trajectories, which are orthogonal to the surfaces of constant  $W$  since the momentum is the gradient of this function. In the classical limit, the behavior of the quantum system defined by the wave function  $\phi = Ae^{\frac{i}{\hbar}W}$  is thus described by a classical trajectory that is orthogonal to the surfaces of constant phase  $W$ .

It should be emphasized that whenever  $\hbar$  is non-zero, the Schrödinger equation is intrinsically complex and physical states are described by a complex wave function. This suggests that even in the classical limit derived above, where the wave function is parametrized as  $\psi = e^{\frac{i}{\hbar}S}$  or  $\phi = e^{\frac{i}{\hbar}W}$  and the functions  $S$  and  $W$  are determined by a real Hamilton-Jacobi equation, one can nevertheless associate a meaning also to complex solutions for  $S$  and  $W$ . More precisely, we know that the solutions for  $S$  and  $W$  are respectively given by the classical indefinite action and the classical indefinite reduced action, and it turns out that these functions of the coordinates are real in classically allowed regions and imaginary in the classically forbidden regions. As a result, the wave function in the classical limit behaves as a rapidly oscillating wave in the classically allowed regions and a strongly suppressed exponential profile in the classically forbidden regions:

$$\text{Classically allowed regions: rapidly oscillating wave function,} \quad (1.2.55)$$

$$\text{Classically forbidden regions: strongly damped wave function.} \quad (1.2.56)$$

Of course, in the formal limit where one brutally sends  $\hbar \rightarrow 0$ , the wave function can be approximated with a smooth average amplitude that is non-zero only in classically allowed regions and vanishes in classically forbidden regions. To reliably compute the position dependence of this amplitude, one needs however to take into account at least the first subleading correction in the Schrödinger equation. Indeed, subleading corrections to the quantities  $S$  or  $W$  of order  $\hbar$  induce a non-trivial correction to the exponents  $\hbar S$  or  $\hbar W$  of the wave function that is independent of  $\hbar$ , and therefore modulate the amplitude in a significant way.

### 1.3 Validity of the classical approximation

The above argumentation shows the transition from quantum mechanics to classical mechanics is formally perfectly analogous to the transition from wave optics to geometrical optics. In both cases, a wave propagation is traded with a trajectory, the velocity being orthogonal to the wave fronts. We will now see that the classical limit of quantum mechanics is essentially applicable in the regime in which the De Broglie wave length  $\lambda = \hbar/p$  is small compared to the length-scales characterizing the system, very much like the geometrical limit of wave optics is applicable when the optical wave length  $\lambda$  is small compared to the length scales of the problem.

In a generic situation, the condition for the classical approximation to be reliable is that the last term in (1.2.41) that we have dropped to arrive to (1.2.42) should have a negligible effect, in particular with respect to the first term. This implies the condition  $\hbar|\Delta S| \ll (\vec{\nabla}S)^2$ , which can be rewritten as  $\hbar|\vec{\nabla} \cdot \vec{p}| \ll p^2$  since  $\vec{p} = \vec{\nabla}S$ . Similarly, in a stationary situation, the condition for the classical approximation to be reliable is similarly that the last term in (1.2.47) that we have dropped to arrive to (1.2.51) should have a negligible effect, in particular with respect to the first term. This implies that  $\hbar|\Delta W| \ll (\vec{\nabla}W)^2$ , which can again be written as  $\hbar|\vec{\nabla} \cdot \vec{p}| \ll p^2$  since  $\vec{p} = \vec{\nabla}W$ . A general necessary condition for the validity of the semiclassical approximation is therefore that

$$\hbar|\vec{\nabla} \cdot \vec{p}| \ll p^2. \quad (1.3.57)$$

At the quantitative level, this requires in general that  $p$  is large on average and varies slowly from point to point, implying that the De Broglie wave length  $\lambda$  is small and slowly varying, as expected from the analogy with optics. At the quantitative level, these conditions for the applicability of a classical approximation based on trajectories depend on the form of the potential  $V(\vec{x})$  in the quantum theory, very much like they depend on the refraction index in optics.

For one-dimensional systems, the situation further simplifies and the above condition simply reads

$$\frac{\hbar}{p^2} \left| \frac{dp}{dx} \right| \ll 1. \quad (1.3.58)$$

The restriction (1.3.58) can then be rewritten as a condition involving only the De Broglie wave length  $\lambda$ . Indeed, using the relations

$$\lambda = \frac{\hbar}{p}, \quad \frac{d\lambda}{dx} = -\frac{\hbar}{p^2} \frac{dp}{dx}, \quad (1.3.59)$$

one finds that the condition simply becomes the requirement that the De Broglie wave length should vary slowly over space:

$$\left| \frac{d\lambda}{dx} \right| \ll 1. \quad (1.3.60)$$

For a system of finite size  $a$  in which  $\lambda$  does not vary too rapidly, one has  $d\lambda/dx \sim \lambda/a$  and this condition reduces to the requirement that the wave length should be small compared

to the dimensions of the system:

$$|\lambda| \ll a. \quad (1.3.61)$$

The restriction (1.3.58) can also be rephrased in an alternative way as a condition involving the potential. Indeed, the momentum  $p$  is related to the potential by the equation of motion  $dp/dt = -dV/dx$  and also by the relation  $p = \sqrt{2m(V - E)}$ , which both imply that

$$\frac{dp}{dx} = -\frac{m}{p} \frac{dV}{dx}. \quad (1.3.62)$$

Substituting this into (1.3.58) one finds that the potential should vary slowly over space, and more precisely

$$\left| \frac{m\hbar}{p^3} \frac{dV}{dx} \right| \ll 1. \quad (1.3.63)$$

In terms of the force  $F = -dV/dx$ , this implies that the momentum  $p$  should be much larger than  $|m\hbar F|^{1/3}$ , or in other words that the particle should not be too slow:

$$|p| \gg |m\hbar F|^{1/3}. \quad (1.3.64)$$

This finally implies that the De Broglie wave length should be smaller than a certain quantum-mechanical length scale determined by the mass  $m$ , the force  $F$  and the Planck constant  $\hbar$ :

$$|\lambda| \ll \left| \frac{mF}{\hbar^2} \right|^{-1/3}. \quad (1.3.65)$$

## 1.4 The semiclassical expansion

Whenever the quantum effects correcting the behavior of the classical limit are small, one may compute these by using a perturbative expansion. Since the last term in eq. (1.2.41) that is responsible for these corrections is proportional to  $\hbar$ , this is formally equivalent to solve eq. (1.2.41) through a series expansion in powers of  $\hbar$ .

From now on, we shall focus on stationary states of the quantum theory, which possess a definite energy  $E$ . We shall then start from the stationary Schrödinger equation (1.2.50). For convenience, we start by rewriting this equation by bringing the potential term on the right-hand side and multiplying by  $2m$ , in the form

$$(\vec{\nabla}W)^2 - i\hbar\Delta W = 2m(E - V). \quad (1.4.66)$$

We then look for a solution for  $W$  taking the form of a series expansion in  $-i\hbar$ :

$$W(\vec{x}) = W_0(\vec{x}) + (-i\hbar)W_1(\vec{x}) + (-i\hbar)^2W_2(\vec{x}) + \dots \quad (1.4.67)$$



Plugging back into (1.4.66) and requiring the coefficients of all orders in  $-\hbar$  to vanish, one finds an infinite set of coupled equations for the coefficients  $W_n$ . The first ones read:

$$\left\{ \begin{array}{l} (\vec{\nabla}W_0)^2 = 2m(E - V), \\ \vec{\nabla}W_0 \cdot \vec{\nabla}W_1 + \frac{1}{2}\Delta W_0 = 0, \\ (\vec{\nabla}W_1)^2 + 2\vec{\nabla}W_0 \cdot \vec{\nabla}W_2 + \Delta W_1 = 0, \\ \dots \end{array} \right. \quad (1.4.68)$$

These equations for  $W_0, W_1, W_2, \dots$  can be solved in sequence and allow in principle to determine the solution  $W$  up to any order in  $\hbar$ . This procedure defines what is called the semiclassical expansion, and is clearly well-defined only under the hypothesis that the series converges.

In practice, the semiclassical expansion is useful only when quantum effects are small compared to classical effects. It is then usually enough to restrict to the first two terms in the expansion and write:

$$W \simeq W_0 - i\hbar W_1. \quad (1.4.69)$$

In such an approximation,  $W_0$  describes the classical behavior whereas  $W_1$  encodes the leading quantum effects. The wave function then takes the following form:

$$\phi(x) = A e^{W_1(\vec{x})} e^{\frac{i}{\hbar}W_0(\vec{x})}. \quad (1.4.70)$$

We see that, as already remarked, the leading term  $W_0$  controls the coefficient of the  $1/\hbar$  exponent and therefore determines the length scale on which the wave function oscillates or dies out, while the subleading term  $W_1$  controls the amplitude of the wave function.

For simplicity, let us consider again a one-dimensional problem. Since the quantity  $2m(E - V)$  corresponds to the classical momentum  $p$ , we shall introduce the short hand notation

$$p(x) = \sqrt{2m(E - V(x))}. \quad (1.4.71)$$

The two equations determining  $W_0$  and  $W_1$  then simply read:

$$\left\{ \begin{array}{l} W_0'^2 = p^2, \\ W_0'W_1' + \frac{1}{2}W_0'' = 0. \end{array} \right. \quad (1.4.72)$$

The first equation directly implies that  $W_0' = \pm p$ , whereas the second can be rewritten as  $W_1' = -\frac{1}{2}W_0''/W_0'$  and therefore implies, together with the first one, that  $W_1' = -\frac{1}{2}p'/p$ . The general solution is then given by:

$$\left\{ \begin{array}{l} W_0(x) = \pm \int^x p(x')dx' + \text{constant}, \\ W_1(x) = -\ln \sqrt{p(x)} + \text{constant}. \end{array} \right. \quad (1.4.73)$$

The semiclassical stationary wave function  $\phi = Ae^{\frac{i}{\hbar}W}$  then takes the following simple form, where the two constants of integration have been reabsorbed into the arbitrary normalization  $A$ :

$$\phi(x) \simeq \frac{A}{\sqrt{p(x)}} \exp \left\{ \pm \frac{i}{\hbar} \int^x p(x') dx' \right\}. \quad (1.4.74)$$

The general structure of this result for  $\phi$  is easy to interpret from the classical point of view. The form of the phase  $\arg \phi$  is related to the classical motion of the particle. Indeed, the gradient of this phase  $(\arg \phi)'(x)$  must be proportional to the momentum  $p(x)$ , and this implies that  $\arg \phi(x)$  should be proportional to the reduced action  $\int^x p(x') dx'$ . The form of the amplitude  $|\phi|$  is instead related to the classical probability distribution of finding the particle. Indeed, the infinitesimal probability  $|\phi(x)|^2 dx$  of finding the particle between  $x$  and  $x + dx$  must be proportional to the time  $dt$  spent by the particle in this interval, which is given by  $dx/v(x)$  in terms of the velocity  $v(x)$  and is thus proportional to  $dx/p(x)$  where  $p(x)$  is the momentum. This implies that  $|\phi(x)|$  should be proportional to  $1/\sqrt{p(x)}$ .

## 1.5 The semiclassical wave function

The result (1.4.74) represents the general form taken by the wave function in the semiclassical approximation, whenever this approximation is defined. The two possible signs in the exponent define two linearly independent solutions of the semiclassical Schrödinger equation. The general solution is then given by a linear combination of these two independent solutions with arbitrary coefficients  $A_+$  and  $A_-$ :

$$\phi(x) = \frac{A_+}{\sqrt{p(x)}} \exp \left\{ \frac{i}{\hbar} \int^x p(x') dx' \right\} + \frac{A_-}{\sqrt{p(x)}} \exp \left\{ -\frac{i}{\hbar} \int^x p(x') dx' \right\}. \quad (1.5.75)$$

From the definition of the classical momentum  $p(x) = \sqrt{2m(E - V)}$ , we see that the semiclassical wave function has a radically different behavior depending on whether the energy  $E$  is larger, smaller or equal to the potential  $V$  at the point under consideration, so that the momentum is correspondingly real, imaginary or vanishing. Let us then consider these three cases separately.

### 1.5.1 Classically allowed regions

In the regions of space  $x$  where  $E > V(x)$ , which are classically allowed, the particle has a positive kinetic energy and  $p(x)$  is real. The semiclassical wave function is correspondingly an oscillating function and the density of probability of finding the particle in such a region is sizable. It is then convenient to rewrite the wave function in terms of the real and positive quantum-mechanical wave number  $k(x)$  that locally corresponds to the classical momentum  $p(x)$ , which is defined as

$$k(x) = \frac{1}{\hbar} p(x) = \frac{1}{\hbar} \sqrt{2m(E - V(x))}. \quad (1.5.76)$$

The general solution in this region can then be written as the superposition of progressive and a regressive waves with amplitudes weighted by two arbitrary coefficients  $B_+$  and  $B_-$ :

$$\phi(x) = \frac{B_+}{\sqrt{k(x)}} \exp \left\{ i \int^x k(x') dx' \right\} + \frac{B_-}{\sqrt{k(x)}} \exp \left\{ -i \int^x k(x') dx' \right\}. \quad (1.5.77)$$

Alternatively, one may write this solution as a standing wave with amplitude weighted by an arbitrary coefficient  $B$  and phase determined by an arbitrary angle  $\delta$ :

$$\phi(x) = \frac{B}{\sqrt{k(x)}} \sin \left\{ \int^x k(x') dx' + \delta \right\}. \quad (1.5.78)$$

### 1.5.2 Classically forbidden regions

In the regions of space  $x$  where  $E < V(x)$ , which are classically forbidden, the particle formally has a negative kinetic energy and  $p(x)$  is imaginary. The semiclassical wave function is correspondingly an exponentially localized function and the density of probability of finding the particle in such a region is tiny, although not zero. It is then convenient to rewrite the wave function in terms of a real and positive quantum-mechanical penetration-number  $\beta(x)$  that locally corresponds to the classical momentum  $p(x)$ , which is defined as

$$\beta(x) = -\frac{i}{\hbar} p(x) = \frac{1}{\hbar} \sqrt{2m(V(x) - E)}. \quad (1.5.79)$$

The general solution in this region can then be written as the superposition of decreasing and increasing exponentials with amplitudes weighted by two arbitrary coefficients  $D_\downarrow$  and  $D_\uparrow$ :

$$\phi(x) = \frac{D_\downarrow}{\sqrt{\beta(x)}} \exp \left\{ -\int^x \beta(x') dx' \right\} + \frac{D_\uparrow}{\sqrt{\beta(x)}} \exp \left\{ \int^x \beta(x') dx' \right\}. \quad (1.5.80)$$

### 1.5.3 Classical turning points

Finally, at the points  $x_0$  where  $E = V(x_0)$ , which are turning points of the classical trajectories, the particle has vanishing kinetic energy and  $p(x_0)$  is zero. The semiclassical wave function is correspondingly ill defined and the probability of finding the particle in such points cannot be computed. However, at such points the semiclassical approximation clearly breaks down and the approximate result derived for the wave function is in fact not reliable, since when  $p = 0$  and  $F = -V' \neq 0$  the condition (1.3.64) is clearly brutally violated.

### 1.5.4 Matching strategy

We thus learn that the semiclassical approximation of the wave function is never reliable in the neighborhood of turning points, whereas far away from these turning points it might be reliable under suitable circumstances and behaves respectively as an oscillating wave and a damped profile in classically allowed and classically forbidden regions sufficiently far

away from the turning points. At first sight, one would then be tempted to conclude that this matter of fact represents a severe limitation on the application of the semiclassical approximation to the standard problems encountered in quantum mechanics, since in those problems the basic physical properties of the system precisely emerge from the constraints imposed by the transition between oscillatory behavior in classically allowed regions and damped behavior in classically forbidden regions across turning points.

Happily, there exists a general way out of this problem, which provides a method to derive the glueing conditions between the semiclassical wave functions that are valid in classically allowed and forbidden regions sufficiently apart from a turning point. The idea consists in noticing that in the immediate neighborhood of a turning point, where the semiclassical approximation is not reliable, it is possible to use another approximation to derive in a reliable way the behavior of the wave function, at least under the assumption that the potential is a sufficiently slowly varying function. This consists in approximating the potential in such a neighborhood with the linear potential defined by its first order expansion around the turning point:

$$V(x) \simeq V(x_0) + V'(x_0)(x - x_0) \simeq E - F(x_0)(x - x_0). \quad (1.5.81)$$

It turns out that the Schrödinger equation in such a linear potential can be solved exactly, as will be described in next subsection, and this allows to determine the true behavior of the wave function in the neighborhood of a turning point.

The basic question is then whether it is possible to reliably glue the approximate oscillatory and damped wave functions obtained in the semiclassical approximation in classically allowed and forbidden regions away from turning points with the wave function obtained in the linearized potential approximation close to the fixed point. For this to be possible, there should be an overlap among the validity regions of these two different approximations. It turns out that in most of the situations this is indeed the case. To argue this, let us start by imagining to be sufficiently close to the turning point for the linearization of the potential to be a reliable approximation. In such a region, we can compute the size of the momentum  $p(x)$  as

$$|p(x)| \simeq |p'(x)(x - x_0)| \simeq \sqrt{2m|F(x)||x - x_0|}. \quad (1.5.82)$$

Inserting this in the necessary condition (1.3.64) for the applicability of the semiclassical approximation, we see that this requires that  $|x - x_0| \gg \frac{1}{2}\hbar|m\hbar F(x)|^{-1/3} \gg \hbar/|p(x)|$ , which in terms of the De Broglie wave length  $\lambda = \hbar/p$  reads:

$$|x - x_0| \gg \frac{1}{2}|\lambda(x)|. \quad (1.5.83)$$

On the other hand, the other necessary condition (1.3.61) for the validity of the semiclassical approximation implies that  $\lambda$  must be small. In that situation the condition (1.5.83) for the applicability of the semiclassical approximation will then usually start to be satisfied already very close to the turning point, where the linearization of  $V$  is still comfortably reliable, and the regions of validity of the two approximations will indeed sufficiently overlap to be able to match the two types of wave functions.

## 1.6 Behavior in a linear potential

Let us then study the wave function of a one-dimensional particle subject to a linear potential with overall constant equal to the energy  $E$  of the particle and a slope corresponding to an arbitrary force  $F_0 = F(x_0)$ :

$$V(x) = E - F_0(x - x_0). \quad (1.6.84)$$

The stationary Schrödinger equation for the wave function  $\phi(x)$ , which can be written as  $\phi'' + 2m/\hbar^2(E - V)\phi = 0$ , then becomes:

$$\frac{d^2}{dx^2}\phi(x) + \frac{2mF_0}{\hbar^2}(x - x_0)\phi(x) = 0. \quad (1.6.85)$$

It is then convenient to change from the variable  $x$ , which has dimensions of a length and where the turning point is located in  $x_0$ , to a new variable  $z$ , which is dimensionless and where the turning point is located in 0. Since the quantity  $2mF_0/\hbar^2$  has dimensions of a length to the power  $-3$ , the appropriate change of variable is:

$$z = -\text{sign}(F_0) \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} (x - x_0). \quad (1.6.86)$$

It follows that

$$\frac{d}{dz} = -\text{sign}(F_0) \left| \frac{2mF_0}{\hbar^2} \right|^{-1/3} \frac{d}{dx}. \quad (1.6.87)$$

In this new variable, the stationary Schrödinger equation reduces to the simple ordinary differential equation

$$\frac{d^2}{dz^2}\phi(z) - z\phi(z) = 0. \quad (1.6.88)$$

The solution of this equation can be found in integral form by using the method of Laplace. This consists in writing the wave function  $\phi(z)$  depending on the real variable  $z$  in terms of an integral along some path  $\gamma$  in the complex plane involving an other function  $\varphi(s)$  depending on a complex variable  $s$ . More precisely, we look for solutions of the form

$$\phi(z) = \frac{1}{2\pi i} \int_{\gamma} \varphi(s) e^{zs} ds. \quad (1.6.89)$$

Inserting this into eq. (1.6.88), one deduces that

$$\int_{\gamma} (s^2 - z)\varphi(s) e^{zs} ds = 0. \quad (1.6.90)$$

Rewriting now  $ze^{zs} = d(e^{zs})/ds$  in the integrand and integrating by parts, this can be equivalently rewritten in the following form, where  $s_1$  and  $s_2$  denote the end-points of the path  $\gamma$ :

$$\int_{\gamma} \left( \frac{d}{ds}\varphi(s) + s^2\varphi(s) \right) e^{zs} ds - \varphi(s) e^{zs} \Big|_{s_1}^{s_2} = 0. \quad (1.6.91)$$

It is now clear that we can find solutions of this equation by choosing  $\varphi$  in such a way that the integrand of the bulk term vanishes, and the path  $\gamma$  in such a way that the boundary term vanishes. The first requirement implies that  $\varphi(s)$  should satisfy the first order differential equation

$$\frac{d}{ds}\varphi(s) + s^2\varphi(s) = 0, \quad (1.6.92)$$

whose general solution is determined modulo an arbitrary normalization  $A$  and reads:

$$\phi(s) = A e^{-s^3/3}. \quad (1.6.93)$$

The second requirement implies that the function  $\varphi(s)e^{zs}$  should take the same value at  $s_1$  and  $s_2$ :

$$\varphi(s)e^{zs} \Big|_{s_1}^{s_2} = 0. \quad (1.6.94)$$

Without loss of generality, we can focus on open infinite paths where the end-points  $s_1$  and  $s_2$  are at infinity in some direction in the complex  $s$  plane, and require that the function  $\varphi(s)e^{zs}$  tends to 0 at the infinite end-points of  $\gamma$ . Using the explicit form derived for  $\varphi(s)$ , this implies that:

$$\lim_{s \rightarrow s_{1,2}} e^{zs-s^3/3} = 0. \quad (1.6.95)$$

Writing  $s_{1,2} = |s_{1,2}|e^{i\alpha_{1,2}}$  and taking the modulus  $|s_{1,2}|$  to infinity, this condition is realized only if  $\text{Re } s_{1,2}^3 > 0$  and thus constrains the phase  $\alpha_{1,2}$  to be such that  $\cos(3\alpha_{1,2}) > 0$ . This allows for three disjoint intervals of values for  $\alpha_{1,2}$  within  $]-\pi, \pi[$ , namely:

$$I_- = \left] -\frac{5\pi}{6}, -\frac{\pi}{2} \right[ , \quad I_0 = \left] -\frac{\pi}{6}, \frac{\pi}{6} \right[ , \quad I_+ = \left] \frac{\pi}{2}, \frac{5\pi}{6} \right[ . \quad (1.6.96)$$

Putting everything together, we finally find that the general solution for the wave function  $\phi(z)$  is given by:

$$\phi(z) = \frac{A}{2\pi i} \int_{\gamma} e^{zs-s^3/3} ds, \quad (1.6.97)$$

where  $\gamma$  is an open infinite path with starting point  $s_1$  and ending point  $s_2$  in any of the regions of the complex plane defined by the intervals  $I_-$ ,  $I_0$ ,  $I_+$ , as shown in fig. 1.1:

$$\gamma = \text{infinite open path with end-points in any of the regions } I_-, I_0, I_+. \quad (1.6.98)$$

It is straightforward to verify that there are as expected two independent solutions, corresponding to two independent choices for  $\gamma$ . Indeed, a basis of possible choices for  $\gamma$  is given by the paths  $\gamma_{-+}$ ,  $\gamma_{-0}$  and  $\gamma_{+0}$  going respectively from  $I_-$  to  $I_+$ , from  $I_-$  to  $I_0$  and from  $I_+$  to  $I_0$ . However, this basis is not linearly independent, because the difference of the paths  $\gamma_{-0}$  and  $\gamma_{+0}$  is equivalent to the path  $\gamma_{-+}$ . Schematically this means that

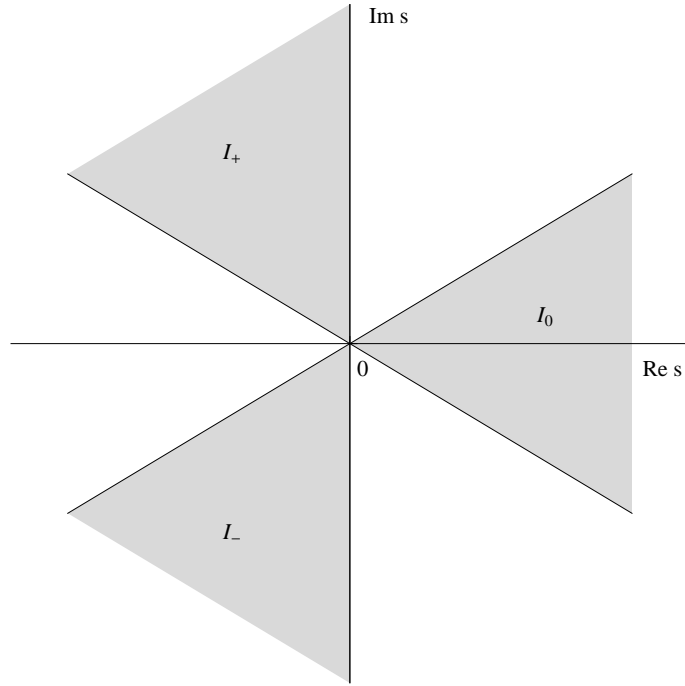


Figure 1.1: Plot of the three domains  $I_0$ ,  $I_+$  and  $I_-$ .

$\gamma_{-+} \simeq \gamma_{-0} - \gamma_{+0}$ . A convenient choice for the two linearly independent paths is then given by  $\gamma_{-+}$  and the sum of the paths  $\gamma_{-0}$  and  $\gamma_{+0}$ :

$$\gamma_A \simeq \gamma_{-+}, \quad (1.6.99)$$

$$\gamma_B \simeq \gamma_{-0} + \gamma_{+0}. \quad (1.6.100)$$

The corresponding solutions for the wave function are given by the so-called Airy functions of first and second kind, which are more precisely defined as:

$$\text{Ai}(z) = \frac{1}{2\pi i} \int_{\gamma_{-+}} e^{zs-s^3/3} ds, \quad (1.6.101)$$

$$\text{Bi}(z) = \frac{1}{2\pi} \int_{\gamma_{-0}} e^{zs-s^3/3} ds + \frac{1}{2\pi} \int_{\gamma_{+0}} e^{zs-s^3/3} ds. \quad (1.6.102)$$

A more explicit representation of these functions in terms of real integrals can be obtained by choosing special representatives for the paths  $\gamma_{-+}$ ,  $\gamma_{-0}$  and  $\gamma_{+0}$  in terms of straight lines. Their asymptotic behaviors are instead most easily derived by using the saddle-point or steepest-descent method. This consists in choosing the complex path defining the function in such a way that this passes exactly through the special points where the exponent  $zs - s^3/3$  of the integrand becomes stationary and moreover with an orientation which corresponds to the maximal rate of variation of the whole integrand. In this way, the main contribution to the integral arises from regions close to these stationary points, and when  $z \rightarrow \mp\infty$  the approximate value of the integral can be obtained from a simple Gaussian integral based on the quadratic approximation for the phase of the integrand

around stationary points. In our case, there are always two stationary points at  $s = \pm\sqrt{z}$ , but their location depends on the sign of  $z$ . For  $z \rightarrow -\infty$ ,  $z$  is negative and the two saddle points are on the imaginary axis at  $s = \pm i\sqrt{|z|}$ . For  $z \rightarrow \infty$ ,  $z$  is instead positive and the two saddle points are on the real axis at  $s = \pm\sqrt{|z|}$ .

For the first solution  $\text{Ai}(z)$ , one may choose the path  $\gamma_{-+}$  to tend to the imaginary axis parametrized by  $s = it$  with  $t \in ]-\infty, +\infty[$ . One then arrives at the following representation:

$$\begin{aligned}\text{Ai}(z) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i(zt+t^3/3)} dt \\ &= \frac{1}{\pi} \int_0^{+\infty} \cos(zt + t^3/3) dt.\end{aligned}\tag{1.6.103}$$

The asymptotic behavior for  $z \rightarrow -\infty$  can be obtained by choosing  $\gamma_{-+}$  to pass through to both of the saddle points at  $s = \pm i\sqrt{|z|}$ . Dropping the details, one finds:

$$\text{Ai}(z) \simeq \frac{1}{\sqrt{\pi}|z|^{1/4}} \sin\left(\frac{2}{3}|z|^{3/2} + \frac{\pi}{4}\right), \quad z \ll 0.\tag{1.6.104}$$

The asymptotic behavior for  $z \rightarrow \infty$  can be obtained by choosing the path  $\gamma_{-+}$  in such a way that it passes through one of the saddle points at  $s = \pm\sqrt{|z|}$ . Dropping again the details, one finds:

$$\text{Ai}(z) \simeq \frac{1/2}{\sqrt{\pi}z^{1/4}} e^{-\frac{2}{3}z^{3/2}}, \quad z \gg 0.\tag{1.6.105}$$

The function  $\text{Ai}(z)$  is therefore an oscillating wave in the classical allowed region  $z < 0$  and an exponentially damped function in the classically forbidden region  $z > 0$ . Its behavior across the turning point at  $z = 0$  is shown in fig. 1.2.

For the second solution  $\text{Bi}(z)$ , one may choose the paths  $\gamma_{\pm 0}$  to be the union of the positive real axis, parametrized by  $s = t$  with  $t \in ]0, +\infty[$ , and respectively the positive and negative imaginary axis with suitable orientation, parametrized by  $s = \mp it$  with  $t \in ]-\infty, 0[$ . One then arrives at the following expression:

$$\begin{aligned}\text{Bi}(z) &= \frac{1}{2\pi} \int_0^{+\infty} e^{zt-t^3/3} dt - \frac{i}{2\pi} \int_{-\infty}^0 e^{-i(zt+t^3/3)} dt \\ &\quad + \frac{1}{2\pi} \int_0^{+\infty} e^{zt-t^3/3} dt + \frac{i}{2\pi} \int_{-\infty}^0 e^{i(zt+t^3/3)} dt \\ &= \frac{1}{\pi} \int_0^{+\infty} e^{zt-t^3/3} dt + \frac{1}{\pi} \int_0^{+\infty} \sin(zt + t^3/3) dt.\end{aligned}\tag{1.6.106}$$

The asymptotic behavior for  $z \rightarrow -\infty$  can be obtained by choosing  $\gamma_{-0}$  and  $\gamma_{+0}$  to respectively pass through the saddle points at  $s = \mp i\sqrt{|z|}$ . One finds:

$$\text{Bi}(z) \simeq \frac{-1}{\sqrt{\pi}|z|^{1/4}} \sin\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right), \quad z \ll 0.\tag{1.6.107}$$



The asymptotic behavior for  $z \rightarrow +\infty$  can be obtained by choosing the paths  $\gamma_{-0}$  and  $\gamma_{+0}$  in such a way that they both pass through one of the saddle points at  $s = \pm\sqrt{|z|}$ . One finds:

$$\text{Bi}(z) \simeq \frac{1}{\sqrt{\pi}z^{1/4}}e^{\frac{2}{3}z^{3/2}}, \quad z \gg 0. \quad (1.6.108)$$

The function  $\text{Bi}(z)$  is therefore an oscillating wave in the classical allowed region  $z < 0$  and an exponentially growing function in the classically forbidden region  $z > 0$ . Its behavior across the turning point at  $z = 0$  is shown in fig. 1.2.

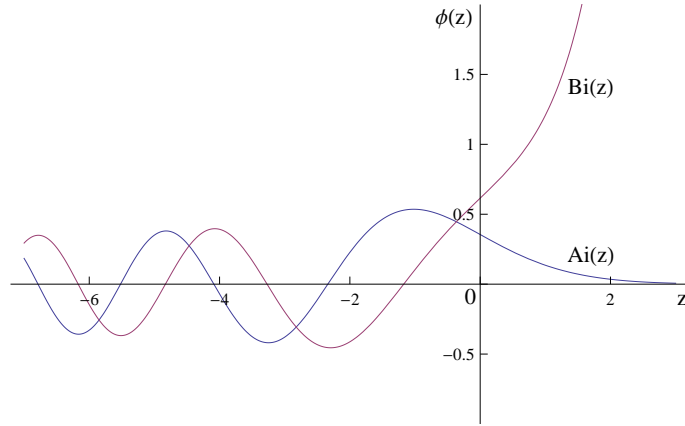


Figure 1.2: Plot of the two Airy functions  $\text{Ai}(z)$  and  $\text{Bi}(z)$ .

Summarizing, the general solution for the wave function in the neighborhood of a turning point is a generic linear combination of the two Airy functions  $\text{Ai}(z)$  and  $\text{Bi}(z)$  with arbitrary coefficients  $C_A$  and  $C_B$ :

$$\phi(z) = C_A \text{Ai}(z) + C_B \text{Bi}(z). \quad (1.6.109)$$

The asymptotic behaviors of such a solution for  $z \rightarrow \mp\infty$  are moreover given by:

$$\begin{aligned} \phi(z) &\simeq \frac{C_A}{\sqrt{\pi}|z|^{1/4}} \sin\left(\frac{2}{3}|z|^{3/2} + \frac{\pi}{4}\right) - \frac{C_B}{\sqrt{\pi}|z|^{1/4}} \sin\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \\ &\simeq \frac{C_+}{\sqrt{\pi}|z|^{1/4}} e^{-i\frac{2}{3}|z|^{3/2}} + \frac{C_-}{\sqrt{\pi}|z|^{1/4}} e^{i\frac{2}{3}|z|^{3/2}}, \quad z \ll 0, \end{aligned} \quad (1.6.110)$$

and

$$\phi(z) \simeq \frac{C_A/2}{\sqrt{\pi}z^{1/4}} e^{-\frac{2}{3}z^{3/2}} + \frac{C_B}{\sqrt{\pi}z^{1/4}} e^{\frac{2}{3}z^{3/2}}, \quad z \gg 0, \quad (1.6.111)$$

where we have defined

$$C_+ = \frac{1}{2}\left(e^{i\frac{\pi}{4}}C_A + e^{-i\frac{\pi}{4}}C_B\right), \quad C_- = \frac{1}{2}\left(e^{-i\frac{\pi}{4}}C_A + e^{i\frac{\pi}{4}}C_B\right). \quad (1.6.112)$$

An interesting check on the behaviors of the two independent solutions can be done by recalling that the Wronskian  $\phi_A\phi'_B - \phi'_A\phi_B$  of two independent solutions  $\phi_A$  and  $\phi_B$  of

the Schrödinger equation must be constant. In our case, this Wronskian is equal to  $1/\pi$ , as a result of the following property of Airy functions:

$$\text{Ai}(z)\text{Bi}'(z) - \text{Ai}'(z)\text{Bi}(z) = \frac{1}{\pi}. \quad (1.6.113)$$

It is straightforward to check that this relation is indeed satisfied by the above-derived asymptotic behaviors of the Airy functions for  $z \rightarrow \pm\infty$ .

It is worth mentioning that the two asymptotic behaviors in the classically allowed region where  $z \rightarrow -\infty$  and in the classically forbidden regions where  $z \rightarrow +\infty$  are actually related by an analytic continuation and both descend from the asymptotic behavior of the wave function  $\phi(z)$  for  $|z| \rightarrow +\infty$  in the complex  $z$  plane. As a result, the matching between these two asymptotic behaviors can actually be determined without ever needing the exact behavior of the wave function close to the turning point. The idea is to move from  $z = \rho$  to  $z = -\rho$ , with  $\rho \gg 1$  real and positive, on a semicircle avoiding the origin in the complex  $z$  plane, parametrized by  $z = \rho e^{\pm i\phi}$  with  $\phi \in [0, \pi]$ . Taking this point of view, it becomes clear that when moving from the classically forbidden region  $z \gg 0$  to the classically allowed region  $z \ll 0$ , the real exponents  $\pm \frac{2}{3}z^{3/2}$  map to the imaginary phases  $\pm i\frac{2}{3}|z|^{3/2}$  and the prefactor  $z^{-1/4}$  maps to the prefactor  $|z|^{-1/4}$  times some additional phase factors of the form  $e^{\pm i\frac{\pi}{4}}$ . But determining the precise connection formulae between the two kinds of asymptotic behaviors is not completely trivial even with this method, because while phases factors of different signs are on the same footing, real exponents of different signs have hierarchically different magnitudes.

## 1.7 Matching conditions across turning points

The results that we have obtained clearly show that the exact wave function around a turning point has a behavior which as expected interpolates from an oscillatory behavior in the classically allowed region to an exponentially damped behavior in the classically forbidden region. It is now straightforward to verify that these behaviors away from the turning point are precisely of the general form obtained for the wave functions in such regions in the semiclassical approximation. This allows to derive matching conditions for the semiclassical behaviors on the two different sides of a turning point.

To work out the details, we need to switch back from the dimensionless variable  $z$  to the original coordinate  $x$ , and figure out what the quantities  $k(x)$  and  $\beta(x)$  look like. For concreteness, we shall study separately the two cases of turning points with increasing and decreasing potential, where  $F_0 < 0$  and  $F_0 > 0$ . Moreover, it will be convenient to introduce new normalization constants  $C_{0A}$ ,  $C_{0B}$  related to  $C_A$ ,  $C_B$  by the relations

$$C_{0A,B} = \frac{1}{\sqrt{\pi}} \left| \frac{2mF_0}{\hbar^2} \right|^{1/6} C_{A,B}. \quad (1.7.114)$$

We also define in the same way as before

$$C_{0+} = \frac{1}{2} \left( e^{i\frac{\pi}{4}} C_{0A} + e^{-i\frac{\pi}{4}} C_{0B} \right), \quad C_{0-} = \frac{1}{2} \left( e^{-i\frac{\pi}{4}} C_{0A} + e^{i\frac{\pi}{4}} C_{0B} \right). \quad (1.7.115)$$

### 1.7.1 Turning points with increasing potential

Consider first the case of increasing potential with  $F_0 < 0$ , as shown in fig. 1.3. In this case, the relation between  $z$  and  $x$  reads:

$$z = \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} (x - x_0). \quad (1.7.116)$$

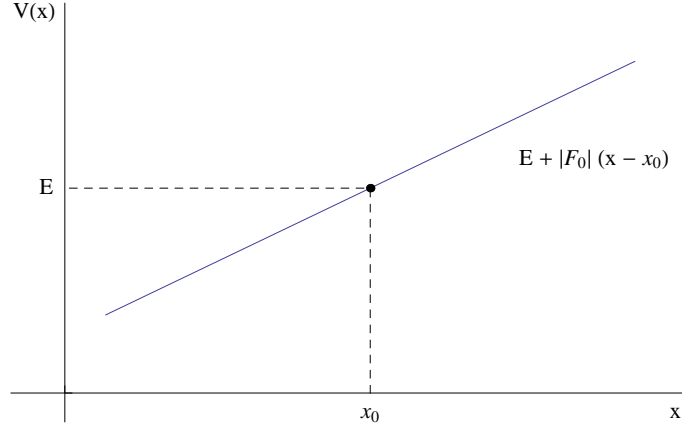


Figure 1.3: Turning point with an increasing potential.

In the classically allowed region, where  $z < 0$  and therefore  $x < x_0$ , one easily computes that the wave number is locally given by

$$\begin{aligned} k(x) &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x_0 - x)^{1/2} \\ &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} |z|^{1/2}, \end{aligned} \quad (1.7.117)$$

and its integral yields

$$\begin{aligned} \int_x^{x_0} k(x') dx' &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} \int_x^{x_0} (x_0 - x')^{1/2} dx' = \frac{2}{3} \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x_0 - x)^{3/2} \\ &= \frac{2}{3} |z|^{3/2}. \end{aligned} \quad (1.7.118)$$

Using these results, we see that the wave function far inside the allowed region, which is determined by the asymptotic behavior (1.6.110), can be rewritten in a way that manifestly matches the general form (1.5.78) of the semiclassical wave function in a classically allowed region:

$$\begin{aligned} \phi(x) &\simeq \frac{C_{0A}}{\sqrt{k(x)}} \sin \left( \int_x^{x_0} k(x') dx' + \frac{\pi}{4} \right) - \frac{C_{0B}}{\sqrt{k(x)}} \sin \left( \int_x^{x_0} k(x') dx' - \frac{\pi}{4} \right) \\ &\simeq \frac{C_{0+}}{\sqrt{k(x)}} \exp \left\{ -i \int_x^{x_0} k(x') dx' \right\} + \frac{C_{0-}}{\sqrt{k(x)}} \exp \left\{ i \int_x^{x_0} k(x') dx' \right\}, \quad x \ll x_0. \end{aligned} \quad (1.7.119)$$

Notice that  $C_{0+}$  and  $C_{0-}$  control in this case the progressive and regressive components of the wave, since the quantity  $\int_x^{x_0} k(x') dx'$  decreases when  $x$  increases.

In the classically forbidden region, where  $z > 0$  and therefore  $x > x_0$ , one easily finds that the penetration factor is locally given by

$$\begin{aligned}\beta(x) &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x - x_0)^{1/2} \\ &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} z^{1/2},\end{aligned}\tag{1.7.120}$$

and its integral yields

$$\begin{aligned}\int_{x_0}^x \beta(x') dx' &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} \int_{x_0}^x (x' - x_0)^{1/2} dx' = \frac{2}{3} \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x - x_0)^{3/2} \\ &= \frac{2}{3} z^{3/2}.\end{aligned}\tag{1.7.121}$$

Using these results, we see that the wave function far inside the forbidden region, which is determined by the asymptotic behavior (1.6.111), can be rewritten in a way that manifestly matches the general form (1.5.80) of the semiclassical wave function in a classically forbidden region:

$$\phi(x) \simeq \frac{C_{0A}/2}{\sqrt{\beta(x)}} \exp \left\{ - \int_{x_0}^x \beta(x') dx' \right\} + \frac{C_{0B}}{\sqrt{\beta(x)}} \exp \left\{ \int_{x_0}^x \beta(x') dx' \right\}, \quad x \gg x_0 \tag{1.7.122}$$

### 1.7.2 Turning points with decreasing potential

Consider next the case of decreasing potential with  $F_0 > 0$ , as shown in fig. 1.4. In this case, the relation between  $z$  and  $x$  reads:

$$z = \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} (x_0 - x).\tag{1.7.123}$$

In the classically allowed region, where  $z < 0$  and therefore  $x > x_0$ , the wave number is given by

$$\begin{aligned}k(x) &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x - x_0)^{1/2} \\ &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} |z|^{1/2},\end{aligned}\tag{1.7.124}$$

and its integral yields

$$\begin{aligned}\int_{x_0}^x k(x') dx' &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} \int_{x_0}^x (x' - x_0)^{1/2} dx' = \frac{2}{3} \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x - x_0)^{3/2} \\ &= \frac{2}{3} |z|^{3/2}.\end{aligned}\tag{1.7.125}$$

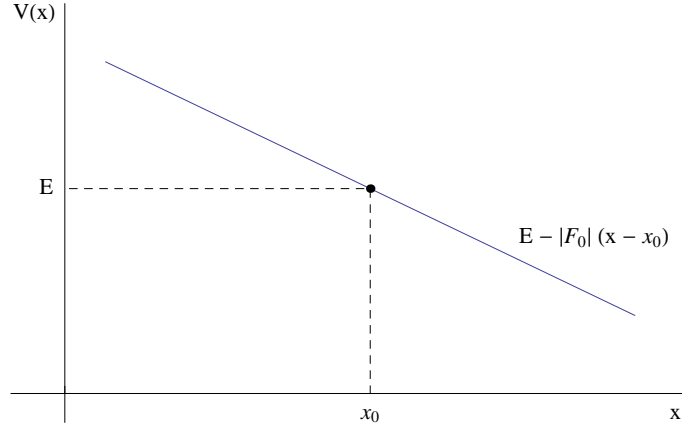


Figure 1.4: Turning point with an decreasing potential.

Using these results, we see that the wave function far inside the allowed region, which is determined by the asymptotic behavior (1.6.110), can be rewritten in a way that manifestly matches the general form (1.5.78) of the semiclassical wave function in a classically allowed region:

$$\begin{aligned} \phi(x) &\simeq \frac{C_{0A}}{\sqrt{k(x)}} \sin \left( \int_{x_0}^x k(x') dx' + \frac{\pi}{4} \right) - \frac{C_{0B}}{\sqrt{k(x)}} \sin \left( \int_{x_0}^x k(x') dx' - \frac{\pi}{4} \right) \quad (1.7.126) \\ &\simeq \frac{C_{0+}}{\sqrt{k(x)}} \exp \left\{ -i \int_{x_0}^x k(x') dx' \right\} + \frac{C_{0-}}{\sqrt{k(x)}} \exp \left\{ i \int_{x_0}^x k(x') dx' \right\}, \quad x \gg x_0. \end{aligned}$$

Notice that  $C_{0+}$  and  $C_{0-}$  control in this case the regressive and progressive components of the wave, since the quantity  $\int_{x_0}^x k(x') dx'$  increases when  $x$  increases.

In the classically forbidden region, where  $z > 0$  and therefore  $x < x_0$ , the penetration factor is given by

$$\begin{aligned} \beta(x) &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x_0 - x)^{1/2} \\ &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/3} z^{1/2}, \quad (1.7.127) \end{aligned}$$

and its integral yields

$$\begin{aligned} \int_x^{x_0} \beta(x') dx' &= \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} \int_x^{x_0} (x_0 - x')^{1/2} dx' = \frac{2}{3} \left| \frac{2mF_0}{\hbar^2} \right|^{1/2} (x_0 - x)^{3/2} \\ &= \frac{2}{3} z^{3/2}. \quad (1.7.128) \end{aligned}$$

Using these results, we see that the wave function far inside the forbidden region, which is determined by the asymptotic behavior (1.6.111) can be rewritten in a way that matches the general form (1.5.80) of the semiclassical wave function in a classically forbidden region:

$$\phi(x) \simeq \frac{C_{0A}/2}{\sqrt{\beta(x)}} \exp \left\{ -\int_x^{x_0} \beta(x') dx' \right\} + \frac{C_{0B}}{\sqrt{\beta(x)}} \exp \left\{ \int_x^{x_0} \beta(x') dx' \right\}, \quad x \ll x_0 \quad (1.7.129)$$

## Chapter 2

# One-dimensional problems in the semiclassical approximation

In this chapter, we shall apply the general results derived in the previous chapter for the semiclassical form of the wave function to study a number of standard one-dimensional problems. We will first study the spectrum of localized bound states admitted by a generic potential well and show how the Bohr-Sommerfeld quantization rules naturally emerge in the semiclassical approximation. We will then study the reflection and transmission coefficients for delocalized scattering states for a generic potential barrier, and display how the quantum mechanical tunnel effect is captured by the semiclassical approximation. We will finally study the properties of the quasi stationary states allowed by a generic potential well associated to a finite barrier, and derive the energy spectrum and the life time of such states in the semiclassical approximation. In all these cases, we will moreover discuss how the results can be understood in terms of the quantities characterizing the classical motion. To conclude, we will also present a systematic approach to deal with more complicated potentials involving several wells and barriers, and use it to illustrate some interesting phenomena that can occur in these settings, like for instance level splitting in double wells or resonance and opacity phenomena in double barriers.

### 2.1 Energy levels in a generic potential well

One of the most interesting and important applications of the semiclassical approximation is the study of the energy levels of a generic one-dimensional potential well with arbitrary shape. This directly leads to the Bohr-Sommerfeld quantization conditions, which were postulated in the early days of quantum mechanics but are then understood to really emerge and hold only in the semiclassical approximation.

Consider a particle moving in a one-dimensional potential well  $V(x)$ , with some definite energy  $E$ . There are then two classical turning points  $x_1$  and  $x_2$  with  $x_1 < x_2$  where  $V(x_1) = V(x_2) = E$  and  $V'(x_1) < 0$ ,  $V'(x_2) > 0$ , as depicted in fig. 2.1. This defines a finite central region  $II = ]x_1, x_2[$  that is classically allowed and two infinite boundary

regions  $I = ]-\infty, x_1[$  and  $III = ]x_2, +\infty[$  that are classically forbidden. The semiclassical wave function must be an oscillating wave in the classically allowed region  $II$  and an exponentially suppressed function in the classically forbidden regions  $I$  and  $III$ . The condition that the wave function should vanish at  $x \rightarrow \pm\infty$  selects one particular solution in the two forbidden regions  $I$  and  $III$ . The continuation of these semiclassical behaviors across the two turning points, into the region  $x \in ]x_1, x_2[$ , can then be done as explained in previous section. This selects one particular solution in the classically allowed region and also imposes a quantization condition on the spectrum of allowed energies  $E$ , which should take discrete values parametrized by an integer quantum number related to the number of nodes of the wave function.

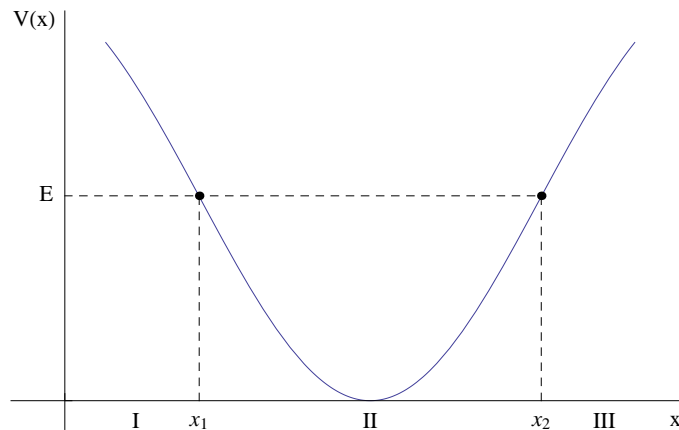


Figure 2.1: Turning points in a potential well.

### 2.1.1 Evaluation of the semiclassical wave function

By applying the reasoning of last section to the first classical turning point at  $x_1$  where the potential is decreasing, we deduce that the wave function in the regions  $I$  and  $II$  separated by this turning point takes the forms (1.7.129) and (1.7.126), with arbitrary coefficients now renamed  $C_{1A}$  and  $C_{1B}$ . The boundary condition that the wave function should vanish for  $x \rightarrow -\infty$  implies that  $C_{1B} = 0$ , and there is thus only one non-vanishing coefficient  $C_{1A} \neq 0$ , so that:

$$\phi_I(x) \simeq \frac{C_{1A}/2}{\sqrt{\beta(x)}} \exp \left\{ - \int_x^{x_1} \beta(x') dx' \right\}, \quad (2.1.1)$$

$$\phi_{II}(x) \simeq \frac{C_{1A}}{\sqrt{k(x)}} \sin \left( \int_{x_1}^x k(x') dx' + \frac{\pi}{4} \right). \quad (2.1.2)$$

By applying similarly the reasoning of last section to the second turning point at  $x_2$  where the potential is increasing, we deduce that the wave function in the regions  $II$  and  $III$  separated by this turning point takes the forms (1.7.119) and (1.7.122), with arbitrary coefficients now called  $C_{2A}$  and  $C_{2B}$ . The boundary condition that the wave function should vanish for  $x \rightarrow +\infty$  implies that  $C_{2B} = 0$ , and there is thus only one non-vanishing

coefficient  $C_{2A} \neq 0$ , so that:

$$\phi_{II}(x) \simeq \frac{C_{2A}}{\sqrt{k(x)}} \sin \left( \int_x^{x_2} k(x') dx' + \frac{\pi}{4} \right), \quad (2.1.3)$$

$$\phi_{III}(x) \simeq \frac{C_{2A}/2}{\sqrt{\beta(x)}} \exp \left\{ - \int_{x_2}^x \beta(x') dx' \right\}. \quad (2.1.4)$$

We now have to require that the two different expressions derived above for  $\phi_{II}$  should be identical. The corresponding condition is most easily written down by writing:

$$\int_x^{x_2} k(x') dx' = J - \int_{x_1}^x k(x') dx', \quad (2.1.5)$$

where

$$J = \int_{x_1}^{x_2} k(x') dx'. \quad (2.1.6)$$

Rewriting then (2.1.3) and (2.1.2) in terms of exponentials and using the above relation, we see that they match if

$$\begin{aligned} & \frac{1}{2} C_{1A} e^{-i\frac{\pi}{4}} \exp \left\{ i \int_{x_1}^x k(x') dx' \right\} + \frac{1}{2} C_{1A} e^{i\frac{\pi}{4}} \exp \left\{ -i \int_{x_1}^x k(x') dx' \right\} \\ &= \frac{1}{2} C_{2A} e^{-i\frac{\pi}{4}} e^{iJ} \exp \left\{ -i \int_{x_1}^x k(x') dx' \right\} + \frac{1}{2} C_{2A} e^{i\frac{\pi}{4}} e^{-iJ} \exp \left\{ i \int_{x_1}^x k(x') dx' \right\}. \end{aligned} \quad (2.1.7)$$

This condition is identically satisfied for all  $x \in ]x_1, x_2[$  if and only if the coefficients of the progressive and regressive waves both match. This yields the following two conditions:

$$e^{-2iJ} = -1, \quad \frac{C_{1A}}{C_{2A}} = ie^{-iJ}. \quad (2.1.8)$$

For future reference, notice that these can also be rewritten in an equivalent real form by using the identities  $\cot J = i(1 + e^{-2iJ})(1 - e^{-2iJ})^{-1}$  and  $\sin J = -\frac{i}{2}e^{-iJ}(e^{2iJ} - 1)$ :

$$\cot J = 0, \quad \frac{C_{1A}}{C_{2A}} = \sin J. \quad (2.1.9)$$

The solutions of these conditions are labeled by a non-negative integer number  $n = 0, 1, \dots$  and read:

$$J = \left( n + \frac{1}{2} \right) \pi, \quad \frac{C_{1A}}{C_{2A}} = (-1)^n, \quad n = 0, 1, \dots. \quad (2.1.10)$$

Summarizing, there is an infinite number of stationary modes labelled by an integer  $n$ , whose wave functions are determined in terms of a single overall constant  $C$ . Choosing the parametrization  $C_{1A} = C$  and  $C_{2A} = (-1)^n C$ , these wave functions are given by

$$\begin{cases} \phi_I(x) \simeq \frac{C}{2\sqrt{\beta(x)}} \exp \left\{ - \int_x^{x_1} \beta(x') dx' \right\}, \\ \phi_{II}(x) \simeq \frac{C}{\sqrt{k(x)}} \sin \left( \int_{x_1}^x k(x') dx' + \frac{\pi}{4} \right), \\ \phi_{III}(x) \simeq \frac{(-1)^n C}{2\sqrt{\beta(x)}} \exp \left\{ - \int_{x_2}^x \beta(x') dx' \right\}, \end{cases} \quad (2.1.11)$$



with the energy quantization condition

$$\int_{x_1}^{x_2} k(x') dx' = \left( n + \frac{1}{2} \right) \pi. \quad (2.1.12)$$

It is straightforward to verify that the quantum number  $n$  corresponds to the number of nodes possessed by the wave function in the classically allowed region.

The overall constant  $C$  in the wave function can be fixed by requiring this to be properly normalized. Since the classically allowed region is finite, the wave function is normalizable. In the semiclassical approximation, one can neglect the contribution coming from the classically forbidden regions, since in those regions the wave function is exponentially suppressed. One can moreover evaluate the contribution to the total probability from the classically allowed region by replacing the square of the sine function by its average value  $1/2$ , since the wave length must be much smaller than the size of the well for the semiclassical approximation to hold. With these approximations, one finds:

$$\begin{aligned} \int_{-\infty}^{+\infty} |\phi(x)|^2 dx &\simeq \int_{x_1}^{x_2} |\phi_{II}(x)|^2 dx \simeq \frac{1}{2} \int_{x_1}^{x_2} \frac{dx}{k(x)} |C|^2 \\ &\simeq \frac{\hbar^2}{2m} \frac{\partial J}{\partial E} |C|^2, \end{aligned} \quad (2.1.13)$$

where in the last step we have used the fact that from the definition of  $k$  it follows that  $\partial k / \partial E = m / (\hbar^2 k)$  and therefore:

$$\frac{\partial J}{\partial E} = \frac{m}{\hbar^2} \int_{x_1}^{x_2} \frac{dx}{k(x)}. \quad (2.1.14)$$

Requiring the above result to be unity fixes the constant  $C$  to be, modulo an irrelevant phase:

$$C \simeq \frac{\sqrt{2m}}{\hbar} \left( \frac{\partial J}{\partial E} \right)^{-1/2}. \quad (2.1.15)$$

In order to assess the validity range of the above general results, we have now to recall that the semiclassical approximation is valid only at points whose distance from classical turning points is much bigger than the local De Broglie wave length  $\lambda(x) = 1/k(x)$  characterizing the wave function. This implies in particular that the wave function must have a large number of nodes within the classically allowed region, meaning that the quantum number  $n$  should be large:

$$n \gg 1. \quad (2.1.16)$$

It is only in this limit of large quantum number that the semiclassical approximation is justified. In this regime, the  $1/2$  shift obtained in the quantization condition (2.1.12) formally represents a small effect. In practice, however, it happens quite often that (2.1.12) yields a rather accurate result even for the low-lying energy levels, with the  $1/2$  shift playing a quantitatively important role. In some particular cases, it even happens that the semiclassical approximation accidentally yields the exact spectrum of energy levels.

### 2.1.2 Quantum spectrum and classical interpretation

The way in which the system behaves at the quantum level admits a nice interpretation based on the classical trajectory. Recall for this that the classical motion is periodic, and a full cycle starts at  $x_1$  reaches  $x_2$  and goes back to  $x_1$ . During this cycle, the classically allowed region  $II$  is therefore spanned twice. Since the classical momentum is given by  $p(x) = m dx/dt$ , the period  $T$  and the angular frequency  $\omega$  of this motion are given by

$$T = \oint dt = m \oint \frac{dx}{p(x)}, \quad (2.1.17)$$

$$\omega = \frac{2\pi}{T}. \quad (2.1.18)$$

The functions  $J$  and  $\partial J/\partial E$  that determine the quantization condition and the normalization of the semiclassical wave function can then be rewritten as follows in terms of classical quantities:

$$J = \frac{1}{2\hbar} \oint p(x) dx, \quad (2.1.19)$$

$$\frac{\partial J}{\partial E} = \frac{m}{2\hbar} \oint \frac{dx}{p(x)} = \frac{T}{2\hbar} = \frac{1}{2h\omega}. \quad (2.1.20)$$

Let us first discuss the interpretation of the quantization condition. Using (2.1.19), it is straightforward to recognize that (2.1.12) can be rewritten as a Bohr-Sommerfeld type quantization condition on the energy  $E$ , except for the shift by  $1/2$  in the quantum number  $n$ :

$$\oint p(x) dx = \left(n + \frac{1}{2}\right) h. \quad (2.1.21)$$

The  $1/2$  shift emerges automatically and is directly linked to the uncertainty principle that is inherent to the exact formulation of quantum mechanics. It corresponds to a zero-point energy and reflects the fact that for a bound quantum system even the ground state corresponding to  $n = 0$  cannot have an exactly vanishing momentum, because of the finite uncertainty on its position. However, the semiclassical approximation is strictly speaking valid only in the limit of large quantum numbers  $n \gg 1$ , and in this limit the shift represent a quantitatively unimportant effect that can be neglected. With this consideration, the condition (2.1.21) allows to interpret quantum states as classical states with a particular quantized value for the quantity  $\oint p dx$ , which corresponds to the area delimited by the periodic classical motion in phase space. The Bohr-Sommerfeld condition then means that this area should be quantized in units of a minimal area in phase space determined by the fundamental constant  $h$ . Moreover, since the number  $n$  corresponds to the number of different quantum states with energies less that the energy  $E$  associated to the considered value of  $\oint p dx$ , we can conclude that to each distinct quantum state we can associate a cell in phase space of area  $h$ . The number of quantum states associated to an area  $\Delta p \Delta x$  in phase space is therefore given by:

$$\frac{\Delta p \Delta x}{h} \simeq \# \text{ of quantum states}. \quad (2.1.22)$$

The Bohr-Sommerfeld quantization condition (2.1.21) also allows to deduce some general properties of the energy spectrum in terms of the quantities characterizing the classical motion. In particular, the energy separation  $\Delta E$  between two contiguous levels with  $\Delta n = 1$  is much smaller than their average energy  $E$  associated to some large  $n \gg 1$ . Applying then  $\Delta E \partial/\partial E = \Delta n \partial/\partial n$  to the two sides of the quantization condition, one deduces that

$$\Delta E \oint \frac{\partial p}{\partial E}(x) dx \simeq h. \quad (2.1.23)$$

But  $\partial E/\partial p = p/m$ , so that

$$\oint \frac{\partial p}{\partial E}(x) dx = m \oint \frac{dx}{p(x)} = T = \frac{2\pi}{\omega}. \quad (2.1.24)$$

Its then follows that:

$$\Delta E = \hbar \omega. \quad (2.1.25)$$

This means that in the region of the spectrum where the semiclassical approximation holds true, the separation  $\Delta E$  between levels is approximately given by  $\hbar$  times the frequency  $\omega$  associated to the classical motion with energy  $E$ . This implies in particular that transitions between neighbor levels through the emission or absorption of electromagnetic radiation will involve photons of frequency  $\omega$ .

Let us next discuss the interpretation of the normalization of the wave function. Using (2.1.20), we deduce that the normalization constant (2.1.15) of the semiclassical wave function can be expressed as

$$C \simeq \sqrt{\frac{4m}{\hbar T}} \simeq \sqrt{\frac{4m\omega}{h}}. \quad (2.1.26)$$

With this result we can now compute the classical density of probability  $\rho(x)$  for finding the particle at the position  $x$ , which is obtained by averaging the semiclassical density of probability  $|\phi(x)|^2$  over distances much larger than the wavelength  $\lambda(x)$ . In the forbidden regions, the suppressed exponential can be neglected and  $\rho_{I,III} \simeq 0$ , while in the allowed region the square of the sine function can be approximated with its average value 1/2 and  $\rho_{II} \simeq \frac{\hbar}{2} |C|^2/p(x)$ . Using the above value of  $C$ , one then finds:

$$\begin{cases} \rho_I(x) \simeq 0, \\ \rho_{II}(x) \simeq \frac{2m}{T} \frac{1}{p(x)} \simeq \frac{m\omega}{\pi} \frac{1}{p(x)}, \\ \rho_{III}(x) \simeq 0. \end{cases} \quad (2.1.27)$$

As a final general comment, let us mention that there exists a general technique to evaluate the phase space integral  $\oint p(x) dx$  as a function of the energy, in order to derive the explicit form of a spectrum for a given potential  $V(x)$ . This is based on the observation that the phase space integral is equal to twice the integral of  $p(x) = \sqrt{2m(E - V(x))}$  between the turning points  $x_1$  and  $x_2$  where  $V(x_1) = V(x_2) = E$  and thus  $p(x_1) =$

$p(x_2) = 0$ . In the complex plane, where  $p(z)$  has a branch cut ranging between the two turning points  $x_1$  and  $x_2$  on the real axis, this phase space integral can then be written as the integral of  $p(z) = \sqrt{2m(E - V(z))}$  along a closed contour  $c$  encircling the cut. The integral can then be evaluated by using Cauchy's theorem for the reversed contour, which encircles the rest of the complex plane. Assuming that  $V(z)$  is analytic everywhere except the cut, the result of this integral is then simply  $-2\pi i$  times the residue of the function  $p(z)$  at infinity, which is equal to minus the coefficient of the  $1/z$  term in the Laurent expansion of this function around infinity. In summary, we thus have:

$$\oint_c p(x) dx = \oint_c p(z) dz = -2\pi i \operatorname{Res} \{p(z)\}_{z=\infty}. \quad (2.1.28)$$

Of course, in simple cases one may also directly evaluate the result by computing the original real integral by means of ordinary techniques.

### 2.1.3 Example

To illustrate the general result derived in this section, let us apply it to the simple case of the one-dimensional harmonic oscillator, defined by a potential of the form

$$V(x) = \frac{1}{2}m\omega^2 x^2. \quad (2.1.29)$$

For a given energy  $E$ , there are two classical turning points at  $\pm x_0$ , such that  $V(\pm x_0) = E$ , with:

$$x_0 = \sqrt{\frac{2E}{m\omega^2}} \quad (2.1.30)$$

We can then rewrite

$$V(x) = E \left(\frac{x}{x_0}\right)^2. \quad (2.1.31)$$

The classically allowed region is given by the interval  $]-x_0, x_0[$ , and the momentum in this region is given by

$$\begin{aligned} p(x) &= \sqrt{2m(E - V(x))} \\ &= \sqrt{2mE} \frac{\sqrt{x_0^2 - x^2}}{x_0}. \end{aligned} \quad (2.1.32)$$

To compute the integral  $\oint p(x) dx$ , we can deform it in the complex plane and use (2.1.28). Expanding  $p(z)$  around  $z = \infty$ , one finds:

$$\begin{aligned} p(z) &= i\sqrt{2mE} \frac{z}{x_0} \sqrt{1 - \left(\frac{x_0}{z}\right)^2} \\ &= \sqrt{2mE} \left[ \frac{i}{x_0} z - \frac{i}{2} x_0 \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^3}\right) \right]. \end{aligned} \quad (2.1.33)$$

It follows that:

$$\operatorname{Res} \{p(z)\}_{z=\infty} = \sqrt{2mE} \left[ \frac{i}{2} x_0 \right]. \quad (2.1.34)$$

Using this in (2.1.28), one then finds:

$$\begin{aligned}\oint p(x)dx &= -2\pi i \operatorname{Res} \{p(z)\}_{z=\infty} \\ &= \sqrt{2mE} \pi x_0.\end{aligned}\tag{2.1.35}$$

The same result can also be obtained by evaluating directly the original real integral:

$$\begin{aligned}\oint p(x)dx &= 2\sqrt{2mE} \int_{-x_0}^{x_0} \frac{\sqrt{x_0^2 - x^2}}{x_0} dx \\ &= \sqrt{2mE} \left[ \frac{x}{x_0} \sqrt{x_0^2 - x^2} + x_0 \arcsin\left(\frac{x}{x_0}\right) \right]_{-x_0}^{x_0} \\ &= \sqrt{2mE} \pi x_0.\end{aligned}\tag{2.1.36}$$

Recalling the definition of  $x_0$ , the integral is finally found to take the following form:

$$\oint p(x)dx = \frac{2\pi E}{\omega}.\tag{2.1.37}$$

Plugging this result into the condition (2.1.21), one finally deduces that the semiclassical spectrum coincides in this case with the well-know exact spectrum, namely:

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega.\tag{2.1.38}$$

#### 2.1.4 Generalizations

The above semiclassical analysis of the spectrum of energy levels in a potential well can be generalized from the case of one degree of freedom associated to the coordinate  $x$  to an arbitrary number  $d$  of degrees of freedom associated to equally many coordinates  $x_i$ , provided the potential  $V(x_i)$  is such that the classical motion is periodic and that the problem is completely separable. After performing the separation of variable, one then arrives at  $d$  independent quantization conditions, which are defined in terms of the variables  $x_i$  and their canonically conjugate momenta  $p_i$  and involve equally many quantum numbers  $n_i$ . These quantization conditions have the same form as the one derived above for a single degree of freedom, but with more general zero-point shifts  $\gamma_i \in [0, 1]$ . For each  $i = 1, \dots, d$ , one gets:

$$\oint p_i(x)dx_i = (n_i + \gamma_i)h.\tag{2.1.39}$$

Again, the semiclassical approximation holds a priori true only for large quantum numbers,  $n_i \gg 1$ , and in this limit the above conditions reduce to the Bohr-Sommerfeld quantization rules.

## 2.2 Tunneling probability through a generic barrier

Another very relevant application of the semiclassical approximation is the study of the tunneling probability through a generic one-dimensional potential barrier with arbitrary shape. This leads to a very useful approximate general result for such a probability.

Consider a particle moving in a one-dimensional potential barrier  $V(x)$ , with some energy  $E$ . There are then two classical turning points  $x_1$  and  $x_2$  with  $x_1 < x_2$  where  $V(x_1) = V(x_2) = E$  and  $V'(x_1) > 0$ ,  $V'(x_2) < 0$ , as depicted in fig. 2.2. This defines a finite central region  $II = ]x_1, x_2[$  that is classically forbidden and where the semiclassical wave function is exponentially suppressed and two infinite boundary regions  $I = ]-\infty, x_1[$  and  $III = ]x_2, +\infty[$  that are classically allowed and where the semiclassical wave function is oscillating. By matching these semiclassical behaviors across the two turning points, one finds a relation between the amplitudes of the waves in the two classically allowed regions, which allows to compute the transmission coefficient  $T$ . More specifically, let us assume that the particle comes from the left in region  $I$  and is then partly reflected back to the left in region  $I$  and partly transmitted to the right in region  $III$ . This setup specifies as usual a definite boundary condition, which allows to solve for the complete wave function in the three regions in terms of a single overall normalization constant. To do this, we again use the joining conditions to continue the semiclassical wave function across turning points.

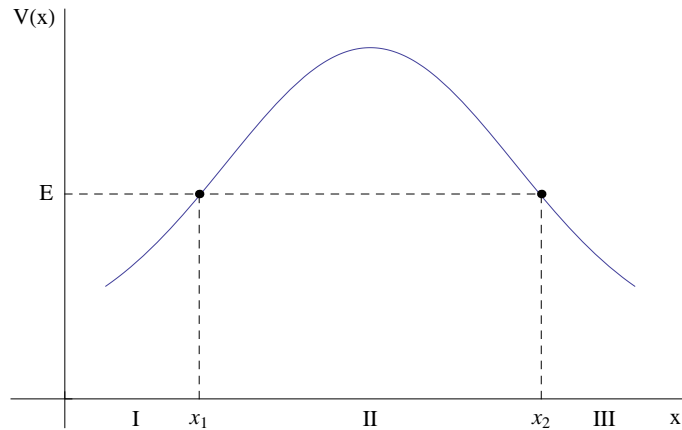


Figure 2.2: Turning points in a potential barrier.

### 2.2.1 Evaluation of the semiclassical wave function

By looking at the first classical turning point at  $x_1$  where the potential is increasing, we deduce that the wave functions in the regions  $I$  and  $II$  take the form (1.7.119) and (1.7.122), with arbitrary coefficients  $C_{1A}$  and  $C_{1B}$  or equivalently  $C_{1+}$  and  $C_{1-}$ , which respectively control the progressive and regressive components in the region  $I$ . In this case there is no boundary condition on the wave function for  $x \rightarrow -\infty$ , since in that asymptotic region there is both an incident and a reflected wave, and there are thus two independent coefficients  $C_{1A} \neq 0$  and  $C_{1B} \neq 0$ , or  $C_{1+} \neq 0$  and  $C_{1-} \neq 0$ , so that:

$$\phi_I(x) \simeq \frac{C_{1+}}{\sqrt{k(x)}} \exp \left\{ -i \int_x^{x_1} k(x') dx' \right\} + \frac{C_{1-}}{\sqrt{k(x)}} \exp \left\{ i \int_x^{x_1} k(x') dx' \right\}, \quad (2.2.40)$$

$$\phi_{II}(x) \simeq \frac{C_{1A}/2}{\sqrt{\beta(x)}} \exp \left\{ -\int_{x_1}^x \beta(x') dx' \right\} + \frac{C_{1B}}{\sqrt{\beta(x)}} \exp \left\{ \int_{x_1}^x \beta(x') dx' \right\}. \quad (2.2.41)$$

By looking at the second classical turning point at  $x_2$  where the potential is decreasing, we similarly deduce that the wave functions in the regions *II* and *III* take the form (1.7.129) and (1.7.126), with arbitrary coefficients renamed as  $C_{2A}$  and  $C_{2B}$  or equivalently  $C_{2+}$  and  $C_{2-}$ , which respectively control the regressive and progressive components in the region *III*. In this case there is a definite boundary condition on the wave function for  $x \rightarrow +\infty$ , since in that asymptotic region one should find only a transmitted wave, and there is thus only one independent coefficient out of  $C_{2A}$  and  $C_{2B}$ , or equivalently  $C_{2+}$  and  $C_{2-}$ . More precisely, one has to choose  $C_{2B} = -iC_{2A}$ , so that the coefficient of the regressive wave vanishes,  $C_{2+} = 0$ , and the coefficient of the progressive wave is then given by  $C_{2-} = e^{-i\frac{\pi}{4}}C_{2A}$ . One then finds:

$$\phi_{II}(x) \simeq \frac{C_{2A}/2}{\sqrt{\beta(x)}} \exp \left\{ - \int_x^{x_2} \beta(x') dx' \right\} - \frac{iC_{2A}}{\sqrt{\beta(x)}} \exp \left\{ \int_x^{x_2} \beta(x') dx' \right\}, \quad (2.2.42)$$

$$\phi_{III}(x) \simeq \frac{e^{-i\frac{\pi}{4}}C_{2A}}{\sqrt{k(x)}} \exp \left\{ i \int_{x_2}^x k(x') dx' \right\}. \quad (2.2.43)$$

We must now require that the two different expressions derived for  $\phi_{II}(x)$  coincide. The corresponding condition is most easily analyzed by rewriting:

$$\int_x^{x_2} \beta(x') dx' = K - \int_{x_1}^x \beta(x') dx' \quad (2.2.44)$$

where

$$K = \int_{x_1}^{x_2} \beta(x') dx'. \quad (2.2.45)$$

One must then have:

$$\begin{aligned} & \frac{1}{2}C_{1A} \exp \left\{ - \int_{x_1}^x \beta(x') dx' \right\} + C_{1B} \exp \left\{ \int_{x_1}^x \beta(x') dx' \right\} \\ &= \frac{1}{2}C_{2A}e^{-K} \exp \left\{ \int_{x_1}^x \beta(x') dx' \right\} - iC_{2A}e^K \exp \left\{ - \int_{x_1}^x \beta(x') dx' \right\}. \end{aligned} \quad (2.2.46)$$

This condition can be satisfied for all  $x \in ]x_1, x_2[$  if and only if the coefficients of the increasing and decreasing exponentials separately match. This leads to the following two relations among the coefficients:

$$\frac{C_{1A}}{C_{2A}} = -2ie^K, \quad \frac{C_{1B}}{C_{2A}} = \frac{1}{2}e^{-K}, \quad (2.2.47)$$

or equivalently

$$\frac{C_{1+}}{C_{2A}} = e^{-i\frac{\pi}{4}} \left( e^K + \frac{1}{4}e^{-K} \right), \quad \frac{C_{1-}}{C_{2A}} = -e^{i\frac{\pi}{4}} \left( e^K - \frac{1}{4}e^{-K} \right), \quad (2.2.48)$$

Summarizing, there is an infinite number of stationary modes labelled by a continuous value  $E$  for the energy, whose wave functions are determined in terms of a single constant  $C$ . Choosing the parametrization  $C_{1+} = C$ , so that  $C_{1-} = -i(1 - \frac{1}{4}e^{-2K})(1 + \frac{1}{4}e^{-2K})^{-1}C$ ,

$C_{1A} = 2e^{-i\frac{\pi}{4}}(1 + \frac{1}{4}e^{-2K})^{-1}C$ ,  $C_{1B} = \frac{1}{2}e^{i\frac{\pi}{4}}e^{-2K}(1 + \frac{1}{4}e^{-2K})^{-1}C$  and for the last one  $C_{2A} = e^{i\frac{\pi}{4}}e^{-K}(1 + \frac{1}{4}e^{-2K})^{-1}C$ , these wave functions take the form

$$\left\{ \begin{array}{l} \phi_I(x) \simeq \frac{C}{\sqrt{k(x)}} \left[ \exp \left\{ -i \int_x^{x_1} k(x') dx' \right\} - i \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ i \int_x^{x_1} k(x') dx' \right\} \right], \\ \phi_{II}(x) \simeq \frac{C}{\sqrt{\beta(x)}} \left[ \frac{e^{-i\frac{\pi}{4}}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ - \int_{x_1}^x \beta(x') dx' \right\} \right. \\ \quad \left. + \frac{1}{2} \frac{e^{i\frac{\pi}{4}}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ \int_{x_1}^x \beta(x') dx' \right\} \right], \\ \phi_{III}(x) \simeq \frac{C}{\sqrt{k(x)}} \left[ \frac{e^{-K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ i \int_{x_2}^x k(x') dx' \right\} \right]. \end{array} \right. \quad (2.2.49)$$

The overall constant  $C$  can be fixed by requiring that the wave function is properly normalized. But since the classically allowed regions are infinite, the wave function is not normalizable in the usual sense. One then has to use a  $\delta$ -function normalization, as usual with plane waves. We will however not do this explicitly, because it is not needed to extract the main physical properties of the barrier.

To compute the reflection and transmission coefficients of the barrier, we can now study the form of the wave function in the asymptotic regions  $x \rightarrow \mp\infty$ . In those regions the potential is assumed to tend to zero,  $V(x) \rightarrow 0$ , and the wave number then tends to a constant,  $k(x) \rightarrow \sqrt{2mE}/\hbar$ . Moreover,  $\int_x^{x_1} k(x') dx'$  decreases and  $\int_{x_2}^x k(x') dx'$  increases when  $x$  grows. One then deduces that the incident and reflected waves for  $x \rightarrow -\infty$  and the transmitted wave for  $x \rightarrow +\infty$  are given by

$$\phi_{\text{inc}}(x) \simeq \frac{A_{\text{inc}}}{\sqrt{k(x)}} \exp \left\{ -i \int_x^{x_1} k(x') dx' \right\}, \quad A_{\text{inc}} = C, \quad (2.2.50)$$

$$\phi_{\text{ref}}(x) \simeq \frac{A_{\text{ref}}}{\sqrt{k(x)}} \exp \left\{ i \int_x^{x_1} k(x') dx' \right\}, \quad A_{\text{ref}} = -i \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} C, \quad (2.2.51)$$

$$\phi_{\text{tra}}(x) \simeq \frac{A_{\text{tra}}}{\sqrt{k(x)}} \exp \left\{ i \int_{x_2}^x k(x') dx' \right\}, \quad A_{\text{tra}} = \frac{e^{-K}}{1 + \frac{1}{4}e^{-2K}} C. \quad (2.2.52)$$

For each of these, we can now evaluate the density of probability current, which is defined to be:

$$j(x) = -\frac{i\hbar}{2m} (\phi^* \phi' - \phi'^* \phi)(x). \quad (2.2.53)$$

One can neglect the terms where the derivative acts on the prefactor of the wave function, since this is proportional to  $k^{-1/2}(k^{-1/2})' \sim k'/k^2 \sim \lambda'$ , and this must be small for the semiclassical approximation to be valid. One then finds that the currents associated to the incident, the reflected and the transmitted waves are constant and given by

$$j_{\text{inc}} \simeq \frac{\hbar}{m} |A_{\text{inc}}|^2, \quad j_{\text{ref}} \simeq -\frac{\hbar}{m} |A_{\text{ref}}|^2, \quad j_{\text{tra}} \simeq \frac{\hbar}{m} |A_{\text{tra}}|^2. \quad (2.2.54)$$



It follows that the reflection and transmission coefficients associated to the potential barrier are given by:

$$R = \left| \frac{j_{\text{ref}}}{j_{\text{inc}}} \right| \simeq \left( \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \right)^2, \quad T = \left| \frac{j_{\text{tra}}}{j_{\text{inc}}} \right| \simeq \left( \frac{e^{-K}}{1 + \frac{1}{4}e^{-2K}} \right)^2. \quad (2.2.55)$$

Notice that  $|j_{\text{ref}}| + |j_{\text{tra}}| = |j_{\text{inc}}|$ , reflecting the usual conservation of the density of probability current  $j$ , and one thus finds:

$$R + T \simeq 1. \quad (2.2.56)$$

Notice finally that in most of the situations one has  $K \gg 1$ , and in that limit the reflection and transmission coefficients of the barrier further simplify to

$$R \simeq 1 - e^{-2K}, \quad T \simeq e^{-2K}. \quad (2.2.57)$$

To estimate the validity range of the above general results, we have now to check under which instances the conditions for the validity of the semiclassical approximation really hold true. It is not totally straightforward to determine what kind of constraints this implies on the form of the barrier. On general grounds, one could expect that the approximation is justified only whenever the wave function in the forbidden region is strongly suppressed, and this usually implies that the exponent  $K$  should be large, as assumed to arrive at the final expressions (2.2.57):

$$K \gg 1. \quad (2.2.58)$$

In addition, one must require that the potential varies sufficiently slowly. In situations where instead the potential varies rapidly at a turning point, for instance, the above formula is a priori not valid, because the general gluing rules derived in section 1.7 cannot be applied. However, it turns out that the corrections to the semiclassical approximation are in fact quite mild, and consist in an additional non-trivial power-law prefactor multiplying the exponential suppression factor in the tunneling probability. An interesting case where this can be verified explicitly is for instance that of barriers with sharp discontinuities. In those cases, the semiclassical approximation breaks down, but actually only right at the turning point, since away from that point the potential is slowly varying. It is then usually possible to solve the problem of joining the oscillating and damped semiclassical wave functions that are valid on the two sides of such a turning point by simply imposing the continuity of the wave function and its first derivative. In this way, one can derive a reliable result including also the prefactor.

## 2.2.2 Tunneling probability and classical interpretation

Once again, the general results derived by using the semiclassical approximation admit a nice interpretation in terms of classical trajectories. However, since the tunneling process is controlled by the behavior of the wave function in the classically forbidden region, the relevant trajectories are in this case not true classical trajectories in the classically

allowed region but fake complex trajectories in the classically forbidden region, defined by going to complex position  $x$ . The basic observation behind this is that the quantity  $\beta(x)$  entering the definition of the exponential factor  $K$  controlling the tunneling probability is actually defined out of the analytic continuation of the classical momentum to the classically forbidden region. More precisely, we have defined  $\beta(x) = -(i/\hbar)p(x)$ , where  $p(x) = \sqrt{2m(E - V(x))}$  is now purely imaginary. Correspondingly, we can write:

$$K = \int_{x_1}^{x_2} \beta(x') dx' = -\frac{i}{\hbar} \int_{x_1}^{x_2} p(x') dx'. \quad (2.2.59)$$

We conclude from this expression that the real factor  $K$  is  $-i$  times the imaginary reduced action associated to the complex trajectory that solves the classical equations of motion in the classically forbidden region, after extension to the complex plane.

The general result (2.2.57) can be used to draw some general conclusions about the opacity against tunneling of a generic barrier as a function of its typical height  $H$  and with  $W$ . To do so, we parametrize the form of the effective barrier above the energy  $E$  in terms of these typical scales and a dimensionless function  $f$  with values of order 1 between  $x_1$  and  $x_2$ , in such a way that form:

$$V(x) - E = Hf\left(\frac{x}{W}\right) \quad (2.2.60)$$

We can then estimate the exponent  $K$  by switching to the new dimensionless variable  $y = x/W$ , which is of order unity and ranges between  $y_1 = x_1/W$  and  $y_2 = x_2/W$ :

$$\begin{aligned} K &= \frac{1}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} dx = \frac{\sqrt{2mH}}{\hbar} \int_{x_1}^{x_2} \sqrt{f(x/W)} dx \\ &= \frac{\sqrt{2mHW}}{\hbar} \int_{y_1}^{y_2} \sqrt{f(y)} dy. \end{aligned} \quad (2.2.61)$$

The integral is now a number of order unity, and the scaling of  $K$  with  $H$ ,  $W$  and  $m$  is therefore given by:

$$K \propto \frac{m^{1/2} H^{1/2} W}{\hbar}. \quad (2.2.62)$$

### 2.2.3 Example

To illustrate the above results, let us apply them to the simple case of a square potential barrier with height  $V_0$  and width  $L_0$ :

$$V(x) = \begin{cases} V_0, & |x| \leq L_0/2, \\ 0, & |x| > L_0/2. \end{cases} \quad (2.2.63)$$

For a given energy  $E < V_0$ , the classical turning points are located at  $x_1 = -L_0/2$  and  $x_2 = L_0/2$ . One then computes

$$\begin{aligned} K &= \frac{1}{\hbar} \int_{-L_0/2}^{L_0/2} \sqrt{2m(V_0 - E)} dx, \\ &= \frac{\sqrt{2m(V_0 - E)} L_0}{\hbar}. \end{aligned} \quad (2.2.64)$$

In this simple case, one can work out explicitly the constraints imposed on the validity regime of this result by the two necessary conditions described in last chapter. Firstly, the De Broglie wave length of the wave function should be much smaller than the typical size characterizing the system. In this case, this means that  $|\lambda| \simeq \hbar/\sqrt{2m(V_0 - E)}$  should be much smaller than  $L_0$ :  $|\lambda| \ll L_0$ . This implies that  $K \gg 1$ , as expect on more general grounds. Secondly, the derivative of the potential at the turning points should not be too large. In our case, this derivative is actually infinite, and the gluing prescriptions of section 1.7 are therefore strictly speaking not applicable. However, one should nevertheless get the correct exponential suppression factor and miss only a relatively unimportant multiplicative correction prefactor  $A$ . We can thus infer that the reflection and transmission coefficients should be given by the following approximate formulae, with  $K$  given by eq. (2.2.64) and  $A$  representing an unknown prefactor depending polynomially on the parameters of the problem:

$$R \simeq 1 - A e^{-2K}, \quad T \simeq A e^{-2K}. \quad (2.2.65)$$

In this case, it is actually straightforward to compute the exact wave function and derive from it the exact expressions for the reflection and transmission coefficients. These are found to be given by:

$$R = \frac{1}{1 + (4/A)^{-1} \sinh^{-2} K}, \quad T = \frac{1}{1 + (4/A) \sinh^2 K}. \quad (2.2.66)$$

where  $K$  is given by eq. (2.2.64) and  $A$  is found to be given by

$$A = 16 \frac{E}{V_0} \left( 1 - \frac{E}{V_0} \right). \quad (2.2.67)$$

We see that for  $K \gg 1$ , the above result does indeed take the approximate form (2.2.65), and the prefactor  $A$  has as promised only a mild polynomial dependence on the parameters.

#### 2.2.4 Generalizations

The above semiclassical analysis of the probability of tunneling through a potential barrier can be generalized from the case of one degree of freedom associated to the coordinate  $x$  to an arbitrary number  $d$  of degrees of freedom associated to equally many coordinates  $x_i$ . The general  $d$ -dimensional result has the same general form as the one-dimensional result derived above, but with an exponent  $K$  given by:

$$K = \min \int_{\vec{x}_1}^{\vec{x}_2} \beta(\vec{x}') dl(\vec{x}'). \quad (2.2.68)$$

Pictorially, this means that in the semiclassical approximation a  $d$ -dimensional tunneling process is dominated by a one-dimensional tunneling process that proceeds along the section of the barrier along which it appears most transparent.

## 2.3 Lifetime of a metastable state

Another interesting application of the semiclassical approximation is the study of the quasi-localized states arising in a potential well involving a finite rather infinite barrier against escape at infinity. In such a situation, we expect that due to the possibility of tunneling through the barrier, there will be no strictly localized states associated to the well, but only quasi-localized states involving not only a localized component inside the well but also a delocalized component escaping outside the barrier. If the tunneling effect is small, we can interpret this situation as leading to metastable localized state with a finite lifetime against decay through the barrier. The corresponding energy will then be complex, with a real part controlling the energy of the level and the usual stationary behavior in time, and the imaginary part controlling the decay width and a damped behavior in time. Such states are then called quasi-stationary.

Consider a particle moving in one-dimensional potential  $V(x)$  consisting of a well with an infinite barrier on the left but a finite barrier on the right, with some energy  $E$ . There are then three turning points  $x_1$ ,  $x_2$  and  $x_3$  with  $x_1 < x_2 < x_3$  where  $V(x_1) = V(x_2) = V(x_3) = E$  and  $V'(x_1) < 0$ ,  $V'(x_2) > 0$ ,  $V'(x_3) < 0$ , as depicted in fig. 2.3. This defines two classically allowed regions  $II = ]x_1, x_2[$  and  $IV = ]x_3, +\infty[$ , and two classically forbidden regions  $I = ]-\infty, x_1[$  and  $III = ]x_2, x_3[$ . By matching the semiclassical behaviors across the three turning points, one finds a relation between the amplitudes of the wave function in the classically forbidden region on the far left and the classically allowed region on the far right. In region  $I$ , the wave function must be exponentially suppressed, but in region  $IV$  we allow the wave function to consist of a progressive wave resulting from the tunneling of the localized state in the well. This setup specifies a definite boundary condition, which allows to solve for the complete wave function in the four regions in terms of a single overall normalization constant. The energy spectrum follows as before from a quantization condition, but in this case the values are complex, even if the Hamiltonian is real, simply because one of the boundary condition is complex.

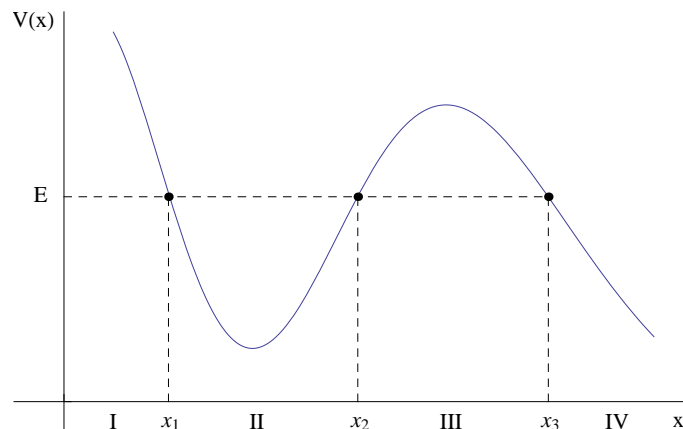


Figure 2.3: Turning points in a potential well with a finite barrier.

### 2.3.1 Evaluation of the semiclassical wave function

The semiclassical wave function can be derived by proceeding as in the cases of a single well or barrier and exploiting the calculations that have already been done for those cases. The wave function in the regions *I* and *II* around the first turning point, with the boundary condition that it vanishes at  $x \rightarrow -\infty$ , has the same form as for the potential well:

$$\phi_I(x) \simeq \frac{C}{2\sqrt{\beta(x)}} \exp \left\{ - \int_x^{x_1} \beta(x') dx' \right\}, \quad (2.3.69)$$

$$\phi_{II}(x) \simeq \frac{C}{2\sqrt{k(x)}} \left[ e^{i\frac{\pi}{4}} \exp \left\{ -i \int_{x_1}^x k(x') dx' \right\} + e^{-i\frac{\pi}{4}} \exp \left\{ i \int_{x_1}^x k(x') dx' \right\} \right]. \quad (2.3.70)$$

The wave function in the regions *II*, *III* and *IV* across the barrier defined by the turning points  $x_2$  and  $x_3$ , with the boundary condition that it reduces to a progressive wave at  $x \rightarrow +\infty$ , has instead the same form as for the potential barrier:

$$\phi_{II}(x) \simeq \frac{D}{\sqrt{k(x)}} \left[ \exp \left\{ -i \int_x^{x_2} k(x') dx' \right\} - i \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ i \int_x^{x_2} k(x') dx' \right\} \right] \quad (2.3.71)$$

$$\begin{aligned} \phi_{III}(x) \simeq \frac{D}{\sqrt{\beta(x)}} & \left[ \frac{e^{-i\frac{\pi}{4}}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ - \int_{x_2}^x \beta(x') dx' \right\} \right. \\ & \left. + \frac{1}{2} \frac{e^{i\frac{\pi}{4}} e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ \int_{x_2}^x \beta(x') dx' \right\} \right], \end{aligned} \quad (2.3.72)$$

$$\phi_{IV}(x) \simeq \frac{D}{\sqrt{k(x)}} \left[ \frac{e^{-K}}{1 + \frac{1}{4}e^{-2K}} \exp \left\{ i \int_{x_3}^x k(x') dx' \right\} \right]. \quad (2.3.73)$$

where

$$K = \int_{x_2}^{x_3} \beta(x') dx'. \quad (2.3.74)$$

The two different expressions for the wave function in the region *II* must now be matched. The corresponding condition is most easily formulated after rewriting

$$\int_x^{x_2} k(x') dx' = J - \int_{x_1}^x k(x') dx', \quad (2.3.75)$$

where

$$J = \int_{x_1}^{x_2} k(x') dx'. \quad (2.3.76)$$

One must then require that:

$$\begin{aligned} & \frac{1}{2} C e^{i\frac{\pi}{4}} \exp \left\{ -i \int_{x_1}^x k(x') dx' \right\} + \frac{1}{2} C e^{-i\frac{\pi}{4}} \exp \left\{ i \int_{x_1}^x k(x') dx' \right\} \\ & = D e^{-iJ} \exp \left\{ i \int_{x_1}^x k(x') dx' \right\} - i D \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} e^{iJ} \exp \left\{ -i \int_{x_1}^x k(x') dx' \right\}. \end{aligned} \quad (2.3.77)$$

The above condition is identically satisfied for every  $x \in ]x_1, x_2[$  if and only if the coefficients of the progressive and the regressive waves both match. These two equations yield a quantization condition on  $J$  and a relation between the two constants  $C$  and  $D$ :

$$e^{-2iJ} = -\frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}}, \quad \frac{C}{D} = 2e^{i\frac{\pi}{4}}e^{-iJ}. \quad (2.3.78)$$

Equivalently, these may also be written as:

$$\cot J = \frac{i}{4}e^{-2K}, \quad \frac{C}{D} = 2e^{-i\frac{\pi}{4}}\frac{\sin J}{1 + i \cot J}. \quad (2.3.79)$$

In both of these forms, we see that the quantization condition cannot be satisfied with real  $J$  but only with complex  $J$ . As expected, this implies complex values of the energy. The general solution can again be parametrized in terms of a non-negative integer  $n = 0, 1, \dots$  and reads:

$$J = \left(n + \frac{1}{2}\right)\pi + \frac{i}{2} \log \left(\frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}}\right), \quad \frac{C}{D} = 2e^{i\frac{\pi}{4}}(-1)^n \sqrt{\frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}}}. \quad (2.3.80)$$

Summarizing, the system admits an infinite set of quasi-localized modes with complex energies  $E$  and wave function given in terms of a single overall coefficient  $C$  by:

$$\left\{ \begin{array}{l} \phi_I(x) \simeq \frac{C}{2\sqrt{\beta(x)}} \exp \left\{ -\int_x^{x_1} \beta(x') dx' \right\}, \\ \phi_{II}(x) \simeq \frac{C}{\sqrt{k(x)}} \sin \left( \int_{x_1}^x k(x') dx' + \frac{\pi}{4} \right), \\ \phi_{III}(x) \simeq \frac{(-1)^n C}{2\sqrt{\beta(x)}} \left[ \frac{1}{\sqrt{1 - \frac{1}{16}e^{-4K}}} \exp \left\{ -\int_{x_2}^x \beta(x') dx' \right\} \right. \\ \quad \left. + \frac{i}{2} \frac{e^{-2K}}{\sqrt{1 - \frac{1}{16}e^{-4K}}} \exp \left\{ \int_{x_2}^x \beta(x') dx' \right\} \right], \\ \phi_{IV}(x) \simeq \frac{(-1)^n C}{2\sqrt{k(x)}} \left[ \frac{e^{i\frac{\pi}{4}} e^{-K}}{\sqrt{1 - \frac{1}{16}e^{-4K}}} \exp \left\{ i \int_{x_3}^x k(x') dx' \right\} \right], \end{array} \right. \quad (2.3.81)$$

with the quantization condition:

$$\int_{x_1}^{x_2} k(x') dx' = \left(n + \frac{1}{2}\right)\pi + \frac{i}{2} \log \left(\frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}}\right). \quad (2.3.82)$$

As already explained, the allowed energies  $E$  are complex. They are conventionally written in the following form:

$$E = E_0 - i\frac{\Gamma}{2}. \quad (2.3.83)$$

The states are correspondingly not really stationary. This can be seen by computing the probability density defined by the full wave function  $\psi(x, t) = e^{-\frac{i}{\hbar}Et}\phi(x)$  describing a

state with such a complex energy. One finds:

$$\begin{aligned}\rho(x, t) &= |\psi(x, t)|^2 = |e^{-\frac{i}{\hbar}Et}|^2 |\phi(x)|^2 \\ &= e^{-\frac{1}{\hbar}\Gamma t} |\phi(x)|^2.\end{aligned}\tag{2.3.84}$$

We see that the overall normalization decreases exponentially in time, as a result of the non-zero imaginary part in the energy. This corresponds to the fact that a state that is initially localized in the barrier can decay by tunneling through the barrier to a delocalized state. One can then define the lifetime of such an initially localized state as the time scale of this exponential decay, that is the time by which the probability to find the state localized in the well decreases by a factor of  $e$ . From the above result for the density of probability, we then conclude that the lifetime is related to the imaginary part of the energy by the following relation:

$$\tau = \frac{\hbar}{\Gamma}.\tag{2.3.85}$$

The quantity  $\Gamma$ , which has the dimension of an energy, has also a direct physical interpretation. This is related to the fact that when trying to measure the energy  $E$  of an unstable state, by any kind of physical process, the uncertainty relation  $\Delta E \Delta t \geq \frac{\hbar}{2}$  sets a limitation on how small an uncertainty  $\Delta E$  on the result one can get depending on how large an observation time  $\Delta T$  one can afford:  $\Delta E \geq \hbar/(2\Delta T)$ . When the state has a finite lifetime  $\tau = \hbar/\Gamma$ , one is limited to  $\Delta T \lesssim \tau$  and therefore  $\Delta E \geq \Gamma/2$ . This means that  $\Gamma$  represents an intrinsic uncertainty on the energy that can be associated to the state. In a spectroscopy experiment in which the levels are measured from some peaks in the response of a system to radiation,  $E_0$  will then represent the location of the peaks and  $\Gamma$  their widths. For this reason,  $\Gamma$  is often called the width of the state.

As usual, the validity of the semiclassical approximation normally requires that the tunneling probability through the barrier is small and therefore

$$K \gg 1.\tag{2.3.86}$$

In that case, the factor controlling the tunneling probability through the finite barrier is small,  $e^{-2K} \ll 1$ , and one can approximate the right-hand side of the quantization condition with the simpler expression

$$\frac{i}{2} \log \left( \frac{1 - \frac{1}{4}e^{-2K}}{1 + \frac{1}{4}e^{-2K}} \right) \simeq -\frac{i}{4}e^{-2K}.\tag{2.3.87}$$

Correspondingly, the imaginary part of the energy is much smaller than the real part, and one has:

$$\Gamma \ll E_0.\tag{2.3.88}$$

In such a situation, the state is a long-lived quasi-stationary state, and one can derive an explicit expression for its lifetime. To do this one may expand the left-hand side of the quantization condition around  $E_0$  at first order in powers of  $\Gamma$ :

$$J|_E \simeq J|_{E_0} - i \frac{\Gamma}{2} \left. \frac{\partial J}{\partial E} \right|_{E_0}.\tag{2.3.89}$$

Plugging back these expressions into the quantization condition, one finally deduces that the real and imaginary parts of the energy are approximately determined by two independent equations:

$$E_0 : J|_{E_0} \simeq \left(n + \frac{1}{2}\right)\pi, \quad (2.3.90)$$

$$\Gamma = \frac{1}{2} \left( \frac{\partial J}{\partial E} \right)_{E_0}^{-1} e^{-2K}. \quad (2.3.91)$$

The lifetime is then

$$\tau = 2\hbar \left( \frac{\partial J}{\partial E} \right)_{E_0} e^{2K}. \quad (2.3.92)$$

### 2.3.2 Decay width and classical interpretation

In this case too, the results that we have obtained in the semiclassical approximation admit a nice interpretation in terms of the quantities characterizing the classical trajectory. Recall in particular that the period  $T$  and the frequency  $\omega$  are given by

$$T = \oint dt = m \oint \frac{dx}{p(x)}, \quad (2.3.93)$$

$$\omega = \frac{2\pi}{T}, \quad (2.3.94)$$

and that the functions  $J$  and  $\partial J/\partial E$  can then be rewritten as follows in terms of these quantities:

$$J = \frac{1}{2\hbar} \oint p(x) dx, \quad (2.3.95)$$

$$\frac{\partial J}{\partial E} = \frac{m}{2\hbar} \oint \frac{dx}{p(x)} = \frac{T}{2\hbar} = \frac{1}{2\hbar\omega}. \quad (2.3.96)$$

We see that the energy  $E_0$  of the levels are determined by the same quantization condition as for a normal well, namely the Bohr-Sommerfeld type of condition:

$$\oint p(x) dx = \left(n + \frac{1}{2}\right)h. \quad (2.3.97)$$

The implications and the interpretation of this result are exactly the same as those already discussed for a simple well.

The width  $\Gamma$ , which is the new physical quantity associated the finite barrier attached to the well, is instead given by the following expression in terms of classical quantities:

$$\Gamma = \frac{\hbar}{T} e^{-2K}. \quad (2.3.98)$$

The corresponding lifetime is then

$$\tau = T e^{2K}. \quad (2.3.99)$$



This result can be understood in the following way. We know from the study of the tunneling through a potential barrier that the probability for a particle at the turning point to tunnel through it and escape is equal to  $e^{-2K} \ll 1$ . Now, in the classical approximation the particle undergoes a periodic motion with period  $T$  in the well, and during some large time  $t \gg T$  it therefore arrives at the relevant turning point a number of times  $t/T \gg 1$ . The probability that the particle decays during this large time is given by  $1 - (1 - e^{-2K})^{t/T} \simeq 1 - e^{-t/Te^{-2K}}$ . The lifetime  $\tau$  should then be equal to the time  $t$  for which this probability becomes equal to  $1 - 1/e$ . This reproduces the result  $\tau = Te^{2K}$ .

## 2.4 Multiple wells and barrier

The computations done in the last three sections can be generalized to one-dimensional situations where the potential involves several wells and barrier. In these more complicated cases, it is convenient to proceed in the following way. First one determines the general form of the semiclassical wave function in terms of two independent coefficients. Then one imposes on it the boundary conditions at infinity that are appropriate to the problem. Finally, one extracts the relevant information.

The general computation that has to be done is to find the relation between the two coefficient parametrizing the general form of the wave function for  $x \rightarrow +\infty$  in terms of the two coefficients parametrizing the general form of the wave function for  $x \rightarrow -\infty$ , by suitably gluing these coefficients across each turning point. From the three examples that were worked out in detail, it is clear that this can be done according to some simple and universal general rules. More precisely, putting the pair of coefficients describing the wave-function in each region into a two-dimensional vector, the gluing across each turning point amounts to the action of two by two matrix on this. More precisely, we shall track the coefficients controlling the two independent exponentials describing the solution, and we therefore define the following notation:

$$C_i^{\text{all}} = \begin{pmatrix} C_{i+} \\ C_{i-} \end{pmatrix}, \quad C_i^{\text{for}} = \begin{pmatrix} C_{iA} \\ C_{iB} \end{pmatrix}. \quad (2.4.100)$$

When crossing a turning point  $x_i$ , the coefficients in the two regions that it separates are related by the expression linking the coefficients  $C_{i+}$ ,  $C_{i-}$  and the coefficients  $C_{iA}$ ,  $C_{iB}$ . For a turning point  $x_i$  with raising potential with  $V'(x_i) > 0$ , the coefficients  $C_i^{\text{for}}$  in the forbidden region on the right are linked to the coefficients  $C_i^{\text{all}}$  in the allowed region on the left by the relation

$$C_i^{\text{for}} = M_{\uparrow} \cdot C_i^{\text{all}}, \quad (2.4.101)$$

where:

$$M_{\uparrow} = \begin{pmatrix} e^{-i\frac{\pi}{4}} & e^{i\frac{\pi}{4}} \\ e^{i\frac{\pi}{4}} & e^{-i\frac{\pi}{4}} \end{pmatrix}. \quad (2.4.102)$$

Similarly, for a turning point  $x_i$  with falling potential with  $V'(x_i) < 0$ , the coefficients  $C_i^{\text{all}}$  in the allowed region on the right are linked to the coefficients  $C_i^{\text{for}}$  in the for region on the left by the relation

$$C_i^{\text{all}} = M_{\downarrow} \cdot C_i^{\text{for}}, \quad (2.4.103)$$

where:

$$M_{\downarrow} = \frac{1}{2} \begin{pmatrix} e^{i\frac{\pi}{4}} & e^{-i\frac{\pi}{4}} \\ e^{-i\frac{\pi}{4}} & e^{i\frac{\pi}{4}} \end{pmatrix}. \quad (2.4.104)$$

When moving from one turning point  $x_i$  to the next turning point  $x_{i+1}$ , one must then rewrite the wave function by expressing the integrals of the form  $\int_{x_i}^x$  in terms of integrals of the form  $\int_x^{x_{i+1}}$ , before proceeding to the next gluing. When  $x_i$  and  $x_{i+1}$  are separated by a well with factor  $J_i = \int_{x_i}^{x_{i+1}} k(x') dx'$ , one can use the simple relation  $\int_{x_i}^x k(x') dx' = J_i - \int_x^{x_{i+1}} k(x') dx'$ , and the coefficients  $C_{i+1}^{\text{all}}$  describing the wave function as seen from the turning point  $x_{i+1}$  on its left are linked to the coefficients  $C_i^{\text{all}}$  describing the wave function as seen from the turning point  $x_i$  on its right by the relation

$$C_{i+1}^{\text{all}} = M_{W_i} \cdot C_i^{\text{all}}, \quad (2.4.105)$$

where:

$$M_{W_i} = \begin{pmatrix} 0 & e^{iJ_i} \\ e^{-iJ_i} & 0 \end{pmatrix}, \quad J_i = \int_{x_i}^{x_{i+1}} k(x') dx'. \quad (2.4.106)$$

Similarly, when  $x_i$  and  $x_{i+1}$  are separated by a barrier with factor  $K_i = \int_{x_i}^{x_{i+1}} \beta(x') dx'$ , one can use the relation  $\int_{x_i}^x \beta(x') dx' = K_i - \int_x^{x_{i+1}} \beta(x') dx'$ , and the coefficients  $C_{i+1}^{\text{for}}$  describing the wave function as seen from the turning point  $x_{i+1}$  on its left are linked to the coefficients  $C_i^{\text{for}}$  describing the wave function as seen from the turning point  $x_i$  on its right by the relation

$$C_{i+1}^{\text{for}} = M_{B_i} \cdot C_i^{\text{for}}, \quad (2.4.107)$$

where:

$$M_{B_i} = \begin{pmatrix} 0 & 2e^{K_i} \\ \frac{1}{2}e^{-K_i} & 0 \end{pmatrix}, \quad K_i = \int_{x_i}^{x_{i+1}} \beta(x') dx'. \quad (2.4.108)$$

Using the above rules, one can then find the matrix relating the coefficients on the far right of the potential to those on the far left of the potential by simply multiplying the matrices associated to each raising or falling turning point and to each well or barrier.

### 2.4.1 Multiple wells

As a first application, let us consider localized states in a multiple well potential, where both the asymptotic regions are classically forbidden. The coefficients  $C_{>}^{\text{for}}$  describing the

wave function for  $x \rightarrow +\infty$  are linked to the coefficients  $C_{<}^{\text{for}}$  describing the wave function for  $x \rightarrow -\infty$  by some matrix  $M$  as

$$C_{>}^{\text{for}} = M \cdot C_{<}^{\text{for}}, \quad (2.4.109)$$

The form of the physical wave function is now obtained by imposing the boundary conditions that it is a falling exponential for  $x \rightarrow -\infty$  and  $x \rightarrow +\infty$ . This implies that  $C_{<A} \neq 0$ ,  $C_{<B} = 0$  and  $C_{>A} \neq 0$ ,  $C_{>B} = 0$ . The gluing equation is then:

$$\begin{pmatrix} C_{>A} \\ 0 \end{pmatrix} = \begin{pmatrix} M_{AA} & M_{AB} \\ M_{BA} & M_{BB} \end{pmatrix} \cdot \begin{pmatrix} C_{<A} \\ 0 \end{pmatrix}. \quad (2.4.110)$$

This implies the following two conditions, which are respectively the quantization condition and the relation between the two coefficients:

$$M_{BA} = 0, \quad \frac{C_{>A}}{C_{<A}} = M_{AA}. \quad (2.4.111)$$

For the case of a single well, which has already been studied, it is straightforward to recover the known results. The relevant matrix is  $M = M_{\uparrow} \cdot M_W \cdot M_{\downarrow}$ , and one easily computes  $M_{BA} = \cos J$ . This gives back correct quantization condition  $\cot J = 0$ , whose solution is parametrized by one non-negative integer  $n$  and reads  $J = (n + \frac{1}{2})h$ .

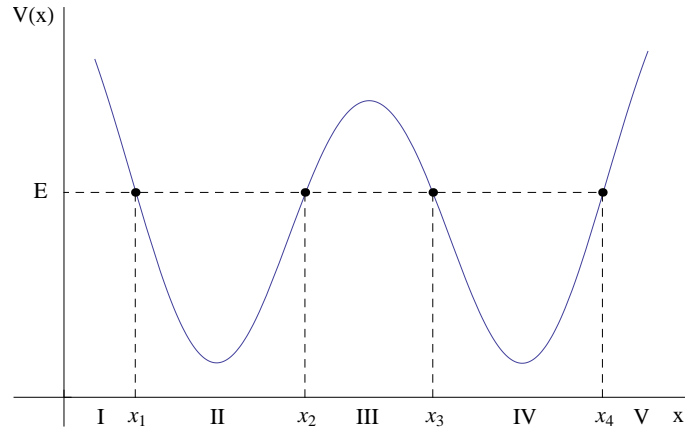


Figure 2.4: Turning points in a double potential well with a finite barrier.

For the case of a double well of the type depicted in fig. 2.4, one can proceed exactly in the same way, without much more effort. The relevant matrix is in this case:

$$M = M_{\uparrow} \cdot M_{W_2} \cdot M_{\downarrow} \cdot M_B \cdot M_{\uparrow} \cdot M_{W_1} \cdot M_{\downarrow}. \quad (2.4.112)$$

A straightforward computation yields:

$$M_{BA} = 2 e^K \cos J_1 \cos J_2 - \frac{1}{2} e^{-K} \sin J_1 \sin J_2. \quad (2.4.113)$$

It follows that the quantization condition is given by:

$$\cot J_1 \cot J_2 = \frac{1}{4} e^{-2K}. \quad (2.4.114)$$

Assuming that  $e^{-2K} \ll 1$ , the allowed levels are then in first approximation those of the two wells considered separately, plus some small real corrections suppressed as  $e^{-2K}$  induced by tunneling effects. In the particular case of a symmetric double well, for which  $J_1 = J_2 = J$ , this effect is however enhanced and is only suppressed as  $e^{-K}$ , due to the fact that it lifts a two-fold degeneration of the levels. Indeed, the quantization condition becomes:

$$\cot J = \pm \frac{1}{2} e^{-K}. \quad (2.4.115)$$

Let us then write the energy as a main contribution  $E_0$  plus a small correction  $\Delta E$  due to tunneling effects:

$$E = E_0 + \Delta E \quad (2.4.116)$$

One can then expand the left-hand side of the quantization condition as follows:

$$\cot J|_E \simeq \cot J|_{E_0} - \left[ \sin^{-2} J \frac{\partial J}{\partial E} \right]_{E_0} \Delta E. \quad (2.4.117)$$

The leading part of the quantization condition states that the spectrum for the leading values  $E_0$  is twice degenerate satisfies the quantization condition of each single well taken separately:

$$E_0 : \cot J|_{E_0} = 0. \quad (2.4.118)$$

The general solution is, as already seen, labelled by a non-negative integer  $n$  and is defined by:

$$E_0 : J|_{E_0} = \left( n + \frac{1}{2} \right) \pi. \quad (2.4.119)$$

The subleading terms in the quantization condition then determine the correction  $\Delta E$  to these levels induced by the tunneling effect through the finite barrier separating them. One finds:

$$\Delta E = \mp \frac{1}{2} \left( \frac{\partial J}{\partial E} \right)_{E_0}^{-1} e^{-K}. \quad (2.4.120)$$

Each degenerate pair of levels therefore splits, as a result of the tunneling effect. The lowest corresponds to a parity-even wave-function and the upper one to a parity-odd wave function. Recalling finally that  $\partial J / \partial E = T / (2\hbar)$  in terms of the period  $T$  of the classical motion within each well, the above result can also be written as

$$\Delta E = \mp \frac{\hbar}{T} e^{-K}. \quad (2.4.121)$$

## 2.4.2 Multiple barriers

As a second application, let us consider delocalized states in a multiple barrier potential, where both the left and the right asymptotic regions are allowed. The coefficients  $C_{>}^{\text{all}}$  describing the wave function for  $x \rightarrow +\infty$  are linked to the coefficients  $C_{<}^{\text{all}}$  describing the wave function for  $x \rightarrow -\infty$  by some matrix  $M$  as

$$C_{>}^{\text{all}} = M \cdot C_{<}^{\text{all}}, \quad (2.4.122)$$

Conservation of the current density of probability  $j$  implies that the two pairs of coefficients satisfy

$$|C_{<+}|^2 - |C_{<-}|^2 = |C_{>-}|^2 - |C_{>+}|^2. \quad (2.4.123)$$

This guarantees that the above matrix  $M$  must satisfy the following general properties:

$$|M_{-+}|^2 - |M_{++}|^2 = 1, \quad (2.4.124)$$

$$|M_{+-}|^2 - |M_{--}|^2 = 1, \quad (2.4.125)$$

$$M_{++}M_{+-}^* - M_{-+}M_{--}^* = 0. \quad (2.4.126)$$

Combining these three equations, one also deduces that:

$$|M_{++}| = |M_{--}|, \quad |M_{+-}| = |M_{-+}|, \quad |\det M| = 1. \quad (2.4.127)$$

The form of the physical wave function is now obtained by imposing the boundary conditions that it is an incident plus a reflected wave for  $x \rightarrow -\infty$  and an transmitted wave for  $x \rightarrow +\infty$ . This implies that  $C_{<+} \neq 0$ ,  $C_{<-} \neq 0$  and  $C_{>+} = 0$ ,  $C_{>-} \neq 0$ . The gluing equation is then:

$$\begin{pmatrix} 0 \\ C_{>-} \end{pmatrix} = \begin{pmatrix} M_{++} & M_{+-} \\ M_{-+} & M_{--} \end{pmatrix} \cdot \begin{pmatrix} C_{<+} \\ C_{<-} \end{pmatrix}. \quad (2.4.128)$$

This implies the following two conditions, which are the relation between the three coefficients:

$$\frac{C_{<+}}{C_{<-}} = -\frac{M_{+-}}{M_{++}}, \quad \frac{C_{>-}}{C_{<-}} = \frac{\det M}{M_{++}}. \quad (2.4.129)$$

Using (2.4.127), it follows that the reflection and transmission coefficients are given by:

$$R = \left| \frac{C_{<-}}{C_{<+}} \right|^2 = \left| \frac{M_{++}}{M_{+-}} \right|^2, \quad (2.4.130)$$

$$T = \left| \frac{C_{>-}}{C_{<+}} \right|^2 = |M_{+-}|^{-2}. \quad (2.4.131)$$

Thanks to (2.4.124)–(2.4.126), these add up to one as they should:

$$R + T = 1. \quad (2.4.132)$$

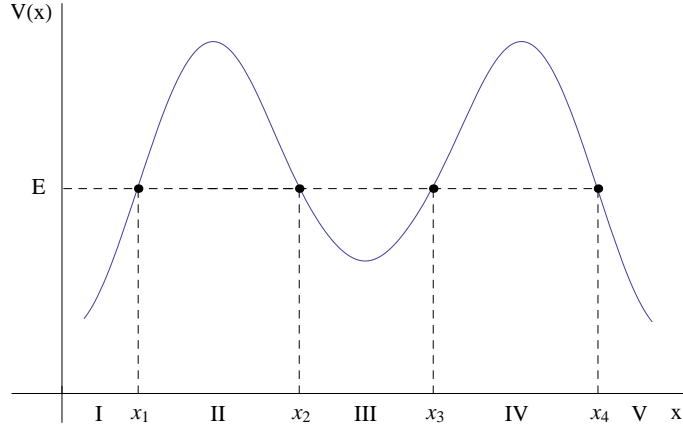


Figure 2.5: Turning points in a double potential barrier.

For the case of a single barrier, which has already been studied, it is straightforward to recover the correct results. The relevant matrix is in this case  $M = M_{\downarrow} \cdot M_B \cdot M_{\uparrow}$ , and one easily finds that  $M_{++} = i(e^K - \frac{1}{4}e^{-K})$  and  $M_{+-} = e^K + \frac{1}{4}e^{-K}$ . It follows that  $R = (1 - \frac{1}{4}e^{-2K})^2(1 + \frac{1}{4}e^{-2K})^{-2}$  and  $T = e^{-2K}(1 + \frac{1}{4}e^{-2K})^{-2}$ .

For the case of a double barrier of the type depicted in fig. 2.5, one can proceed in the same way. In that case one has to consider the following matrix:

$$M = M_{\downarrow} \cdot M_{B_2} \cdot M_{\uparrow} \cdot M_W \cdot M_{\downarrow} \cdot M_{B_1} \cdot M_{\uparrow}. \quad (2.4.133)$$

After a straightforward computation one finds:

$$M_{++} = 2i \left( e^{K_1+K_2} - \frac{1}{16}e^{-K_1-K_2} \right) \cos J + \frac{1}{2} \left( e^{K_1-K_2} - e^{-K_1+K_2} \right) \sin J, \quad (2.4.134)$$

$$M_{+-} = 2 \left( e^{K_1+K_2} + \frac{1}{16}e^{-K_1-K_2} \right) \cos J - \frac{i}{2} \left( e^{K_1-K_2} + e^{-K_1+K_2} \right) \sin J. \quad (2.4.135)$$

For simplicity, let us from now on focus on the simplest case of a symmetric barrier with  $K_1 = K_2 = K$ . In that case the above expressions reduce to:

$$M_{++} = 2i \left( e^{2K} - \frac{1}{16}e^{-2K} \right) \cos J, \quad (2.4.136)$$

$$M_{+-} = 2 \left( e^{2K} + \frac{1}{16}e^{-2K} \right) \cos J - i \sin J. \quad (2.4.137)$$

The reflection and transmission coefficients are then found to be given by the following expressions:

$$R = \frac{\cos^2 J}{\cos^2 J + \frac{1}{4}e^{-4K} \left(1 - \frac{1}{16}e^{-4K}\right)^{-2}}, \quad (2.4.138)$$

$$T = \frac{\frac{1}{4}e^{-4K} \left(1 - \frac{1}{16}e^{-4K}\right)^{-2}}{\cos^2 J + \frac{1}{4}e^{-4K} \left(1 - \frac{1}{16}e^{-4K}\right)^{-2}}. \quad (2.4.139)$$

Under the conservative assumption that  $K \gg 1$ , these results further simplify to

$$R \simeq \frac{\cos^2 J}{\cos^2 J + \frac{1}{4}e^{-4K}}, \quad (2.4.140)$$

$$T \simeq \frac{\frac{1}{4}e^{-4K}}{\cos^2 J + \frac{1}{4}e^{-4K}}. \quad (2.4.141)$$

The above reflection and transmission coefficients display peaks of transparency, where  $R = 0$ ,  $T = 1$ , in correspondence to energies  $E_0$  for which  $\cos J = 0$ . These are recognized to be the energy levels of the well:

$$E_0 : J|_{E_0} = \left(n + \frac{1}{2}\right)\pi. \quad (2.4.142)$$

We know that these levels are actually only quasi-stationary states, due to the possibility of escaping the well by tunneling through any of the two finite barriers. We then expect the width of these states also to play a role in the above formulae. This is indeed the case. To see it, let us anticipate that this width is equal to twice the one computed in section 1.10, due to the presence of two identical barriers, as we will confirm by an explicit computation in next subsection. We are thus led to define

$$\Gamma = \left(\frac{\partial J}{\partial E}\right)_{E_0}^{-1} e^{-2K}. \quad (2.4.143)$$

Using this definition, we can then write down a simple expression for the dependence on the energy  $E$  of the reflection and transmission coefficients close to the special energies  $E_0$ . To do so, we expand around  $E_0$  and compute:

$$\begin{aligned} \cos^2 J|_E &\simeq \cos^2 J|_{E_0} - \left[2 \cos J \sin J \frac{\partial J}{\partial E}\right]_{E_0} (E - E_0) \\ &\quad - \left[(\cos^2 J - \sin^2 J) \left(\frac{\partial J}{\partial E}\right)^2 - \cos J \sin J \frac{\partial^2 J}{\partial E^2}\right]_{E_0} (E - E_0)^2 \\ &\simeq \Gamma^{-2} e^{-4K} (E - E_0)^2. \end{aligned} \quad (2.4.144)$$

Plugging back into the expressions for  $R$  and  $T$ , one finally finds that for  $E$  close to  $E_0$  the behavior of the reflection and transmission coefficients is simply

$$R \simeq \frac{(E - E_0)^2}{(E - E_0)^2 + \Gamma^2/4}, \quad (2.4.145)$$

$$T \simeq \frac{\Gamma^2/4}{(E - E_0)^2 + \Gamma^2/4}. \quad (2.4.146)$$

These approximate formulae clearly display that the appearance of peaks is directly related to the existence of quasi stationary states in the well between the two barriers, and that the energy  $E_0$  and the width  $\Gamma$  determine the location and the width of these peaks. One is then in presence of a resonance phenomenon, and the above formulae display the universal Breit-Wigner behavior associated to such phenomena. In the situation studied here, this

phenomenon can be visualized as an enhancement factor  $e^{4K}$  related to the resonance phenomenon that exactly compensates the suppression factor  $e^{-4K}$  related to the barriers in the transmission coefficient. But this type of phenomenon can actually occur also in more more general situations.

The above reflection and transmission coefficients also display peaks of opacity, where  $R$  goes through a local maximum and  $T$  through a local minimum, in correspondence to energies  $E_1$  for which  $\cos J = 1$ , that is:

$$E_1 : J|_{E_1} = n\pi. \quad (2.4.147)$$

These energies do not correspond to any physical state of the well, but rather to the particular energies for which a maximal destructive interference of the scattering wave occurs inside the well. At such points one gets

$$R \simeq 1 - \frac{1}{4}e^{-4K}, \quad (2.4.148)$$

$$T \simeq \frac{1}{4}e^{-4K}. \quad (2.4.149)$$

In the situation at hand, this suppression effect can be visualized as due to the expected suppression factor  $e^{-4K}$  related to the barriers, which is no-longer compensated by any enhancement factor. But this type of suppression effect can occur also in more general situations.

### 2.4.3 Multiple metastable wells

As a last application, let us consider quasi-localized states in a multiple metastable well potential, where one or both of the left and right asymptotic regions are classically allowed. Let us consider these two possible situations separately.

In the first general case, where the left region is forbidden and the right region is allowed, the coefficients  $C_{>}^{\text{all}}$  describing the wave function for  $x \rightarrow +\infty$  are linked to the coefficients  $C_{<}^{\text{for}}$  describing the wave function for  $x \rightarrow -\infty$  by some matrix  $M$  as

$$C_{>}^{\text{all}} = M \cdot C_{<}^{\text{for}}, \quad (2.4.150)$$

The form of the physical wave function is now obtained by imposing the boundary conditions that it is a damped exponential for  $x \rightarrow -\infty$  and a progressive wave for  $x \rightarrow +\infty$ , resulting from the decay of the quasi-localized state in the well. This implies that  $C_{<A} \neq 0$ ,  $C_{<B} = 0$  and  $C_{>+} = 0$ ,  $C_{>-} \neq 0$ . The gluing equation is then:

$$\begin{pmatrix} 0 \\ C_{>-} \end{pmatrix} = \begin{pmatrix} M_{+A} & M_{+B} \\ M_{-A} & M_{-B} \end{pmatrix} \cdot \begin{pmatrix} C_{<A} \\ 0 \end{pmatrix}. \quad (2.4.151)$$

This implies the following two conditions, which are the quantization condition and the relation between the two coefficients:

$$M_{+A} = 0, \quad \frac{C_{>-}}{C_{<A}} = M_{-A}. \quad (2.4.152)$$



For the case of a single well followed by a single barrier, which has already been studied, it is straightforward to recover the correct result. The relevant matrix is in this case  $M = M_{\downarrow} \cdot M_B \cdot M_{\uparrow} \cdot M_W \cdot M_{\downarrow}$ , and one easily finds  $M_{+A} = e^{i\frac{\pi}{4}} (e^K \cos J - \frac{i}{4} e^{-K} \sin J)$ . This gives back the quantization condition  $\cot J = \frac{i}{4} e^{-2K}$ , whose solution for  $K \gg 1$  is a complex energy  $E = E_0 - i\Gamma/2$  where  $E_0 : J|_{E_0} \simeq (n + \frac{1}{2})\pi$  and  $\Gamma = \frac{1}{2} (\partial J / \partial E)^{-1} e^{-2K}$ .

In the second general case, where both the left and the right regions are allowed, the coefficients  $C_{>}^{\text{all}}$  describing the wave function for  $x \rightarrow +\infty$  are linked to the coefficients  $C_{<}^{\text{all}}$  describing the wave function for  $x \rightarrow -\infty$  by some matrix  $M$  as

$$C_{>}^{\text{all}} = M \cdot C_{<}^{\text{all}}. \quad (2.4.153)$$

The form of the physical wave function is obtained by imposing the boundary conditions that it is a regressive wave for  $x \rightarrow -\infty$  and a progressive wave for  $x \rightarrow +\infty$ , resulting from the decay of the quasi-localized state in the well. This implies that  $C_{<+} = 0$ ,  $C_{<-} \neq 0$  and  $C_{>+} = 0$ ,  $C_{>-} \neq 0$ . The gluing equation is then:

$$\begin{pmatrix} 0 \\ C_{>-} \end{pmatrix} = \begin{pmatrix} M_{++} & M_{+-} \\ M_{-+} & M_{--} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ C_{<-} \end{pmatrix}. \quad (2.4.154)$$

This implies the following two conditions, which are the quantization condition and the relation between the two coefficients:

$$M_{+-} = 0, \quad \frac{C_{>-}}{C_{<-}} = M_{--}. \quad (2.4.155)$$

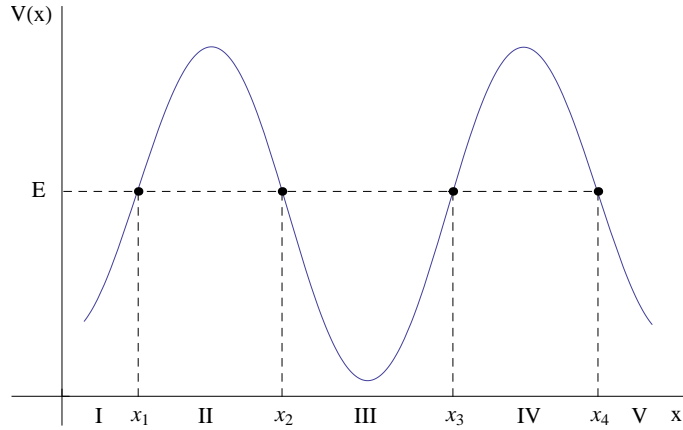


Figure 2.6: Turning points in a well with two barriers.

In the case of a simple well surrounded by two barriers of the type depicted in fig. 2.6, one has to consider the following matrix:

$$M = M_{\downarrow} \cdot M_{B_2} \cdot M_{\uparrow} \cdot M_W \cdot M_{\downarrow} \cdot M_{B_1} \cdot M_{\uparrow}. \quad (2.4.156)$$

One easily finds:

$$M_{+-} = 2 \left( e^{K_1+K_2} + \frac{1}{16} e^{-K_1-K_2} \right) \cos J - \frac{i}{2} \left( e^{K_1-K_2} + e^{-K_1+K_2} \right) \sin J. \quad (2.4.157)$$

In the simplest case of a symmetric barrier with  $K_1 = K_2 = K$ , and under the assumption that  $K \gg 1$ , this reduces to

$$M_{+-} \simeq 2e^{2K} \cos J - i \sin J. \quad (2.4.158)$$

The quantization condition then reads:

$$\cot J \simeq \frac{i}{2} e^{-2K}. \quad (2.4.159)$$

The general solution of this equation is again a complex energy  $E = E_0 - i\Gamma/2$ , with the same real part  $E_0$  as before but an imaginary part  $\Gamma$  that is twice as big:

$$E_0 : J|_{E_0} \simeq \left(n + \frac{1}{2}\right)\pi, \quad (2.4.160)$$

$$\Gamma = \left(\frac{\partial J}{\partial E}\right)_{E_0}^{-1} e^{-2K}. \quad (2.4.161)$$

Recalling finally that  $\partial J/\partial E = T/(2\hbar)$  in terms of the period  $T$  of the classical motion within the well, the lifetime  $\tau = \hbar/\Gamma$  is found to be twice smaller as in the case of a single barrier, as expected:

$$\tau = \frac{1}{2} T e^{2K}. \quad (2.4.162)$$



## Chapter 3

# Central problems and the semiclassical approximation

In this chapter we will consider three-dimensional spherically symmetric problems with a central potential and apply the semiclassical approximation to the study of a number of typical problems in this setting. We will start by reviewing how the radial and angular parts of this kind of problems can be separated, and how the angular wave function can be decomposed in terms of spherical harmonics. We will then discuss the general features of the radial part of the wave function and describe how one may compute it in the semiclassical approximation, by treating the radial problem as an effective one-dimensional problem. We will finally study the various typical problems that can arise in this context. These include localized bound states and their spectrum of levels, delocalized states and their scattering amplitude, and metastable states and their life time.

### 3.1 Separation of radial and angular parts

We shall start by summarizing the basic tools to treat spherically symmetric problems, where the potential depends only on the distance. Using polar coordinates  $r$ ,  $\theta$  and  $\varphi$ , the problem is completely separable. The Hamiltonian takes the form

$$H = \frac{1}{2m} \left( p_r^2 + \frac{L^2}{r^2} \right) + V(r), \quad (3.1.1)$$

where  $p_r$  is the Hermitian radial momentum

$$p_r = -i\hbar \left( \frac{\partial}{\partial r} + \frac{1}{r} \right), \quad (3.1.2)$$

and  $L^2$  is the square angular momentum

$$L^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right). \quad (3.1.3)$$

These operators also commute with the third component  $L_z$  of the angular momentum:

$$L_z = -i\hbar \frac{\partial}{\partial \varphi}. \quad (3.1.4)$$

The Schrödinger equation for a stationary state of fixed energy  $E$  and wave function  $\psi(r, \theta, \varphi, t) = \phi(r, \theta, \varphi)e^{-\frac{i}{\hbar}Et}$  implies that the stationary wave function  $\phi(r, \theta, \varphi)$  should be an eigenvector of  $H$  with eigenvalue  $E$ :

$$H \phi(r, \theta, \varphi) = E \phi(r, \theta, \varphi). \quad (3.1.5)$$

In general the eigenvalue  $E$  can be either quantized in terms of some quantum number  $n = 0, 1, 2, \dots$  if the state is a localized bound state, or allowed to take a continuum of values, if the state is a delocalized wave state:

$$E = \begin{cases} \text{quantized in terms of } n = 0, 1, 2, \dots \text{ for localized states} \\ \text{continuous for delocalized states} \end{cases}. \quad (3.1.6)$$

Moreover, since  $L^2$  and  $L_z$  commute with  $H$  and among themselves, one can also require that the stationary wave function  $\phi(r, \theta, \varphi)$  should be an eigenvector of  $L^2$  with eigenvalue  $\lambda^2$  and of  $L_z$  with eigenvalue  $\lambda_z$ :

$$L^2 \phi(r, \theta, \varphi) = \lambda^2 \phi(r, \theta, \varphi), \quad (3.1.7)$$

$$L_z \phi(r, \theta, \varphi) = \lambda_z \phi(r, \theta, \varphi). \quad (3.1.8)$$

From the algebraic properties of the angular momentum operators, we finally know that the eigenvalues of  $L^2$  are quantized in terms of a first quantum number  $l = 0, 1, 2, \dots$ , and those of  $L_z$  are quantized in terms of an other quantum number  $m = -l, \dots, l$ :

$$\lambda^2 = l(l+1)\hbar^2, \quad l = 0, 1, 2, \dots, \quad (3.1.9)$$

$$\lambda_z = m\hbar, \quad m = -l, \dots, l. \quad (3.1.10)$$

We can then separate the problem into radial and angular parts by taking the following factorized form for the wave function:

$$\phi(r, \theta, \varphi) = \phi_l(r)Y_l^m(\theta, \varphi). \quad (3.1.11)$$

## 3.2 Exact angular wave function

The angular part  $Y_l^m(\theta, \varphi)$  of the wave function corresponding to given values of  $l$  and  $m$  satisfies the eigenvalue equations

$$L^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi), \quad (3.2.12)$$

$$L_z Y_l^m(\theta, \varphi) = \hbar m Y_l^m(\theta, \varphi). \quad (3.2.13)$$

The problem is separable and can be reduced to two independent one-dimensional problems by posing:

$$Y_l^m(\theta, \varphi) = N_{lm} u_{lm}(\theta) \rho_m(\varphi). \quad (3.2.14)$$

The functions  $u_{lm}(\theta)$  and  $\rho_m(\varphi)$  then satisfy some ordinary differential equations, which happen to be exactly solvable, while the constant  $N_{lm}$  is an arbitrary normalization.

The differential equation for  $\rho_m(\varphi)$  arises from the eigenvalue equation for  $L_z$  and takes the following simple form:

$$\rho_m''(\varphi) + m^2 \rho_m(\varphi) = 0. \quad (3.2.15)$$

This is of the same form as the Schrödinger wave equation for a one-dimensional problem with a constant wave number:  $k = m$ . Modulo an arbitrary overall normalization, the solution of this equation is just a simple phase:

$$\rho_m(\varphi) = e^{im\varphi}. \quad (3.2.16)$$

The differential equation for  $u_{lm}(\theta)$  arises from the eigenvalue equation for  $L^2$  and takes the following form:

$$u_{lm}''(\theta) + \cot \theta u_{lm}'(\theta) + \left[ l(l+1) - \frac{m^2}{\sin^2 \theta} \right] u_{lm}(\theta) = 0. \quad (3.2.17)$$

To eliminate the term involving the first derivative, one can redefine  $u_{lm}$  by extracting a factor of  $\sqrt{\sin \theta}$  and posing

$$u_{lm}(\theta) = \frac{v_{lm}(\theta)}{\sqrt{\sin \theta}}. \quad (3.2.18)$$

In this way one finds the following equation for  $v_{lm}(\theta)$ :

$$v_{lm}''(\theta) + \left[ \left( l + \frac{1}{2} \right)^2 + \frac{1 - 4m^2}{4 \sin^2 \theta} \right] v_{lm}(\theta) = 0. \quad (3.2.19)$$

This is again of the same form as the Schrödinger wave equation for a one-dimensional problem, but now with a non-constant wave number that depends on the coordinate:  $k(\theta) = \sqrt{(l+1/2)^2 - (m^2 - 1/4) \sin^{-2} \theta}$ . Nevertheless, the regular solution of this equation can be found in closed form, and modulo an arbitrary overall normalization, it is given by:

$$v_{lm}(\theta) = \sqrt{\sin \theta} P_l^m(\cos \theta), \quad (3.2.20)$$

in the terms of the associated Legendre polynomials  $P_l^m(z)$  defined as

$$P_l^m(z) = \frac{1}{2^l l!} (1 - z^2)^{m/2} \frac{d^{l+m}}{dz^{l+m}} (z^2 - 1)^l, \quad (3.2.21)$$

Finally, the normalization constant  $N_{lm}$  can be fixed to any convenient value. It is conventionally chosen to be

$$N_{lm} = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}. \quad (3.2.22)$$

In this way, the angular part of the wave function is finally given by the following spherical harmonic function:

$$Y_l^m(\theta, \varphi) = N_{lm} P_l^m(\cos \theta) e^{im\varphi}, \quad (3.2.23)$$

These functions satisfy the following completeness and orthonormality conditions:

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l Y_l^m(\theta, \varphi) Y_l^{m*}(\theta', \varphi') = \delta(\cos \theta - \cos \theta') \delta(\varphi - \varphi'), \quad (3.2.24)$$

$$\int_{-1}^1 \int_0^{2\pi} Y_l^{m*}(\theta, \varphi) Y_{l'}^{m'}(\theta, \varphi) d(\cos \theta) d\varphi = \delta_{ll'} \delta_{mm'}. \quad (3.2.25)$$

### 3.3 Semiclassical angular wave function

As we have seen in the previous section, the angular part  $Y_l^m(\theta, \varphi) = N_{lm} u_{lm}(\theta) \rho_m(\varphi)$  of the wave function is universal and can be determined exactly in closed form. There is therefore no practical need to apply the semiclassical approximation in this case. However, we will nevertheless shortly discuss what one would find for such a wave function by applying the semiclassical approximation, and what is the regime of applicability of this approximate result. This will allow us later on to discuss more precisely the classical limit of the full three-dimensional problem.

The exact wave equation for  $\rho_m(\varphi)$  involves a constant wave number, which is related to the quantum number  $m$  and is given by:

$$k(\varphi) = m. \quad (3.3.26)$$

The De Broglie wave length  $\lambda = 1/k$  is then also constant, and one finds  $|d\lambda/d\varphi| = 0$ . This is always identically vanishing and in particular small. The semiclassical approximation is then formally applicable for any  $m$ :

$$m : \text{arbitrary}. \quad (3.3.27)$$

Moreover, the semiclassical form of the wave function reproduces in this case accidentally the exact form of the wave function.

The exact wave equation for  $u_{lm}(\theta)$  involves instead a non-constant wave number, which depends on both quantum numbers  $l$  and  $m$  and reads:

$$k(\theta) = \sqrt{(l + 1/2)^2 - (m^2 - 1/4) \sin^{-2} \theta}. \quad (3.3.28)$$

The De Broglie wave length  $\lambda = 1/k$  is then also a non-trivial function of  $\theta$ , and one finds  $|d\lambda/d\theta| = |m^2 - 1/4| |\cos \theta| [(l + 1/2)^2 \sin^2 \theta - (m^2 - 1/4)]^{-3/2}$ . This is small only if  $|(l + 1/2)^2 \sin^2 \theta - (m^2 - 1/4)|$  is large. A necessary condition for this to be possible is that  $l \sin \theta \gg 1$  should be large, which implies that  $l \gg 1$  and  $\theta, \pi - \theta \gg 1/l$ . The semiclassical approximation is therefore in this case applicable only when  $l$  is large and  $\theta$  is not too close to the extreme values 0 or  $\pi$ :

$$l \gg 1, \quad \theta, \pi - \theta \gg l^{-1}. \quad (3.3.29)$$

In this case, the semiclassical form of the wave function will only approximate the exact form of the wave function.

### 3.4 Exact radial wave function

The radial part  $\phi_l(r)$  of the wave function corresponding to given values of  $l$  and  $E$  satisfies instead the eigenvalue equation

$$H_{\text{eff}} \phi_l(r) = E \phi_l(r), \quad (3.4.30)$$

where, using the definition of  $p_r^2$  and the eigenvalue of  $L^2$ , the effective Hamiltonian is found to be given by

$$H_{\text{eff}} = T_{\text{eff}} + V_{\text{eff}}, \quad (3.4.31)$$

with effective kinetic and potential energies given by

$$T_{\text{eff}} = -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right), \quad V_{\text{eff}} = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (3.4.32)$$

More explicitly, the radial wave equation then reads:

$$\phi_l'' + \frac{2}{r} \phi_l' + \left[ \frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] \phi_l = 0. \quad (3.4.33)$$

To get rid of the term of first order in the radial derivative, it is sometimes convenient to further redefine the radial wave function by extracting a factor of  $r$ :

$$\phi_l(r) = r^{-1} \chi_l(r) \quad (3.4.34)$$

The new radial wave function  $\chi(r)$  then satisfies an equation that is very similar to the Schrödinger equation for a single degree of freedom associated to the radial coordinate  $r$ . More precisely, one now finds

$$H_{\text{eff}} \chi_l(r) = E \chi_l(r), \quad (3.4.35)$$

with

$$H_{\text{eff}} = T_{\text{eff}} + V_{\text{eff}}, \quad (3.4.36)$$

where now

$$T_{\text{eff}} = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2}, \quad V_{\text{eff}} = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \quad (3.4.37)$$

More explicitly, the reduced form of the radial wave equation is then:

$$\chi_l'' + \left[ \frac{2m}{\hbar^2} (E - V(r)) - \frac{l(l+1)}{r^2} \right] \chi_l = 0. \quad (3.4.38)$$

The exact behavior of the radial wave function depends on the form of the potential  $V(r)$  and can in general not be determined in closed form. However, its asymptotic behaviors turn out to be universal, under some mild assumptions. More precisely, let us assume that  $V(r)$  is less singular than  $1/r^2$  for  $r \rightarrow 0$  and that it tends to 0 for  $r \rightarrow +\infty$ .



In such a situation, the behavior for  $r \rightarrow 0$  is determined by the centrifugal potential and is universal, while the behavior for  $r \rightarrow \infty$  is essentially free and thus also universal. For concreteness we focus here on the case where the energy  $E$  is positive. The results can then be expressed in terms of the real asymptotic wave number defined by:

$$k = \frac{\sqrt{2mE}}{\hbar}. \quad (3.4.39)$$

The results for negative energy  $E$  can be obtained by an analytic continuation and essentially correspond to having an imaginary wave number, as usual. But we will not work them out in detail here. We shall moreover discuss the asymptotic behaviors of  $\phi_l(r)$ . The asymptotic behaviors of the corresponding  $\chi_l(r)$  are easily deduced by using the relation  $\chi_l(r) = r\phi(r)$ .

### 3.4.1 Asymptotic behavior in the origin

Consider first the behavior in the region  $r \rightarrow 0$ . In that region, the differential equation for  $\phi_l$  is approximately given by

$$\phi_l'' + \frac{2}{r}\phi_l' - \frac{l(l+1)}{r^2}\phi_l \simeq 0. \quad (3.4.40)$$

The solutions of this equation are proportional to the function  $\phi_l(r) \simeq r^\alpha$ , where  $\alpha$  must satisfy  $\alpha^2 + \alpha - l(l+1) = 0$ , implying  $\alpha = l, -l-1$ . Introducing some peculiar normalizations that will be convenient later on, and noting  $(2n+1)!! = (2n+1)(2n-1)\cdots 1$ , the two independent solutions can then be taken to be :

$$\phi_{lj}(r) \simeq \frac{1}{(2l+1)!!} (kr)^l, \quad (3.4.41)$$

$$\phi_{ln}(r) \simeq -(2l-1)!! (kr)^{-l-1}. \quad (3.4.42)$$

The first of these two solutions is regular in the origin and therefore physically acceptable, while the second is singular in the origin and must therefore be discarded.

### 3.4.2 Asymptotic behavior at infinity

Consider next the behavior in the region  $r \rightarrow +\infty$ . In that region, the differential equation for  $\phi_l$  simplifies to

$$\phi_l'' + \frac{2}{r}\phi_l' + k^2\phi_l \simeq 0. \quad (3.4.43)$$

The solutions of this equation are proportional to the function  $\phi_l(r) \simeq r^{-1}\sin(kr + \delta)$ , with arbitrary  $\delta$ . Introducing again some specific normalizations that will be convenient later on, the two independent solutions can then be taken to be

$$\phi_{lj}(r) \simeq \frac{1}{kr} \sin\left(kr - l\frac{\pi}{2}\right), \quad (3.4.44)$$

$$\phi_{ln}(r) \simeq -\frac{1}{kr} \cos\left(kr - l\frac{\pi}{2}\right). \quad (3.4.45)$$

Both of these solutions are bounded at infinity and therefore acceptable.

### 3.4.3 Relative asymptotic behaviors for vanishing potential

In the particular case of a free particle subject to no potential, the radial wave function can be determined exactly. The differential equation for  $\phi_l$  is in that case given by

$$\phi_l'' + \frac{2}{r}\phi_l' + \left[ k^2 - \frac{l(l+1)}{r^2} \right] \phi_l \simeq 0. \quad (3.4.46)$$

This is the spherical Bessel equation, modulo a simple rescaling of the variable  $r$  by  $k$ . The two independent solutions of this equation can be chosen to be the spherical Bessel functions  $j_l(kr)$  and  $n_l(kr)$ :

$$\phi_{lj}(r) \simeq j_l(kr), \quad (3.4.47)$$

$$\phi_{ln}(r) \simeq n_l(kr). \quad (3.4.48)$$

The functions  $j_l(z)$  and  $n_l(z)$  have a typical behavior that is displayed in fig. 3.1 and are given by the following expressions:

$$j_l(z) = (-z)^l \left( \frac{1}{z} \frac{d}{dz} \right)^l \frac{\sin z}{z}, \quad (3.4.49)$$

$$n_l(z) = -(-z)^l \left( \frac{1}{z} \frac{d}{dz} \right)^l \frac{\cos z}{z}. \quad (3.4.50)$$

These satisfy the following property, which reflects the fact that  $zj_l(z)$  and  $zn_l(z)$  are the two independent solutions of a differential equation without first derivative term and must therefore have a constant Wronskian:

$$j_l(z)n_l(z)' - j_l(z)'n_l(z) = 1. \quad (3.4.51)$$

The exact solutions (3.4.47) and (3.4.48) can be shown to have precisely the asymptotic behaviors reported above, namely (3.4.41) and (3.4.42) for  $r \rightarrow 0$  and (3.4.44) and (3.4.45) for  $r \rightarrow +\infty$ , including the numerical coefficients, and the transition between the oscillatory and the power behavior is seen from the differential equation to occur for  $r \simeq \sqrt{l(l+1)}/k$ . We then conclude that only the first of these solution is acceptable, while the second must be discarded, due to the behavior at the origin. The asymptotic behaviors of this regular combination  $\phi_{l\text{reg}}(r)$  will then be the following:

$$\phi_{l\text{reg}}(r) \simeq \frac{1}{(2l+1)!!} (kr)^l, \quad r \rightarrow 0, \quad (3.4.52)$$

$$\phi_{l\text{reg}}(r) \simeq \frac{1}{kr} \sin \left( kr - l\frac{\pi}{2} \right), \quad r \rightarrow +\infty. \quad (3.4.53)$$

In other words, once the regular behavior is chosen in the origin, the behavior at infinity has a fixed amplitude and phase.

### 3.4.4 Relative asymptotic behavior for non-vanishing potential

In the case of a particle subject to a non-trivial potential, one can in general not find the explicit form of the two independent solutions of the differential equation defining

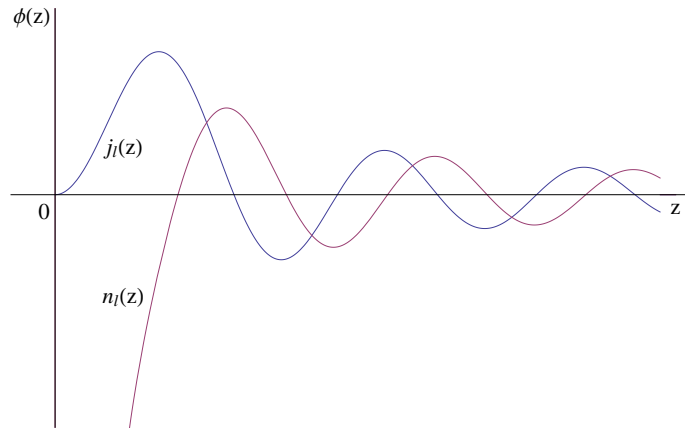


Figure 3.1: Typical form for spherical Bessel functions  $j_l(z)$  and  $n_l(z)$ .

the radial wave function. Still, the asymptotic behaviors for  $r \rightarrow 0$  and  $r \rightarrow \infty$  must correspond to linear combinations of the universal asymptotic behaviors that we have deduced above. However, due to the effect of the potential, it will no longer be true that the solution that has the  $j$ -type or the  $n$ -type behavior for  $r \rightarrow 0$  will have the  $j$ -type or the  $n$ -type behavior for  $r \rightarrow +\infty$ . In fact, the acceptable solution with the regular  $j$ -type behavior at  $r \rightarrow 0$  will behave as some linear combination of the  $j$ -type and  $n$ -type behaviors at  $r \rightarrow +\infty$ . The asymptotic behaviors of this regular combination  $\phi_{l\text{reg}}(r)$  will then have the following general form:

$$\phi_{l\text{reg}}(r) \simeq \frac{1}{(2l+1)!!} (kr)^l, \quad r \rightarrow 0, \quad (3.4.54)$$

$$\phi_{l\text{reg}}(r) \simeq \frac{A_l}{kr} \sin\left(kr - l\frac{\pi}{2} + \delta_l\right), \quad r \rightarrow +\infty. \quad (3.4.55)$$

The only possible effect of the potential on the asymptotic behavior of the radial wave function is therefore an amplitude rescaling  $A_l$  and a phase shift  $\delta_l$ , which depend on the angular momentum quantum number  $l$  and tend respectively to 1 and 0 in the limit of vanishing potential.

### 3.5 Semiclassical radial wave function

As discussed in the previous section, the radial part  $\chi_l(r)$  of the wave function is determined by a one-dimensional schrödinger-like equation involving an effective potential  $V_{\text{eff}}(r) = V(r) + \hbar^2 l(l+1)/(2mr^2)$ , and can in general not be determined exactly in closed form. It is then interesting to address the problem in the semiclassical approximation. To do so, we can simply apply the general formulae obtained for the semiclassical wave function of one-dimensional problems, after substituting the wave number  $k$  and the penetration number  $\beta$  in the classically allowed and forbidden regions with the following

effective expressions including the effect of the angular momentum:

$$k_{\text{eff}}(r) = \frac{1}{\hbar} \sqrt{2m(E - V_{\text{eff}}(r))}, \quad (3.5.56)$$

$$\beta_{\text{eff}}(r) = \frac{1}{\hbar} \sqrt{2m(V_{\text{eff}}(r) - E)}. \quad (3.5.57)$$

Let us now investigate under which conditions the semiclassical approximation is applicable. For simplicity, we shall again suppose that the potential has a behavior which is less singular than  $1/r^2$  for  $r \rightarrow 0$  and that it tends to 0 for  $r \rightarrow +\infty$ . For small values of  $r$ ,  $V_{\text{eff}}(r)$  is then dominated by the centrifugal term and  $|k_{\text{eff}}| \simeq \sqrt{l(l+1)}/r$ . It follows that  $|\lambda_{\text{eff}}| \simeq r/\sqrt{l(l+1)}$  and  $|d\lambda_{\text{eff}}/dr| \simeq 1/\sqrt{l(l+1)}$ . The condition  $|d\lambda_{\text{eff}}/dr| \ll 1$  then implies that

$$l \gg 1. \quad (3.5.58)$$

For large values of  $r$ , the whole  $V_{\text{eff}}(r)$  tends to zero in a smooth way and the semiclassical approximation is therefore always valid. Finally, for intermediate values of  $r$ ,  $V_{\text{eff}}$  depends in a significant way on the potential, and one may get further restrictions on the applicability of the semiclassical approximation.

By applying the semiclassical approximation as describe above, one obtains results that work well in situations where the semiclassical approximation holds true, that is for  $l \gg 1$ . However, it turns out that a minor modification of the above formulae, called Langer modification, allows to further improve the accuracy of the results. It consists in replacing the coefficient  $l(l+1)$  in front of the effective centrifugal potential with the factor  $(l+1/2)^2$ , and therefore use the following modified effective potential for the evaluation of the above wave number and penetration number to define the semiclassical wave function:

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2(l+1/2)^2}{2mr^2}. \quad (3.5.59)$$

This modification is clearly quantitatively irrelevant in the limit of large quantum number  $l$ , in which the semiclassical approximation is a priori expected to be reliable. However, it significantly improves the accuracy of the results for small  $l$ . There exist various arguments to justify the above modification and explain why it leads to an improvement. One of the simplest and most transparent of these arguments is related to the asymptotic behavior of the semiclassical wave function  $\chi_l(r)$  for  $r \rightarrow 0$ . Indeed, we shall see below that with this modification the semiclassical wave function displays for  $r \rightarrow 0$  precisely the universal asymptotic behavior that the exact wave function must have, while without this modification its behavior would involve small deviations from the exact behavior that are negligible only for large  $l$ .

The behavior of the semiclassical wave function close to  $r \simeq 0$  is easily computed. Notice for this that the neighborhood of the origin always corresponds to a classically forbidden region, at least for not too singular potentials, since the effective potential tends to  $+\infty$  at this point. The semiclassical wave function in that region must then be

a superposition of the following two expressions:

$$\chi_{lj}(r) \simeq \frac{C_{lj}}{\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ -\int_r \beta_{\text{eff}}(r') dr' \right\}, \quad (3.5.60)$$

$$\chi_{ln}(r) \sim \frac{C_{ln}}{\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ \int_r \beta_{\text{eff}}(r') dr' \right\}. \quad (3.5.61)$$

For  $r \rightarrow 0$ , one finds that the effective potential with Langer's modification behaves as  $V_{\text{eff}}(r) \simeq \hbar^2(l+1/2)^2/(2mr^2)$ , so that

$$\beta_{\text{eff}}(r) \simeq \frac{l+1/2}{r}, \quad (3.5.62)$$

$$\int_r \beta_{\text{eff}}(r') dr' \simeq -(l+1/2) \ln r + \text{constant}. \quad (3.5.63)$$

It follows that the two linearly independent semiclassical solutions do indeed display respectively the  $j$ -type and  $n$ -type universal asymptotic behaviors that the exact wave function  $\chi_l(r) \sim r\phi_l(r)$  is allowed to have close to the origin, namely

$$\chi_{lj}(r) \sim r^{1/2} e^{(l+1/2)\ln r} \sim r^{l+1}, \quad (3.5.64)$$

$$\chi_{ln}(r) \sim r^{1/2} e^{-(l+1/2)\ln r} \sim r^{-l}. \quad (3.5.65)$$

From these behaviors we also learn that the acceptable solution that is regular in the origin is given by (3.5.60), while the other solution (3.5.61) is singular and must therefore be discarded.

### 3.6 Localized stationary states

As a first application, let us consider the study of localized stationary states. To illustrate the situation, we consider a generic attractive potential  $V(r)$ , which is negative, tends to 0 for  $r \rightarrow +\infty$  and is negligible with respect to the centrifugal term proportional to  $1/r^2$  for  $r \rightarrow 0$ . In this situation, there can be a competition between the two terms in the effective potential  $V_{\text{eff}}(r)$ , and this can give rise to a finite well. There can then be localized stationary states with a discrete spectrum of negative energies.

For a negative energy  $E$  there can be two classical turning points  $r_1$  and  $r_2$  in the radial motion, where  $V_{\text{eff}}(r_1) = E$ ,  $V_{\text{eff}}(r_2) = E$  and  $V'_{\text{eff}}(r_1) < 0$ ,  $V'_{\text{eff}}(r_2) > 0$ , as depicted in fig. 3.2. This defines a classically allowed region  $II = ]r_1, r_2[$  and two classically forbidden regions  $I = [0, r_1[$  and  $III = ]r_2, +\infty[$ . The parameter describing the well is:

$$J = \int_{r_1}^{r_2} k_{\text{eff}}(r') dr'. \quad (3.6.66)$$

One can then determine the semiclassical radial wave function by using the usual joining prescriptions. Requiring that the wave function should vanish in the origin and proceeding as in the case of a one-dimensional well, one then deduces that the semiclassical radial

wave function is given by

$$\begin{cases} \chi_{II}(r) \simeq \frac{C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ -\int_r^{r_1} \beta_{\text{eff}}(r') dr' \right\}, \\ \chi_{III}(r) \simeq \frac{C_l}{\sqrt{k_{\text{eff}}(r)}} \sin \left( \int_{r_1}^r k_{\text{eff}}(r') dr' + \frac{\pi}{4} \right), \\ \chi_{lIII}(r) \simeq \frac{(-1)^n C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ -\int_{r_2}^r \beta_{\text{eff}}(r') dr' \right\}, \end{cases} \quad (3.6.67)$$

with the energy quantization condition

$$J = \left( n + \frac{1}{2} \right) \pi. \quad (3.6.68)$$

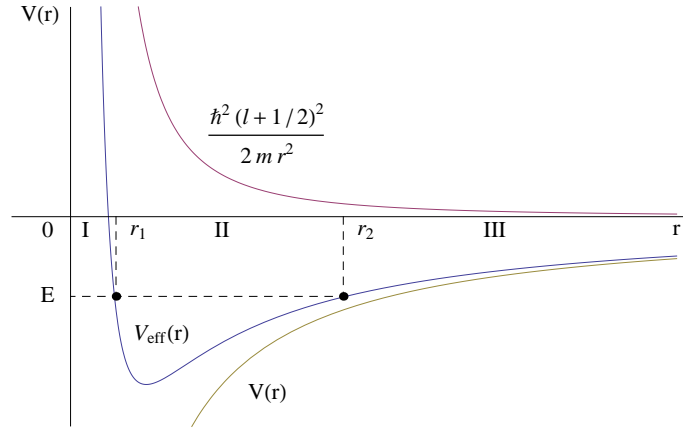


Figure 3.2: Turning points in an attractive central potential.

### 3.6.1 Spectrum and quantization rule

The above result has the same kind of classical interpretation as in the one-dimensional case. In particular, the quantization condition can be rewritten in the form of a Bohr-Sommerfeld quantization rule involving the phase space integral of the radial part of the problem. More precisely, one can write:

$$\oint p_{\text{eff}}(r) dr = \left( n + \frac{1}{2} \right) h. \quad (3.6.69)$$

where

$$p_{\text{eff}}(r) = \sqrt{2m(E - V(r)) - \frac{\hbar^2(l+1/2)^2}{r^2}}. \quad (3.6.70)$$

The integral  $\oint p_{\text{eff}}(r) dr$  over the radial phase space that enters the above quantization condition can be evaluated explicitly as a function of the energy  $E$  for a given potential  $V(r)$  by using the same general technique already explained for the one-dimensional case.

This is again based on the observation that this integral is equal to twice the integral of  $p_{\text{eff}}(r) = \sqrt{2m(E - V_{\text{eff}}(r))}$  between the points  $r_1$  and  $r_2$  where  $V_{\text{eff}}(r_1) = V_{\text{eff}}(r_2) = E$  and thus  $p_{\text{eff}}(r_1) = p_{\text{eff}}(r_2) = 0$ . In the complex plane, where  $p_{\text{eff}}(z)$  has a branch cut ranging between the two turning points  $r_1$  and  $r_2$  on the real axis, this phase space integral can then be written as the integral of  $p_{\text{eff}}(z) = \sqrt{2m(E - V_{\text{eff}}(z))}$  along a closed contour  $c$  encircling the cut. The integral can then be evaluated by using Cauchy's theorem for the reversed contour, which encircles the rest of the complex plane. Assuming that  $V_{\text{eff}}(z)$  is analytic everywhere, except at most in  $z = 0$  where the centrifugal term is divergent, the result of this integral is then simply  $-2\pi i$  times the sum of the residues of the function  $p(z)$  at  $z = \infty$  and at  $z = 0$ , which are respectively equal to minus and plus the coefficients of the  $1/z$  terms in the Laurent expansions of  $p(z)$  around these points. In summary, we thus have:

$$\oint p_{\text{eff}}(r) dr = \oint_c p_{\text{eff}}(z) dz = -2\pi i \left[ \text{Res} \{p_{\text{eff}}(z)\}_{z=\infty} + \text{Res} \{p_{\text{eff}}(z)\}_{z=0} \right]. \quad (3.6.71)$$

In this case, it is usually rather difficult to directly evaluate the result by computing the original real integral by means of ordinary techniques, due to the non-trivial form of the centrifugal barrier.

### 3.6.2 Example

As an application of this result, let us work out the spectrum of bound states in a Coulomb potential, of the type:

$$V(r) = -\frac{\alpha}{r}. \quad (3.6.72)$$

The effective potential then reads:

$$V_{\text{eff}}(r) = -\frac{\alpha}{r} + \frac{\hbar^2(l + 1/2)^2}{2m r^2}. \quad (3.6.73)$$

For a given negative energy  $E$ , there are two classical turning points at  $r_1$  and  $r_2$ , such that  $V(r_1) = V(r_2) = E$ , with:

$$r_{1,2} = -\frac{\alpha}{2E} \left[ 1 \mp \sqrt{1 + \frac{2E\hbar^2(l + 1/2)^2}{\alpha^2 m}} \right]. \quad (3.6.74)$$

These satisfy the relations

$$r_1 + r_2 = -\frac{\alpha}{E}, \quad \sqrt{r_1 r_2} = \frac{\hbar(l + 1/2)}{\sqrt{-2mE}} \quad (3.6.75)$$

We can then rewrite

$$V_{\text{eff}}(r) = E \left[ \frac{r_1 + r_2}{r} - \frac{r_1 r_2}{r^2} \right] = E \left[ 1 + \frac{(r_2 - r)(r - r_1)}{r^2} \right]. \quad (3.6.76)$$

The classically allowed region is the interval  $]r_1, r_2[$ , and the momentum in this region is given by

$$\begin{aligned} p_{\text{eff}}(r) &= \sqrt{2m(E - V_{\text{eff}}(r))} \\ &= \sqrt{-2mE} \frac{\sqrt{(r_2 - r)(r - r_1)}}{r}. \end{aligned} \quad (3.6.77)$$

To compute the integral  $\oint p_{\text{eff}}(x) dx$ , we can deform it in the complex plane and use (3.6.71). Expanding  $p_{\text{eff}}(z)$  around  $z = \infty$  and  $z = 0$ , and taking care of choosing the correct definition of the square root, one respectively finds:

$$\begin{aligned} p_{\text{eff}}(z) &= i\sqrt{-2mE} \sqrt{\left(1 - \frac{r_1}{z}\right)\left(1 - \frac{r_2}{z}\right)} \\ &= \sqrt{-2mE} \left[ i - \frac{i}{2}(r_1 + r_2) \frac{1}{z} + \mathcal{O}\left(\frac{1}{z^2}\right) \right], \end{aligned} \quad (3.6.78)$$

$$\begin{aligned} p_{\text{eff}}(z) &= -i\sqrt{-2mE} \frac{\sqrt{r_1 r_2}}{z} \sqrt{\left(1 - \frac{z}{r_1}\right)\left(1 - \frac{z}{r_2}\right)} \\ &= \sqrt{-2mE} \left[ -i\sqrt{r_1 r_2} \frac{1}{z} + \frac{i}{2} \frac{r_1 + r_2}{\sqrt{r_1 r_2}} + \mathcal{O}(z) \right]. \end{aligned} \quad (3.6.79)$$

It follows that:

$$\text{Res} \{p_{\text{eff}}(z)\}_{z=\infty} = \sqrt{-2mE} \left[ \frac{i}{2}(r_1 + r_2) \right], \quad (3.6.80)$$

$$\text{Res} \{p_{\text{eff}}(z)\}_{z=0} = \sqrt{-2mE} \left[ -i\sqrt{r_1 r_2} \right]. \quad (3.6.81)$$

Using these results into the general formula (3.6.71), one finds

$$\begin{aligned} \oint p_{\text{eff}}(r) dr &= -2\pi i \left[ \text{Res} \{p_{\text{eff}}(z)\}_{z=\infty} + \text{Res} \{p_{\text{eff}}(z)\}_{z=0} \right] \\ &= \sqrt{-2mE} \pi \left[ r_1 + r_2 - 2\sqrt{r_1 r_2} \right]. \end{aligned} \quad (3.6.82)$$

The same result can also be derived by evaluating explicitly the original real integral:

$$\begin{aligned} \oint p_{\text{eff}}(r) dr &= 2\sqrt{-2mE} \int_{r_1}^{r_2} \frac{\sqrt{(r_2 - r)(r - r_1)}}{r} dr \\ &= 2\sqrt{-2mE} \left[ \sqrt{(r - r_1)(r_2 - r)} - \frac{1}{2}(r_1 + r_2) \arcsin\left(\frac{r_1 + r_2 - 2r}{r_2 - r_1}\right) \right. \\ &\quad \left. - \sqrt{r_1 r_2} \arcsin\left(\frac{(r_1 + r_2)r - 2r_1 r_2}{r(r_2 - r_1)}\right) \right]_{r_1}^{r_2} \\ &= \sqrt{-2mE} \pi \left[ r_1 + r_2 - 2\sqrt{r_1 r_2} \right]. \end{aligned} \quad (3.6.83)$$

Recalling the definitions of  $r_1$  and  $r_2$ , the integral is finally found to take the following form:

$$\oint p_{\text{eff}}(r) dr = 2\pi \left[ \sqrt{\frac{-m\alpha^2}{2E}} - \hbar(l + 1/2) \right], \quad (3.6.84)$$

Plugging this result into the condition (3.6.69), one finally deduces that the semiclassical spectrum accidentally coincides in this case with the well-known exact spectrum, namely:

$$E = -\frac{m\alpha^2}{2\hbar^2} \frac{1}{(n + l + 1)^2}. \quad (3.6.85)$$



### 3.7 Delocalized stationary states

As a second application, let us next consider the study of delocalized stationary states. To illustrate the situation, we consider now a generic repulsive potential  $V(r)$ , which is positive, tends to 0 for  $r \rightarrow +\infty$  and is negligible with respect to the centrifugal term proportional to  $1/r^2$  for  $r \rightarrow 0$ . In such a situation, the effective potential  $V_{\text{eff}}(r)$  always displays a infinite barrier at small  $r$ . There can then be delocalized stationary states with a continuous spectrum of positive energies.

For a given positive energy  $E$  there is a single classical turning point  $r_0$  in the radial motion, where  $V_{\text{eff}}(r_0) = E$  and  $V'_{\text{eff}}(r_0) < 0$ , as depicted in fig. 3.3. This defines a classically forbidden region  $I = [0, r_0[$  and a classically allowed region  $II = ]r_0, +\infty[$ . One can then determine the semiclassical radial wave function by using the usual joining prescriptions. Requiring that the wave function should vanish at the origin, and allowing both progressive and regressive waves at infinity, one finds:

$$\begin{cases} \chi_{II}(r) \simeq \frac{C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ - \int_r^{r_0} \beta_{\text{eff}}(r') dr' \right\}, \\ \chi_{III}(r) \simeq \frac{C_l}{\sqrt{k_{\text{eff}}(r)}} \sin \left( \int_{r_0}^r k_{\text{eff}}(r') dr' + \frac{\pi}{4} \right). \end{cases} \quad (3.7.86)$$

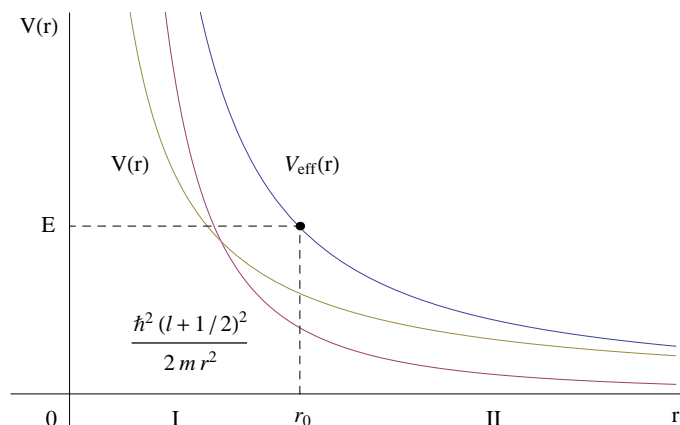


Figure 3.3: Turning point in a repulsive central potential.

We see that the semiclassical wave function that we have obtained describes a radial wave coming in from  $r \rightarrow +\infty$  and a radial wave going out to  $r \rightarrow +\infty$ . The reflection is complete and no transmission by tunneling is allowed. The waves come in from large  $r$ , bounce on the barrier at  $r_0$  and get out to large  $r$  again. However, the boundary condition at the origin in the classically forbidden region imposes as expected a definite value for the phase of the wave at infinity. In fact, we see that the asymptotic form of the semiclassical wave function  $\phi_l(r) = r^{-1}\chi_l(r)$  defined by (3.7.86) does indeed have the expected universal behavior (3.4.55), where  $k$  is the asymptotic wave number

$$k = \frac{\sqrt{2mE}}{\hbar}. \quad (3.7.87)$$

In the free case with  $V(r) = 0$ , one may verify that the phase of the wave function behaves for large  $r$  as expected from eq. (3.4.53). Indeed, in such a situation one has

$$k_{\text{eff}}(r) \Big|_0 = \sqrt{k^2 - \frac{(l + 1/2)^2}{r^2}}. \quad (3.7.88)$$

The turning point where this vanishes is located at  $r_0|_0 = (l + 1/2)/k$ . One may then rewrite  $k_{\text{eff}} = k\sqrt{1 - r_0^2/r^2}$ , and evaluate, for  $r \gg r_0$ :

$$\begin{aligned} \int_{r_0}^r k_{\text{eff}}(r') dr' \Big|_0 &= k \int_{r_0}^r \frac{\sqrt{r'^2 - r_0^2}}{r'} dr' \\ &= k \left[ \sqrt{r'^2 - r_0^2} - r_0 \arccos\left(\frac{r_0}{r'}\right) \right]_{r_0}^r \simeq k \left[ r - r_0 \frac{\pi}{2} \right] \\ &\simeq kr - l \frac{\pi}{2} - \frac{\pi}{4}. \end{aligned} \quad (3.7.89)$$

It follows that the semiclassical wave function behaves in this case as:

$$\chi_l(r) \Big|_0 \propto \sin\left(kr - l \frac{\pi}{2}\right), \quad r \gg r_0. \quad (3.7.90)$$

In the interacting case with  $V(r) \neq 0$ , one gets instead a different behavior for large  $r$ , which is of the form implied by eq. (3.4.55) and involves an extra shift  $\delta_l$  in the phase compared to the free case. Indeed, in such a situation one has:

$$k_{\text{eff}}(r) \Big|_V = \sqrt{k^2 - \frac{2m}{\hbar^2} V(r) - \frac{(l + 1/2)^2}{r^2}}. \quad (3.7.91)$$

The turning point where this vanishes is now located at some  $r_0|_V \neq (l + 1/2)/k$ . One then finds the following type of result, for  $r \gg r_0$

$$\int_{r_0}^r k_{\text{eff}}(r) dr \Big|_V \simeq kr - l \frac{\pi}{2} - \frac{\pi}{4} + \delta_l. \quad (3.7.92)$$

It follows that the semiclassical wave function behaves in this case as

$$\chi_l(r) \Big|_V \propto \sin\left(kr - l \frac{\pi}{2} + \delta_l\right), \quad r \gg r_0. \quad (3.7.93)$$

The phase shift  $\delta_l$  induced by the presence of a non-trivial potential  $V$  can be computed more explicitly in the semiclassical approximation as the following difference of integrals:

$$\begin{aligned} \delta_l &\simeq \int_{r_0}^{\infty} k_{\text{eff}}(r) dr \Big|_0^V \\ &\simeq \frac{1}{\hbar} \int_{r_0}^{\infty} \sqrt{2m(E - V(r)) - \frac{\hbar^2(l + 1/2)^2}{r^2}} dr \Big|_0^V. \end{aligned} \quad (3.7.94)$$

We have here implicitly assumed that the difference of the two integrals converges and thus sent  $r \rightarrow \infty$  in the upper extremum of the integration. We see that this is the case when  $V(r)$  tends to zero faster than  $1/r$  for large  $r$ . On the other hand, when  $V(r)$  tends to zero slower than  $1/r$ , even the difference of the two integrals diverges, and

one finds an infinite result for  $\delta_l$ . However, since this divergence is controlled by the potential and is independent of the centrifugal barrier, it is actually independent of  $l$  and therefore universal. One may then rewrite  $\delta_l$  as the sum of an  $l$ -independent and potentially divergent part  $\delta$  plus an  $l$ -dependent and always finite part  $\hat{\delta}_l$ :

$$\delta_l = \delta + \hat{\delta}_l. \quad (3.7.95)$$

### 3.7.1 Scattering amplitude and cross section

Let us now see how one can characterize the scattering process for the original three-dimensional problem. The typical experimental setting to study such a process consists in sending in an incident beam of particles from a given direction and measuring the scattered beam of particles in some other arbitrary direction. In such a setting, one may then consider the so-called differential cross section  $\sigma(\Omega)$  associated to the problem. This is an observable quantity that is defined as follows for a general scattering problem. One first considers the quantity  $d\sigma$  defined by the ratio of the number of particles scattered per unit time within some infinitesimal solid angle  $d\Omega$  and the number of incident particles per unit time and unit surface. One then divides this quantity by the infinitesimal solid angle element  $d\Omega$  to define  $\sigma(\Omega) = d\sigma/d\Omega$ . Summarizing:

$$\sigma(\Omega) = \frac{\# \text{ scattered particles in } d\Omega \text{ per unit time divided by } d\Omega}{\# \text{ incident particles per unit time and surface}}. \quad (3.7.96)$$

This quantity has the dimension of a length squared and measures the effective transversal section that particles scattered with a certain energy and in a certain direction feel for the target that generates the potential. It is the closest three-dimensional analogue of the reflection coefficient for one-dimensional problems. But its normalization is not directly constrained by the conservation of the probability density current, and it can be non-trivial even at the classical level. One may also define the total cross section  $\sigma_{\text{tot}}$  as the integral of the differential cross section  $\sigma(\Omega)$  over the solid angle:

$$\sigma_{\text{tot}} = \int \sigma(\Omega) d\Omega. \quad (3.7.97)$$

For general non-central problems, the scattering process depends both on  $\theta$  and on  $\varphi$ . One must then look at  $\theta$  in the interval  $[\theta, \theta + d\theta]$  and  $\varphi$  in the interval  $[\varphi, \varphi + d\varphi]$ , and use  $d\Omega = d(\cos \theta)d\varphi$  as infinitesimal solid angle element. This gives  $\sigma(\Omega) = \sigma(\theta, \varphi)$ . For central problems, on the other hand, one can choose the  $z$  axis to coincide with the direction of the incident particles, and the scattering process then depends only on  $\theta$  and not on  $\varphi$ . One can then look at  $\theta$  in the interval  $[\theta, \theta + d\theta]$  and  $\varphi$  anywhere in the interval  $[0, 2\pi]$ , and use  $d\Omega = 2\pi d(\cos \theta)$  as infinitesimal solid angle element. One then finds  $\sigma(\Omega) = \sigma(\theta)$ .

Let us now see how one can compute the differential cross section at the quantum level for central problems. Choosing the direction of the incident wave to be parallel to the  $z$  axis, the scattered wave can only depend on the angle  $\theta$ , while the angle  $\varphi$  must

remain constant. In fact, in such a situation  $L_z = 0$  and the whole wave function  $\phi(r, \theta, \varphi)$  describing the complete scattering state must be independent of  $\varphi$ :

$$\phi(r, \theta) = \text{full wave-function of the delocalized stationary state.} \quad (3.7.98)$$

The boundary condition that we would now like to impose on this three-dimensional wave function is that for  $r \rightarrow +\infty$  it should be the sum of an incident plane wave of the form  $\phi_{\text{inc}}(r, \theta) = e^{ikr \cos \theta}$ , which travels along the  $z$  axis with some wave number  $k$ , and a scattered spherical wave of the form  $\phi_{\text{sca}}(r, \theta) = f(\theta)r^{-1}e^{ikr}$ , which has an amplitude that falls off as  $1/r$  and is modulated by some function  $f(\theta)$  of the scattering angle. The common overall normalization of these two asymptotic waves will not be important for our purposes and for simplicity we conventionally set it to one. We then require that:

$$\phi(r, \theta) \simeq e^{ikr \cos \theta} + \frac{f(\theta)}{r}e^{ikr}, \quad r \rightarrow +\infty. \quad (3.7.99)$$

The fluxes of particles described by this asymptotic wave can be computed by using the usual expression for the density of probability current:

$$\vec{j} = -\frac{i\hbar}{2m} \left( \phi^* \vec{\nabla} \phi - \phi \vec{\nabla} \phi^* \right). \quad (3.7.100)$$

For the incident plane wave  $\phi_{\text{inc}}(r, \theta) = e^{ikr \cos \theta}$ , the current is oriented along the  $z$  direction and has a modulus given by:

$$\begin{aligned} j_{\text{inc}}(r, \theta) &= -\frac{i\hbar}{2m \cos \theta} \left( \phi_{\text{inc}}^* \frac{\partial}{\partial r} \phi_{\text{inc}} - \phi_{\text{inc}} \frac{\partial}{\partial r} \phi_{\text{inc}}^* \right)(r, \theta) \\ &= \frac{\hbar k}{m}. \end{aligned} \quad (3.7.101)$$

For the scattered spherical wave  $\phi_{\text{sca}}(r, \theta) = f(\theta)r^{-1}e^{ikr}$ , on the other hand, this current is oriented radially and has a modulus given at large  $r$  by

$$\begin{aligned} j_{\text{sca}}(r, \theta) &= -\frac{i\hbar}{2m} \left( \phi_{\text{sca}}^* \frac{\partial}{\partial r} \phi_{\text{sca}} - \phi_{\text{sca}} \frac{\partial}{\partial r} \phi_{\text{sca}}^* \right)(r, \theta) \\ &\simeq \frac{\hbar k}{m} \frac{|f(\theta)|^2}{r^2}. \end{aligned} \quad (3.7.102)$$

To compute the differential cross section  $\sigma(\theta)$ , we now observe that the number of incident particles per unit time and surface is just  $j_{\text{inc}}$ , while the number of scattered particles per unit time in the solid angle element  $d\Omega$  defining a surface element  $dS = r^2 d\Omega$  is given by  $j_{\text{sca}} dS = j_{\text{sca}} r^2 d\Omega$ . It then follows that

$$\sigma(\theta) = \frac{j_{\text{sca}}(r, \theta)}{j_{\text{inc}}(r, \theta)} r^2 \quad (3.7.103)$$

Using the expressions (3.7.101) and (3.7.102), we see that the dependence on  $r$  cancels out and the differential cross section  $\sigma(\theta)$  is finally given simply by the squared norm of the function  $f(\theta)$  modulating the amplitude of the scattered wave relative to the amplitude of the incident wave, namely:

$$\sigma(\theta) = |f(\theta)|^2. \quad (3.7.104)$$

The corresponding total cross section is:

$$\sigma_{\text{tot}} = 2\pi \int_{-1}^1 |f(\theta)|^2 d(\cos \theta). \quad (3.7.105)$$

The above quantities can be expressed in terms of properties of the infinitely many radial problems corresponding to each value of the angular momentum quantum number  $l$ . To see this, we start by expanding the full wave function  $\phi(r, \theta)$  on the complete set of spherical harmonics  $Y_l^m(\theta, \varphi)$  with coefficients  $\phi_l(r)$ . Since there is no dependence on the angle  $\varphi$ , the expansion actually involves only the simplest spherical harmonics with arbitrary  $l$  but  $m = 0$ . These depend only on  $\theta$ , through a Legendre polynomial  $P_l(\cos \theta)$  of degree  $l$  in  $\cos \theta$ :

$$Y_l^0(\theta) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta). \quad (3.7.106)$$

The explicit form of the Legendre polynomials  $P_l(z)$  is:

$$P_l(z) = \frac{1}{2^l l!} \frac{d^l}{dz^l} (z^2 - 1)^l. \quad (3.7.107)$$

They moreover satisfy the following completeness and orthonormality relations:

$$\sum_{l=0}^{\infty} (2l+1) P_l(x) P_l(x') = 2 \delta(x - x'), \quad (3.7.108)$$

$$\int_{-1}^1 P_l(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{ll'}. \quad (3.7.109)$$

With a suitable redefinition of the normalization factor in the coefficients  $\phi_l(r)$  of the original expansion, one may then write:

$$\phi(r, \theta) = \sum_{l=0}^{\infty} i^l (2l+1) \phi_l(r) P_l(\cos \theta). \quad (3.7.110)$$

On the other hand, a plane wave propagating along the  $z$  axis with wave number  $k$  also admits a similar expansion, since it is a solution of the Schrödinger equation for the spherically symmetric setting of a free particle. Moreover we know that the coefficients in this expansion must be proportional to the spherical Bessel functions  $j_l(r)$ , since these determine the allowed form of the radial wave function with definite angular momentum for a free particle. The proportionality constants can be fixed by multiplying this expansion by  $P_{l'}(\cos \theta)$ , integrating over  $\theta$  and using the orthogonality property of the Legendre polynomials. The precise formula is found to be:

$$e^{ikr \cos \theta} = \sum_{l=0}^{\infty} i^l (2l+1) j_l(kr) P_l(\cos \theta). \quad (3.7.111)$$

Finally, a spherical wave with an amplitude modulated by a function  $f(\theta)$  can also be expanded in this way. The non-trivial part is the arbitrary function  $f(\theta)$ , which can be

expanded with some arbitrary coefficients  $f_l$  as:

$$f(\theta) = \sum_{l=0}^{\infty} (2l+1) f_l P_l(\cos \theta). \quad (3.7.112)$$

With this parametrization, the differential cross section  $\sigma(\theta)$  can be expressed as follows in terms of the coefficients  $f_l$ :

$$\sigma(\theta) = \left| \sum_{l=0}^{\infty} (2l+1) f_l P_l(\cos \theta) \right|^2. \quad (3.7.113)$$

The total cross section  $\sigma_{\text{tot}}$  is then obtained by integrating the differential cross section  $\sigma(\theta)$  over the full solid angle:  $\sigma_{\text{tot}} = 2\pi \int_{-1}^1 \sigma(\theta) d(\cos \theta)$ . Using the expression (3.7.113) and the orthonormality relation (3.7.109) for Legendre polynomials, one finds:

$$\sigma_{\text{tot}} = 4\pi \sum_{l=0}^{\infty} (2l+1) |f_l|^2. \quad (3.7.114)$$

It turns out that the partial amplitudes  $f_l$  defining  $\sigma(\theta)$  and  $\sigma_{\text{tot}}$  are fully determined by the knowledge of the phase shifts  $\delta_l$  characterizing the asymptotic form of the radial wave functions for arbitrary angular momentum  $l$ . To find the relation between  $f_l$  and  $\delta_l$ , we have to look at the asymptotic behavior of the above expansions for  $r \rightarrow +\infty$ . By comparing (3.7.110) with (3.7.111), we see that the normalization implied for  $\phi_l(r)$  is such that in the case of a free particle subject to no potential this reduces to  $j_l(kr)$ . With this normalization, we then know from (3.4.55) that the full radial wave function must behave as  $\phi_l(r) \simeq A_l (kr)^{-1} \sin(kr - l\frac{\pi}{2} + \delta_l)$  for  $r \rightarrow +\infty$ . The asymptotic behavior of the full wave function is thus determined by the following expression in terms of the phase shifts  $\delta_l$ :

$$\phi(r, \theta) \simeq \sum_{l=0}^{\infty} i^l (2l+1) \left[ \frac{A_l}{kr} \sin\left(kr - l\frac{\pi}{2} + \delta_l\right) \right] P_l(\cos \theta), \quad r \rightarrow +\infty. \quad (3.7.115)$$

Similarly, we know that  $j_l(kr) \simeq (kr)^{-1} \sin(kr - l\frac{\pi}{2})$  for  $r \rightarrow \infty$ . The asymptotic behavior of the sum of the incident and the scattered wave is then given by

$$e^{ikr \cos \theta} + \frac{f(\theta)}{r} e^{ikr} \simeq \sum_{l=0}^{\infty} i^l (2l+1) \left[ \frac{1}{kr} \sin\left(kr - l\frac{\pi}{2}\right) + \frac{f_l}{i^l r} e^{ikr} \right] P_l(\cos \theta), \quad r \rightarrow +\infty. \quad (3.7.116)$$

These two expressions are seen to be equal, as required by the boundary condition (3.7.99), if and only if:

$$A_l (-i)^l e^{i\delta_l} e^{ikr} - A_l (i)^l e^{-i\delta_l} e^{-ikr} = (-i)^l (1 + 2ik f_l) e^{ikr} - (i)^l e^{-ikr}. \quad (3.7.117)$$

Matching the progressive and regressive waves implies the following two conditions:

$$A_l = e^{i\delta_l}, \quad f_l = \frac{1}{2ik} (e^{2i\delta_l} - 1). \quad (3.7.118)$$

The second of these relations provides the relation between  $f_l$  and  $\delta_l$  we were looking for. It can be written in the following equivalent forms:

$$f_l = \frac{1}{2ik} (e^{2i\delta_l} - 1) = \frac{1}{k} e^{i\delta_l} \sin \delta_l = \frac{1}{k \cot \delta_l - i} \quad (3.7.119)$$

From this we see that the modulus of this partial amplitude is bounded by above for a fixed energy corresponding to a fixed wave number  $k$ :

$$|f_l| = \frac{1}{k} |\sin \delta_l| \leq \frac{1}{k}. \quad (3.7.120)$$

The scattering amplitude is then found to be expressed in terms of the phase shifts  $\delta_l$  by the following relation:

$$\begin{aligned} f(\theta) &= \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) (e^{2i\delta_l} - 1) P_l(\cos \theta) \\ &= \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta). \end{aligned} \quad (3.7.121)$$

The first term in the bracket involving the factor  $e^{2i\delta_l}$  controls the deflected part of the scattered wave in a generic direction, while the second term in the bracket involving the factor  $-1$  is instead relevant only for the undeflected part of the scattered wave in the forward direction. For  $\theta = 0$  both terms contribute and the result can be simplified by using the fact that  $P_l(1) = 1$ . For  $\theta \neq 0$ , on the other hand, only the first term contributes, while the second drops, as can be verified by using the identity (3.7.108) together with  $P_l(1) = 1$ . In these two situations one then finds:

$$\begin{cases} f(0) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l, \\ f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) e^{2i\delta_l} P_l(\cos \theta), \quad \theta \neq 0. \end{cases} \quad (3.7.122)$$

The differential cross section for arbitrary  $\theta$  finally reads

$$\sigma(\theta) = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta) \right|^2. \quad (3.7.123)$$

In the two cases where  $\theta = 0$  and  $\theta \neq 0$ , this can also be rewritten as

$$\begin{cases} \sigma(0) = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l \right|^2, \\ \sigma(\theta) = \frac{1}{k^2} \left| \sum_{l=0}^{\infty} (2l+1) e^{2i\delta_l} P_l(\cos \theta) \right|^2, \quad \theta \neq 0. \end{cases} \quad (3.7.124)$$

The total cross section  $\sigma_{\text{tot}}$  is finally given by the following simple expression involving a single series of partial square amplitudes:

$$\sigma_{\text{tot}} = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l. \quad (3.7.125)$$

We see that this satisfies the following relation, which shows up here as a matter of fact but actually has a much more general validity and is called optical theorem:

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im}f(0). \quad (3.7.126)$$

Let us finally analyze the physical relevance of the potentially divergent universal part in the phase shifts  $\delta_l = \delta + \hat{\delta}_l$ . We see that the differential cross section for  $\theta \neq 0$  does not depend on the overall term  $\delta$ , while the forward differential cross section for  $\theta = 0$  and the total cross section do instead depend on the overall term  $\delta$ . This means that only the forward scattering at vanishing angle is sensitive to the potentially divergent  $\delta$ , while the scattering at any non-vanishing angle only depends on the finite  $\hat{\delta}_l$ . This is compatible with the fact that the quantum cross section can display a divergence related to small angle scattering when the potential does not fall off sufficiently fastly at infinity. We shall see below that the same type of divergence related to small angle scattering is actually already displayed by the classical cross section, for any long range potential, and that it admits a clear semiclassical interpretation.

### 3.7.2 Classical interpretation

To conclude, let us discuss the classical interpretation of these results and see how a classical scattering trajectory can emerge in situations where the whole scattering process is semiclassical. Recall in this respect that the radial part of the problem is semiclassical when  $l \gg 1$ , while the angular part of the problems is semiclassical when  $\theta l, (\pi - \theta)l \gg 1$ . This means that in situations where the semiclassical approximation is applicable, the infinite sum over  $l$  defining the scattering amplitude must be dominated by terms with  $l \gg 1$ , and moreover the scattering angle must be such that  $\theta, \pi - \theta \gg 1/l$ . We thus assume that we can restrict to

$$l \gg 1, \quad \theta, \pi - \theta \gg 1/l. \quad (3.7.127)$$

To proceed, we may then substitute the Legendre polynomials  $P_l(\cos \theta)$  with their asymptotic form for  $l \sin \theta \gg 1$ . This corresponds to use for the angular part of the wave function  $Y_l^0(\theta) = \sqrt{(2l+1)/(4\pi)} P_l(\cos \theta)$  the approximate expression that one would find in a semiclassical rather than an exact treatment. From our discussion of section 3.3, we see that when  $l \sin \theta \gg 1$  and  $m = 0$  the relevant wave number (3.3.28) is approximately constant and given by  $k \simeq l + 1/2$ , and this semiclassical angular wave function must therefore involve a plane wave with this wave number. More precisely, one can show that the asymptotic form to be used is given by:

$$P_l(\cos \theta) \simeq \sqrt{\frac{2}{\pi}} \frac{\sin \left[ \left( l + \frac{1}{2} \right) \theta + \frac{\pi}{4} \right]}{\sqrt{l \sin \theta}}, \quad l \sin \theta \gg 1. \quad (3.7.128)$$

Plugging this expression into the scattering amplitude for  $\theta \neq 0$  given by the second of (3.7.122) and rewriting the sine in the numerator in terms of exponentials, we then arrive



at the following expression:

$$f(\theta) \simeq \sum_{l \gg 1}^{\infty} \sqrt{\frac{l}{2\pi \sin \theta}} \frac{1}{k} \left( \exp \left\{ i \left[ 2\delta_l - \left( l + \frac{1}{2} \right) \theta - \frac{\pi}{4} \right] \right\} - \exp \left\{ i \left[ 2\delta_l + \left( l + \frac{1}{2} \right) \theta + \frac{\pi}{4} \right] \right\} \right). \quad (3.7.129)$$

When written in this semiclassical form, we see that the scattering amplitude is an infinite sum over  $l$  of terms that involve large phases that rapidly oscillate when  $l$  is changed. As a result, most of these terms cancel out from the infinite sum over  $l$ , and the main contribution comes from values of  $l$  close to the special value for which the phase of one of the two terms is extremal and stationary. This happens whenever the derivative of these phases with respect to  $l$  vanishes, that is when  $2 d\delta_l/dl \mp \theta \simeq 0$  or equivalently:

$$\frac{d\delta_l}{dl} \simeq \pm \frac{\theta}{2}. \quad (3.7.130)$$

Notice that this relation implies that  $\delta_l \simeq \pm \theta l/2 + \text{constant}$ , and since  $l\theta \gg 1$  it follows that the semiclassical phase shifts are large:

$$|\delta_l| \gg 1. \quad (3.7.131)$$

Since the phase shifts  $\delta_l$  depend on the energy, the constraint (3.7.130) represents a sharp relation between the energy, the angular momentum and the deflection angle, as required by the emergence of a definite classical trajectory. Using the previously derived semiclassical form (3.7.94) of these phase shifts, it is straightforward to show that this relation indeed corresponds to the one implied by the classical trajectory followed by the particle during the scattering process. To see this, let us start from the semiclassical expression (3.7.94) for  $\delta_l$ . Since we know that  $\int_{r_0}^r k_{\text{eff}}(r) dr|_0 = kr - (l + 1/2)\frac{\pi}{2}$ , the term associated to the free motion can be written more explicitly as  $\int_{r_0}^{+\infty} k_{\text{eff}}(r) dr|_0 = \int_{r_0}^{+\infty} k dr + kr_0 - (l + 1/2)\frac{\pi}{2}$ . Recalling also that  $k = \sqrt{2mE}/\hbar$  and  $L \simeq \hbar(l + 1/2)$ , one can then write

$$\delta_l \simeq \frac{1}{\hbar} \int_{r_0}^{\infty} \left( \sqrt{2m(E - V(r)) - \frac{L^2}{r^2}} - \sqrt{2mE} \right) dr + \frac{1}{\hbar} \left( L \frac{\pi}{2} - \sqrt{2mE} r_0 \right). \quad (3.7.132)$$

The derivative  $d\delta_l/dl$  can now be easily computed. Using  $dL/dl = \hbar$  and noticing that although  $dr_0/dl \neq 0$  the two terms that this induces cancel out, one finds:

$$\frac{d\delta_l}{dl} \simeq - \int_{r_0}^{\infty} \frac{L}{r^2} \left[ 2m(E - V(r)) - \frac{L^2}{r^2} \right]^{-1/2} dr + \frac{\pi}{2}. \quad (3.7.133)$$

Plugging this into the condition (3.7.130) one finally deduces the following relation between the energy  $E$ , the angular momentum  $L$  and the scattering angle  $\theta$ :

$$\int_{r_0}^{\infty} \frac{L}{r^2} \left[ 2m(E - V(r)) - \frac{L^2}{r^2} \right]^{-1/2} dr \simeq \frac{\pi \mp \theta}{2}. \quad (3.7.134)$$

This is recognized to be the general classical relation between the energy  $E$ , the angular momentum  $L$  and the asymptotic deflection angle  $\theta$  for a particle moving in a central

potential  $V(r)$ . This relation can also be rewritten in a different way in terms of the impact parameter  $b$ . Indeed, for a classical particle one has  $L = pb$  and  $E = p^2/(2m)$ , where  $p$  is the momentum at infinity. For a given energy  $E$ , the impact parameter  $b$  is then related to the angular momentum  $L$  by the following expression:

$$b = \frac{L}{\sqrt{2mE}}. \quad (3.7.135)$$

Using this new variable, the formula (3.7.134) can be rewritten as a relation between the deflection angle  $\theta$  and the impact parameter  $b$  for fixed energy  $E$ :

$$\int_{r_0}^{\infty} \frac{b}{r^2} \left[ 1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right]^{-1/2} dr \simeq \frac{\pi \mp \theta}{2}. \quad (3.7.136)$$

This leads to the classical picture of the scattering process illustrated in 3.4. The negative sign applies to repulsive potentials and the positive sign to attractive potentials, as can be seen by requiring that the argument of the square root should admit one root  $r_0$ . It should however be recalled that this semiclassical picture holds true only when the original assumptions that  $\theta, \pi - \theta \gg 1/l$  is fulfilled. In the semiclassical limit  $l \simeq L/\hbar$ , and these conditions can therefore be rephrased as the requirement that

$$\theta, \pi - \theta \gg \hbar/L. \quad (3.7.137)$$

We can now understand that this restriction is related to the limitations imposed by the quantum mechanical uncertainty relations. Indeed, a classical interpretation requires that for an impact parameter  $b$  determined with a small uncertainty  $\Delta b \ll b$  one should be able to associate a deflection angle  $\theta$  with a small uncertainty  $\Delta\theta \ll \theta, \pi - \theta$ . But denoting with  $p$  the momentum and with  $\Delta p$  its uncertainty in the transverse direction, one has  $\Delta\theta \sim \Delta p/p$ . The usual uncertainty principle then implies that  $\Delta b \Delta p \gtrsim \hbar$  and therefore  $\Delta\theta \gtrsim \hbar/(p\Delta b)$ . This finally implies that  $\theta, \pi - \theta \gg \Delta\theta \gtrsim \hbar/(p\Delta b) \gg \hbar/(pb) \sim \hbar/L$ .

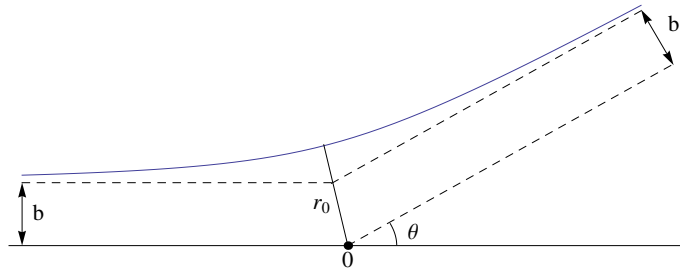


Figure 3.4: Classical scattering in a central potential.

In the above fully semiclassical situation, we may also compute more explicitly the cross section and compare it to the classical result. To do so, we have to evaluate explicitly the infinite sum defining  $f(\theta)$ . We have seen that this receives its dominant contribution from terms where  $l$  is close to a special value  $l_0$ , which depends on the energy  $E$  and the

scattering angle  $\theta$  as implied by eq. (3.7.134) with  $L \simeq \hbar l_0$ . To evaluate this contribution, we may now define the new variable  $l' = l - l_0$ , and expand the phases appearing in (3.7.129) up to quadratic order in  $l'$ . Since  $l_0$  is defined by eq. (3.7.130), one deduces that  $d\delta_l/dl|_{l_0} \simeq \pm\theta/2$  and thus  $d^2\delta_l/dl^2|_{l_0} \simeq \pm(d\theta/dl)/2|_{l_0}$ . One then finds:

$$\left[2\delta_l \mp \left(l + \frac{1}{2}\right)\theta \mp \frac{\pi}{4}\right] \simeq \left[2\delta_{l_0} \mp \left(l_0 + \frac{1}{2}\right)\theta \mp \frac{\pi}{4}\right] \pm \frac{1}{2} \frac{d\theta}{dl_0} l'^2 + \mathcal{O}(l'^3). \quad (3.7.138)$$

Using this expression for the phases in (3.7.129) and setting  $l \simeq l_0$  everywhere else, one can then compute the sum over the values  $l'$  around 0. After rewriting  $d\theta/dl_0 = \hbar d\theta/dL$  and introducing  $\xi = \hbar l'$ , one may think of  $\hbar$  as being very small. This allows to convert the sum into an integral over  $\xi$  with  $d\xi = \hbar$  and evaluate this with the saddle point method. In this way, assuming that  $d\theta/dL < 0$  one finds the following expression:

$$\begin{aligned} I &\simeq \sum_{l' \gg 1} \exp \left\{ \pm \frac{i}{2} \frac{d\theta}{dl_0} l'^2 \right\} \simeq \frac{1}{\hbar} \int_{-\infty}^{\infty} d\xi \exp \left\{ \mp \frac{i}{2\hbar} \left| \frac{d\theta}{dL} \right| \xi^2 \right\} = \sqrt{\frac{2\pi}{\hbar}} \left| \frac{dL}{d\theta} \right|^{1/2} e^{\mp i \frac{\pi}{4}} \\ &\simeq \sqrt{2\pi} \left| \frac{dl_0}{d\theta} \right|^{1/2} e^{\mp i \frac{\pi}{4}}. \end{aligned} \quad (3.7.139)$$

The scattering amplitude then becomes

$$\begin{aligned} f(\theta) &\simeq \pm \sqrt{\frac{l_0}{2\pi \sin \theta}} \frac{1}{k} \exp \left\{ i \left[ 2\delta_{l_0} \mp \left(l_0 + \frac{1}{2}\right)\theta \mp \frac{\pi}{4} \right] \right\} I \\ &\simeq \pm \sqrt{\frac{l_0}{\sin \theta}} \frac{1}{k} \left| \frac{dl_0}{d\theta} \right|^{1/2} \exp \left\{ i \left[ 2\delta_{l_0} \mp \left(l_0 + \frac{1}{2}\right)\theta \mp \frac{\pi}{2} \right] \right\}. \end{aligned} \quad (3.7.140)$$

The differential cross section  $\sigma(\theta) = |f(\theta)|^2$  is finally found to be:

$$\sigma(\theta) = \frac{l_0}{k^2 \sin \theta} \left| \frac{dl_0}{d\theta} \right| = -\frac{l_0}{k^2 \sin \theta} \frac{dl_0}{d\theta}. \quad (3.7.141)$$

Noticing now that eq. (3.7.135) implies that  $b \simeq l_0/k$  and recalling that  $d\Omega = 2\pi d(\cos \theta)$ , we may finally write this formula in the following way:

$$\sigma(\theta) = \frac{d(\pi b^2)}{d\Omega}. \quad (3.7.142)$$

This is recognized to be the classical result for  $\sigma(\theta)$ . Indeed, for a classical particle of fixed energy, the impact parameter  $b$  and the deflection angle  $\theta$  are sharply related. As a result, we see from fig. 3.4 that the number of particles scattered per unit time in the solid angle element  $d\Omega$  must be equal to the number of incident particles per unit time per unit surface times the surface element defined by impact parameters  $b$  in the interval  $[b, b+db]$  and arbitrary angles  $\varphi$  in the interval  $[0, 2\pi]$ , which is given by  $dS = d(\pi b^2)$ . The differential cross section is then simply  $\sigma(\theta) = dS/d\Omega = d(\pi b^2)/d\Omega$ . The total cross section is straightforwardly evaluated by integrating the above expression for the differential cross section over the solid angle. Calling  $b_{\max}$  the maximal value of the impact parameter for which the differential cross section is non-vanishing, one trivially finds:

$$\sigma_{\text{tot}} = \pi b_{\max}^2. \quad (3.7.143)$$

This shows that in the classical limit the total cross section is equal to the transversal surface in which the incident particles undergo a deflection due to the effect of the potential, no matter how big this deflection is. This quantity is therefore finite for potentials with a finite range and infinite for potentials with an infinite range.

### 3.7.3 Example

As an important example of scattering process, let us consider the case of an attractive Coulomb potential of the form

$$V(r) = -\frac{\alpha}{r}. \quad (3.7.144)$$

In this case,  $r_0$  is determined by the equation  $1 + (\alpha/E)r_0^{-1} - b^2r_0^{-2} = 0$  and is found to be given by:

$$r_0 = -\frac{\alpha}{2E} + \sqrt{\frac{\alpha^2}{4E^2} + b^2}. \quad (3.7.145)$$

It follows that:

$$\begin{aligned} \int_{r_0}^{\infty} \frac{b}{r^2} \left[ 1 - \frac{V(r)}{E} - \frac{b^2}{r^2} \right]^{-1/2} dr &= \int_{r_0}^{\infty} \frac{b}{r} \left[ \left( r - r_0 \right) \left( r + \frac{b^2}{r_0} \right) \right]^{-1/2} dr \\ &= 2 \arctan \frac{b}{r_0}. \end{aligned} \quad (3.7.146)$$

The equation (3.7.136) then gives:

$$\frac{b}{r_0} = \tan \frac{\pi + \theta}{4}. \quad (3.7.147)$$

Using the expression of  $r_0$  it follows that

$$\frac{\alpha}{Eb} = \frac{b}{r_0} - \frac{r_0}{b} = 2 \tan \frac{\theta}{2}. \quad (3.7.148)$$

Finally, this leads to the following expression for the impact parameter in terms of the deflection angle:

$$b = \frac{\alpha}{2E} \cot \frac{\theta}{2}. \quad (3.7.149)$$

The differential cross section may now be computed according to the classical formula

$$\sigma(\theta) = \frac{bdb}{d(\cos \theta)} = -\frac{b}{\sin \theta} \frac{db}{d\theta} \quad (3.7.150)$$

One finds in this way the Rutherford formula:

$$\sigma(\theta) = \left( \frac{\alpha}{4E} \right)^2 \sin^{-4} \frac{\theta}{2}. \quad (3.7.151)$$

The total cross section is in this case divergent:

$$\sigma_{\text{tot}} = +\infty. \quad (3.7.152)$$

It turns out that the above semiclassical results for the differential and total cross section accidentally coincide with the exact quantum result, which can be derived by solving the differential equation for the radial wave function exactly in terms of hypergeometric functions.

### 3.8 Metastable quasi-stationary states

As a third application, let us consider the study of metastable quasi stationary states. To illustrate the situation, we imagine a repulsive potential  $V(r)$ , which is positive, tends to 0 for  $r \rightarrow +\infty$  and remains smaller than  $1/r^2$  for  $r \rightarrow 0$ . In such a situation, the effective potential can give rise to a finite well followed by a finite barrier. There can then be metastable quasi-stationary states with a discrete spectrum of complex energies.

For a given energy  $E$  there are three classical turning points  $r_1$ ,  $r_2$  and  $r_3$ , where  $V_{\text{eff}}(r_1) = V_{\text{eff}}(r_2) = V_{\text{eff}}(r_3) = 0$  and  $V'_{\text{eff}}(r_1) < 0$ ,  $V'_{\text{eff}}(r_2) > 0$ ,  $V'_{\text{eff}}(r_3) < 0$ , as depicted in fig. 3.5. This defines two classically allowed regions  $II = ]r_1, r_2[$ ,  $IV = ]r_3, +\infty[$  and two classically forbidden regions  $I = ]0, r_1[$ ,  $III = ]r_2, r_3[$ . The parameters describing the well and the barrier are:

$$J = \int_{r_1}^{r_2} k_{\text{eff}}(r') dr', \quad (3.8.153)$$

$$K = \int_{r_2}^{r_3} \beta_{\text{eff}}(r') dr'. \quad (3.8.154)$$

One can then determine the semiclassical radial wave function by using the usual joining prescriptions. Requiring that the wave function should vanish at the origin and consist only of a progressive wave at infinity, and proceeding as in the case of a one-dimensional well associated to a barrier and focusing on the case where  $K \gg 1$ , one finds:

$$\left\{ \begin{array}{l} \chi_{II}(r) \simeq \frac{C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ - \int_r^{r_1} \beta_{\text{eff}}(r') dr' \right\}, \\ \chi_{III}(r) \simeq \frac{C_l}{\sqrt{k_{\text{eff}}(r)}} \sin \left( \int_{r_1}^r k_{\text{eff}}(r') dr' + \frac{\pi}{4} \right), \\ \chi_{III}(r) \simeq \frac{(-1)^n C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \left[ \exp \left\{ - \int_{r_2}^r \beta_{\text{eff}}(r') dr' \right\} + \frac{i}{2} e^{-2K} \exp \left\{ \int_{r_2}^r \beta_{\text{eff}}(r') dr' \right\} \right], \\ \chi_{IV}(r) \simeq \frac{(-1)^n C_l}{2\sqrt{k_{\text{eff}}(r)}} \left[ e^{i\frac{\pi}{4}} e^{-K} \exp \left\{ i \int_{r_3}^r k_{\text{eff}}(r') dr' \right\} \right], \end{array} \right. \quad (3.8.155)$$

with the quantization condition  $\cot J \simeq \frac{i}{4} e^{-2K}$  or more explicitly:

$$J \simeq \left( n + \frac{1}{2} \right) \pi - \frac{i}{4} e^{-2K}. \quad (3.8.156)$$

By proceeding as in the corresponding one-dimensional problem, we then deduce that the complex energy levels  $E = E_0 - \frac{i}{2} \Gamma$  have real and an imaginary parts determined as follows:

$$J|_{E_0} = \left( n + \frac{1}{2} \right) \pi, \quad (3.8.157)$$

$$\Gamma = \frac{1}{2} \left( \frac{\partial J}{\partial E} \right)_{E_0}^{-1} e^{-2K}. \quad (3.8.158)$$

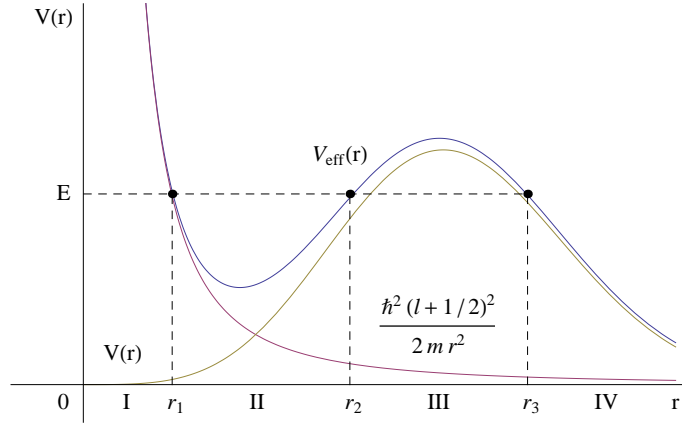


Figure 3.5: Turning points in a peculiar central potential.

### 3.8.1 Energy and width

The classical interpretation of the above results is the same as in the one-dimensional case. The real part  $E_0$  of the energy is determined by a Bohr-Sommerfeld quantization rule on the phase space integral of the radial part of the problem:

$$\oint p_{\text{eff}}(r) dr = \left(n + \frac{1}{2}\right) h. \quad (3.8.159)$$

The width  $\Gamma$  associated to the imaginary part of the energy can instead again be written in terms of the period  $T$  of the classical motion:

$$\Gamma = \frac{\hbar}{T} e^{-2K}. \quad (3.8.160)$$

The associated lifetime is:

$$\tau = T e^{2K}. \quad (3.8.161)$$

## 3.9 Resonance effects

As a last application, let us consider the possibility of having resonance effects in delocalized stationary states describing a scattering process. To illustrate the situation, we imagine again a repulsive potential  $V(r)$ , which is positive, tends to 0 for  $r \rightarrow +\infty$  and remains smaller than  $1/r^2$  for  $r \rightarrow 0$ . In such a situation, the effective potential can give rise to a finite well followed by a finite barrier. There can then be resonance effects in delocalized stationary states with a continuous spectrum of real energies, which arise whenever the energy gets close to one of the discrete values of the energy associated to metastable quasi stationary states admitted by the effective potential.

For a given energy  $E$  there are three classical turning points  $r_1$ ,  $r_2$  and  $r_3$ , where  $V_{\text{eff}}(r_1) = V_{\text{eff}}(r_2) = V_{\text{eff}}(r_3) = 0$  and  $V'_{\text{eff}}(r_1) < 0$ ,  $V'_{\text{eff}}(r_2) > 0$ ,  $V'_{\text{eff}}(r_3) < 0$ , as depicted in fig. 3.5. This defines two classically allowed regions  $II = ]r_1, r_2[$ ,  $IV = ]r_3, +\infty[$  and

two classically forbidden regions  $I = ]0, r_1[$ ,  $III = ]r_2, r_3[$ . The parameters describing the well and the barrier are as before:

$$J = \int_{r_1}^{r_2} k_{\text{eff}}(r') dr' , \quad (3.9.162)$$

$$K = \int_{r_2}^{r_3} \beta_{\text{eff}}(r') dr' . \quad (3.9.163)$$

One can then once again determine the semiclassical radial wave function by using the usual joining prescriptions. Requiring that the wave function should vanish at the origin and allowing both a progressive and a regressive wave at infinity, and focusing on the case where  $K \gg 1$ , one finds after a straightforward computation:

$$\left\{ \begin{array}{l} \chi_{II}(r) \simeq \frac{C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \exp \left\{ - \int_r^{r_1} \beta_{\text{eff}}(r') dr' \right\} , \\ \chi_{III}(r) \simeq \frac{C_l}{\sqrt{k_{\text{eff}}(r)}} \sin \left( \int_{r_1}^r k_{\text{eff}}(r') dr' + \frac{\pi}{4} \right) , \\ \chi_{IIII}(r) \simeq \frac{C_l}{2\sqrt{\beta_{\text{eff}}(r)}} \left[ \sin J \exp \left\{ - \int_{r_2}^r \beta_{\text{eff}}(r') dr' \right\} + 2 \cos J \exp \left\{ \int_{r_2}^r \beta_{\text{eff}}(r') dr' \right\} \right] , \\ \chi_{IIV}(r) \simeq \frac{C_l}{\sqrt{k_{\text{eff}}(r)}} \left[ e^{-i\frac{\pi}{4}} \left( \cos J e^K + \frac{i}{4} \sin J e^{-K} \right) \exp \left\{ i \int_{r_3}^r k_{\text{eff}}(r') dr' \right\} \right. \\ \left. + e^{i\frac{\pi}{4}} \left( \cos J e^K - \frac{i}{4} \sin J e^{-K} \right) \exp \left\{ -i \int_{r_3}^r k_{\text{eff}}(r') dr' \right\} \right] . \end{array} \right. \quad (3.9.164)$$

As a check, notice that the above expression reduces to (3.8.155) for complex energies satisfying the quantization condition rule (3.8.156), which implies that  $\cos J \simeq \frac{i}{4}(-1)^n e^{-2K}$  and  $\sin J \simeq (-1)^n$ . For generic and real values of the energy, on the other hand, we see that the last term is non-vanishing and there is not only a progressive wave but also a regressive wave for large  $r$ . One is then in a situation where one has a delocalized scattering state consisting of a radial wave coming in from  $r \rightarrow +\infty$  and a radial wave getting out to  $r \rightarrow +\infty$ . The reflection is complete, as before, because there is nowhere else than  $r \rightarrow +\infty$  that the wave can end. However, in this case only part of the wave bounces back at the classical turning point  $r_3$  that it meets. The other part tunnels through the barrier and bounces back only at the classical turning point  $r_1$ .

The wave function is seen to have a behavior for large  $r$  which is of the expected type, and can be rewritten in the following more convenient form:

$$\chi_l(r) \propto \sin \left[ \int_{r_3}^r k_{\text{eff}}(r') dr' + \frac{\pi}{4} + \arg \left( \cot J + \frac{i}{4} e^{-2K} \right) \right] . \quad (3.9.165)$$

From this expression, we see that the phase shifts  $\delta_l$  are the sum of two terms,

$$\delta_l = \delta_l^{\text{nor}} + \delta_l^{\text{res}} . \quad (3.9.166)$$

The first term is the one that one would get in the absence of tunneling and is given by the normal expression:

$$\delta_l^{\text{nor}} = \int_{r_3}^r k_{\text{eff}}(r') dr' \Big|_0^V. \quad (3.9.167)$$

The second term is instead due to the possibility of tunneling and represents an extra effect that can display a resonance phenomenon:

$$\delta_l^{\text{res}} = \arg \left( \cot J + \frac{i}{4} e^{-2K} \right). \quad (3.9.168)$$

Let us now consider the behavior of the phase shift for energies  $E$  close to the energy  $E_0$  of a quasi-stationary state:

$$E_0 : J|_{E_0} = \left( n + \frac{1}{2} \right) \pi. \quad (3.9.169)$$

We also recall that the width of the quasi-stationary states, which is expected to play a role, is given by

$$\Gamma = \frac{1}{2} \left( \frac{\partial J}{\partial E} \right)_{E_0}^{-1} e^{-2K}. \quad (3.9.170)$$

One may now expand around  $E_0$  in powers of  $E - E_0$ . Working at first order and neglecting terms involving both  $e^{-2K}$  and  $E - E_0$  unless they come with a  $\Gamma^{-1}$ , one finds:

$$\begin{aligned} \left[ \cot J + \frac{i}{4} e^{-2K} \right]_E &\simeq \left[ \cot J + \frac{i}{4} e^{-2K} \right]_{E_0} - \left[ \sin^{-2} J \frac{\partial J}{\partial E} \right]_{E_0} (E - E_0) \\ &\simeq \frac{i}{4} e^{-2K} - \frac{1}{2} \Gamma^{-1} e^{-2K} (E - E_0) \\ &\simeq \frac{1}{2} \Gamma^{-1} e^{-2K} \left( -E + E_0 + i \frac{\Gamma}{2} \right). \end{aligned} \quad (3.9.171)$$

Using this expression and assuming that the normal part of the phase shifts is a slowly varying function of  $E$  close to  $E_0$ , one may then approximate:

$$\delta_l^{\text{nor}} \simeq \delta_l^{\text{nor}}(E_0), \quad (3.9.172)$$

$$\delta_l^{\text{res}} \simeq \arg \left( -E + E_0 + i \frac{\Gamma}{2} \right). \quad (3.9.173)$$

The total phase shift is therefore:

$$\delta_l \simeq \delta_l^{\text{nor}} + \arg \left( -E + E_0 + i \frac{\Gamma}{2} \right). \quad (3.9.174)$$

When increasing  $E$  from values smaller than  $E_0$  to values larger than  $E_0$ , we see that the resonance term changes from 0 to  $\pi$ , going very sharply through  $\pi/2$  around  $E_0$ . To see the impact of this behavior in the scattering amplitude, we compute:

$$e^{2i\delta_l} \simeq e^{2i\delta_l^{\text{nor}}} \frac{E - E_0 - i\Gamma/2}{E - E_0 + i\Gamma/2} \simeq \left( 1 - \frac{i\Gamma}{E - E_0 + i\Gamma/2} \right) e^{2i\delta_l^{\text{nor}}}, \quad (3.9.175)$$

$$e^{2i\delta_l} - 1 \simeq e^{2i\delta_l^{\text{nor}}} - 1 - \frac{i\Gamma}{E - E_0 + i\Gamma/2} e^{2i\delta_l^{\text{nor}}}. \quad (3.9.176)$$



It follows that the partial scattering amplitude  $f_l = (e^{2i\delta_l} - 1)/(2ik)$  can be written as the sum of a normal term and a resonance term,

$$f_l \simeq f_l^{\text{nor}} + f_l^{\text{res}}, \quad (3.9.177)$$

where:

$$f_l^{\text{nor}} = \frac{1}{2ik} (e^{2i\delta_l^{\text{nor}}} - 1), \quad (3.9.178)$$

$$f_l^{\text{res}} \simeq -\frac{1}{k} \frac{\Gamma/2}{E - E_0 + i\Gamma/2} e^{2i\delta_l^{\text{nor}}}. \quad (3.9.179)$$

We discover that the partial scattering amplitude  $f_l(E)$  has a pole in the complex energy plane, which is located at the complex energy  $E_0 - i\Gamma/2$  of the quasi-stationary state. For real values of  $E$  considered in scattering processes, this does not lead to any singularity, but since  $\Gamma$  was assumed to be small it results in a strong enhancement in the neighborhood of  $E_0$ . Indeed, for  $E$  close to  $E_0$  the resonance term tends to dominate over the normal term and in such a situation one then finds a Breit-Wigner behavior:

$$|f_l(E)|^2 \simeq \frac{\Gamma^2/4}{(E - E_0)^2 + \Gamma^2/4} \frac{1}{k^2}. \quad (3.9.180)$$

We see from this expression that for  $E \simeq E_0$  the square modulus of the partial amplitude for the value of  $l$  for which the metastable state exists takes the maximal possible value:  $|f_l(E_0)|^2 \simeq 1/k^2$ . If for some reason the contribution from this partial wave dominates over the others, this peak may also show up in the cross section. This is a resonance effect that is perfectly analogous to the one encountered in section 2.4 for the transmission coefficient associated to a one-dimensional potential consisting of a symmetric double barrier, where peaks of maximal transparency arise in correspondence of the energies of metastable states allowed by the well between the two barriers. Here the resonance effect concerns the radial problem associated to a definite partial wave with fixed  $l$ , and although there is a single barrier this has to be crossed twice by the wave: once when it comes in and once when gets out. The two situations are thus indeed very similar.

An other extreme behavior of the phase shifts occurs for energies  $E$  close to some particular energy  $E_1$  satisfying:

$$E_1 : J|_{E_1} = n\pi. \quad (3.9.181)$$

In such a situation, we see that  $\cot J + \frac{i}{4}e^{-2K}$  tends to  $\pm\infty$  and therefore its argument is equal to 0 modulo  $\pi$ . One then finds:

$$\delta_l^{\text{nor}} \simeq \delta_l^{\text{nor}}(E_1), \quad (3.9.182)$$

$$\delta_l^{\text{res}} \simeq 0 \text{ mod } \pi. \quad (3.9.183)$$

The total phase shift is then equal to the normal one, modulo  $\pi$ :

$$\delta_l \simeq \delta_l^{\text{nor}} \text{ mod } \pi. \quad (3.9.184)$$

It then follows that the resonance effect is totally absent and the partial amplitude is equal to the normal one:

$$f_l = f_l^{\text{nor}}. \quad (3.9.185)$$

## Chapter 4

# Approximation methods for central scattering problems

In this chapter, we will present several alternative approximation methods for computing the scattering amplitude, which can be applied in different regimes and become helpful in many situations where a semiclassical approach is not possible and there are important quantum effects. We will start with some general considerations concerning the computation of the scattering amplitude. We will then study the case of weak coupling, where one can use a perturbative expansion where the potential is treated as a small correction to the energy. We will next consider the case of high energy scattering, where the wave length is much smaller than the typical range of the potential and the scattering process displays a classical behavior in its radial part and a simple small angle behavior in its angular part. We will finally consider the case of low-energy scattering, where the wave length is much larger than the typical range of the potential and the scattering process displays a threshold behavior dominated by quantum effects.

### 4.1 General behavior of the partial-wave expansion

We have seen in the previous chapter that the scattering amplitude defining the differential and the total cross sections is given for central problems by an infinite sum over partial waves. This takes the general form

$$f(\theta) = \sum_{l=0}^{+\infty} (2l+1) f_l P_l(\cos \theta), \quad (4.1.1)$$

where the partial amplitudes  $f_l$  are related to the phase shifts  $\delta_l$  displayed by the radial wave function  $\chi_l(r)$  in the presence of the potential as compared to the free wave function  $\chi_0(r) = r j_l(kr)$  that would arise in the absence of the potential:

$$f_l = \frac{1}{2ik} (e^{2i\delta_l} - 1) = \frac{1}{k} e^{i\delta_l} \sin \delta_l = \frac{1}{k} \frac{1}{\cot \delta_l - i} \quad (4.1.2)$$

The determination of the phase shifts  $\delta_l$  and the partial amplitudes  $f_l$  requires in principle the knowledge of the radial wave functions  $\chi_l(r)$  solving the radial Schrödinger equation.

An important point about the above partial wave expansion is the range of values of  $l$  that significantly contributes. This strongly depends on the situation that is considered. In situations where the semiclassical approximation can be applied, we have seen in previous chapter that for given wave number  $k$  and scattering angle  $\theta$  the sum over  $l$  is dominated by values close to the special value  $l_0$  associated to the definite angular momentum  $L \simeq \hbar l_0$  or impact parameter  $b \simeq l_0/k$  corresponding to the classical trajectory. But to look at all the possible scattering angles, one needs in general to include all the possible angular momenta and impact parameters, and a priori all the values of  $l$  can contribute. In situations where quantum effects are important, the situation is yet more complicated, and even for given wave number  $k$  and scattering angle  $\theta$ , a wider range of values of  $l$  can give significant contributions. And in order to look at all the possible scattering angles, one needs once again to include all the possible values of  $l$ , in general.

To gain some intuition on which values of  $l$  can really give a significant contribution, let us suppose for concreteness that the potential has a finite range  $a$  beyond which it is strongly suppressed and below which it is significant. When looking at all the possible scattering angles but some definite wave number  $k$ , we then expect partial waves to significantly contribute only when  $l$  is smaller than or comparable to but not much larger than a certain maximal value given by

$$l_{\max} \simeq ka. \quad (4.1.3)$$

In situations where the semiclassical approximation is valid, this corresponds to the fact that if  $l \gg ka$  then  $b \gg a$  and the particle cannot be significantly deflected because it does never pass at distances  $r \lesssim a$  within the range of action of the potential. In situations where quantum effects are important, this can instead be motivated through the following observation. If  $l \gg ka$ , the region of  $r \lesssim a$  where the potential can have a significant effect is such that  $kr \ll l$ . In such a region, the free radial wave function  $\phi_0(r) = j_l(kr)$  is then well approximated by a power law of the form  $\chi_0(r) \sim (kr)^l$ , and is thus tiny and damped. It is then reasonable to expect that it should be very little affected by the presence of the potential. This implies that the phase shift  $\delta_l$  should correspondingly be very small, and there should thus be no significant contribution to the scattering amplitude.

Armed with these general considerations, we shall now study three different general situations where it is possible to find a concrete approximate expression for the scattering amplitude in terms of the potential.

## 4.2 Weak coupling scattering and the Born approximation

In many cases, the effects of the potential can be considered as small. In such a situation, the scattering amplitude will also be small, although still a non-trivial function of the wave number and the scattering angle. One can then compute it by taking into account the effects of the potential in a perturbative way. The systematics of such a perturbative expansion will be described in detail later on. But it turns out that the leading first order approximation can be easily obtained with very elementary considerations, and we will therefore discuss it here.

The basic idea is that when the potential is small, the exact radial wave function  $\chi_l(r)$  in the presence of the potential differs only mildly from the free radial wave function  $\chi_l^0(r) = rj_l(kr)$ . One may then try to exploit this to find an approximate expression for the phase shifts  $\delta_l$ . To do so, let us start from the two differential equations satisfied by these two functions. Denoting as usual with  $k = \sqrt{2mE}/\hbar$  the asymptotic momentum, these can be written in the following form:

$$\chi_l''(r) + \left[ k^2 - \frac{l(l+1)}{r^2} \right] \chi_l(r) = \frac{2m}{\hbar^2} V(r) \chi_l(r), \quad (4.2.4)$$

$$\chi_l^{0''}(r) + \left[ k^2 - \frac{l(l+1)}{r^2} \right] \chi_l^0(r) = 0. \quad (4.2.5)$$

Multiplying the first of these equations by  $\chi_l^0(r)$  and the second by  $\chi_l(r)$ , and taking the difference, one deduces that:

$$\chi_l''(r)\chi_l^0(r) - \chi_l^{0''}(r)\chi_l(r) = \frac{2m}{\hbar^2} V(r)\chi_l(r)\chi_l^0(r). \quad (4.2.6)$$

We now see that the left-hand side of this equation is in fact a total derivative, since one has  $\chi_l''\chi_l^0 - \chi_l^{0''}\chi_l = (\chi_l'\chi_l^0 - \chi_l^0'\chi_l)'$ . Integrating over  $r \in [0, +\infty[$ , and using the fact that the behavior at  $r \rightarrow 0$  is universal and therefore identical for  $\chi_l(r)$  and  $\chi_l^0(r)$ , one then deduces that:

$$\lim_{r \rightarrow \infty} \left[ \chi_l'(r)\chi_l^0(r) - \chi_l^0'(r)\chi_l(r) \right] = \frac{2m}{\hbar^2} \int_0^{+\infty} V(r)\chi_l(r)\chi_l^0(r) dr. \quad (4.2.7)$$

Using the asymptotic forms  $\chi_l^0(r) \simeq k^{-1} \sin(kr - l\frac{\pi}{2})$  and  $\chi_l(r) \simeq k^{-1} e^{i\delta_l} \sin(kr - l\frac{\pi}{2} + \delta_l)$  valid for large  $r$ , we further deduce after a trivial computation that the left-hand side of this expression is directly related to the partial scattering amplitude:

$$\lim_{r \rightarrow \infty} \left[ \chi_l'(r)\chi_l^0(r) - \chi_l^0'(r)\chi_l(r) \right] = -\frac{1}{k} e^{i\delta_l} \sin \delta_l = -f_l. \quad (4.2.8)$$

Using the expression  $\chi_l^0(r) = rj_l(kr)$  in the right-hand side, it finally follows that:

$$f_l = -\frac{2m}{\hbar^2} \int_0^{+\infty} V(r)\chi_l(r) [rj_l(kr)] dr. \quad (4.2.9)$$

This is an exact relation between the partial scattering amplitude  $f_l$  and the corresponding exact radial wave function  $\chi_l(r)$ .

In the case where the effect of the potential on the radial wave function  $\chi_l$  is small, we may determine this in a perturbative expansion in powers of the potential. This will yield a result of the form  $\chi_l = \chi_l^0 + \chi_l^1 + \dots$ , where the  $n$ -th term  $\chi_l^n$  will be suppressed by  $n$  powers of the potential. In first approximation, we may then take  $\chi_l(r) \simeq \chi_l^0(r) = rj_l(kr)$ . Plugging this in the above formula, we then deduce the following approximate result for the partial scattering amplitude, which goes under the name of Born approximation:

$$f_l \simeq -\frac{2m}{\hbar^2} \int_0^{+\infty} V(r) [rj_l(kr)]^2 dr. \quad (4.2.10)$$

Notice that this approximation requires that  $|f_l| \ll 1$ , which implies that  $\delta_l \ll 1$ . In this situation we therefore have the approximate relation  $\delta_l \simeq kf_l$ , and the above formula also directly yields an approximate expression for the phase shifts:

$$\delta_l \simeq -\frac{2mk}{\hbar^2} \int_0^{+\infty} V(r) [rj_l(kr)]^2 dr. \quad (4.2.11)$$

Using the above expressions, we can now compute the scattering amplitude  $f(\theta)$ . This is found to be given by:

$$\begin{aligned} f(\theta) &= \sum_{l=0}^{+\infty} (2l+1) f_l P_l(\cos \theta) \\ &= -\frac{2m}{\hbar^2} \int_0^{+\infty} V(r) \left[ \sum_{l=0}^{+\infty} (2l+1) [j_l(kr)]^2 P_l(\cos \theta) \right] r^2 dr. \end{aligned} \quad (4.2.12)$$

It turns out that this result can be most conveniently expressed in terms of the momentum that is transferred from the potential (or more precisely the body generating it) to the particle during the scattering process:

$$\vec{q} = \vec{k}_{\text{sca}} - \vec{k}_{\text{inc}}. \quad (4.2.13)$$

Notice that the modulus of the momentum of the particle is the same before and after the scattering, since the potential tends to zero at infinity:  $k_{\text{sca}} = k_{\text{inc}} = k$ . But its orientation can change, and this results in a non-zero  $\vec{q}$ , whose modulus is related to the scattering angle  $\theta$ . Since  $\theta$  is the angle between  $\vec{k}_{\text{sca}}$  and  $\vec{k}_{\text{inc}}$ , one has  $\vec{k}_{\text{sca}} \cdot \vec{k}_{\text{inc}} = k^2 \cos \theta$ . It follows that:

$$\begin{aligned} q^2 &= k_{\text{sca}}^2 + k_{\text{inc}}^2 - 2\vec{k}_{\text{sca}} \cdot \vec{k}_{\text{inc}} = 2k^2(1 - \cos \theta) \\ &= 4k^2 \sin^2 \frac{\theta}{2}, \end{aligned} \quad (4.2.14)$$

and therefore that

$$q = 2k \sin \frac{\theta}{2}. \quad (4.2.15)$$

The infinite sum appearing in the (4.2.12) can now be evaluated explicitly without too much difficulty. To do so, one may start from the plane wave  $e^{i\vec{q} \cdot \vec{r}} = e^{i\vec{k}_{\text{sca}} \cdot \vec{r}} e^{-i\vec{k}_{\text{inc}} \cdot \vec{r}}$ , reexpress each of the two factors on the right hand side by an expansion of the type (3.7.111) and integrate over the orientation of  $\vec{r}$  relative to  $\vec{q}$ . In this way one finds an expression for the sum (4.2.12) in terms of the integral of  $e^{i\vec{q} \cdot \vec{r}}$  over the orientation of  $\vec{r}$  relative to  $\vec{q}$ . The result turns out to be given by the following expression in terms of  $q$ :

$$\sum_{l=0}^{+\infty} (2l+1) [j_l(kr)]^2 P_l(\cos \theta) = \frac{\sin(qr)}{qr}, \quad (4.2.16)$$

It then follows that the scattering amplitude is given as a function of  $q$  by

$$f(q) \simeq -\frac{2m}{\hbar^2} \int_0^{+\infty} V(r) \frac{\sin(qr)}{qr} r^2 dr. \quad (4.2.17)$$

We can now easily recognize that the integral appearing in this expression is proportional to the Fourier transform of the potential evaluated at the momentum transfer. Indeed:

$$\begin{aligned}\int V(r) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r} &= 2\pi \int_0^{+\infty} V(r) \left[ \int_{-1}^1 e^{-iqr \cos \theta} d(\cos \theta) \right] r^2 dr \\ &= 4\pi \int_0^{+\infty} V(r) \left[ \frac{\sin(qr)}{qr} \right] r^2 dr.\end{aligned}\quad (4.2.18)$$

One finally finds the following simple expression for the scattering amplitude in the Born approximation:

$$f(q) \simeq -\frac{m}{2\pi\hbar^2} \int V(r) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}.\quad (4.2.19)$$

The corresponding differential cross section is given by:

$$\sigma(q) = \left( \frac{m}{2\pi\hbar^2} \right)^2 \left| \int V(r) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r} \right|^2.\quad (4.2.20)$$

Notice finally that since  $q^2 = 2k^2(1 - \cos \theta)$  one has  $dq^2 = -2k^2 d(\cos \theta)$ , and the total cross section can be written as an integral over  $q^2$ :

$$\sigma_{\text{tot}} = \frac{\pi}{k^2} \int_0^{4k^2} \sigma(q^2) dq^2.\quad (4.2.21)$$

It should also be emphasized that the Born approximations for  $f(\theta)$  and  $\sigma_{\text{tot}}$  do not satisfy the optical theorem exactly, but rather in an approximate perturbative way. Indeed, the first order expression for  $f(\theta)$  is real and an imaginary part can arise only at second order in perturbation theory, corresponding to the fact that the leading effect in  $\sigma_{\text{tot}}$  is quadratic in the potential.

### 4.2.1 Example

As an example, let us consider the case of a screened repulsive Coulomb potential of the type:

$$V(r) = \frac{\alpha}{r} e^{-r/a}.\quad (4.2.22)$$

The scattering amplitude in the Born approximation is given by (4.2.17), which reads in this case:

$$f(q) \simeq -\frac{2m\alpha}{\hbar^2 q} \int_0^{+\infty} e^{-r/a} \sin(qr) dr\quad (4.2.23)$$

The integral that appears in this expression is easily calculated:

$$\begin{aligned}\int_0^{+\infty} e^{-r/a} \sin(qr) dr &\simeq \frac{1}{2i} \int_0^{+\infty} \left[ e^{-(1/a-iq)r} - e^{-(1/a+iq)r} \right] dr \\ &\simeq \frac{1}{2i} \left[ \frac{1}{1/a-iq} - \frac{1}{1/a+iq} \right] \\ &\simeq \frac{q}{q^2 + a^{-2}}.\end{aligned}\quad (4.2.24)$$

One then finds:

$$f(q) \simeq -\frac{2m\alpha}{\hbar^2} \frac{1}{q^2 + a^{-2}}. \quad (4.2.25)$$

The differential cross section then reads:

$$\sigma(q^2) \simeq \left(\frac{2m\alpha}{\hbar^2}\right)^2 \frac{1}{(q^2 + a^{-2})^2}. \quad (4.2.26)$$

Finally, the total cross section is

$$\sigma_{\text{tot}} \simeq \frac{\pi}{k^2} \int_0^{4k^2} \sigma(q^2) dq^2 = \frac{\pi}{k^2} \left(\frac{2m\alpha}{\hbar^2}\right)^2 \int_0^{4k^2} \frac{dq^2}{(q^2 + a^{-2})^2}. \quad (4.2.27)$$

The integral in this expression is evaluated to be:

$$\begin{aligned} \int_0^{4k^2} \frac{dq^2}{(q^2 + a^{-2})^2} &= \left[ -\frac{1}{q^2 + a^{-2}} \right]_0^{4k^2} = -\frac{1}{4k^2 + a^{-2}} + \frac{1}{a^{-2}} \\ &= \frac{4k^2 a^4}{1 + 4k^2 a^2} \end{aligned} \quad (4.2.28)$$

It follows that:

$$\sigma_{\text{tot}} \simeq \pi \left(\frac{4m\alpha}{\hbar^2}\right)^2 \frac{a^4}{1 + 4k^2 a^2}. \quad (4.2.29)$$

Notice that in the limit  $a \rightarrow \infty$ , in which one recovers the case of an unscreened Coulomb potential, the differential cross section reduces to the Rutherford cross section, while the total cross section diverges. In that situation the born approximation accidentally yields the exact result.

### 4.3 High energy scattering and the eikonal approximation

Another situation in which there is a significant simplification is that of the scattering of very high energy particles from a potential with a finite range  $a$ . More precisely, let us suppose that  $V$  is strongly suppressed for  $r$  larger than  $a$ , and that the energy of the incoming particles is such that  $E \gg |V|$  and  $k \gg 1/a$ , meaning that  $\lambda \ll a$ . This is a situation where according to our discussion of section 4.1  $l_{\text{max}} \simeq ka \gg 1$ . The main contribution to the scattering amplitude therefore comes from partial waves with large angular quantum number  $l$  and is restricted to small scattering angles. We may then assume that  $l \gg 1$  and  $\theta \ll 1$ . This implies that the radial part of the problem is semiclassical. One can then use the semiclassical approximation for the phase shifts derived in previous chapter. The angular part of the problem is instead not semiclassical but rather dominated by quantum effects. One can then not use the semiclassical result for the cross section, but one may derive another simple result for it by exploiting the fact that the scattering angle is very small.

To derive an approximate formula for the scattering amplitude in the above situation, let us then start from the semiclassical approximation for the phase shifts, which is valid for  $l \gg 1$  and can be rewritten in the following way:

$$\delta_l \simeq \int_{r_0}^{\infty} \sqrt{k^2 - \frac{2m}{\hbar^2} V(r) - \frac{l^2}{r^2}} dr - \int_{r_0}^{\infty} \sqrt{k^2 - \frac{l^2}{r^2}} dr. \quad (4.3.30)$$

In the situation at hand, the potential term has a small effect in this semiclassical formula. In particular, the turning point  $r_0$  is dominantly determined by the centrifugal barrier and can be taken in both integrals to be approximately given by

$$r_0 \simeq \frac{l}{k}. \quad (4.3.31)$$

Moreover, one may expand the integrand of the first integral in powers of  $V(r)$ . The zeroth order term then just cancels against the second integral, while the first order term gives a good approximation of the result:

$$\begin{aligned} \delta_l &\simeq -\frac{m}{\hbar^2} \int_{l/k}^{\infty} V(r) \left[ k^2 - \frac{l^2}{r^2} \right]^{-1/2} dr \\ &\simeq -\frac{m}{\hbar^2 k} \int_{r_0}^{\infty} V(r) \left[ 1 - \frac{r_0^2}{r^2} \right]^{-1/2} dr. \end{aligned} \quad (4.3.32)$$

Finally, one may rewrite this integral in a more convenient way as an integral over the  $z$  coordinate. Writing  $r = \sqrt{r_0^2 + z^2}$  one has  $z = \sqrt{r^2 - r_0^2}$  and  $dz = r/\sqrt{r^2 - r_0^2} dr$ , and since  $r_0 \simeq l/k$  it follows that:

$$\delta_l \simeq -\frac{m}{2\hbar^2 k} \int_{-\infty}^{\infty} V(\sqrt{z^2 + l^2/k^2}) dz. \quad (4.3.33)$$

This simple result can be interpreted in the following way. In a truly semiclassical situation, the phase of the wave function would be given by  $S/\hbar$ , where  $S$  is the classical action evaluated along the classical trajectory. In the regime of very high energy scattering we are considering, the situation is not really semiclassical, but it turns out that one may nevertheless use in a meaningful way the same formula with  $S$  evaluated on a trajectory that is a straight line with fixed impact parameter  $b$  and  $z$  going from  $-\infty$  to  $+\infty$ , corresponding to the fact that the scattering angle must be very small. The asymptotic form for  $z \rightarrow +\infty$  of the true scattering wave function in the presence of the potential and the free wave-function that one would have in the absence of the potential are then related by a factor  $e^{2i\delta(b)}$  where  $\delta(b) = (S(b)|_V - S(b)|_0)/(2\hbar)$ . The scattering amplitude must then involve the factor  $e^{2i\delta(b)} - 1$ , and this suggests that it should be possible to relate  $\delta(b)$  to the phase shifts  $\delta_l$  computed in this situation. As a matter of fact, one finds that  $\delta(b)$  is given by the following expression in the high-energy limit:

$$\begin{aligned} \delta(b) &\simeq \frac{1}{2} \int_{-\infty}^{+\infty} \sqrt{k^2 - \frac{2m}{\hbar^2} V(\sqrt{z^2 + b^2})} dz - \frac{1}{2} \int_{-\infty}^{+\infty} k dz \\ &\simeq -\frac{m}{2\hbar^2 k} \int_{-\infty}^{+\infty} V(\sqrt{z^2 + b^2}) dz. \end{aligned} \quad (4.3.34)$$



We can now make contact with our previous expression (4.3.33) by taking  $b \simeq r_0 \simeq l/k$ . We then see that one indeed finds

$$\delta_l \simeq \delta(b), \quad (4.3.35)$$

with  $b$  given by

$$b \simeq \frac{l}{k}. \quad (4.3.36)$$

To continue and derive an approximate expression for the scattering amplitude, we now have to plug the above approximate expression for the phase shifts into the sum over partial waves defining the scattering amplitude and evaluate this sum. To do so, we may use the approximate behavior of the Legendre polynomials for small angles  $\theta \ll 1$  and large angular momenta  $l \gg 1$ . This can be obtained by solving the angular wave equation in the limit  $\theta \ll 1$  and for  $l \gg 1$ , which reads  $u_l''(\theta) + 1/\theta u_l'(\theta) + l^2 u_l(\theta) \simeq 0$ . In this way one deduces that

$$P_l(\cos \theta) \simeq J_0(l\theta), \quad \theta \ll 1, \quad l \gg 1, \quad (4.3.37)$$

in terms of the zeroth order Bessel function  $J_0(z)$ , which is defined by the differential equation  $J_0''(z) + 1/z J_0'(z) + J_0(z) = 0$  and admits the following integral representation:

$$J_0(z) = \frac{1}{2\pi} \int_0^{2\pi} e^{-iz \cos \varphi} d\varphi. \quad (4.3.38)$$

Substituting this in the infinite sum defining the scattering amplitude, one may now evaluate the latter more concretely. To do so, we switch to the new variable  $b \simeq l/k$  and rewrite  $\delta_l = \delta(b)$  and  $J_0(l\theta) = J_0(k\theta b)$ . One may then treat  $k$  as a large quantity and approximate the infinite sum as an integral over  $b$  with  $db \simeq 1/k$ . Proceeding in this way one finds:

$$\begin{aligned} f(\theta) &\simeq \frac{1}{2ik} \sum_{l \gg 1}^{+\infty} (2l+1)(e^{2i\delta_l} - 1) P_l(\cos \theta) \simeq \frac{1}{ik} \sum_{l \gg 1}^{+\infty} (e^{2i\delta_l} - 1) J_0(l\theta) l \\ &\simeq -ik \int_0^{+\infty} (e^{2i\delta(b)} - 1) J_0(k\theta b) b db. \end{aligned} \quad (4.3.39)$$

Using the integral representation (4.3.38) for  $J_0(k\theta b)$ , one may finally write this as:

$$f(\theta) \simeq \frac{k}{2\pi i} \int_0^{+\infty} \int_0^{2\pi} (e^{2i\delta(b)} - 1) e^{-ik\theta b \cos \varphi} b db d\varphi. \quad (4.3.40)$$

This result can be rewritten in a yet more convenient way in terms of the transferred momentum  $\vec{q}$ . Indeed, for a very high energy scattering process involving a small deflection angle  $\theta \ll 1$ , this lies approximately in the  $xy$  plane, like the impact parameter  $\vec{b}$ , and has a modulus that is simply given by  $k\theta$ :

$$\vec{q} \perp \hat{z}, \quad q \simeq k\theta. \quad (4.3.41)$$

We may then identify the angle  $\varphi$  in (4.3.40) with the arbitrary angle between the vectors  $\vec{b}$  and  $\vec{q}$  in the  $xy$  plane. In this way, we have  $\vec{q} \cdot \vec{b} \simeq k\theta b \cos \varphi$  and  $d^2\vec{b} = b db d\varphi$ , and the scattering amplitude (4.3.40) can be rewritten as a two-dimensional integral over the impact parameter vector, namely:

$$f(q) \simeq \frac{k}{2\pi i} \int (e^{2i\delta(b)} - 1) e^{-i\vec{q}\cdot\vec{b}} d^2\vec{b}. \quad (4.3.42)$$

The result (4.3.42), or equivalently (4.3.39), is called the eikonal approximation to the scattering amplitude, in reference to the fact that it is determined by a semiclassical phase  $\delta(b)$ , which we recall is given by

$$\delta(b) \simeq -\frac{m}{2\hbar^2 k} \int_{-\infty}^{+\infty} V(\sqrt{z^2 + b^2}) dz. \quad (4.3.43)$$

One can show that the eikonal approximation satisfies the optical theorem exactly. As a result, one can exploit the optical theorem to compute the total cross section out of the imaginary part of the forward scattering amplitude:

$$\begin{aligned} \sigma_{\text{tot}} &\simeq \frac{4\pi}{k} \text{Im} f(0) \\ &\simeq 4 \int \sin^2 \delta(b) d^2\vec{b}. \end{aligned} \quad (4.3.44)$$

Notice that in the special situations where the interaction is weak and the potential can be treated as small, the phase  $\delta(b)$  is small, since it is linear in the potential. One may then make the further expansion  $e^{2i\delta(b)} - 1 \simeq 2i\delta(b)$ , and the eikonal approximation reduces to the Born approximation:

$$\begin{aligned} f(q) &\simeq -\frac{m}{2\pi\hbar^2} \int_{-\infty}^{+\infty} \int V(\sqrt{z^2 + b^2}) e^{-i\vec{q}\cdot\vec{b}} d^2\vec{b} dz \\ &\simeq -\frac{m}{2\pi\hbar^2} \int V(r) e^{-i\vec{q}\cdot\vec{r}} d^3\vec{r}. \end{aligned} \quad (4.3.45)$$

As already mentioned, when doing this further approximation the optical theorem holds only approximately.

### 4.3.1 Example

As a simple example, let us consider the high-energy scattering by a spherical barrier of the form:

$$V(r) = \begin{cases} V_0, & r < a, \\ 0, & r > a. \end{cases} \quad (4.3.46)$$

In such a situation, the eikonal phase is given by:

$$\delta(b) = -\nu_0 \sqrt{1 - b^2/a^2} \theta(a - b). \quad (4.3.47)$$

in terms of the following parameter:

$$\nu_0 = \frac{mV_0a}{\hbar^2k}. \quad (4.3.48)$$

It follows that the scattering amplitude in the eikonal approximation is given by the following integral:

$$f(\theta) \simeq -ik \int_0^a \left[ \exp \left\{ -2i\nu_0 \sqrt{1 - b^2/a^2} \right\} - 1 \right] J_0(k\theta b) b db \quad (4.3.49)$$

In the totally forward direction  $\theta = 0$ , one can use  $J_0(0) = 1$  and performing the change of variable  $x = \sqrt{1 - b^2/a^2}$ ,  $dx = -a^{-2}/\sqrt{1 - b^2/a^2} b db$  one therefore finds:

$$\begin{aligned} f(0) &\simeq -ika^2 \int_0^1 \left[ \exp \left\{ -2i\nu_0 x \right\} - 1 \right] x dx \\ &\simeq \frac{ka^2}{2} \left[ i + \frac{1}{\nu_0} e^{-2i\nu_0} - \frac{i}{2\nu_0^2} (e^{-2i\nu_0} - 1) \right] \\ &\simeq \frac{ka^2}{2} \left[ \left( \frac{\cos(2\nu_0)}{\nu_0} - \frac{\sin(2\nu_0)}{2\nu_0^2} \right) + i \left( 1 + \frac{1}{2\nu_0^2} - \frac{\sin(2\nu_0)}{\nu_0} - \frac{\cos(2\nu_0)}{2\nu_0^2} \right) \right] \end{aligned} \quad (4.3.50)$$

Using the optical theorem, one finally deduces that the total cross section is given by:

$$\begin{aligned} \sigma_{\text{tot}} &= \frac{4\pi}{k} \text{Im}f(0) \\ &\simeq 2\pi a^2 \left[ 1 + \frac{1}{2\nu_0^2} - \frac{\sin(2\nu_0)}{\nu_0} - \frac{\cos(2\nu_0)}{2\nu_0^2} \right]. \end{aligned} \quad (4.3.51)$$

In the case of a very low barrier with  $\nu_0 \ll 1$ , this simplifies to the following result (which coincides with what one would obtain by using the Born approximation and taking the high energy limit  $ka \gg 1$ ):

$$\sigma_{\text{tot}} \simeq 2\pi a^2 \nu_0^2, \quad \nu_0 \ll 1. \quad (4.3.52)$$

In the case of a very high barrier with  $\nu_0 \gg 1$ , one finds instead the following very simple result:

$$\sigma_{\text{tot}} \simeq 2\pi a^2, \quad \nu_0 \gg 1. \quad (4.3.53)$$

This is a factor of 2 bigger than the classical result  $\pi a^2$  for an unpenetrable spherical barrier. The extra contribution can be interpreted as a diffraction effect related to the shadow that must arise behind the spherical barrier in the forward direction.

## 4.4 Low energy scattering and the threshold approximation

Another situation in which there is a significant simplification is that of the scattering of very low energy particles from a potential with a finite range  $a$ . More precisely, let us suppose that  $V$  is strongly suppressed for  $r$  larger than  $a$ , and that the energy of the incoming particles is such that  $k \ll 1/a$ , meaning that  $\lambda \gg a$ . This is a situation

where the scattering process is totally dominated by quantum effects and does not admit a semiclassical picture. However, there is an important simplification: according to our discussion of section 4.1  $l_{\max} \simeq ka \ll 1$ . All the partial waves with  $l \neq 0$  then give a suppressed contribution, and the scattering amplitude is dominated by the  $l = 0$  term, also called *s*-wave. Intuitively, the reason for this can also be understood as follows. At distances  $r \gtrsim a$ , the potential is negligible and  $V_{\text{eff}}$  is therefore dominated by the centrifugal barrier. In particular, at  $r \sim a$  one has  $V_{\text{eff}}(a) \sim \hbar^2 l(l+1)/(2ma^2)$ . In order for a radial mode with  $l \neq 0$  to penetrate down to this distance and feel the potential, it would then need to have an energy  $E \sim \hbar^2 l(l+1)/(2ma^2)$ , corresponding to a wave number  $k \sim \sqrt{l(l+1)}/a$ . If instead  $k \ll 1/a$ , the radial mode cannot penetrate to small distances and significantly feel the potential. As a consequence, the radial wave function is essentially the free one and the phase shifts approximately vanish. The only exception to this arises for the  $l = 0$  mode, for which the centrifugal barrier is absent and the effect of the potential can then be felt significantly.

A more quantitative information about the low-energy behavior of the phase shifts, also called threshold behavior, can be obtained by studying the radial wave equation, which reads:

$$\phi_l''(r) + \frac{2}{r}\phi_l'(r) + \left[ k^2 - \frac{l(l+1)}{r^2} \right] \phi_l(r) = \frac{2m}{\hbar^2} V(r) \phi_l(r). \quad (4.4.54)$$

Recall that in general the behaviors for  $r \rightarrow 0$  and for  $r \rightarrow +\infty$  are universal and independent of the potential, while the phase shift observed at large  $r$  depends instead on the effect of the potential in the whole region of finite  $r$ . In the situation at hand, however, the potential affects the wave function only for  $r$  much smaller than  $a$ . For  $r$  much larger than  $a$ , the potential is negligible and the wave function must therefore be a linear combination of the two independent solutions of the free radial wave equation. We may write this general form of the wave function in the following way:

$$\phi_l(r) \simeq A_l \left[ \cos \delta_l j_l(kr) - \sin \delta_l n_l(kr) \right], \quad r \gg a. \quad (4.4.55)$$

Notice now that since  $k \ll 1/a$ , the distance of order  $1/k$  where this solution changes its behavior from power law to oscillatory is much larger than  $a$ . Using the asymptotic behaviors (3.4.41), (3.4.42) and (3.4.44), (3.4.45) one then finds:

$$\phi_l(r) \simeq A_l \left[ \cos \delta_l \frac{(kr)^l}{(2l+1)!!} + \sin \delta_l \frac{(2l-1)!!}{(kr)^{l+1}} \right], \quad a \ll r \ll 1/k, \quad (4.4.56)$$

$$\phi_l(r) \simeq \frac{A_l}{kr} \sin \left( kr - l\frac{\pi}{2} + \delta_l \right), \quad r \gg 1/k. \quad (4.4.57)$$

The constant  $\delta_l$  that has been used to parametrize the relative weight of the two linearly independent solutions is now recognized to be precisely the asymptotic phase shift. It is determined by the matching across the region of  $r \sim a$  the above free wave function valid for  $r \gg a$  to the potential-influenced wave function valid for  $r \ll a$ . The precise numerical value of  $\delta_l$  can be determined only once the exact behavior of the wave function in the region where the potential is relevant is known. However, one may deduce the

general way it can depend on  $k$  by a simple argument. The basic observation is that in the region  $a \ll r \ll 1/k$  the  $k^2$  term in the differential equation can still be neglected, and the solution should therefore not depend on  $k$ . This means that the coefficients  $A_l \cos \delta_l k^l$  and  $-A_l \sin \delta_l k^{-l-1}$  of the two independent solutions  $r^l$  and  $r^{-l-1}$  in (4.4.56) should be independent of  $k$ , modulo an overall normalization. In particular, their ratio  $-\tan \delta_l k^{-2l-1}$  should be a constant  $\alpha_l$  depending only on  $l$  and not on  $k$ . This implies that  $\tan \delta_l = -\alpha_l k^{2l+1}$ , and the phase shifts  $\delta_l$  can therefore be parametrized in terms of the constants  $\alpha_l$  as:

$$\delta_l \simeq -\arctan(\alpha_l k^{2l+1}). \quad (4.4.58)$$

Notice now that since  $k$  is assumed to be small, it is rather natural to have  $\delta_l \ll 1$ . In that case, the arctangent can be linearized to give  $\delta_l \simeq -\alpha_l k^{2l+1}$ , and the partial scattering amplitude is simply  $f_l \simeq \delta_l/k \simeq -\alpha_l k^{2l}$ . However, it may also happen that some of the  $\alpha_l$  are big, and that  $\delta_l \sim 1$ . In that case, one has to keep the arctangent in the above expression for  $\delta_l$  to compute the partial scattering amplitude, and one finds:

$$\begin{aligned} f_l &\simeq \frac{1}{k \cot \delta_l - ik} \simeq \frac{1}{-\alpha_l^{-1} k^{-2l} - ik} \\ &\simeq -\frac{\alpha_l k^{2l}}{1 + i\alpha_l k^{2l+1}}. \end{aligned} \quad (4.4.59)$$

In this general expression, we can now safely approximate the denominator with 1, since the extra term is further suppressed by an extra factor of  $k$ , even when  $\alpha_l k^{2l}$  is sizable. So finally:

$$f_l \simeq -\alpha_l k^{2l}. \quad (4.4.60)$$

As expected, in a generic situation with small  $k$  the dominant effect is represented by the  $l = 0$  partial amplitude, while the  $l \neq 0$  partial amplitudes are smaller and smaller when  $l$  is increased. One may then perform a kind of multipole expansion where one retains a finite number of partial waves according to the accuracy that one wants to achieve. In this respect, it should be noticed that for small but finite  $k$ , the quantities  $\alpha_l = -\tan \delta_l/k^{2l+1}$  are actually only approximately constant and can be expanded in powers of  $k^2$ . But the contributions of different partial waves are nevertheless distinguished by the fixed dependence on  $\theta$  through  $P_l(\cos \theta)$  that they induce in the full scattering amplitude  $f(\theta)$ . The  $s$ -wave has partial amplitude  $f_0 = -\alpha_0$  and gives an isotropic contribution since  $P_0(\cos \theta) = 1$ . The  $p$  wave has partial amplitude  $f_1 = -\alpha_1 k^2$  and gives an anisotropic contribution controlled by  $P_1(\cos \theta) = \cos \theta$ . The  $d$  wave has partial amplitude  $f_2 = -\alpha_2 k^4$  and gives an anisotropic contribution controlled by  $P_2(\cos \theta) = 3/2 \cos^2 \theta - 1/2$ . And so on. In situations where  $k$  is very small, one may in first approximation restrict to the  $s$  wave and write  $f(\theta) \simeq f_0$ , or:

$$f(\theta) \simeq -\alpha_0. \quad (4.4.61)$$

The scattering amplitude is thus approximately constant and independent of the angle at very low energies. The number  $\alpha_0$ , which has the dimension of a length and depends on

the form of the potential, is called the scattering length. Its general definition is:

$$\alpha_0 = - \lim_{k \rightarrow 0} \frac{\tan \delta_0}{k}. \quad (4.4.62)$$

The differential cross section is then given by

$$\sigma(\theta) \simeq \alpha_0^2, \quad (4.4.63)$$

and finally the total cross section is simply:

$$\sigma_{\text{tot}} \simeq 4\pi\alpha_0^2. \quad (4.4.64)$$

It is worth emphasizing that the optical theorem, which implies that  $\sigma_{\text{tot}} = 4\pi/k \text{Im}f(0)$ , cannot be sensibly applied with these formulae for the threshold approximation, since one has both  $k \rightarrow 0$  and  $\text{Im}f(0) \rightarrow 0$ .

Whenever the potential is weak, the quantities  $\alpha_l$  are small and can be easily computed at first order in perturbation theory. The result can be obtained immediately by starting from the Born approximation (4.2.11). Replacing the spherical Bessel function with its behavior for small argument, one deduces that as expected  $\delta_l \simeq -\alpha_l k^{2l+1}$ , with:

$$\alpha_l \simeq \frac{2m}{\hbar^2} \frac{1}{[(2l+1)!!]^2} \int_0^{+\infty} V(r) r^{2l+2} dr. \quad (4.4.65)$$

In particular, the approximate scattering length at weak coupling is given by

$$\alpha_0 \simeq \frac{2m}{\hbar^2} \int_0^{+\infty} V(r) r^2 dr. \quad (4.4.66)$$

This formula shows that in the weak coupling limit  $\alpha_0$  is positive for repulsive potentials and negative for attractive potentials, and small in absolute value.

In general situations where the potential is not weak, the quantities  $\alpha_l$  can be computed by determining the exact behavior of the wave function in the region  $r \lesssim a$  and then matching this to the general free form (4.4.56) for  $r \gtrsim a$  to determine the parameters of the latter. One interesting situation where this matching can be carried out more explicitly is that of potentials which exactly vanish for  $r$  larger than some finite range  $a$ . The matching of the wave function can then be done by requiring the continuity of its logarithmic derivative in  $r = a$ . More precisely, suppose that we know the exact wave function  $\phi_l(r)$  for  $r \leq a$ . We may then compute its logarithmic derivative in  $r = a$  and get some number  $\gamma_l$ :

$$\left. \frac{r\phi_l'}{\phi_l} \right|_a = \left. \frac{r\chi_l'}{\chi_l} \right|_a - 1 = \gamma_l. \quad (4.4.67)$$

We must then compare this with the logarithmic derivative of the free wave function  $\phi_l^0(r) = A_l[\cos \delta_l j_l(kr) - \sin \delta_l n_l(kr)]$  valid for  $r \geq a$  evaluated in  $r = a$ , which is given by:

$$\left. \frac{r\phi_l^{0\prime}}{\phi_l^0} \right|_a = \left. \frac{r\chi_l^{0\prime}}{\chi_l^0} \right|_a - 1 = ka \frac{\cos \delta_l j_l'(ka) - \sin \delta_l n_l'(ka)}{\cos \delta_l j_l(ka) - \sin \delta_l n_l(ka)}. \quad (4.4.68)$$

Matching these two expressions one deduces that the phase shifts  $\delta_l$  are related to the logarithmic derivatives  $\gamma_l$  of the exact wave function by the following relation:

$$\delta_l = \arctan\left(\frac{ka j_l'(ka) - \gamma_l j_l(ka)}{ka n_l'(ka) - \gamma_l n_l(ka)}\right). \quad (4.4.69)$$

For small  $k$ , one may now use the asymptotic behavior of the spherical Bessel functions for small argument. In this way, one arrives at an expression for  $\delta_l$  which has indeed the expected form

$$\delta_l \simeq -\arctan(\alpha_l k^{2l+1}), \quad (4.4.70)$$

with  $\alpha_l$  given by the following expression:

$$\alpha_l = \frac{\gamma_l - l}{\gamma_l + l + 1} \frac{a^{2l+1}}{(2l+1)!!(2l-1)!!}. \quad (4.4.71)$$

This means that the partial amplitudes behave as  $f_l \propto (ka)^{2l}a$ , showing once again that the contribution of higher and higher partial waves is a priori more and more suppressed for  $ka \ll 1$ , unless the dimensionless coefficient controlling them grows large. Looking at the dominant  $l = 0$  case, one deduces in particular that the scattering length is given by

$$\alpha_0 \simeq \frac{\gamma_0}{1 + \gamma_0} a. \quad (4.4.72)$$

There exist in this case an interesting pictorial interpretation for the scattering length  $\alpha_0$ , which is based on the form of the wave function for  $k \rightarrow 0$ . In such a extreme low-energy limit,  $1/k \rightarrow +\infty$ , and therefore there are essentially only two regions to be considered. In the region  $r \in [0, a[$  the wave function depends on the potential. In the region  $r \in [a, +\infty[$ , on the other hand, it is universal and given by the expression (4.4.56) with  $\delta_0 \simeq -\arctan(\alpha_0 k)$ , from which we deduce that  $\phi_0(r) \propto 1 + \tan \delta_0 / (kr) = 1 - \alpha_0 / r$  and therefore that  $\chi_0(r) = r\phi_0(r)$  has a simple linear behavior:

$$\chi_0(r) \propto r - \alpha_0, \quad r > a. \quad (4.4.73)$$

This shows that  $\alpha_0$  corresponds to the value of  $r$  where the extrapolation of this behavior for the wave function crosses zero, that is the intercept of the free wave function evaluated at  $r = a$ :

$$\alpha_0 = \text{intercept of the wave function at } r = a. \quad (4.4.74)$$

It should be emphasized that depending on the value of  $\gamma_0$ , which is the value of the logarithmic derivative of the  $s$ -wave at the boundary of the region where the potential is non-vanishing, the scattering length  $\alpha_0$  may differ significantly from the range of the potential  $a$ . To be more precise, let us distinguish the two situations of repulsive and attractive potentials. For increasingly strong repulsive potentials, the wave function in the region  $r \leq a$  is more and more damped, as shown in fig. 4.1. The scattering length  $\alpha_0$  then monotonically increases from 0 up to the maximal value  $a$ , which is reached

when  $\gamma_0 = +\infty$ . For increasingly strong attractive potentials, on the contrary, the wave function in the region  $r \leq a$  is more and more enhanced and can even develop one or several nodes, as shown in fig. 4.2. The scattering length  $\alpha_0$  then monotonically decreases from 0 to  $-\infty$ , jumps from  $-\infty$  to  $+\infty$  when the first node appears and  $\gamma_0 = -1$ , decreases monotonically from  $+\infty$  to  $-\infty$ , jumps again from  $-\infty$  to  $+\infty$  when the second node appears and  $\gamma_0 = -1$ , and so on and so forth.

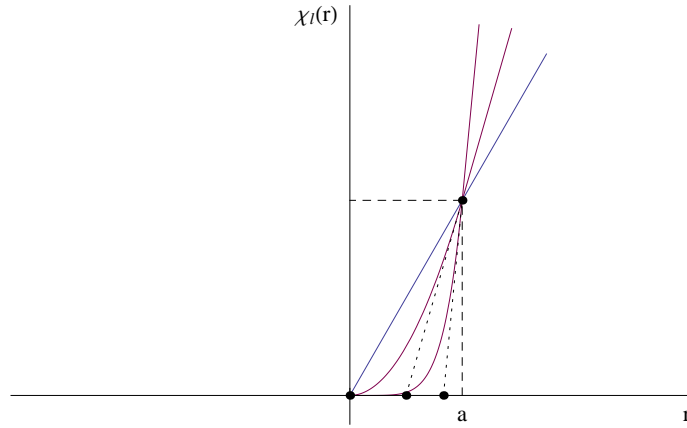


Figure 4.1: Pictorial representation of the scattering length for more and more repulsive potentials.

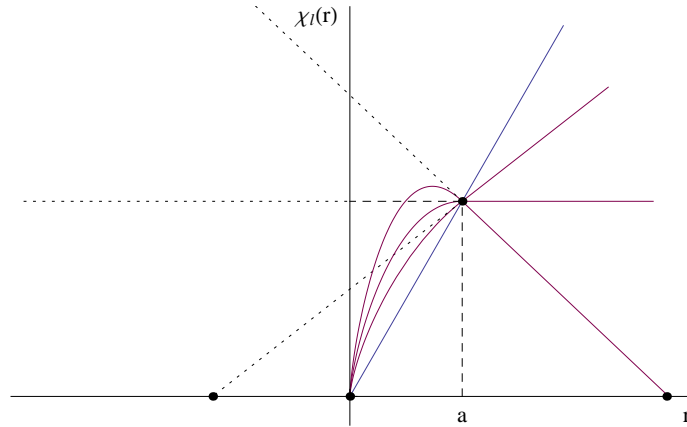


Figure 4.2: Pictorial representation of the scattering length for more and more attractive potentials.

The above picture allows to give simple and physical interpretation to the fact that  $\alpha_0 \rightarrow \infty$  whenever it happens that  $\gamma_0 \rightarrow -1$ :

$$\alpha_0 \rightarrow \infty, \text{ when } \gamma_0 \rightarrow -1. \quad (4.4.75)$$

Recall for this that  $\gamma_0$  corresponds to the logarithmic derivative of  $\phi_0(r)$  at  $r \simeq a$ , and therefore  $1 + \gamma_0$  similarly corresponds to the logarithmic derivative of  $\chi_0(r)$  at  $r \simeq a$ . The case where  $\gamma_0 \simeq -1$  thus corresponds to a situation in which the logarithmic derivative



of  $\chi_0(r)$  in  $r \simeq a$  vanishes and the wave function tends to a small constant at infinity. This signals the fact that in such a situation the attractive potential develops a bound state with very small negative energy, and the absolute value of the scattering length then takes its maximal value, namely  $|\alpha_0| \rightarrow +\infty$ , due to a resonance phenomenon involving this bound state. This effect is perfectly analogous to the resonance on a metastable state of positive energy  $E_0$  and finite width  $\Gamma$ , which appears when  $E \simeq E_0$ . In this case, the resonance is on a stable state of negative but very tiny energy  $E_0 \rightarrow 0^-$  and vanishing width  $\Gamma \rightarrow 0$ , which appears when  $E \rightarrow 0^+$ .

In fact, whenever a very large and positive scattering length  $\alpha_0^{\text{res}}$  appears due to the resonance on a bound state with very small negative energy  $E_0$ , one can relate  $\alpha_0^{\text{res}}$  to  $E_0$  by comparing the wave functions of the scattering state and the bound state. For  $r \leq a$ , the two wave functions must approximately coincide, since the former essentially corresponds to  $E \simeq 0^+$  and the latter essentially to  $E \simeq 0^-$ . For  $r \geq a$ , on the other hand, the two wave functions are parametrized by different quantities. For the scattering state we have  $\chi_0(r) \propto 1 - r/\alpha_0$ , where  $\alpha_0$  is the scattering length. For the bound state we have instead  $\chi_0(r) \propto e^{-\beta_0 r}$ , where  $\beta_0 = \sqrt{-2mE_0}/\hbar$  is the damping factor associated to the bound state energy. Comparing these two expressions for  $r \sim a$  and assuming that  $\beta_0 a \ll 1$  so that we can expand the exponential at first order, we deduce that  $\alpha_0 \simeq \beta_0^{-1}$ , that is:

$$\alpha_0^{\text{res}} \simeq \frac{\hbar}{\sqrt{-2mE_0}}. \quad (4.4.76)$$

#### 4.4.1 Example

As a simple example, let us consider the low-energy scattering by a spherical barrier of the form:

$$V(r) = \begin{cases} V_0, & r < a, \\ 0, & r > a. \end{cases} \quad (4.4.77)$$

The wave equation for  $r < a$  is:

$$\phi_l''(r) + \frac{2}{r}\phi_l'(r) + \left[ -\beta^2 - \frac{l(l+1)}{r^2} \right] \phi_l(r) = 0. \quad (4.4.78)$$

where:

$$\beta = \sqrt{-k^2 + \frac{2m}{\hbar^2}V_0} \simeq \frac{\sqrt{2mV_0}}{\hbar}. \quad (4.4.79)$$

The general solution is given by spherical Bessel functions with imaginary argument  $i\beta r$ , and the one that is regular in the origin is:

$$\phi_l(r) = A_l j_l(i\beta r), \quad r \leq a. \quad (4.4.80)$$

From this, we compute that the logarithmic derivative of the wave function at  $r = a$  is given by:

$$\gamma_l = i\beta a \frac{j_l'(i\beta a)}{j_l(i\beta a)} \quad (4.4.81)$$

For the case  $l = 0$ , we can use  $j_0(z) = \sin z/z$  and obtain:

$$\gamma_0 = \beta a \coth(\beta a) - 1. \quad (4.4.82)$$

It then follows from (4.4.72) that the scattering length and the total low-energy cross section are given by the following monotonic functions:

$$\alpha_0 = \left(1 - \frac{\tanh(\beta a)}{\beta a}\right)a, \quad \sigma_{\text{tot}} = 4 \left(1 - \frac{\tanh(\beta a)}{\beta a}\right)^2 \pi a^2. \quad (4.4.83)$$

For a very low barrier with small  $V_0$  such that  $\beta a \ll 1$ , representing an easily penetrable sphere, one finds the following result (which coincides with what one would find by using the Born approximation and taking the low-energy limit  $ka \ll 1$ ):

$$\alpha_0 \simeq \frac{1}{3}(\beta a)^2 a, \quad \sigma_{\text{tot}} \simeq \frac{4}{3}(\beta a)^4 \pi a^2, \quad \text{for } \beta a \ll 1. \quad (4.4.84)$$

For a very high barrier with large  $V_0$  such that  $\beta a \gg 1$ , representing an almost unpenetrable sphere, one finally finds instead:

$$\alpha_0 \simeq a, \quad \sigma_{\text{tot}} \simeq 4\pi a^2, \quad \text{for } \beta a \gg 1. \quad (4.4.85)$$

This behavior is very similar to the one displayed by the low-energy behavior of the reflection coefficient  $R$  for a one-dimensional square barrier, which monotonically increases from the minimal value 0 to the maximal classical value 1 when the height  $V_0$  is increased. In this three-dimensional case, however, we see that the total cross section  $\sigma_{\text{tot}}$  monotonically increases from the minimal value 0 to a maximal value  $4\pi a^2$ , which is four times larger than the classical maximal cross section  $\pi a^2$ . This reflects the fact that in the low-energy regime the scattering process is not semiclassical at all. The enhancement factor of 4 is due to a maximal quantum interference between the incoming and scattered waves, which is possible in the three-dimensional setting but not in the one-dimensional setting.

An other simple and interesting example, which can be studied in a very similar way, is that of the low-energy scattering by a spherical well of the form:

$$V(r) = \begin{cases} -V_0, & r < a, \\ 0, & r > a. \end{cases} \quad (4.4.86)$$

The wave equation for  $r < a$  is:

$$\phi_l''(r) + \frac{2}{r}\phi_l'(r) + \left[\alpha^2 - \frac{l(l+1)}{r^2}\right]\phi_l(r) = 0. \quad (4.4.87)$$

where:

$$\alpha = \sqrt{k^2 + \frac{2m}{\hbar^2}V_0} \simeq \frac{\sqrt{2mV_0}}{\hbar}. \quad (4.4.88)$$

The general solution is given by spherical Bessel functions with real argument  $\alpha r$ , and the one that is regular in the origin is:

$$\phi_l(r) = A_l j_l(\alpha r), \quad r \leq a. \quad (4.4.89)$$

From this, we compute that the logarithmic derivative of the wave function at  $r = a$  is given by:

$$\gamma_l = \alpha a \frac{j_l'(\alpha a)}{j_l(\alpha a)} \quad (4.4.90)$$

For the case  $l = 0$ , we can use  $j_0(z) = \sin z/z$  and obtain:

$$\gamma_0 = \alpha a \cot(\alpha a) - 1. \quad (4.4.91)$$

It then follows from (4.4.72) that the scattering length and the total low-energy cross section are given by the following jumping functions:

$$\alpha_0 = \left(1 - \frac{\tan(\alpha a)}{\alpha a}\right)a, \quad \sigma_{\text{tot}} = 4 \left(1 - \frac{\tan(\alpha a)}{\alpha a}\right)^2 \pi a^2. \quad (4.4.92)$$

For a very low well with small height  $V_0$  such that  $\alpha a \ll 1$ , one finds the following result (which coincides with what one would find by using the Born approximation and taking the low-energy limit  $ka \ll 1$ ):

$$\alpha_0 \simeq -\frac{1}{3}(\alpha a)^2 a, \quad \sigma_{\text{tot}} \simeq \frac{4}{3}(\alpha a)^4 \pi a^2, \quad \text{for } \alpha a \ll 1. \quad (4.4.93)$$

For wells with a height  $V_0$  such that  $\tan(\alpha a) = \alpha a$ , one finds a total suppression of the scattering length and the cross section:

$$\alpha_0 = 0, \quad \sigma_{\text{tot}} = 0, \quad \text{for } \tan(\alpha a) = \alpha a. \quad (4.4.94)$$

For wells with a height  $V_0$  such that  $\tan(\alpha a) = +\infty$ , on the contrary, one finds a maximal enhancement of the scattering length and the cross section:

$$\alpha_0 = +\infty, \quad \sigma_{\text{tot}} = +\infty, \quad \text{for } \tan(\alpha a) = +\infty. \quad (4.4.95)$$

This behavior is very similar to the one displayed by the low-energy behavior of the reflection coefficient  $R$  for a one-dimensional square well, which displays minima and maxima for certain discrete values of  $V_0$ . In this three-dimensional case, we see that the total cross section  $\sigma_{\text{tot}}$  displays minima with the smallest possible value 0 and maxima with the largest possible value  $+\infty$ . The first effect is called Ramsauer-Townsend effect and just corresponds to a situation with maximal destructive interference. The second effect is due to a resonance phenomenon involving bound states with approximately vanishing energy. Indeed, it can be easily verified that such bound states with vanishing energy occur when  $\tan(\alpha a) = +\infty$ , where  $\alpha \simeq \sqrt{2mV_0}/\hbar$ , that is when the well is such that  $\sqrt{2mV_0}a/\hbar \simeq (n + 1/2)\pi$ .

## Chapter 5

# General operatorial formalism for scattering problems

In this chapter, we will set up a more general formalism to study scattering problems which can be applied to any potential, even without spherical symmetry. It is an operatorial formalism based on the reinterpretation of a scattering process as a transition between asymptotic free-particle states as a consequence of the action of the interaction potential during the time evolution of the system. The basic ingredient in this formalism is the time-evolution operator and its infinite-time limit, which defines the scattering operator. We will describe how to compute the scattering amplitude and the cross section in this formalism, and use this to discuss more systematically the perturbative weak-coupling expansion. We will finally see how this formalism reduces to the one based on phase shifts and partial waves in the particular case of central problems, and investigate its relation to the use of Green functions to solve the stationary Schrödinger equation defining the problem.

### 5.1 The time-evolution operator

A scattering process can be viewed as a time-dependent process, where the incoming particle starts as a free particle far away from the interaction region, then feels the potential only for the limited time during which it is in the vicinity of its center, and finally ends up again as a free particle far away from the interaction region. It must then be possible to describe the scattering amplitude in terms of the transition rate between two free particle states with generically different momenta as a result of the application of the time dependent perturbation represented by the effect of the potential. Once this is done, it is possible to compute the scattering amplitude by using time-dependent perturbation theory, where the crucial ingredient is the time-evolution operator.

To set up the problem, let us start from a general Hamiltonian  $H$  which is the sum of the free kinetic energy  $H_0 = \vec{p}^2/(2m)$  and a time-independent potential  $V(\vec{r})$ :

$$H = H_0 + V. \tag{5.1.1}$$

In the usual Schrödinger picture, the time evolution of the states is determined by the full Hamiltonian while the time evolution of the operators is trivial:

$$i\hbar \frac{d}{dt} |\psi_S(t)\rangle = H |\psi_S(t)\rangle, \quad (5.1.2)$$

$$i\hbar \frac{d}{dt} \mathcal{O}_S(t) = 0. \quad (5.1.3)$$

The finite form of the time evolution is:

$$|\psi_S(t)\rangle = e^{-\frac{i}{\hbar} H(t-t_0)} |\psi_S(t_0)\rangle, \quad (5.1.4)$$

$$\mathcal{O}_S(t) = \mathcal{O}_S(t_0). \quad (5.1.5)$$

The usual description in terms of a time-dependent wave function  $\psi_S(\vec{r}, t)$  satisfying the Schrödinger equation can be obtained by using the coordinate representation  $|\vec{r}\rangle$  of the Hilbert space and defining:

$$\psi_S(\vec{r}, t) = \langle \vec{r} | \psi_S(t) \rangle. \quad (5.1.6)$$

One may switch from the Schrödinger picture to the interaction picture by performing a norm-preserving change of basis in the Hilbert space generated by the unitary transformation  $e^{i/\hbar H_0 t}$ . More precisely, we have:

$$|\phi_I(t)\rangle = e^{\frac{i}{\hbar} H_0 t} |\psi_S(t)\rangle, \quad (5.1.7)$$

$$\mathcal{O}_I(t) = e^{\frac{i}{\hbar} H_0 t} \mathcal{O}_S(t) e^{-\frac{i}{\hbar} H_0 t}. \quad (5.1.8)$$

In the interaction picture, the time evolution of the states is dictated by the potential, while the time evolution of the operators is dictated by the free Hamiltonian. More precisely, one easily shows that the time evolution of the states and the operators is determined by the following differential equations:

$$i\hbar \frac{d}{dt} |\phi_I(t)\rangle = V_I(t) |\phi_I(t)\rangle, \quad (5.1.9)$$

$$i\hbar \frac{d}{dt} \mathcal{O}_I(t) = [\mathcal{O}_I(t), H_0]. \quad (5.1.10)$$

The finite form of these are given by:

$$|\phi_I(t)\rangle = e^{\frac{i}{\hbar} H_0 t} e^{-\frac{i}{\hbar} H(t-t_0)} e^{-\frac{i}{\hbar} H_0 t_0} |\phi_I(t_0)\rangle, \quad (5.1.11)$$

$$\mathcal{O}_I(t) = e^{\frac{i}{\hbar} H_0(t-t_0)} \mathcal{O}_I(t_0) e^{-\frac{i}{\hbar} H_0(t-t_0)}. \quad (5.1.12)$$

Finally, a description in terms of a time-dependent wave function  $\phi_I(\vec{r}, t)$ , which however reduces to a stationary wave function associated to a given energy in the absence of interaction potential and has more in general a time dependence that is directly related to the effect of the potential, can be obtained by using the coordinate representation  $|\vec{r}\rangle$  of the Hilbert space and defining:

$$\phi_I(\vec{r}, t) = \langle \vec{r} | \phi_I(t) \rangle. \quad (5.1.13)$$

The interesting feature of the interaction picture is that the effect of the interaction potential is entirely encoded in the evolution of the states. Indeed, we see from eq. (5.1.11) that this time evolution can be written in terms of the unitary operator  $U_I(t, t_0) = e^{\frac{i}{\hbar}H_0 t} e^{-\frac{i}{\hbar}H(t-t_0)} e^{-\frac{i}{\hbar}H_0 t_0}$ , which reduces to the identity in the absence of any potential:

$$|\phi_I(t)\rangle = U_I(t, t_0)|\phi_I(t_0)\rangle. \quad (5.1.14)$$

However, in this picture the potential is effectively described by the time-dependent operator  $V_I(t)$ , whose form is dictated by the definition (5.1.8):

$$V_I(t) = e^{\frac{i}{\hbar}H_0 t} V e^{-\frac{i}{\hbar}H_0 t} \quad (5.1.15)$$

We observe now that since  $[H_0, V] \neq 0$  in the general situation that we are considering,  $U_I(t, t_0) \neq e^{-i/hV(t-t_0)}$  and similarly  $V_I(t) \neq V$ . However, it turns out that there exists a simple formal relation between  $U_I(t, t_0)$  and  $\int_{t_0}^t V_I(t') dt'$ . This can be derived by finding out the differential equation satisfied by  $U_I(t, t_0)$  and then solving it. The searched differential equation can be deduced by taking a time derivative of (5.1.14) and using (5.1.9). In this way one deduces that:

$$i\hbar \frac{d}{dt} U_I(t, t_0) = V_I(t) U_I(t, t_0). \quad (5.1.16)$$

This must now be solved with the boundary condition that

$$U_I(t_0, t_0) = 1. \quad (5.1.17)$$

The simplest way to proceed is to convert this into an integral equation, by integrating it over time between  $t_0$  and  $t$ :

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V_I(t') U_I(t', t_0) dt'. \quad (5.1.18)$$

This equation can be formally solved by iteratively replacing the  $U_I$  operator appearing under the integral with the expression defined by the above equation. In this way one finds:

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V_I(t') dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t \int_{t_0}^{t'} V_I(t') V_I(t'') dt' dt'' + \dots \quad (5.1.19)$$

Finally, one may rewrite the multiple integrals in such a way that they all range over the full time interval from  $t_0$  to  $t$ , by using the symmetry properties of integration. One standard way of doing this is to use the time-ordering operator  $\mathcal{T}$ , which orders the operators to which it is applied in antichronological order. This allows to formally sum up the whole series, but it is not directly useful for computing the cross section. An other trick that one can use, which proves to be more useful in this context, is to introduce an explicit step function to constrain each successive integration, as we shall see.

At this point, the above result derived for the time-evolution operator in the interaction picture can be used to obtain a similar result for the time-evolution operator in the Schrödinger picture. Indeed, from the relation between the two pictures it follows that

$$U_S(t, t_0) = e^{-\frac{i}{\hbar}H_0 t} U_I(t, t_0) e^{\frac{i}{\hbar}H_0 t_0}. \quad (5.1.20)$$

## 5.2 The scattering matrix

Let us now investigate how one can define a scattering amplitude and a cross section from the operatorial point of view, where the scattering process is viewed as a transition induced by a potential. For definiteness we use the interaction picture, but drop the indices  $I$  specifying this choice for simplicity. We moreover start by temporarily putting the whole system in a box of finite volume, in such a way to work with a discrete spectrum of free particle states, and postpone for a while the discussion of the continuous spectrum emerging in the infinite volume limit.

To describe the scattering process, we consider all the possible initial free-particle states  $|i\rangle$  and all the possible final free-particle states  $|f\rangle$ , both chosen among the complete set of free particle states:

$$|i\rangle = \text{initial free-particle state}, \quad (5.2.21)$$

$$|f\rangle = \text{final free-particle state}. \quad (5.2.22)$$

We use the canonical normalization for these free particles states in terms of Kronecker  $\delta$ -function, so that the orthonormality and completeness relations read:

$$\langle i|j\rangle = \delta_{ij}, \quad \sum_n |n\rangle\langle n| = 1. \quad (5.2.23)$$

The key quantity to describe the dynamics of the scattering process is then the time-evolution operator  $U(t_f, t_i)$ , which relates the full scattering state  $|\phi(t_i)\rangle$  at some initial time  $t_i$  to the full scattering state  $|\phi(t_f)\rangle$  at some final time  $t_f$ :

$$|\phi(t_f)\rangle = U(t_f, t_i)|\phi(t_i)\rangle. \quad (5.2.24)$$

More precisely, we are interested in studying this time evolution for initial times  $t_i \rightarrow -\infty$  in the far past and final times  $t_f \rightarrow +\infty$  in the far future, because we know that at those times the state must be a free particle state. We are then led to define the scattering operator or matrix  $S$  as the limit of the evolution operator  $U(t_f, t_i)$  for these asymptotic times:

$$S = U(+\infty, -\infty). \quad (5.2.25)$$

According to the formula (5.1.19), this is given by:

$$S = 1 - \frac{i}{\hbar} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}H_0 t} V e^{-\frac{i}{\hbar}H_0 t} dt + \dots. \quad (5.2.26)$$

Now, if the scattering state is chosen in such a way that  $|\phi(-\infty)\rangle = |i\rangle$  at  $t_i \rightarrow -\infty$ , then it will evolve to  $|\phi(+\infty)\rangle = S|\phi(-\infty)\rangle = S|i\rangle = \sum_f \langle f|S|i\rangle|f\rangle$  at  $t_f \rightarrow +\infty$ . This shows that the probability that from a definite initial state  $|i\rangle$  we get a definite final state  $|f\rangle$  is given by the square norm of the matrix element of the  $S$  operator between these two states:

$$P_{i \rightarrow f} = |\langle f|S|i\rangle|^2. \quad (5.2.27)$$

The scattering operator  $S$  is by construction unitary, since the evolution operator  $U(t_f, t_i)$  is so:

$$S^\dagger S = 1. \quad (5.2.28)$$

This ensures that the probability that a given initial state  $|i\rangle$  is seen to transform in any of the possible final states  $|f\rangle$  is unity, as it should:

$$\sum_f P_{i \rightarrow f} = \sum_f \langle i | S^\dagger | f \rangle \langle f | S | i \rangle = \langle i | S^\dagger S | i \rangle = 1 \quad (5.2.29)$$

Notice moreover that in the interaction picture the scattering operator consists of a diagonal part which is just the identity and corresponds to the possibility that no diffusion takes place at all, plus an off-diagonal part which describes the possible non-trivial diffusions. It is then convenient to parametrize the scattering operator  $S$  in terms of a transition operator  $T$  as follows:

$$S = 1 - iT. \quad (5.2.30)$$

The unitarity of  $S$  implies that  $T$  should satisfy the following property:

$$i(T - T^\dagger) = T^\dagger T. \quad (5.2.31)$$

The explicit expression for  $T$  descends from that of  $S$ , and one has:

$$T = \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar} H_0 t} V e^{-\frac{i}{\hbar} H_0 t} dt + \dots \quad (5.2.32)$$

In the relevant case where the final state  $|f\rangle$  is not identical to the initial state  $|i\rangle$ , we can compute the transition probability by considering the matrix element of the  $T$  operator rather than the  $S$  operator:

$$P_{i \rightarrow f} = |\langle f | T | i \rangle|^2. \quad (5.2.33)$$

Let us now consider the real situation in which the free particle states form a continuum and are labelled by three-dimensional wave vector  $\vec{k}$ . In such a situation, one may use the canonical normalization involving a Dirac  $\delta$ -function, so that the orthonormality and completeness relations read:

$$\langle i | j \rangle = \delta^{(3)}(\vec{k}_i - \vec{k}_j), \quad \int |n\rangle \langle n| d^3 \vec{k}_n = 1. \quad (5.2.34)$$

In this situation, we may more sensibly compute the differential probability for the transition from an initial state  $|i\rangle$  with definite wave vector  $\vec{k}_i$  to a final state  $|f\rangle$  with wave vector  $\vec{k}_f$  specified with an infinitesimal accuracy  $d^3 \vec{k}_f$ :

$$dP_{i \rightarrow f} = |\langle f | T | i \rangle|^2 d^3 \vec{k}_f. \quad (5.2.35)$$

The evaluation of the matrix element  $\langle f | T | i \rangle$  is in general a difficult task, and the best that one can do is usually to take a perturbative approach and compute it in the weak



potential approximation by retaining only the first few terms of the expansion for the operator  $T$ . The systematics of this expansion will be discussed in a forthcoming section. There is however a simple and important generic feature that emerges for it, which we can anticipate: the matrix element  $\langle f|T|i\rangle$  will vanish whenever  $E_f \neq E_i$ . To see this, let us for a moment return to a situation where  $t_i = -\tau/2$  and  $t_f = \tau/2$  with a total time  $\tau$  that is very large but finite, and check what happens when  $\tau$  is sent to infinity. When evaluating the matrix element  $\langle f|T|i\rangle$ , one always encounters an integral over the time during which the potential is active of the phase  $e^{i/\hbar(E_f-E_i)t}$  that is induced by the operators  $e^{\pm i/\hbar H_0 t}$  involved in the expression for  $U(t_f, t_i)$  when they act on the initial and final states. This integral yields a delta function enforcing energy conservation in the limit of infinite time  $\tau$ , as suggested by the uncertainty relation  $\Delta E \Delta t \gtrsim \hbar$ :

$$\frac{1}{\hbar} \int_{-\tau/2}^{\tau/2} e^{i/\hbar(E_f-E_i)t} dt = \frac{\sin [(E_f - E_i)\tau/(2\hbar)]}{(E_f - E_i)/2} \rightarrow 2\pi\delta(E_f - E_i). \quad (5.2.36)$$

We then expect that the general structure for the matrix element  $\langle f|T|i\rangle$  should consist of the above factor enforcing energy conservation times a residual matrix element for definite energy:

$$\langle f|T|i\rangle = 2\pi\delta(E_f - E_i) T_{fi}^E. \quad (5.2.37)$$

When squaring this matrix element, one encounters the square of the factor (5.2.36). This can be evaluated in the following way:

$$\left[ \frac{1}{\hbar} \int_{-\tau/2}^{\tau/2} e^{i/\hbar(E_f-E_i)t} dt \right]^2 = \frac{\sin^2 [(E_f - E_i)\tau/(2\hbar)]}{(E_f - E_i)^2/4} \rightarrow \frac{2\pi\tau}{\hbar} \delta(E_f - E_i). \quad (5.2.38)$$

We then conclude that we can identify  $2\pi\delta(0) = \tau/\hbar$  and:

$$|\langle f|T|i\rangle|^2 = \frac{2\pi}{\hbar} \delta(E_f - E_i) |T_{fi}^E|^2 \tau. \quad (5.2.39)$$

Because of the special role played by the energy in the computation of the matrix element appearing in (5.2.35), it is convenient to similarly decompose the differential  $d^3\vec{k}_f$  appearing in this quantity. To do so, we observe that a free particle state with wave number  $\vec{k}_f$  can be labeled by the modulus of this vector, which is related to the energy  $E_f$ , and the orientation of this vector, which is labelled by a solid angle element  $\Omega_f$ . Recalling that  $E_f = (\hbar k_f)^2/(2m)$ , we then find that  $d^3\vec{k}_f = k_f^2 dk_f d\Omega_f = mk_f/\hbar^2 dE_f d\Omega_f$ . We may then write

$$d^3\vec{k}_f = \rho(E_f) dE_f d\Omega_f, \quad (5.2.40)$$

in terms of the density of states with a given energy  $E_f$ , defined as:

$$\rho(E_f) = \frac{mk_f}{\hbar^2}. \quad (5.2.41)$$

Using these results, we can finally rewrite (5.2.35) in the following form:

$$dP_{i \rightarrow f} = \frac{2\pi\tau}{\hbar} \delta(E_i - E_f) |T_{fi}^E|^2 \rho(E_f) dE_f d\Omega_f. \quad (5.2.42)$$

Dividing this differential probability by the total time  $\tau$ , we finally conclude that the differential rate of transition per unit time is constant and given by

$$dW_{i \rightarrow f} = \frac{2\pi}{\hbar} \delta(E_f - E_i) |T_{fi}^E|^2 \rho(E_f) dE_f d\Omega_f. \quad (5.2.43)$$

We now recognize that this is simply the generalization of Fermi's golden rule to all orders in perturbation theory.

### 5.3 The cross section

Let us now see how one can relate the above differential transition rate defined by the matrix elements of the transition operator  $T$  to the differential cross section  $\sigma(\Omega)$ . According to its definition (3.7.96),  $\sigma(\Omega)$  is given by the ratio of the number of particles that are scattered per unit time and unit solid angle divided by the number of incoming particles per unit time and unit transverse surface.

To start, we compute the number of scattered particles per unit time through the solid angle element  $d\Omega_f$ . This is given by (5.2.43) integrated over the final energy  $E_f$ , which is fixed by the  $\delta$ -function, namely

$$d\bar{W}_{i \rightarrow f} = \int_0^{+\infty} \frac{dW_{i \rightarrow f}}{dE_f} dE_f = \frac{2\pi}{\hbar} |T_{fi}^E|^2 \rho(E_f) d\Omega_f \quad (5.3.44)$$

We then divide this by the volume element  $d\Omega_f$  itself, to find the number of scattered particles per unit time and unit solid angle, which is the numerator of the definition of the differential cross section:

$$w_{\text{sca}}(\Omega) = \frac{d\bar{W}_{i \rightarrow f}}{d\Omega_f} = \frac{2\pi}{\hbar} |T_{fi}^E|^2 \rho(E_f) = \frac{2\pi m k}{\hbar^3} |T_{fi}^E|^2. \quad (5.3.45)$$

We next compute the number of incident particles per unit time and unit surface. This is just given by the absolute value of the probability density current:

$$\vec{j}_{\text{inc}} = -\frac{i\hbar}{2m} \left( \phi_i^* \vec{\nabla} \phi_i - \phi_i \vec{\nabla} \phi_i^* \right). \quad (5.3.46)$$

The wave function  $\phi_i$  denotes the stationary wave function describing the initial state  $|i\rangle$ . This must be normalized compatibly with our convention (5.2.34), and is given by:

$$\phi_i(\vec{r}) = \langle \vec{r} | i \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}_i \cdot \vec{r}}. \quad (5.3.47)$$

The modulus of the incident flux, which is the denominator in the definition of the differential cross section, is then computed to be

$$j_{\text{inc}} = \frac{\hbar k}{m(2\pi)^3}. \quad (5.3.48)$$

Finally, the differential cross section is given by the ratio between (5.3.45) and (5.3.48), and reads:

$$\sigma(\Omega) = \frac{w_{\text{sca}}(\Omega)}{j_{\text{inc}}} = \frac{(2\pi)^4 m^2}{\hbar^4} |T_{fi}^E|^2. \quad (5.3.49)$$

As a last step, we may now write this as the squared norm of some scattering amplitude  $f(\Omega)$ , to compare with the approach followed in chapters 3 and 4:

$$\sigma(\Omega) = |f(\Omega)|^2. \quad (5.3.50)$$

The phase of  $f(\Omega)$  is not fixed by this reasoning, but we will see that the choice that precisely corresponds to our previous definition of the scattering amplitude is simply:

$$f(\Omega) = -\frac{(2\pi)^2 m}{\hbar^2} T_{fi}^E. \quad (5.3.51)$$

The general expression (5.3.51) is the main formula in this formalism. It relates the scattering amplitude  $f(\Omega)$  to the matrix elements of the transition operator  $T$ . It can now be proven that the unitarity of the scattering matrix  $S = 1 - iT$  implies a more general version of the optical theorem, valid for completely general static potentials. To prove this, let us recall that the unitarity of the  $S$  operator implies the following relation for the  $T$  operator:

$$i(T - T^\dagger) = T^\dagger T. \quad (5.3.52)$$

Taking the matrix element of this relation between a free-particle state  $|i\rangle$  and a free-particle state  $\langle j|$ , and inserting a complete set of free-particle states  $|f\rangle$  between the two operators in the right-hand side, we deduce that:

$$i(T_{ji} - T_{ij}^*) = \int T_{fj}^* T_{fi} d^3 \vec{k}_f. \quad (5.3.53)$$

In the special case where  $|j\rangle = |i\rangle$ , one then finds:

$$\text{Im}(T_{ii}) = -\frac{1}{2} \int |T_{fi}|^2 d^3 \vec{k}_f. \quad (5.3.54)$$

We may now use the expression (5.2.37) for  $T_{ii}$  with the identification  $2\pi\delta(0) \rightarrow \tau/\hbar$  and the expression (5.2.39) for  $|T_{fi}|^2$ , to rewrite:

$$T_{ii} = \frac{\tau}{\hbar} T_{ii}^E, \quad (5.3.55)$$

$$|T_{fi}|^2 = \frac{2\pi\tau}{\hbar} \delta(E_f - E_i) |T_{fi}^E|^2. \quad (5.3.56)$$

We may then also use (5.2.40) and (5.2.41) to write:

$$d^3 \vec{k}_f = \frac{mk}{\hbar^2} dE_f d\Omega_f. \quad (5.3.57)$$

Plugging back these expressions into (5.3.54), dividing by  $\tau/\hbar$  and integrating over  $E_f$ , it follows that:

$$\text{Im}(T_{ii}^E) = -\frac{\pi mk}{\hbar^2} \int |T_{fi}^E|^2 d\Omega_f. \quad (5.3.58)$$

Finally, using the relation (5.3.51) between  $T_{fi}^E$  and  $f(\Omega)$ , one deduces that:

$$\text{Im} f(0) = \frac{k}{4\pi} \int |f(\Omega)|^2 d\Omega. \quad (5.3.59)$$

This generalizes the optical theorem (3.7.126) that we derived with an other method for the special case of central potentials to generic potentials:

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im} f(0). \quad (5.3.60)$$

## 5.4 Systematics of the perturbative expansion

To compute the matrix element defining the scattering amplitude, we may now use a perturbative expansion in powers of  $(-i/\hbar)V$  truncated to some finite order. This will be justified when the interaction potential is weak and this quantity is small. Notice that since an inverse power of  $\hbar$  appears, this expansion is in some sense the opposite of the semiclassical expansion.

The crucial step that allows to simplify the time integrations defining the series expansion of the transition operator  $T$  and to explicitly factorize an energy-conservation delta-function to define  $T^E$  is to introduce the following free time-evolution operator restricted to the future:

$$U_0^+(t_1 - t_2) = e^{-\frac{i}{\hbar}H_0(t_1-t_2)}\theta(t_1 - t_2). \quad (5.4.61)$$

The operator  $T$  may then be rewritten as

$$T = \sum_{n=1}^{\infty} T^{(n)}, \quad (5.4.62)$$

where the operators  $T^{(n)}$  are given by

$$T^{(1)} = i\left(\frac{-i}{\hbar}\right) \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}H_0 t} V e^{-\frac{i}{\hbar}H_0 t} dt, \quad (5.4.63)$$

$$T^{(2)} = i\left(\frac{-i}{\hbar}\right)^2 \int \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}H_0 t} V U_0^+(t - t') V e^{-\frac{i}{\hbar}H_0 t'} dt dt', \quad (5.4.64)$$

$$T^{(3)} = i\left(\frac{-i}{\hbar}\right)^3 \int \int \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}H_0 t} V U_0^+(t - t') V U_0^+(t' - t'') V e^{-\frac{i}{\hbar}H_0 t''} dt dt' dt'', \quad (5.4.65)$$

...

To evaluate the matrix elements of the various contributions  $T^{(n)}$  to the operator  $T$ , one can now use the following Fourier integral representation of  $U_0^+(t_1 - t_2)$ , where the small positive number  $\epsilon$  defines a prescription on how to perform the integration in the vicinity of  $H_0$ , which is crucial to reproduce the  $\theta(t_1 - t_2)$  factor in  $U_0^+(t_1 - t_2)$ :

$$U_0^+(t_1 - t_2) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} e^{-\frac{i}{\hbar}\mathcal{E}(t_1-t_2)} \frac{1}{\mathcal{E} - H_0 + i\epsilon} d\mathcal{E}. \quad (5.4.66)$$

One may verify this expression by extending the integral to the complex  $\mathcal{E}$  plane. One can then close the integration contour at complex  $\infty$  in such a way the factor  $e^{-\frac{i}{\hbar}\mathcal{E}(t_1-t_2)}$  vanishes on the added part of the contour and compute the integral with the help of

Cauchy's theorem. When  $t_1 - t_2 > 0$ , one has to close the contour in the lower half plane, and the result of the integral is non-vanishing, since the integrand has a pole at  $\mathcal{E} = H_0 - i\epsilon$  in such a half plane. When instead  $t_1 - t_2 < 0$ , one has to close the contour in the upper half plane, and the result vanishes, since the integrand has no poles in such a half plane. One may then also interpret the above expression in terms of a real integral. Indeed, from that perspective one has to split the integral into a real principal part plus an imaginary localized contribution, and this amounts to using the following prescription:

$$\frac{1}{\mathcal{E} - H_0 + i\epsilon} \doteq \mathcal{P} \frac{1}{\mathcal{E} - H_0} - i\pi\delta(\mathcal{E} - H_0). \quad (5.4.67)$$

We will now see that by using the representation (5.4.66), one may compute more explicitly the matrix elements  $\langle f|T^{(n)}|i\rangle$  and bring them in the form that we have already anticipated to compute the scattering amplitude, namely:

$$\langle f|T^{(n)}|i\rangle = 2\pi\delta(E_f - E_i) T_{fi}^{E(n)}. \quad (5.4.68)$$

One may then compute the matrix element  $T_{fi}^E$  controlling the scattering amplitude as the following series:

$$T_{fi}^E = \sum_{n=1}^{\infty} T_{fi}^{E(n)}. \quad (5.4.69)$$

The first-order contribution  $T_{fi}^{E(1)}$  is defined through the matrix element of the operator  $T^{(1)}$  given by (5.4.63). This is computed to be

$$\begin{aligned} \langle f|T^{(1)}|i\rangle &= \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(E_f - E_i)t} dt \langle f|V|i\rangle \\ &= 2\pi\delta(E_f - E_i) \langle f|V|i\rangle. \end{aligned} \quad (5.4.70)$$

It follows that:

$$T_{fi}^{E(1)} = \langle f|V|i\rangle. \quad (5.4.71)$$

With a shorter notation, we may write this simply as:

$$T_{fi}^{E(1)} = V_{fi}. \quad (5.4.72)$$

At first order in perturbation theory, the transition amplitude on the fixed-energy shell is thus simply proportional to the matrix element of the interaction potential. This is the analogue of the fact that in time-independent perturbation theory the first order correction to the energy levels is given by the expectation value of the interaction potential.

The second-order contribution  $T_{fi}^{E(2)}$  is defined through the matrix element of the operator  $T^{(2)}$  given by (5.4.64). This is computed to be

$$\begin{aligned} \langle f|T^{(2)}|i\rangle &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(E_f - \mathcal{E})t} dt \frac{1}{\hbar} \int_{-\infty}^{+\infty} e^{\frac{i}{\hbar}(\mathcal{E} - E_i)t'} dt' \langle f|V \frac{1}{\mathcal{E} - H_0 + i\epsilon} V|i\rangle d\mathcal{E} \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} 2\pi\delta(E_f - \mathcal{E}) 2\pi\delta(\mathcal{E} - E_i) \langle f|V \frac{1}{\mathcal{E} - H_0 + i\epsilon} V|i\rangle d\mathcal{E} \\ &= 2\pi\delta(E_i - E_f) \langle f|V \frac{1}{E_i - H_0 + i\epsilon} V|i\rangle. \end{aligned} \quad (5.4.73)$$

It follows, denoting now the conserved energy by  $E_i = E_f = E$ , that:

$$T_{fi}^{E(2)} = \langle f | V \frac{1}{E - H_0 + i\epsilon} V | i \rangle. \quad (5.4.74)$$

Inserting a complete set of free-particle states between each operator, we may finally write this in the following form, with  $E_{k'} = (\hbar^2 k')^2 / (2m)$ :

$$T_{fi}^{E(2)} = \int \frac{V_{fk'} V_{k'i}}{E - E_{k'} + i\epsilon} d^3 \vec{k}'. \quad (5.4.75)$$

At second order in perturbation theory, the transition amplitude on the fixed-energy shell thus receives a contribution involving two matrix elements of the interaction potential, where the transition proceeds via an arbitrary virtual intermediate state with unconstrained wave number. This is the analogue of the fact that in time-independent perturbation theory the second order correction to the energy levels involves two matrix elements of the interaction potential and an intermediate state with unconstrained energy.

The  $n$ -order contribution  $T_{fi}^{E(n)}$  is defined through the matrix element of the operator  $T^{(n)}$ . Proceeding in a similar way as before, this is computed to be

$$T_{fi}^{E(n)} = \langle i | V \frac{1}{E - H_0 + i\epsilon} V \frac{1}{E - H_0 + i\epsilon} V \cdots | f \rangle. \quad (5.4.76)$$

Inserting a complete set of free-particle states between each operator, and using the notation  $E_{k'} = (\hbar^2 k')^2 / (2m)$ ,  $E_{k''} = (\hbar^2 k'')^2 / (2m)$ ,  $\dots$ , we may finally write this as:

$$T_{fi}^{E(n)} = \iint \cdots \frac{V_{fk'} V_{k'k''} V_{k''k'''} \cdots}{(E - E_{k'} + i\epsilon)(E_{k'} - E_{k''} + i\epsilon) \cdots} d^3 \vec{k}' d^3 \vec{k}'' \cdots. \quad (5.4.77)$$

At the  $n$ -th order in perturbation theory, the transition amplitude on the fixed-energy shell thus receives a contribution involving  $n$  matrix elements of the interaction potential, where the transition proceeds via  $n - 1$  arbitrary virtual intermediate states with unconstrained wave numbers. This is again perfectly analogous to what happens in time-independent perturbation theory for the  $n$ -th order correction to the energy levels.

Before evaluating more explicitly the form of the various contributions  $T_{fi}^{E(n)}$ , let us notice that from the above results for the matrix element  $T_{fi}^E = \langle f | T^E | i \rangle$  for arbitrary free particles states it follows that the operator  $T^E$  is given by the following expression:

$$\begin{aligned} T^E &= V + V \frac{1}{E - H_0 + i\epsilon} V + V \frac{1}{E - H_0 + i\epsilon} V \frac{1}{E - H_0 + i\epsilon} V + \cdots \\ &= V + V \left[ \frac{1}{E - H_0 + i\epsilon} + \frac{1}{E - H_0 + i\epsilon} V \frac{1}{E - H_0 + i\epsilon} + \cdots \right] V \\ &= V + V \frac{1}{E - H_0 - V + i\epsilon} V \end{aligned} \quad (5.4.78)$$

Let us now evaluate more explicitly the first few contributions to the matrix element defining the scattering amplitude. To do so, we first compute the matrix element of the potential between two generic free particle states. With the normalization that we have

chosen, this is found to be:

$$\begin{aligned} V_{ij} &= \langle i|V|j\rangle = \int \langle i|\vec{r}\rangle V(\vec{r}) \langle \vec{r}|j\rangle d^3\vec{r} = \frac{1}{(2\pi)^3} \int e^{-i(\vec{k}_i - \vec{k}_j) \cdot \vec{r}} V(\vec{r}) d^3\vec{r} \\ &= \frac{1}{(2\pi)^3} \tilde{V}(\vec{k}_i - \vec{k}_j). \end{aligned} \quad (5.4.79)$$

It follows that

$$\begin{aligned} T_{fi}^E &= V_{fi} + \int \frac{V_{fk'} V_{k'i}}{E - E_{k'} + i\epsilon} d^3\vec{k}' + \dots \\ &= \frac{1}{(2\pi)^3} \tilde{V}(\vec{k}_f - \vec{k}_i) + \frac{1}{(2\pi)^6} \int \frac{\tilde{V}(\vec{k}_f - \vec{k}') \tilde{V}(\vec{k}' - \vec{k}_i)}{E - E_{k'} + i\epsilon} d^3\vec{k}' + \dots \end{aligned} \quad (5.4.80)$$

We conclude from this that the scattering amplitude is given by:

$$f(\vec{k}_i, \vec{k}_f) = -\frac{m}{2\pi\hbar^2} \left[ \tilde{V}(\vec{k}_f - \vec{k}_i) + \frac{1}{(2\pi)^3} \int \frac{\tilde{V}(\vec{k}_f - \vec{k}') \tilde{V}(\vec{k}' - \vec{k}_i)}{E - E_{k'} + i\epsilon} d^3\vec{k}' + \dots \right]. \quad (5.4.81)$$

We see that at first order we recover the Born approximation for the differential cross section, which depends only on the transferred momentum  $\vec{q} = \vec{k}_f - \vec{k}_i$  and is given by the following expression, which coincides with the result (4.2.19) that we have already derived with an other method for the special case of central potentials:

$$f(\vec{q}) \simeq -\frac{m}{2\pi\hbar^2} \tilde{V}(\vec{q}). \quad (5.4.82)$$

Moreover, we can now explicitly verify that the optical theorem is satisfied, provided one works at the appropriate order in the perturbative expansion to evaluate its left-hand and right-hand sides. Indeed, the leading contribution (5.4.82) to the scattering amplitude is real at  $q = 0$ , and the first contribution to the imaginary part of the scattering amplitude at  $\Omega = 0$  therefore arises from the second-order term, as a consequence of the prescription (5.4.67). By decomposing  $d^3k' = mk/\hbar^2 dE_{k'} d\Omega'$ , one easily shows that:

$$\text{Im } f(0) \simeq \frac{k}{4\pi} \left( \frac{m}{2\pi\hbar^2} \right)^2 \int |\tilde{V}(\vec{q})|^2 d\Omega. \quad (5.4.83)$$

The expressions (5.4.82) and (5.4.83) show that the relation (5.3.59) and thus the optical theorem is indeed approximately satisfied.

## 5.5 Central problems

In the special case of central problems with a spherical symmetry, one may choose the states as eigenstates of  $L^2$  and  $L_z$  labeled by the quantum numbers  $l$  and  $m$ . To do so, one may start from the usual description of free particle states in terms of a wave vector  $\vec{k}$ , which treats the three dimensions on equal footing, then switch to a description in terms of a wave number  $k$  and a solid angle direction  $\Omega$ , which refer to the radial and angular parts of the problem, and finally switch to a description in terms of an energy  $E$  for the radial part and an angular momentum specified by  $L^2$  and  $L_z$  for the angular part.

To perform the above change of basis properly, one must be careful with normalizations. To this purpose, let us recall that the asymptotic states  $|i\rangle$  have been chosen with a normalization such that  $\langle i|j\rangle = \delta^{(3)}(\vec{k}_i - \vec{k}_j)$ . When switching from the description in terms of  $\vec{k}_i$  to the description in terms of  $E_i$  and  $\Omega_i$ , one may then write:

$$\langle i|j\rangle = \rho^{-1}(E_i)\delta(E_i - E_j)\delta^{(2)}(\Omega_i - \Omega_j), \quad (5.5.84)$$

where

$$\rho(E) = \frac{mk}{\hbar^2}. \quad (5.5.85)$$

From this we deduce that we may describe the full states  $|i\rangle$  in terms of a radial part  $|E_i\rangle$  and an angular part  $|\Omega_i\rangle$  as

$$|i\rangle = \frac{1}{\sqrt{2\pi}}\rho^{-1/2}(E_i)|E_i\rangle \otimes |\Omega_i\rangle, \quad (5.5.86)$$

where the states  $|E_i\rangle$  and  $|\Omega_i\rangle$  are normalized in the following way:

$$\langle E_i|E_j\rangle = 2\pi\delta(E_i - E_j), \quad (5.5.87)$$

$$\langle \Omega_i|\Omega_j\rangle = \delta^{(2)}(\Omega_i - \Omega_j), \quad (5.5.88)$$

With this decomposition, the expectation value of an operator  $\mathcal{O}$  at fixed energy, as defined by the relation  $\mathcal{O}_{ij} = 2\pi\delta(E_i - E_j)\mathcal{O}_{ij}^E$ , can be rewritten more explicitly in the following way:

$$\mathcal{O}_{ij}^E = \frac{1}{2\pi}\rho^{-1}(E_i)\langle \Omega_i|\mathcal{O}|\Omega_j\rangle. \quad (5.5.89)$$

At this point, we may perform any orthonormal change of basis we like in the angular part. In particular, we may switch from the states  $|\Omega_i\rangle$  to the states  $|l, m\rangle$  by writing

$$|\Omega_i\rangle = \sum_{l=0}^{+\infty} \sum_{m=-l}^l Y_l^{m*}(\Omega_i)|l, m\rangle, \quad (5.5.90)$$

where the states  $|l, m\rangle$  are canonically normalized:

$$\langle l, m|l', m'\rangle = \delta_{ll'}\delta_{mm'}, \quad (5.5.91)$$

and the spherical harmonic functions  $Y_l^m(\Omega_i)$  are defined by the overlap

$$Y_l^m(\Omega_i) = \langle \Omega_i|l, m\rangle. \quad (5.5.92)$$

In the new basis  $|l, m\rangle$ , the expectation value of an operator  $\mathcal{O}$  which is invariant under rotations and commutes with  $L^2$  and  $L_z$  is diagonal and depends only on  $l$  and not on  $m$ , since the choice of the  $z$  axis is clearly arbitrary:

$$\langle l, m|\mathcal{O}|l', m'\rangle = \delta_{ll'}\delta_{mm'}\mathcal{O}_l. \quad (5.5.93)$$



It then follows that the expectation value of such an operator in the original basis  $|\Omega_i\rangle$  can be decomposed as follows:

$$\begin{aligned}\langle \Omega_i | \mathcal{O} | \Omega_j \rangle &= \sum_{l=0}^{+\infty} \sum_{m=-l}^l \sum_{l'=0}^{+\infty} \sum_{m'=-l'}^{l'} Y_l^{m*}(\Omega_i) Y_{l'}^{m'}(\Omega_j) \langle l, m | \mathcal{O} | l', m' \rangle \\ &= \sum_{l=0}^{+\infty} \sum_{m=-l}^l Y_l^{m*}(\Omega_i) Y_l^m(\Omega_j) \mathcal{O}_l.\end{aligned}\quad (5.5.94)$$

Using at this point the relation

$$\sum_{m=-l}^l Y_l^{m*}(\Omega_i) Y_l^m(\Omega_j) = \frac{2l+1}{4\pi} P_l(\cos \theta), \quad (5.5.95)$$

where  $\theta$  is the relative angle between  $\Omega_i$  and  $\Omega_j$ , this matrix element can be written as a partial wave expansion:

$$\langle \Omega_i | \mathcal{O} | \Omega_j \rangle = \frac{1}{4\pi} \sum_{l=0}^{+\infty} (2l+1) \mathcal{O}_l P_l(\cos \theta). \quad (5.5.96)$$

Finally, the expectation value of a rotation-invariant operator  $\mathcal{O}$  at fixed energy can therefore be written in the following form:

$$\mathcal{O}_{ij}^E = \frac{\hbar^2}{8\pi^2 m k} \sum_{l=0}^{+\infty} (2l+1) \mathcal{O}_l P_l(\cos \theta). \quad (5.5.97)$$

At this point, we may use the above results to rewrite the scattering amplitude as a partial wave expansion:

$$f(\Omega) = -\frac{1}{2k} \sum_{l=0}^{+\infty} (2l+1) T_l P_l(\cos \theta). \quad (5.5.98)$$

Recalling that  $T = i(S - 1)$ , this may also be written as:

$$f(\Omega) = \frac{1}{2ik} \sum_{l=0}^{+\infty} (2l+1) (S_l - 1) P_l(\cos \theta), \quad (5.5.99)$$

Comparing with the expression of the scattering amplitude in terms of phase shifts, we conclude that the scattering matrix elements  $S_l$  are related to the phase shifts  $\delta_l$  by the following very simple relation:

$$S_l = e^{2i\delta_l}. \quad (5.5.100)$$

Notice finally that in this basis the unitarity of the scattering matrix  $S$  implies the condition  $|S_l| = 1$ , which translates into the fact that the phase shifts for an elastic scattering process must be real:  $\text{Im } \delta_l = 0$ .

## 5.6 Relation to Green functions

As a final remark concerning the general formalism presented in this section, let us explore the connection with Green functions and the tool that these offer for solving wave equations like the Schrödinger equation through a perturbative expansion. We have seen in previous section that a crucial ingredient in the perturbative expansion of the scattering amplitude is the operator  $1/(E - H_0 + i\epsilon)$ . It turns out that the matrix elements of this operator are directly related to Green functions.

The matrix elements of the operator  $1/(E - H_0 + i\epsilon)$  in wave-vector space are trivially computed. Denoting  $E = (\hbar k)^2/(2m)$  and  $E_{k'} = (\hbar k')^2/(2m)$ , one finds:

$$\langle \vec{k}' | \frac{1}{E - H_0 + i\epsilon} | \vec{k}'' \rangle = \tilde{G}(\vec{k}') \delta^{(3)}(\vec{k}' - \vec{k}''), \quad (5.6.101)$$

where the function  $\tilde{G}$  is given by

$$\tilde{G}(\vec{k}') = \frac{1}{E - E_{k'} + i\epsilon} = \frac{2m}{\hbar^2} \frac{1}{k^2 - k'^2 + i\epsilon}. \quad (5.6.102)$$

This trivially satisfies the algebraic equation:

$$(E - E_{k'}) \tilde{G}(\vec{k}') = \frac{\hbar^2}{2m} (k^2 - k'^2) \tilde{G}(\vec{k}') = 1. \quad (5.6.103)$$

The matrix elements of this same operator in configuration space can instead be computed by inserting twice a complete set of states. One finds:

$$\begin{aligned} \langle \vec{r}' | \frac{1}{E - H_0 + i\epsilon} | \vec{r}'' \rangle &= \int \int \langle \vec{r}' | \vec{k}' \rangle \langle \vec{k}' | \frac{1}{E - H_0 + i\epsilon} | \vec{k}'' \rangle \langle \vec{k}'' | \vec{r}'' \rangle d^3 \vec{k}' d^3 \vec{k}'' \\ &= \frac{1}{(2\pi)^3} \int e^{i\vec{k}' \cdot (\vec{r}' - \vec{r}'')} \frac{1}{E - E_{k'} + i\epsilon} d^3 \vec{k}' \\ &= \frac{m}{2\pi^2 \hbar^2} \int_0^{+\infty} \int_{-1}^1 e^{ik' |\vec{r}' - \vec{r}''| \cos \theta} d \cos \theta \frac{k'^2}{k^2 - k'^2 + i\epsilon} dk' \\ &= \frac{m}{\pi^2 \hbar^2} \frac{1}{|\vec{r}' - \vec{r}''|} \int_0^{+\infty} \frac{k'}{k^2 - k'^2 + i\epsilon} \sin(k' |\vec{r}' - \vec{r}''|) dk' \end{aligned} \quad (5.6.104)$$

To evaluate the last integral explicitly, we may now use complex integration techniques, promoting  $k'$  to a complex variable  $z$ . We notice for this that the integrand is even in  $z$  and has simple poles in  $z = \pm k \pm i\epsilon/(2k)$ . Using the short-hand notation  $r = |\vec{r}' - \vec{r}''|$ , we may then write:

$$\begin{aligned} \int_0^{+\infty} \frac{z}{k^2 - z^2 + i\epsilon} \sin(zr) dz &= \frac{1}{2} \int_{-\infty}^{+\infty} \frac{z}{k^2 - z^2 + i\epsilon} \sin(zr) dz \\ &= -\frac{i}{4} \int_{c_+} \frac{z}{k^2 - z^2 + i\epsilon} e^{izr} dz + \frac{i}{4} \int_{c_-} \frac{z}{k^2 - z^2 + i\epsilon} e^{-izr} dz \\ &= \frac{\pi}{2} \text{Res} \left\{ \frac{z e^{izr}}{k^2 - z^2} \right\}_{z=k} + \frac{\pi}{2} \text{Res} \left\{ \frac{z e^{-izr}}{k^2 - z^2} \right\}_{z=-k} \\ &= -\frac{\pi}{2} e^{ikr} \end{aligned} \quad (5.6.105)$$

It finally follows that

$$\langle \vec{r}' | \frac{i}{E - H_0 + i\epsilon} | \vec{r}'' \rangle = G(\vec{r}' - \vec{r}''), \quad (5.6.106)$$

where the function  $G$  is by construction the three-dimensional Fourier antitransform of  $\tilde{G}$  and has the explicit form

$$G(\vec{r}' - \vec{r}'') = -\frac{2m}{\hbar^2} \frac{e^{ik|\vec{r}' - \vec{r}''|}}{4\pi|\vec{r}' - \vec{r}''|}. \quad (5.6.107)$$

This satisfies the following differential equation, which defines the Green function of the Schrödinger wave operator and represents the configuration space version of (5.6.103):

$$(-H'_0 + E)G(\vec{r}' - \vec{r}'') = \frac{\hbar^2}{2m}(\Delta' + k^2)G(\vec{r}' - \vec{r}'') = \delta^{(3)}(\vec{r}' - \vec{r}''). \quad (5.6.108)$$

We may now reexpress the scattering amplitude (5.4.81) in terms of the potential and the above defined Green function. Using the wave-vector space versions  $\tilde{V}$  and  $\tilde{G}$  of the potential and the Green function, one simply has

$$f(\vec{k}_i, \vec{k}_f) = -\frac{m}{2\pi\hbar^2} \left[ \tilde{V}(\vec{k}_f - \vec{k}_i) + \frac{1}{(2\pi)^3} \int \tilde{V}(\vec{k}_f - \vec{k}') \tilde{G}(\vec{k}') \tilde{V}(\vec{k}' - \vec{k}_i) d^3\vec{k}' + \dots \right]. \quad (5.6.109)$$

Using instead the configuration space versions  $V$  and  $\tilde{G}$  of the potential and the Green function, this expression becomes:

$$f(\vec{k}_i, \vec{k}_f) = -\frac{m}{2\pi\hbar^2} \left[ \int e^{-i\vec{k}_f \cdot \vec{r}'} V(\vec{r}') e^{i\vec{k}_i \cdot \vec{r}'} d^3\vec{r}' + \int e^{-i\vec{k}_f \cdot \vec{r}'} V(\vec{r}') G(\vec{r}' - \vec{r}'') V(\vec{r}'') e^{i\vec{k}_i \cdot \vec{r}''} d^3\vec{r}' d^3\vec{r}'' + \dots \right]. \quad (5.6.110)$$

Let us now come back to the scattering problem we want to solve. This consists in finding the solution with appropriate boundary conditions of the stationary Schrödinger equation, which can be rewritten in the following form:

$$(-H_0 + E)\phi(\vec{r}) = \frac{\hbar^2}{2m}(\Delta + k^2)\phi(\vec{r}) = V(\vec{r})\phi(\vec{r}). \quad (5.6.111)$$

Using the Green function  $G$ , the general solution of this equation can now be formally written in terms of a generic solution  $\phi_0$  of the free equation as:

$$\phi(\vec{r}) = \phi_0(\vec{r}) + \int G(\vec{r} - \vec{r}') V(\vec{r}') \phi(\vec{r}') d^3\vec{r}'. \quad (5.6.112)$$

This is an integral equation for  $\phi(\vec{r})$ , which can be solved in the usual way by iterating it. In this way one finds:

$$\begin{aligned} \phi(\vec{r}) &= \phi_0(\vec{r}) + \int G(\vec{r} - \vec{r}') V(\vec{r}') \phi_0(\vec{r}') d^3\vec{r}' \\ &+ \int \int G(\vec{r} - \vec{r}') V(\vec{r}') G(\vec{r}' - \vec{r}'') V(\vec{r}'') \phi_0(\vec{r}'') d^3\vec{r}' d^3\vec{r}'' + \dots \end{aligned} \quad (5.6.113)$$

The choice of the free solution  $\phi_0(\vec{r})$  is related to the boundary conditions for the true solution  $\phi(\vec{r})$  at large  $r$ . More precisely, it must correspond to the incident wave, since  $\phi(\vec{r}) \rightarrow \phi_0(\vec{r})$  when  $V(\vec{r}) \rightarrow 0$ . We then take  $\phi_0(\vec{r})$  to be a progressive wave with wave vector  $\vec{k}_i = k\hat{z}$  defining the incident wave vector and a conventional normalization equal to unity:

$$\phi_0(\vec{r}) = e^{i\vec{k}_i \cdot \vec{r}}. \quad (5.6.114)$$

The remaining part of the solution  $\phi(\vec{r})$  must then correspond to the scattered wave. To extract the scattering amplitude, we must then study the asymptotic behavior of this part for positions  $\vec{r}$  with large modulus  $r$ . We expect to find a progressive wave with a wave vector  $\vec{k}_f = k\hat{r}$  defining the scattered wave number and an amplitude suppressed by  $1/r$ . To see that this is indeed what emerges, we can go back to eq. (5.6.112) and imagine that the potential has a finite range  $a$ , beyond which it is negligible. In such a situation, the integration over  $\vec{r}'$  may be safely limited to  $r' \lesssim a$ . One can then consider the asymptotic region where  $r \gg a$  and thus  $r \gg r'$ . In such a situation,  $\vec{r} - \vec{r}'$  differs only little from  $\vec{r}$ , and denoting by  $\alpha$  the angle between  $\vec{r}$  and  $\vec{r}'$ , one computes, at leading order in  $r'/r$ :

$$\begin{aligned} |\vec{r} - \vec{r}'| &= \sqrt{r^2 + r'^2 - 2rr' \cos \alpha} = r \sqrt{1 - 2 \cos \alpha \frac{r'}{r} + \frac{r'^2}{r^2}} \simeq r - \cos \alpha r' \\ &\simeq r - \hat{r} \cdot \vec{r}'. \end{aligned} \quad (5.6.115)$$

One may then approximate the Green function with the following expression, after recalling that  $k\hat{r}$  is interpreted as the scattered wave vector  $\vec{k}_f$ :

$$G(\vec{r} - \vec{r}') \simeq -\frac{m}{2\pi\hbar^2} \frac{1}{r} e^{ikr} e^{-i\vec{k}_f \cdot \vec{r}'}. \quad (5.6.116)$$

In this region of large  $r$ , the integral equation (5.6.112) then implies that the exact scattering solution  $\phi(\vec{r})$  has indeed the expected type of asymptotic behavior, namely

$$\phi(\vec{r}) \simeq e^{i\vec{k}_i \cdot \vec{r}} + \frac{f(\vec{k}_i, \vec{k}_f)}{r} e^{ikr}, \quad (5.6.117)$$

with a scattering amplitude identified with the following expression:

$$f(\vec{k}_i, \vec{k}_f) = -\frac{m}{2\pi\hbar^2} \int e^{-i\vec{k}_f \cdot \vec{r}'} V(\vec{r}') \phi(\vec{r}') d^3\vec{r}' \quad (5.6.118)$$

Using finally the formal solution (5.6.113) for  $\phi(\vec{r})$  with  $\phi_0(\vec{r}') = e^{i\vec{k}_i \cdot \vec{r}'}$ , one deduces that the scattering amplitude  $f(\vec{k}_i, \vec{k}_f)$  can be written in the form (5.6.110), or equivalently as (5.6.109) after switching to wave-vector space.

We therefore see that the general result (5.6.109) or (5.6.110) for the scattering amplitude obtained in the operatorial approach can also be derived by using just the Green function of the Schrödinger wave equation. The operatorial formalism has however the advantage over the Green function approach of being more easily and directly generalizable to describe also more complicated situations, like for instance inelastic scattering processes.



## Chapter 6

# Approximation methods for many-body problems

In this final chapter, we shall briefly describe two general classes of approximation methods that can be used to face problems with many identical particles. The first method is based on the idea that a many-body system might be effectively described in terms of a collection of individual particles that behave independently but are subject to an effective potential, which takes into account the presence of all the particles and their mutual interaction. This effective potential is then self-consistently determined in such a way to minimize the energy of the full system. The second method is based on the idea that a many-body system might be effectively described in terms of a density of particles. This density is then self-consistently determined in such a way to minimize the energy of the full system. We shall then discuss the application of these methods to many-electron atoms.

### 6.1 Individual wave functions approach

Let us consider the problem of a system of  $N$  identical particles with coordinates  $\vec{r}_i$  and spins  $s_i$ , where each particle is subject to the action of a potential  $V(\vec{r}_i)$ , which depends only on the position  $\vec{r}_i$  of each particle relative to the center, and each pair of particles is subject to a mutual interaction  $W(\vec{r}_i - \vec{r}_j)$ , which depends only on the relative position  $\vec{r}_i - \vec{r}_j$  of the two particles. The Hamiltonian describing the full system then takes the following form:

$$H = \sum_i \left[ -\frac{\hbar^2}{2m} \Delta_i + V(\vec{r}_i) \right] + \frac{1}{2} \sum_{i,j \text{ diff.}} W(\vec{r}_i - \vec{r}_j). \quad (6.1.1)$$

Under suitable circumstances, one may expect that such a system could be reasonably well described in terms of individual wave functions, whose form take to some extent into account the interaction with the other particles. To determine the best approximation of this kind, we may consider a family of multi-particle wave functions constructed in terms of such individual wave functions, and then apply the variational method to determine the best approximation to the true ground state within this reduced set of wave functions.

### 6.1.1 The Hartree approximation

The simplest possibility is to use a family of trial wave functions taking simply the form of a product of individual stationary wave functions for each particle, ignoring for the moment their statistics:

$$\phi(\vec{r}_1, s_1, \dots, \vec{r}_n, s_n) = \phi_1(\vec{r}_1)\chi_1(s_1) \cdots \phi_N(\vec{r}_N)\chi_N(s_n). \quad (6.1.2)$$

The expectation value of  $H$  on such a trial function is easily found to be:

$$\begin{aligned} \langle \phi | H | \phi \rangle &= -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3\vec{r}_i + \sum_i \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i \\ &\quad + \frac{1}{2} \sum_{i,j \text{ diff.}} \iint W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j. \end{aligned} \quad (6.1.3)$$

The norm of each individual wave function is instead given by:

$$\langle \phi_i | \phi_i \rangle = \int |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i. \quad (6.1.4)$$

We can now determine the individual wave functions  $\phi_i$  by minimizing the above expectation value  $\langle \phi | H | \phi \rangle$  for the energy. In doing so, we impose the constraint that each of the individual wave functions  $\phi_i$  should be normalized to unity, namely  $\langle \phi_i | \phi_i \rangle = 1$ . This ensures not only that the full wave function is properly normalized, but also that it can be effectively interpreted as the product of independent wave functions for individual particles. This constrained minimization problem can be set up with the usual method of Lagrange multipliers. Since we have  $N$  independent constraints we need to introduce  $N$  Lagrange multipliers  $\mathcal{E}_i$  and extremize the following functional:

$$E = \langle \phi | H | \phi \rangle - \sum_i \mathcal{E}_i [\langle \phi_i | \phi_i \rangle - 1]. \quad (6.1.5)$$

Using the expressions (6.1.3) and (6.1.4), we are then led to the following functional:

$$\begin{aligned} E &= -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3\vec{r}_i + \sum_i \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i \\ &\quad + \frac{1}{2} \sum_{i,j \text{ diff.}} \iint W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j \\ &\quad - \sum_i \mathcal{E}_i \left[ \int |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i - 1 \right]. \end{aligned} \quad (6.1.6)$$

The stationarity equations following from the invariance of  $E$  with respect to arbitrary small variations of  $\phi_i^*$  give the following set of  $N$  coupled non-linear differential equations, which determine the  $\phi_i$  for given values of  $\mathcal{E}_i$ :

$$\left[ -\frac{\hbar^2}{2m} \Delta_i + V(\vec{r}_i) + \sum_{j \neq i} \int W(\vec{r}_i - \vec{r}_j) |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_j \right] \phi_i(\vec{r}_i) = \mathcal{E}_i \phi_i(\vec{r}_i). \quad (6.1.7)$$

Notice that these equations have the structure of  $N$  stationary Schrödinger equations for the individual wave functions  $\phi_i$  with energies  $\mathcal{E}_i$ , but with some effective potentials which themselves depend on the form of the other wave functions  $\phi_j$  with  $j \neq i$  and take into account the mutual interaction energy with the density of the remaining particles. The values of  $\mathcal{E}_i$  are then fixed by the stationary conditions for  $E$  with respect to variations of  $\mathcal{E}_i$ , which are nothing but the constraints that the individual wave functions  $\phi_i$  should be properly normalized:

$$\int |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i = 1. \quad (6.1.8)$$

Multiplying eq. (6.1.7) by  $\phi_i^*(\vec{r}_i)$  and integrating over  $\vec{r}_i$ , one finds:

$$\begin{aligned} \mathcal{E}_i = & -\frac{\hbar^2}{2m} \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3\vec{r}_i + \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i \\ & + \sum_{j \neq i} \int \int W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j. \end{aligned} \quad (6.1.9)$$

Once the wave functions  $\phi_i$  and the numbers  $\mathcal{E}_i$  have been derived in this way, the total energy of the system is given by the value of the functional  $E$  at this extremum. This is found to be given by:

$$E = \sum_i \mathcal{E}_i - \frac{1}{2} \sum_{i,j \text{ diff.}} \int \int W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j. \quad (6.1.10)$$

An important shortcoming of this approach, which is called the Hartree method, is that it does not properly implement the quantum statistics of identical particles. In particular, for fermionic particles it does not incorporate Pauli's exclusion principle. One way to partly remediate to this problem is to keep the same kind of trial function but to somehow impose the additional requirement that the individual wave functions  $\phi_i$  should satisfy some orthogonality constraints, in such a way to ensure that all the individual fermions are in a different state. This does however not come out automatically and it is not entirely straightforward to implement this procedure. In particular, two individual wave functions  $\phi_i$  and  $\phi_j$  are in general not orthogonal, even when  $\mathcal{E}_i$  and  $\mathcal{E}_j$  are different, because they do not represent two different eigenvectors of a single differential operator but rather the eigenvectors of two different differential operators.

### 6.1.2 The Hartree-Fock approximation

A more specific possibility to describe systems of identical fermions is to start from a trial function that is completely antisymmetric under permutations, in such a way to properly incorporate the fermionic statistics. This can be taken to be of the standard form of a Slater determinant built out of individual wave functions:

$$\phi(\vec{r}_1, s_1, \dots, \vec{r}_n, s_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1)\chi_1(s_1) & \cdots & \phi_1(\vec{r}_N)\chi_1(s_N) \\ \vdots & & \vdots \\ \phi_N(\vec{r}_1)\chi_N(s_1) & \cdots & \phi_N(\vec{r}_N)\chi_N(s_N) \end{vmatrix}. \quad (6.1.11)$$



The expectation value of  $H$  on such a trial function can now be computed. But this requires slightly more care than before, to take into account the effect of all the permutation terms building up the determinant, besides the one coming from the main diagonal. The result can be derived in a systematic way by rewriting the determinant in terms of a sum over permutations, and going through a sequence of simple manipulations on this sum of permutations. The final result is that one simply finds an additional exchange term for each pair of individual particles with identical spins:

$$\begin{aligned}
\langle \phi | H | \phi \rangle &= -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3\vec{r}_i + \sum_i \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i \\
&+ \frac{1}{2} \sum_{i,j \text{ diff}} \iint W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j \\
&- \frac{1}{2} \sum_{i,j \text{ diff}} \delta_{s_i, s_j} \iint W(\vec{r}_i - \vec{r}_j) \phi_i^*(\vec{r}_i) \phi_j(\vec{r}_i) \phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j) d^3\vec{r}_i d^3\vec{r}_j.
\end{aligned} \tag{6.1.12}$$

The norm of each individual wave function is instead given by:

$$\langle \phi_i | \phi_i \rangle = \int |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i. \tag{6.1.13}$$

We can now proceed exactly as before and determine the individual wave functions  $\phi_i$  by minimizing the above expectation value  $\langle \phi | H | \phi \rangle$  for the energy. In doing so, we impose again the constraint that each of the individual wave functions  $\phi_i$  should be normalized to unity, namely  $\langle \phi_i | \phi_i \rangle = 1$ . To set up this constrained minimization problem we introduce as before  $N$  Lagrange multipliers  $\mathcal{E}_i$  and extremize the following functional:

$$E = \langle \phi | H | \phi \rangle - \sum_i \mathcal{E}_i [\langle \phi_i | \phi_i \rangle - 1]. \tag{6.1.14}$$

Using the expressions (6.1.12) and (6.1.13), and extending the sums over  $i, j \text{ diff}$  to run over all the values of  $i, j$  by exploiting the fact that when  $i = j$  the two  $W$ -dependent terms cancel each other, we are then led to the following functional:

$$\begin{aligned}
E &= -\frac{\hbar^2}{2m} \sum_i \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3\vec{r}_i + \sum_i \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i \\
&+ \frac{1}{2} \sum_{i,j} \iint W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3\vec{r}_i d^3\vec{r}_j \\
&- \frac{1}{2} \sum_{i,j} \delta_{s_i, s_j} \iint W(\vec{r}_i - \vec{r}_j) \phi_i^*(\vec{r}_i) \phi_j(\vec{r}_i) \phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j) d^3\vec{r}_i d^3\vec{r}_j \\
&- \sum_i \mathcal{E}_i \left[ \int |\phi_i(\vec{r}_i)|^2 d^3\vec{r}_i - 1 \right].
\end{aligned} \tag{6.1.15}$$

The stationarity equations following from the invariance of  $E$  with respect to arbitrary small variations of  $\phi_i^*$  give the following set of  $N$  coupled non-linear differential equations,

which determine the  $\phi_i$  for given values of  $E_i$ :

$$\begin{aligned} & \left[ -\frac{\hbar^2}{2m} \Delta_i + V(\vec{r}_i) + \sum_j \int W(\vec{r}_i - \vec{r}_j) |\phi_j(\vec{r}_j)|^2 d^3 \vec{r}_j \right] \phi_i(\vec{r}_i) \\ & - \left[ \sum_j \delta_{s_i, s_j} \int W(\vec{r}_i - \vec{r}_j) \phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j) d^3 \vec{r}_j \right] \phi_j(\vec{r}_i) = \mathcal{E}_i \phi_i(\vec{r}_i). \end{aligned} \quad (6.1.16)$$

These equations have again a structure that is similar to  $N$  stationary Schrödinger equations for the individual wave functions  $\phi_i$  with energies  $\mathcal{E}_i$ , but with some effective potentials which depend on the form of all the wave functions  $\phi_i$  and take into account not only the mutual interaction energy but also an exchange term due to the statistics. The values of  $\mathcal{E}_i$  are then fixed by the stationary conditions for  $E$  with respect to variations of  $\mathcal{E}_i$ , which reduce as before to the constraints that the  $\phi_i$  should be properly normalized:

$$\int |\phi_i(\vec{r}_i)|^2 d^3 \vec{r}_i = 1. \quad (6.1.17)$$

Multiplying eq. (6.1.16) by  $\phi_i^*(\vec{r}_i)$  and integrating over  $\vec{r}_i$ , one finds:

$$\begin{aligned} \mathcal{E}_i = & -\frac{\hbar^2}{2m} \int \phi_i^*(\vec{r}_i) \Delta_i \phi_i(\vec{r}_i) d^3 \vec{r}_i + \int V(\vec{r}_i) |\phi_i(\vec{r}_i)|^2 d^3 \vec{r}_i \\ & + \sum_j \int \int W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3 \vec{r}_i d^3 \vec{r}_j \\ & - \sum_j \delta_{s_i, s_j} \int \int W(\vec{r}_i - \vec{r}_j) \phi_i^*(\vec{r}_i) \phi_j(\vec{r}_i) \phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j) d^3 \vec{r}_i d^3 \vec{r}_j. \end{aligned} \quad (6.1.18)$$

Once the wave functions  $\phi_i$  and the numbers  $\mathcal{E}_i$  have been derived in this way, the total energy of the system is given by the value of the function  $E$  at this extremum. This is found to be given by:

$$\begin{aligned} E = & \sum_i \mathcal{E}_i - \frac{1}{2} \sum_{i,j} \int \int W(\vec{r}_i - \vec{r}_j) |\phi_i(\vec{r}_i)|^2 |\phi_j(\vec{r}_j)|^2 d^3 \vec{r}_i d^3 \vec{r}_j \\ & + \frac{1}{2} \sum_{i,j} \delta_{s_i, s_j} \int \int W(\vec{r}_i - \vec{r}_j) \phi_i^*(\vec{r}_i) \phi_j(\vec{r}_i) \phi_j^*(\vec{r}_j) \phi_i(\vec{r}_j) d^3 \vec{r}_i d^3 \vec{r}_j. \end{aligned} \quad (6.1.19)$$

A crucial advantage of this approach, which is called the Hartree-Fock method, is that it properly implements the fermionic statistics and Pauli's exclusion principle. In fact, two individual wave functions  $\phi_i$  and  $\phi_j$  are automatically orthogonal to each other whenever  $\mathcal{E}_i$  and  $\mathcal{E}_j$  are different, because they correspond to two different eigenvectors of one and the same differential operator, although non-linear.

### 6.1.3 Self-consistent field solution

The above approach, based on individual wave functions, allows to approximate the solutions of the original single linear differential equation involving  $3N$  different variables with the solutions of a system of  $N$  coupled non-linear equations each depending only on 3

variables. With this approximation, an analytical determination of the solution is in general still impossible, but a reliable numerical solution becomes possible. A typical method to solve the non-linear equations (6.1.7) or (6.1.16) is to start with an educated guess for the functions  $\phi_i$ , and then try to determine their true form by making an iterative use of the equations. More precisely, one may start by setting in first approximation the  $\phi_i$  to be equal to the functions that would solve the equations (6.1.7) or (6.1.16) in the linearized approximation. One may then use this solution to evaluate the non-linear  $W$ -dependent terms, and solve the full non-linear equation with these terms fixed to the computed value, to determine a better form for  $\phi_i$ . Iterating this process one may then determine the true solution of the non-linear equations, whenever it converges to a definite result. This then determines self-consistent solutions for the wave functions  $\phi_i$  and the energies  $\mathcal{E}_i$ , which can be associated to individual particles, and the effective potential that they feel.

The precision of this approach is intrinsically limited by the restriction of the set of trial wave functions to those parametrized in terms of uncorrelated individual wave functions. To improve the precision, one needs to include gradually more general wave-functions allowing for some correlation between these individual modes, and this is not easy to implement in a systematic way. However, this type of approximation method has an interesting general property: being based on a variational approach, it always yields upper bounds on the true ground state energy.

## 6.2 Particle density approach

Let us consider again the same problem of a system of  $N$  identical particles with coordinates  $\vec{r}_i$ , where each particle is subject to the action of a potential  $V(\vec{r}_i)$ , which depends only on the position  $\vec{r}_i$  of each particle relative to the center, and each pair of particles is subject to a mutual interaction  $W(\vec{r}_i - \vec{r}_j)$ , which depends only on the relative position  $\vec{r}_i - \vec{r}_j$  of the two particles. The Hamiltonian describing the full system then takes the same form as before, namely:

$$H = \sum_i \left[ -\frac{\hbar^2}{2m} \Delta_i + V(\vec{r}_i) \right] + \frac{1}{2} \sum_{i,j \text{ diff.}} W(\vec{r}_i - \vec{r}_j). \quad (6.2.20)$$

Under favorable circumstances, it may happen that such a system could be reasonably well described in the semi-classical approximation and in a statistical way, in terms of a density of particles. To determine the best approximation of this kind, we may then work out the total energy as a functional of this density of particles and require this to be extremal.

### 6.2.1 The Thomas-Fermi approximation

Let us start by assuming that the potential can be considered as slowly varying and that the semiclassical approximation is justified. We may then reason in classical terms and think of the ground state of the system as a configuration where all the lowest-lying quantum states are optimally occupied, compatibly with Pauli's exclusion principle.

Locally, in the neighborhood of some position  $\vec{r}$ , this means that electrons can have energies up to some maximal value  $E_F(\vec{r})$  and thus momenta up to some maximal momentum  $p_F(\vec{r})$ , the relation between these two maximal quantities being:

$$p_F(\vec{r}) = \sqrt{2m(E_F(\vec{r}) - V(\vec{r}))}. \quad (6.2.21)$$

In such a neighborhood, we may then treat the particles in first approximation as a non-interacting Fermi gas. This allows to relate the density of these particles to the above maximal energy or momentum, at each point  $\vec{r}$ . To find this relation, we may use the semiclassical picture according to which the density of quantum states is given by the action in full phase space divided by  $h^d$ , where  $d$  is the number of degrees of freedom. In our three-dimensional case, the phase space volume  $dS$  corresponding to particles with momentum less than  $p_F$  and position within some volume  $dV$  is given by  $dS = \frac{4}{3}\pi p_F^3 dV$ . The corresponding number of quantum states is obtained by dividing this by  $h^3$  and is thus given by  $d\# = \frac{4}{3}\pi(p_F/h)^3 dV$ , or equivalently  $d\# = \frac{1}{6\pi^2}k_F^3 dV$ . The total number of particles  $dn$  in the volume  $dV$  is instead given by  $dn = \rho dV$ , where  $\rho$  is the density of particles. Taking into account that each quantum state can be occupied by two particles with opposite spins, we conclude that one must have  $2d\# = dn$ , and this implies that:

$$\rho(\vec{r}) = \frac{1}{3\pi^2} k_F^3(\vec{r}), \quad (6.2.22)$$

or viceversa that:

$$k_F(\vec{r}) = (3\pi^2)^{1/3} \rho^{1/3}(\vec{r}). \quad (6.2.23)$$

Let us now calculate the density  $t$  of kinetic energy in the neighborhood of the point  $\vec{r}$ . Observing that the density of free-particle quantum states with momentum between  $p$  and  $p + dp$  and spin up or down is given by  $2 d(\frac{4}{3}\pi p^3)/h^3 = 8\pi p^2/h^3 dp = \frac{1}{\pi^2}k^2 dk$ , this is given by:

$$t(\vec{r}) = \int_0^{k_F(\vec{r})} \frac{\hbar^2 k^2}{2m} \frac{k^2 dk}{\pi^2} = \frac{\hbar^2}{2\pi^2 m} \int_0^{k_F(\vec{r})} k^4 dk = \frac{\hbar^2}{10\pi^2 m} k_F^5(\vec{r}). \quad (6.2.24)$$

Expressing this result in terms of the density of particles  $\rho(\vec{r})$  and integrating it over the whole space, one finally deduces that the kinetic energy is given by:

$$E_{\text{kin}} = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r}, \quad (6.2.25)$$

The potential energy due to the interaction with the external field  $V$  and the mutual interaction  $W$  is instead simply given by:

$$E_{\text{pot}} = \int V(r) \rho(\vec{r}) d^3\vec{r} + \frac{1}{2} \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}'. \quad (6.2.26)$$

Finally, the particle density  $\rho(\vec{r})$  is subject to the constraint that its integral over the whole space should be equal to the number of particles  $N$ :

$$\int \rho(\vec{r}) d^3\vec{r} = N. \quad (6.2.27)$$

The total energy of the full system is given by  $E = E_{\text{kin}} + E_{\text{pot}}$  and is a functional of the density  $\rho(\vec{r})$ . The equilibrium configuration for the latter can then be determined by minimizing this functional, compatibly with the constraint (6.2.27). This constrained minimization problem can be handled by introducing one Lagrange parameter  $\mu$  and extremizing the following functional:

$$E = \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} + \int V(r) \rho(\vec{r}) d^3\vec{r} + \frac{1}{2} \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}' - \mu \left[ \int \rho(\vec{r}) d^3\vec{r} - N \right]. \quad (6.2.28)$$

The stationarity of this functional  $E$  with respect to arbitrary variations of  $\rho(\vec{r})$  implies the following differential equation for  $\rho$ , for fixed numerical value of  $\mu$ :

$$\frac{\hbar^2}{2m} (3\pi^2)^{2/3} \rho^{2/3}(\vec{r}) + V(r) + \int W(\vec{r} - \vec{r}') \rho(\vec{r}') d^3\vec{r}' = \mu. \quad (6.2.29)$$

The stationarity with respect to  $\mu$  implies instead the constraint (6.2.27), which determines the number  $\mu$ :

$$\int \rho(\vec{r}) d^3\vec{r} = N. \quad (6.2.30)$$

Multiplying eq. (6.2.29) by  $\rho(\vec{r})/N$  and integrating over  $\vec{r}$ , one finds:

$$\mu = \frac{1}{N} \left[ \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} + \int V(r) \rho(\vec{r}) d^3\vec{r} + \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}' \right]. \quad (6.2.31)$$

Once the solution for the density profile  $\rho(\vec{r})$  and the chemical potential  $\mu$  has been found, the total energy of the system is given by the functional  $E$  evaluated on this solution. This can be written in the following way:

$$E = N\mu - \frac{\hbar^2}{5m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} - \frac{1}{2} \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}'. \quad (6.2.32)$$

This method is called the Thomas-Fermi method. It has the advantage of being simple and of correctly implementing the fermionic statistics and Pauli's exclusion principle. To compare this method with the Hartree approach, we may identify the density of particles  $\rho(\vec{r})$  with the sum of all the probability densities defined by the individual wave functions  $\phi_i(\vec{r})$ :  $\rho(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$ . By comparing (6.2.28) with (6.1.6), we see that the kinetic energy is described in a different way, which exploits the semiclassical limit, but the potential is essentially the same, at least in the statistical limit of many particles. This comparison also shows that the Thomas-Fermi approach neglects the effects due to the exchange energy.

## 6.2.2 The Thomas-Fermi-Dirac approximation

The exchange energy can be modeled also within this method of approximation. By using a statistical approach that locally treats the system as a Fermi gas, very much as was done above to derive an expression for the kinetic energy in terms of the particle density, one can start from the exchange term in the energy as derived in the Hartree-Fock approach and turn it into a functional of the particle density  $\rho_i(\vec{r})$ . More concretely, this can be done by using free-particle plane-waves  $\phi_i(\vec{r}_i) = (2\pi)^{-3/2} e^{i\vec{k}_i \cdot \vec{r}_i}$  and any sum over  $i$  with an integral over a wave vector  $\vec{k}$  constrained to satisfy  $k \leq k_F$ . In this way one finds a local expression of the general form:

$$E_{\text{exc}} = \int f_W[\rho(\vec{r})] d^3\vec{r}. \quad (6.2.33)$$

The form of the functional  $f_W[\rho]$  depends on the form of the mutual interaction  $W(\vec{r} - \vec{r}')$ . In the simplest case of a Coulomb mutual interaction  $W(\vec{r} - \vec{r}') = \alpha/|\vec{r} - \vec{r}'|$ , one finds for instance that  $f_W[\rho(\vec{r})] = -\frac{3}{4}(3/\pi)^{1/3} \rho^{4/3}(\vec{r})$ . For more general mutual interactions  $W(\vec{r} - \vec{r}')$ , one instead finds a more complicated  $f_W[\rho(\vec{r})]$ . Taking into account this additional contribution describing the exchange energy, the total energy of the full system is given by  $E = E_{\text{kin}} + E_{\text{pot}} + E_{\text{exc}}$  and is again a functional of the density  $\rho(\vec{r})$ . The functional to be minimized to determine the equilibrium configuration then becomes:

$$\begin{aligned} E = & \frac{3\hbar^2}{10m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} + \int V(r) \rho(\vec{r}) d^3\vec{r} \\ & + \frac{1}{2} \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}' + \int f_W[\rho(\vec{r})] d^3\vec{r} \\ & - \mu \left[ \int \rho(\vec{r}) d^3\vec{r} - N \right]. \end{aligned} \quad (6.2.34)$$

The stationarity with respect to  $\rho(\vec{r})$  now implies the following differential equation:

$$\frac{\hbar^2}{2m} (3\pi^2)^{2/3} \rho^{2/3}(\vec{r}) + V(r) + \int W(\vec{r} - \vec{r}') \rho(\vec{r}') d^3\vec{r}' + f'_W[\rho(\vec{r})] = \mu \quad (6.2.35)$$

The stationarity with respect to  $\mu$  implies instead as before that:

$$\int \rho(\vec{r}) d^3\vec{r} = N. \quad (6.2.36)$$

Multiplying eq. (6.2.35) by  $\rho(\vec{r})/N$  and integrating over  $\vec{r}$ , one finds:

$$\begin{aligned} \mu = & \frac{1}{N} \left[ \frac{\hbar^2}{2m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} + \int V(r) \rho(\vec{r}) d^3\vec{r} \right. \\ & \left. + \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}' + \int f'_W[\rho(\vec{r})] \rho(\vec{r}) d^3\vec{r} \right]. \end{aligned} \quad (6.2.37)$$

Once the solution for the density profile  $\rho(\vec{r})$  and the chemical potential  $\mu$  has been found, the total energy of the system is given by the functional  $E$  evaluated on this solution.

This can be written in the following way:

$$\begin{aligned}
E = N\mu - \frac{\hbar^2}{5m} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d^3\vec{r} - \frac{1}{2} \iint W(\vec{r} - \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d^3\vec{r} d^3\vec{r}' \\
+ \int \left( f_W[\rho(\vec{r})] - \rho(\vec{r}) f'_W[\rho(\vec{r})] \right) d^3\vec{r}.
\end{aligned} \tag{6.2.38}$$

This refined approach that includes also the exchange term is called the Thomas-Fermi-Dirac approach.

### 6.2.3 Equilibrium particle density solution

The above approach, based on a particle density, allows to approximate the solutions of the original single linear differential equation involving  $3N$  different variables with the solution of a single non-linear equation depending only on 3 variables. With this approximation, an analytical determination of the solution is in general not possible, but a numerical solution is usually totally straightforward to implement, after imputing an appropriate boundary condition. This then determines the equilibrium particle density  $\rho$ . Once this is known, one can compute the form of the effective potential felt by a probe particle placed into the system, and compute the allowed stationary wave functions  $\phi_i$  and the associated energy levels  $\mathcal{E}_i$ . These can finally be associated to the individual particles forming the system.

The precision of this approach is intrinsically limited by the semiclassical and statistical approximations that have been used. However, it can be proven rather easily that the use of a single particle density to describe the system does not represent any limitation, and one may in principle describe the exact solution in terms of an exact single-particle density distribution rather than in terms of a multi-particle wave function. The difficulty then reduces to find an as accurate energy functional as possible. This has led to the so-called density functional theory.

## 6.3 Application to the structure of atoms

One of the most relevant applications of the above described approximation methods is that of many-electron atoms. In that case, the external potential is given by the electric field created by the nucleus, which is much heavier than the electrons and can therefore be approximately considered to be at rest. The mutual interaction potential is instead the electric repulsion between electrons. We therefore have in this case:

$$V(\vec{r}) = -\frac{Ze^2}{r}, \quad W(\vec{r} - \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|}. \tag{6.3.39}$$

In principle, a many electron atom must be treated as a whole. The allowed configurations are then determined by a multi-particle stationary state. The problem has an overall spherical symmetry, and the total orbital angular momentum  $\vec{L}_{\text{tot}}$  is therefore conserved. Moreover, multi-particle states with definite symmetry properties under permutations of

the individual particles correspond to a definite value of the total spin  $\vec{S}_{\text{tot}}$ , which is also conserved. The atomic energy levels can then be parametrized in terms of two quantum numbers  $L$  and  $S$ , characterizing the sizes of the orbital and spin angular momenta, and have a  $(2L + 1)(2S + 1)$ -fold degeneracy, corresponding to the arbitrary orientation of these angular momenta. However, when relativistic corrections are included, only the total angular momentum  $\vec{J}_{\text{tot}} = \vec{L}_{\text{tot}} + \vec{S}_{\text{tot}}$  remains conserved. The levels are then characterized by a single quantum number  $J$  and have only a  $(2J + 1)$ -fold degeneracy. This means that relativistic effects partially lift the original degeneracy of energy levels, and a so-called fine-structure appears. More precisely, since  $J$  runs from  $|L - S|$  to  $L + S$ , a state with given  $L$  and  $S$ , which was  $(2L + 1)(2S + 1)$  times degenerate, splits into  $2\max(L, S) + 1$  levels labelled by the allowed values of  $J$ , which are each  $2J + 1$  times degenerate. The standard symbology to denote atomic energy levels is to write a capital letter corresponding to the value of  $L = S, P, D, \dots$ , with a lower-right index denoting the value of  $J = 0, 1/2, 1, \dots$  and an upper-left index denoting the value of  $2S + 1 = 1, 2, \dots$ :

$${}^{2S+1}L_J : \text{ atomic level.} \quad (6.3.40)$$

In some approximation, we may however describe a many electron atom as a system composed of individual electrons in single-particle stationary states. As explained above, the effect of the mutual interaction between electrons can be taken into account through the fact that each of them feels a specific effective potential. As already discussed, all the effective potentials felt by the individual electrons must be determined self-consistently, by solving some nonlinear equations. But once this has been done, each of the electrons is described by a one-particle stationary wave function, determined by an effective Hamiltonian. One can then talk about orbital configuration of each of the electrons separately. To very good accuracy, each one-particle problem has an independent spherical symmetry, and the allowed stationary states therefore have a definite individual angular momentum  $\vec{L}$ . Moreover, in each of these problems the spin does not matter and there is therefore a definite individual spin  $\vec{S}$ . The individual electronic energy levels can then be parameterized in terms of the quantum numbers  $l$  and  $s = 1/2$ , and are  $(2l + 1)(2s + 1) = 2(2l + 1)$  times degenerate. Again, relativistic effects partially lift this degeneracy, and only the total angular momentum  $\vec{J} = \vec{L} + \vec{S}$  is conserved. The resulting states are then describe by a single quantum number  $j$  and have only a  $(2j + 1)$ -fold degeneracy. But we shall ignore this here. Finally, we may label all the possible one-electron stationary states of given  $l$  and  $s = 1/2$  and higher and higher energies with a principal quantum number  $n \geq l + 1$ . More precisely,  $n - l - 1$  corresponds to the number of nodes possessed by the radial wave function describing this one-particle state. This is very similar to what occurs in the Hydrogen atom, except that here the energy depends both on  $n$  and  $l$ . The reason for this is that these states describe single-electrons moving in the effective potential generated by all the other electrons, and this potential departs from the simple  $1/r$  potential that was leading to this accidental degeneracy. The standard symbology to denote individual electronic states, which are also called orbitals, is to write a lower-case letter corresponding to the value of  $l = s, p, d, \dots$ , preceded by a number reporting the



value of  $n$ :

$$nl : \text{electronic orbitals.} \quad (6.3.41)$$

One can then specify the electronic structure of a many-electron atom by specifying the orbital of each electron. More and more complicated atoms with growing atomic number  $Z$  will then correspond to filling the allowed single-electron orbitals in the energetically most favorable way and compatibly with Pauli's exclusion principle, which requires that each electron should be in a different state. In this respect, we observe that owing to the  $2(2l + 1)$  degeneracy of the single-electron energy levels of given  $n$  and  $l$ , there may be as many as  $2(2l + 1)$  electrons with the same  $n$  and  $l$ , and thus in first approximation the same energy. For this reason, the group of  $2(2l + 1)$  orbitals with definite  $n$  and  $l$ , which have the same energy and are therefore said to be equivalent, is called a shell. The electronic configuration of a many-electron atom may then be more simply characterized by specifying the numbers of electrons that are present in each different shell. If a number  $\#_{nl}$  of electrons occur in a shell with given  $n$  and  $l$ , this is written simply as  $nl^{\#_{nl}}$ :

$$1s^{\#_{1s}} 2s^{\#_{2s}} 2p^{\#_{2p}} \dots : \text{electronic configuration.} \quad (6.3.42)$$

Notice finally that in order to full specify an atomic state, one needs to specify both the atomic level and the electronic configuration. Indeed, for a given electronic configuration, meaning given numbers of electrons in each  $nl$  shell, one may get different though usually comparable atomic energy levels. This is due to the fact that the total energy depends on the relative orientation of angular momenta of the electrons in each shell. The energetically most favorable configuration can be determined according to Hund's rule: it is the one that has the largest possible value of  $S$  in absolute and the largest value of  $L$  compatible with this value of  $S$ . A qualitative explanation for this statement can be given by considering the resulting symmetry properties of the angular part of the multiparticle wave function describing the full atom and arguing that the above rules lead to a maximization of the average inter-electron distance and therefore a minimization of the repulsion energy between different electrons.

In the above-described framework, the crucial dynamical question is now to understand in which order the atomic shells are filled when the atomic number is increased. For excited states of the Hydrogen atoms, the energy does not depend on  $l$  and increases when  $n$  is increased. If one could fill these levels without affecting their energies, one would thus fill the shells in order of growing  $n$ , and independently of  $l$ . For actual many-electron atoms, however, the filling of each orbital modifies the energies of the following ones, and one has to study the full problem at once to determine the hierarchy of orbital energies. One can then try to compare the spectrum of orbitals that is observed in spectroscopy experiments with the one that can be computed using the Hartree-Fock or Thomas-Fermi approximations. It turns out that one finds a fair agreement. The Hartree-Fock approach is particular suited for small atomic numbers, while the Thomas-Fermi approach is more suited for large atomic numbers. The structure of these spectra of orbitals allows moreover to understand the structure of the periodic table of elements. In particular, it emerges

that different orbital states subdivide into distinct groups, which get progressively filled when the number of electrons is increased, and correspond to the rows of the periodic table:

$1s$	2	electrons	
$2s, 2p$	8	electrons	
$3s, 3p$	8	electrons	
$4s, 3d, 4p$	18	electrons	(6.3.43)
$5s, 4d, 5p$	18	electrons	
$6s, 4f, 5d, 6p$	32	electrons	
$7s, 6d, 5f$	...	electrons	

This observed filling order is in good agreement with the hierarchy of energy levels that can be computed at the theoretical level. As expected, these energies depend not only on the value of  $n$  but also on the value of  $l$ . A first characteristic of the spectrum is that for a given  $n$  the energy increases monotonically when  $l$  increases. A qualitative explanation for this is that for a given  $n$  the states with smaller  $l$  are on average closer to the nucleus and deeper inside the cloud formed by the other electrons, and can therefore feel in a stronger and less shielded way the attraction from the nucleus. An other characteristic that emerges is that in some cases there can be a competition between states with different values of  $n$ , and it may be energetically more favorable to increase  $n$  rather than  $l$ .

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