2 Classical Scattering Theory

Not every collision of microparticles has to be treated using quantum theory and a classical theory may be a perfectly valid approach. Therefore in this chapter we first analyse classical scattering and its limits. This exercise is not self-serving since, as we will see later, the basic ideas of the classical theory translate to the quantum regime too. This includes, for example, the concept of in/out asymptotes and the definition of the scattering cross section.

2.1 Deflection function for single particle collisions

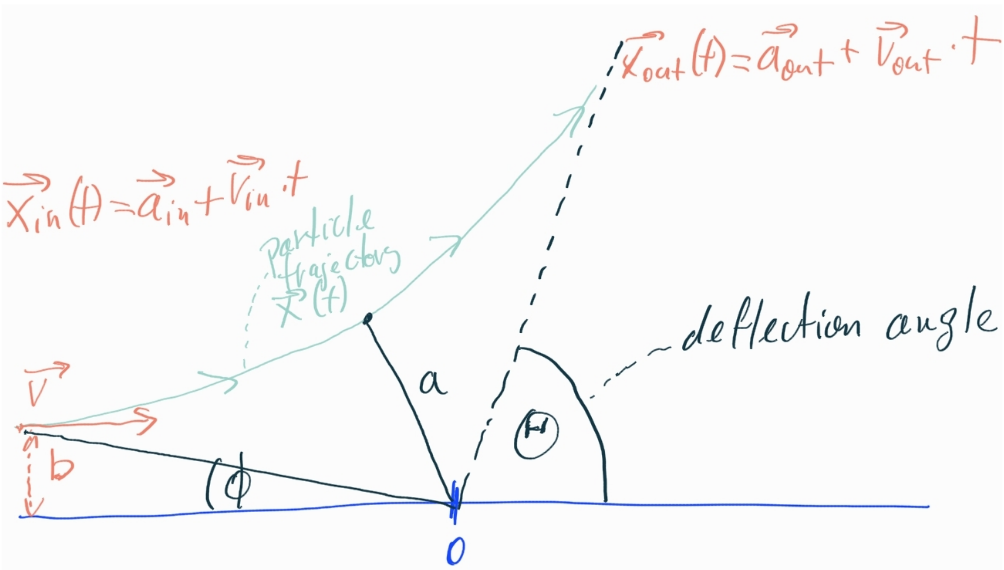

Figure 2.1: Parameters defining a classical collision problem. The particle impinging on the left is characterized by its velocity v and impact parameter b. After the collision the particle is leaving along the line given by the deflection angle Θ. The point of closest approach, where the radial velocity is zero, is denoted by the black dot on the particle's trajectory. The corresponding distance from the origin is a.

We assume that the particle moves in a spherically symmetric potential $V(r)$. The potential can be strictly short-range (i.e. it is exactly zero beyond a certain radius) or a long-range potential which goes smoothly to zero for $r \to \infty$. Energy of the incoming particle is conserved and due to the spherical symmetry its angular momentum is conserved too. Therefore the motion of the particle is constrained to a plane. The particle has a fixed energy E and angular momentum L

$$E = \frac{1}{2}mv^2, \tag{2.1}$$

$$L = mr^2\frac{d\phi}{dt} = mvb. \tag{2.2}$$

Figure 2.1 illustrates the basic setting, defines the polar angle ϕ, the impact parameter b and the deflection angle Θ. We've drawn the coordinate the system so that the horizontal axis is parallel to the particle's velocity. The magnitude of the angular momentum of the particle ($L = rp\sin\phi = mvb$) follows from the triangle on the bottom left of Fig. 2.1.

Before considering a realistic scenario for a collision experiment we'll first develop theory for description of single particle scattering. The trajectory of the incoming particle is specified by a pair of vectors ($\mathbf{a}_{in}, \mathbf{v}_{in}$) corresponding to the particle's displacement and velocity, respectively. After the scattering the outgoing particle is found on the detector and characterized by ($\mathbf{a}_{out}, \mathbf{v}_{out}$). We can expect that any pair of vectors ($\mathbf{a}, \mathbf{v}$) can define in and out asymptotes. However, not every orbit $\mathbf{x}(t)$ has in and out asymptotes (the potential can support bound states).

In scattering experiments involving microparticles we don't have access to the exact orbit $\mathbf{x}(t)$ and we only observe the asymptotic states of the particle. The asymptotic state following the scattering is most conveniently characterized by the deflection angle Θ. This is justified by noticing from Eq (2.2) that the rate of change of ϕ depends inversely on the radial distance of the particle. Hence, the angle ϕ is well defined when the particle is far away from the origin, i.e. before the collision ($\phi = 0$) and after the collision ($\phi \neq 0$).

Our task is therefore to compute the deflection function $\Theta(b, v)$ as a function of the impact parameter b and velocity v (energy) of the incoming particle. It is seen from Fig. 2.1 that the deflection angle is obtained from the angle corresponding to the point of the closest approach

$$\Theta = \pi - 2\phi(a). \tag{2.3}$$

To compute $\phi(a)$ we consider the following quantity:

$$\frac{\frac{d\phi}{dt}}{\frac{dr}{dt}} = \frac{d\phi}{dr}, \tag{2.4}$$

where we have eliminated the time derivatives. The numerator on the left hand side is obtained readily from Eq (2.2) and the denominator from the law of conservation of energy:

$$E = \frac{1}{2}m(r')^2 + \frac{1}{2}m(r\phi')^2 + V(r) = \frac{1}{2}m(r')^2 + \frac{L^2}{2mr^2} + V(r), \tag{2.5}$$

$$r' = \pm\sqrt{(E - V(r) - \frac{L^2}{2mr^2})\frac{2}{m}}. \tag{2.6}$$

The sign of r' is chosen depending on whether we're considering an outward (+) or an inward (−) motion of the particle. Substituting these relations into Eq (2.4) we get

$$\frac{d\phi}{dr} = \frac{\frac{L}{mr^2}}{\pm\sqrt{(E - V(r) - \frac{L^2}{2mr^2})\frac{2}{m}}} = \pm\frac{b}{r^2\sqrt{\left(1 - \frac{V(r)}{E} - \frac{b^2}{r^2}\right)}}. \tag{2.7}$$

In the second step we used $L = mvb$ and $E = 1/2mv^2$. Finally, we obtain $\phi(a)$ and Θ by integration of Eq (2.7)

$$\Theta = \pi + 2b\int_{\infty}^{a} dr\frac{1}{r^2\sqrt{\left(1 - \frac{V(r)}{E} - \frac{b^2}{r^2}\right)}} = \pi - 2b\int_{a}^{\infty} dr\frac{1}{r^2\sqrt{\left(1 - \frac{V(r)}{E} - \frac{b^2}{r^2}\right)}}. \tag{2.8}$$

The two equivalent expressions for Θ were obtained by using the inward and outward type of motion. The point of closest approach a is calculated from Eq (2.6) by requiring $r' = 0$

$$0 = E - V(a) - \frac{L^2}{2ma^2} = 1 - \frac{V(a)}{E} - \frac{b^2}{a^2}. \tag{2.9}$$

We will see later that the deflection angle is the classical analogue of the scattering matrix (S-matrix) while the in/out asymptotes correspond to asymptotic quantum states of the particle which are propagated forward/backward in time into the interaction region where the scattering amplitude is obtained from their overlap.

2.2 General properties of the collision process

One of the goals of scattering experiments is to learn as much as possible about the interaction potential. What parts of the potential we probe depends sensitively on the initial state of the particle. This can be seen by considering the effective potential for the collision

$$V_L(r) = V(r) + \frac{L^2}{2mr^2}, \tag{2.10}$$

which enters into Eq (2.5). Figure 2.2 shows, schematically, the effective potentials plotted for several choices of angular momenta. Several observations can be made based on this plot.

- For a given particle energy increasing the angular momentum (impact parameter) results in pushing of the particle away from the center of force.
- Particle with zero angular momentum experiences the full range of the interaction potential.
- For strictly short-range potentials there is a sharp cut-off on the magnitude of the particle angular momentum that can be scattered.

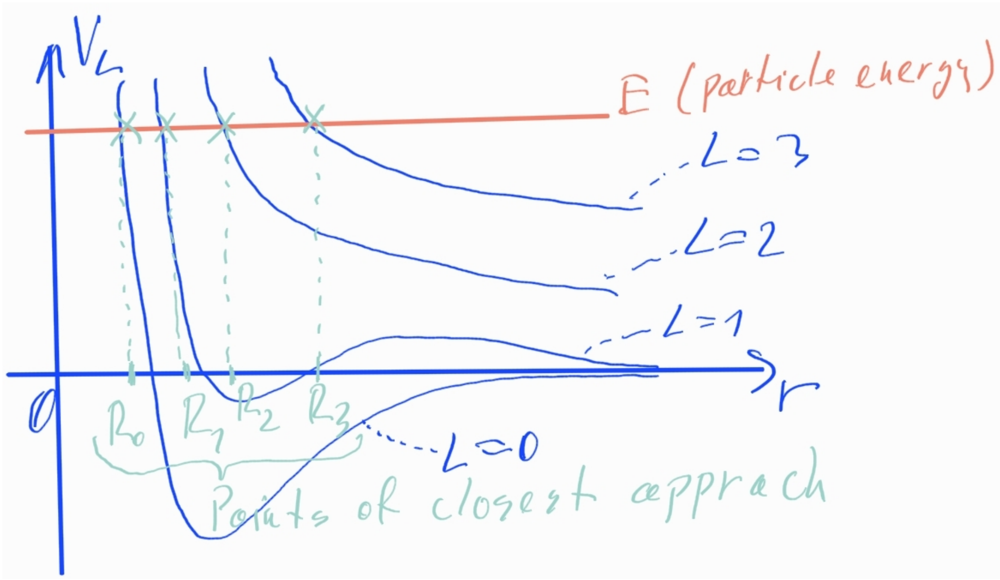

Figure 2.2: Caption

We can consider two limiting cases for the choice of the impact parameter

- $b \to 0$: the deflection angle is zero for attractive potentials since there is no sideways force acting on a particle hitting a spherically symmetric potential head-on. Similarly, for purely repulsive potentials $\Theta = \pi$ since the particle is reflected backwards.

- $b \to \infty$: the deflection angle is zero again but now due to the fact that the asymptotic potential is weak. However, large impact parameters may contribute significantly to small angle scattering.

2.3 Classical Cross Section

In a real experiment we cannot control the impact parameter on a molecular scale. Additionally, we don't learn much from the passage of a single particle either: we only learn if it was scattered or not. Instead, a typical experimental setup consists of a beam of projectiles with a well defined velocity entering into a gas of target particles. The projectiles impinge on the target particles with all possible impact parameters. The projectiles are then detected (counted) following their passage through the reaction chamber. Therefore the experiment effectively repeats the single collision experiment many times each time with a different (random) impact parameter, see Fig. 2.3a.

The incoming beam is characterized by the flux n_{inc}: the number of particles **per area** perpendicular to the momentum of the beam. In the experiment we count the **number** of scattered particles N_{sc}. Therefore we can say that the scattered particles hit a notional

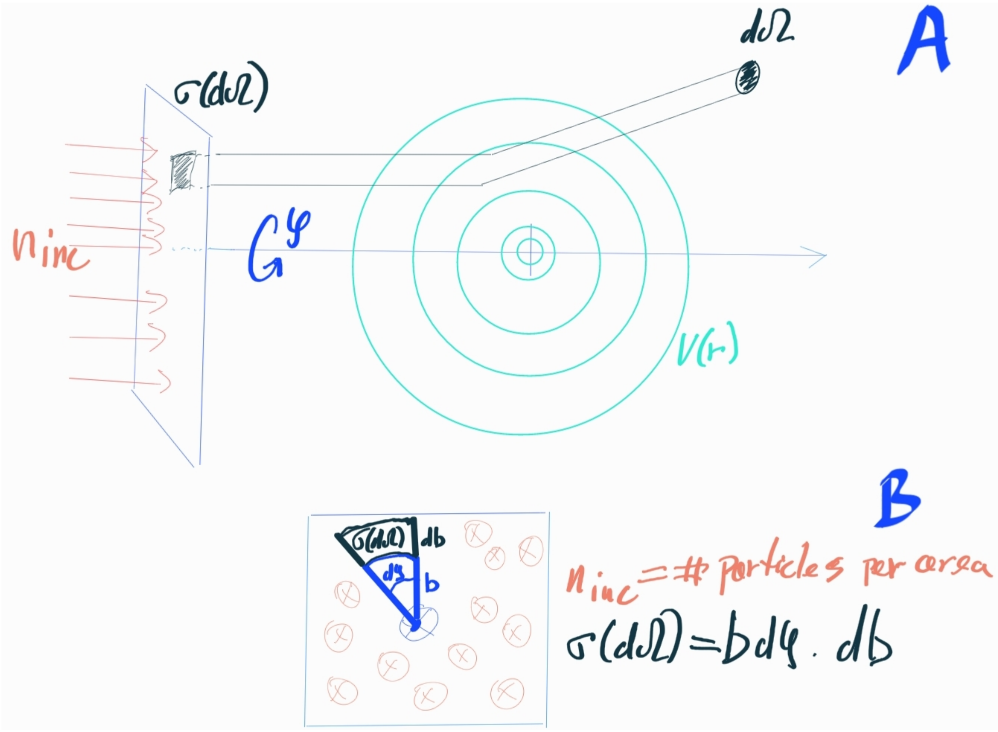

Figure 2.3: Differential cross section for scattering to an element of the solid angle in direction (θ,ϕ).

cross-sectional area σ of the target:

$$N_{sc} = \sigma n_{inc}. \tag{2.11}$$

This expression defines the cross section σ as a constant of proportionality (area) between the incident and the scattered beam of particles. The cross section characterizes properties of the interaction between the projectile and the target. For example, we will see that for scattering of particles from a hard (impenetrable) sphere of radius a the cross section for the collision is exactly πa^2.

We can get a more detailed information by counting the number $N_{sc}(\Delta\Omega)$ of particles scattering into a particular direction (θ,ϕ)

$$N_{sc}(\Delta\Omega) = \sigma(\Delta\Omega) n_{inc}, \tag{2.12}$$

where $\sigma(\Delta\Omega)$ is now that area of the target which scatters particles into the solid angle $\Delta\Omega$. This concept is illustrated on Fig. 2.3b. For small solid angles the cross section $\sigma(\Delta\Omega)$ becomes proportional to the element of solid angle $d\Omega$ and we get

$$N_{sc}(d\Omega) = \left(\frac{d\sigma}{d\Omega}\right) d\Omega n_{inc}. \tag{2.13}$$

The quantity denoted $\frac{d\sigma}{d\Omega}$ is the differential cross section (DCS). It should not be understood as a differentiation of the cross section but a mere notation.

Having defined the cross section we're now in the position to express it in terms of the deflection function. The elementary surface area on crossed by the incoming beam is

$$\sigma(d\Omega) = bd\phi db. \tag{2.14}$$

Combining this expression with the previous two we get

$$bd\phi dbn_{inc} = \left(\frac{d\sigma}{d\Omega}\right) d\Omega n_{inc}, \tag{2.15}$$

$$\tag{2.16}$$

which allows us to straightforwardly express the differential cross section

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{bdbd\phi}{d\Omega} = \frac{bdb}{\sin\theta d\theta} = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right| = \frac{b}{\sin\theta\left|\frac{d\Theta}{db}\right|}. \tag{2.17}$$

The absolute value was inserted since the observed count of particle is always positive regardless of the sign of the term $\frac{db}{d\theta}$. The last form is actually the most convenient formula for computing the cross section since typically we calculate $\Theta(b)$ directly from Eq (2.8) rather than $\theta(b)$.

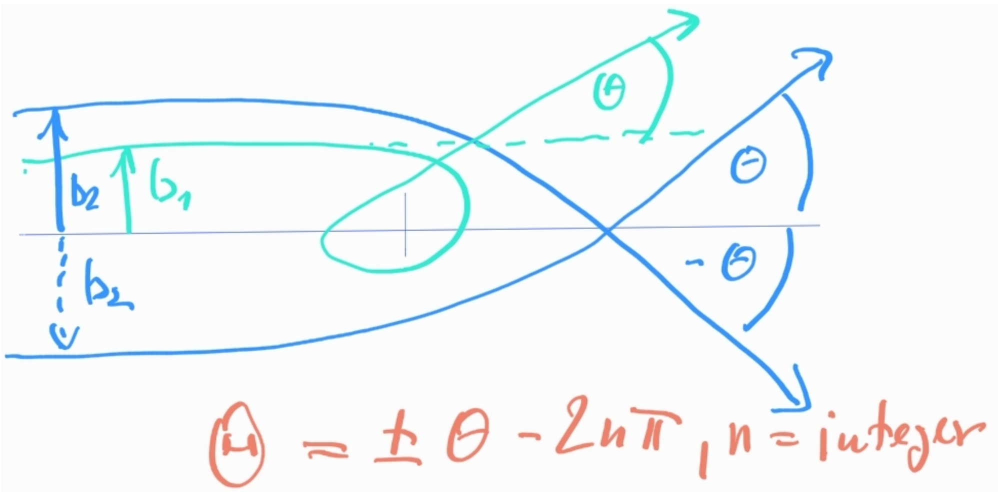

Figure 2.4: Multiple trajectories may correspond to the same scattering angle θ.

Our goal is to express the result in terms of the deflection function. However, that is not the same quantity as the scattering angle $\theta = [0, \pi]$ since the deflection angle Θ may include multiple revolutions of the particle around the scattering center. Additionally, the experiment is not able to distinguish between collisions corresponding to $\pm\theta$, see Fig. 2.4. Therefore the differential cross section for a given angle θ must include a summation over all deflection angles leading to the same scattering angle:

$$\Theta = \pm\theta - 2n\pi, \tag{2.18}$$

$$\left(\frac{d\sigma}{d\Omega}\right) = \sum_i \frac{b_i}{\sin\theta}\left|\frac{db}{d\theta}\right|_{b_i} = \sum_i \frac{b_i}{\sin\theta\left|\frac{d\Theta}{db}\right|_{b_i}}. \tag{2.19}$$

Finally, we remark that scattering cross section in the forward direction is undefined since in this case (elastic scattering) it is impossible to distinguish between scattered and unscattered particles.

Total cross section

The total cross section σ is obtained summing the scattered signal into all directions

$$\sigma = \int d\Omega \left(\frac{d\sigma}{d\Omega}\right) = 2\pi \int_0^{2\pi} \left(\frac{d\sigma}{d\Omega}\right) \sin\theta d\theta. \tag{2.20}$$

Inserting Eq (2.17) into the previous one and assuming a purely short-range interaction with range b_{max} we obtain an important property

$$\sigma = \int d\Omega \left(\frac{d\sigma}{d\Omega}\right) = \int d\phi d\theta b \left|\frac{db}{d\theta}\right| = 2\pi \int_0^{b_{max}} dbb = \pi b_{max}^2, \tag{2.21}$$

where we used substitution to express θ as function of b. We have shown that for all finite range interactions the total cross sections is always equal to the cross sectional area of the potential. In contrast infinite range interactions that go smoothly to zero as $r \to \infty$ always lead to divergent cross sections on account of small-angle scattering coming from the contribution of large impact parameters (even trajectories with large impact parameters scatter to a small but nonvanishing angle). More specifically for potentials behaving as $V(r) \sim 1/r^\alpha$ the deflection function is $\Theta \sim 1/b^\alpha$ showing that the DCS in the forward direction is divergent (CITE Friedrich).

2.3.1 Hard sphere scattering

The simplest scattering process is scattering from an impenetrable sphere of radius a (i.e. $V(r) = \infty, r \leq a$). Clearly, the point of closest approach is equal to the sphere's radius a and the particle only experiences the part of space $r > a$. Starting from the expression Eq (2.8) with $V(r) = 0$ and making the substitution $z = 1/r$ we get

$$\Theta = \pi - 2b \int_0^{1/a} \frac{dz}{\sqrt{1 - b^2 z^2}} = \cdots = \pi - 2\arcsin\left(\frac{b}{a}\right), b \leq a. \tag{2.22}$$

Obviously, $\Theta = 0$ for $b > a$. In this case the deflection function can be obtained directly from the geometry of the problem, see Fig. 2.5. The deflection function is thus a one-to-one mapping of the impact parameter b and $b(\Theta) = b(\theta)$. To compute the DCS we need for example $b(\theta)$ which we obtain readily from the previous equation

$$b = a\sin(\pi/2 - \Theta/2) = a\cos(\Theta/2). \tag{2.23}$$

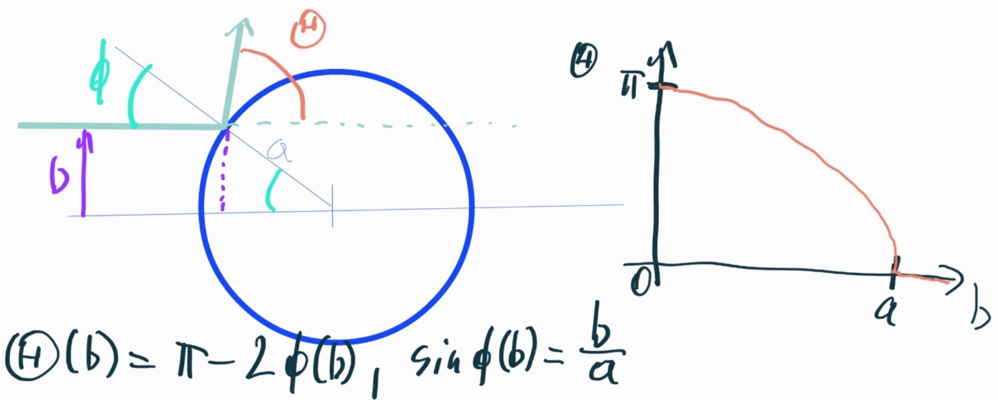

Figure 2.5: Hard sphere scattering

Using the previous equation in Eq (2.17) yields the expected result

$$\frac{d\sigma}{d\Omega} = \frac{a^2}{4}, \tag{2.24}$$

$$\sigma = 4\pi\frac{a^2}{4} = \pi a^2. \tag{2.25}$$

2.3.2 Coulomb (Rutherford) scattering

Coulomb scattering occupies an important place in scattering theory since it was used by Rutherford to explain his famous experiment of scattering of alpha particles on gold foil. His observation of large-angle scattering refuted Thomson's plum pudding model of atom in favour of the planetary model since Thomson's model predicted only small-angle scattering.

We start from Eq (2.8) with $V(r) = B/r$, where B is an arbitrary constant

$$\Theta = \pi - 2b\int_a^\infty \frac{dr}{r^2\sqrt{1 - \frac{b^2}{r^2} - \frac{B}{rE}}}. \tag{2.26}$$

The point of closest approach is obtained solving the equation

$$1 - \frac{b^2}{a^2} - \frac{B}{aE} = 0, \tag{2.27}$$

$$a_{1,2} = \frac{1}{2}\left[\frac{B}{E} \pm \frac{B\sqrt{1 + \frac{4b^2E^2}{B^2}}}{E}\right]. \tag{2.28}$$

Only the positive root is physical. For convenience we now introduce a dimensionless

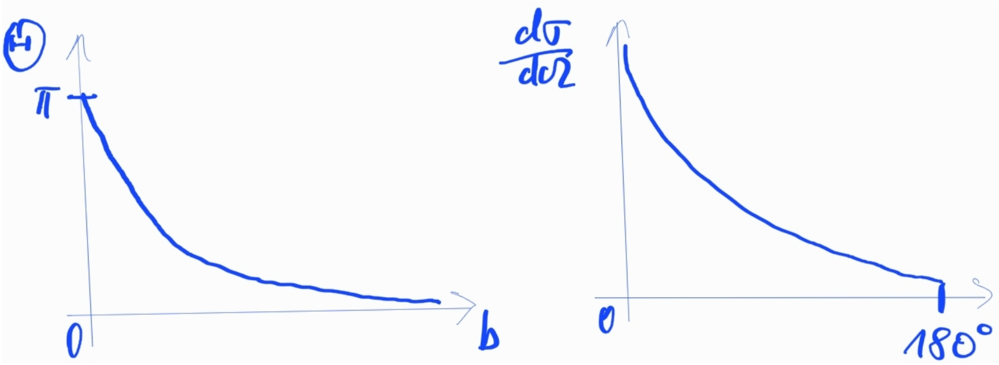

Figure 2.6: Deflection function (left panel) and DCS (right panel) for Coulomb scattering. The deflection function is finite for $b = 0$, $\Theta(0) = \pi$, while the DCS diverges in the forward direction due to the long-range nature of Coulomb interaction and contributions of trajectories with large impact parameters.

constant $\gamma = \frac{B}{2Eb}$ and write

$$a = \frac{B}{2E}\left(1+\sqrt{1+\left(\frac{2bE}{B}\right)^2}\right) = b(\gamma+\sqrt{\gamma^2+1}), \quad (2.29)$$

$$\Theta = \pi - 2b\int_a^{\infty}\frac{dr}{r^2\sqrt{1-\frac{b^2}{r^2}-\frac{B}{rE}}} = |z = \frac{b}{r}| = \pi + 2\int_{b/a}^{0}\frac{dz}{\sqrt{1-z^2-z2\gamma}} \quad (2.30)$$

$$= \cdots = 2\arccos\left(\frac{1}{\sqrt{\gamma^2+1}}\right). \quad (2.31)$$

Again, the deflection function is a one-to-one mapping between b and Θ, see Fig. 2.6. To compute the scattering cross section we express $b(\theta)$ by starting from the expression for cos of the last equation:

$$\cos\frac{\theta}{2} = \frac{1}{\sqrt{\gamma^2+1}}, \quad (2.32)$$

$$\frac{1}{\cos^2(\theta/2)} = 1+\left(\frac{B}{2Eb}\right)^2, \quad (2.33)$$

$$\frac{\sin^2(\theta/2)}{\cos^2(\theta/2)} = \left(\frac{B}{2Eb}\right)^2, \quad (2.34)$$

$$b(\theta) = |\frac{B}{2E}\cot(\theta/2). \quad (2.35)$$

Finally, we get

$$|\frac{db}{d\theta}| = \frac{B}{4E}\frac{1}{\sin^2(\theta/2)}. \quad (2.36)$$

Substitution of this result into Eq (2.17) for the DCS gives

$$\frac{d\sigma}{d\Omega} = \left(\frac{B}{4E}\right)^2 \frac{1}{\sin^4(\theta/2)}. \tag{2.37}$$

This expression has several important properties

- DCS does not depend on the charge B so the DCS is not able to distinguish scattering from a positively and negatively charged center but the trajectories do differ for $\pm B$.
- The DCS (and the total cross section) diverges for $\theta \to 0$ as was already mentioned above.
- The classical DCS is equal to the quantum result. This is a rare (perhaps the only) case for which the two theories give an identical DCS (CITE 1945 Williams paper).

2.3.3 Limitations of classical scattering theory

Was Rutherford's classical treatment of the collision valid? How do we estimate the limits of classical scattering theory? There are two basic conditions that must be satisfied for the classical approach to be valid. The key property of the classical approach is a well-defined trajectory of the particle, i.e. the impact parameter b, the angle of attack ϕ and by inference the deflection function Θ. To make concrete estimates consider scattering by a short-range field with radius a and potential of the order of V.

Well-defined impact parameter b

The impact parameter must be well defined in relation to the field dimensions. The uncertainty relations imply:

$$\Delta b \Delta p \sim a \Delta p \geq \hbar/2, \tag{2.38}$$

$$\Delta p \geq \frac{\hbar}{2a}. \tag{2.39}$$

The uncertainty in the momentum must be much smaller than the momentum itself

$$\Delta p << p, \tag{2.40}$$

$$\frac{\hbar}{2a} << mv. \tag{2.41}$$

The last inequality is equivalent to

$$\frac{\hbar}{mv} = \frac{\lambda}{2\pi} << 2a, \tag{2.42}$$

$$\tag{2.43}$$

that is the de Broglie wavelength of the particle λ must be much smaller than the dimension (diameter) of the scattering region.

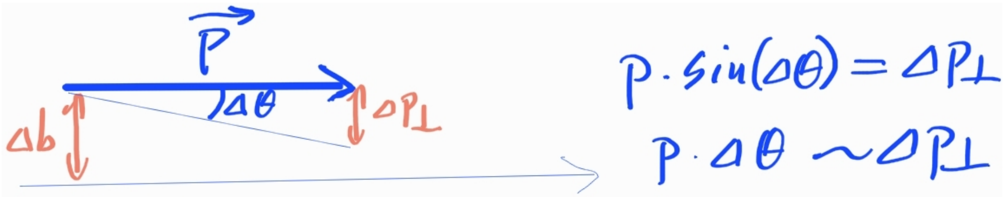

Figure 2.7: Uncertainty in the scattering angle follows from the uncertainty in the impact parameter.

Well-defined deflection angle Θ

We assume that the uncertainties in the impact angle ϕ are small and therefore the uncertainty in this angle is carried over to the deflection angle Θ: $\Delta\phi \sim \Delta\Theta$. We can use the same uncertainty relation as above to express the uncertainty $\Delta\phi$:

$$\Delta b \Delta p \geq \hbar, \tag{2.44}$$
$$p\Delta\theta \sim \Delta p, \tag{2.45}$$
$$\Delta\theta \sim \frac{\Delta p}{mv}, \tag{2.46}$$
$$\Delta\theta \sim \Delta\Theta \geq \frac{\hbar}{mv\Delta b}, \tag{2.47}$$

where the second inequality follows from the triangle on Fig. 2.7. The last inequality implies that exact knowledge of the scattering angle implies complete loss of the concept of impact parameter and vice versa. This uncertainty can be rewritten in an equivalent form as

$$\Delta\theta(mv\Delta b) = \Delta\theta\Delta L \geq \hbar, \tag{2.48}$$

that is complete specification of the scattering angle implies a complete loss of angular momentum information. This is a concept well-known to you from the partial wave expansion of the plane wave for (exact) momentum $\mathbf{k}$

$$\exp[\imath\mathbf{k}.\mathbf{r}] = 4\pi \sum_{L=0}^{\infty} j_L(kr)\imath^L P_L(cos\theta), \tag{2.49}$$

where $j_L(kr)$ is the spherical Bessel function and $P_L(cos\theta) = \sqrt{\frac{4\pi}{2L+1}} Y_{L,0}(\theta,\phi)$ are the Legendre polynomials. So far we have only achieved expressing of the uncertainty relations in a different basis. The real condition on validity of classical scattering is a small uncertainty in the scattering angle in comparison to the actual scattering angle

$$\Delta\Theta << \Theta, \tag{2.50}$$
$$\Delta\Theta \sim \frac{\hbar}{\Delta L} > \frac{\hbar}{L}, \tag{2.51}$$
$$\Theta >> \frac{\hbar}{L}. \tag{2.52}$$

This implies that quantum mechanics implies deviations from the classical theory in the small angle region where a particular care should be applied. However, in many types of collision processes involving for example slow and light particles (e.g. electrons with energies << 100 eV scattering from atoms) the classical theory fails completely and is inadequate in the whole angular range. We will illustrate this criterion in practice later for the case of quantum hard sphere scattering.

Validity of Rutherford's classical treatment

Let's apply the principles above to a more accurate estimate for the validity of Rutherford's experiment. The momentum transferred of the alpha particle can be estimated crudely as

$$\Delta q = F\Delta t, \tag{2.53}$$

where F and Δt are a characteristic force and collision time. Those can be estimated trivially

$$F \sim \frac{V}{a}, \tag{2.54}$$

$$\Delta t \sim \frac{a}{v}. \tag{2.55}$$

Thus our estimate for the momentum transfer is

$$\Delta q \sim \frac{V}{a}\frac{a}{v} = \frac{V}{v}. \tag{2.56}$$

A well-defined trajectory requires

$$\Delta q << \Delta p \sim \frac{\hbar}{a}, \tag{2.57}$$

$$\frac{Va}{\hbar v} >> 1. \tag{2.58}$$

To estimate the interaction potential we use the fact that the atom has finite a finite radius approx. a which screens the pure Coulomb potential and put $V = \frac{Zze^2}{a}$ in the last equation obtaining the condition

$$\frac{Zze^2}{\hbar v} >> 1. \tag{2.59}$$

In the Rutherford experiment $\beta = \frac{v}{c} \sim 0.05$, $z = 2$, $Z = 50$ and remembering that $\frac{\hbar c}{e^2} = 137$ we get

$$\frac{Zz}{137\beta} \sim 20 >> 1. \tag{2.60}$$

That in the Rutherford experiment the use of classical scattering theory was justified.

For pure Coulomb scattering the quantum and the classical result are the same and therefore we would not observe any deviations from the classical DCS for this particular case. However, the point-charge model obviously neglects the atomic electrons: if those are taken into account in a more realistic model, we would expect deviations from the classical result at small scattering angles which are affected by larger impact parameters probing the electronic cloud of the atom. These impact parameters can be roughly estimated as the radius of the atom

$$a \sim a_0 Z^{-1/3}, \tag{2.61}$$

$$\theta_{pc} = 2\arccos\left(\frac{1}{\sqrt{\gamma^2+1}}\right) \sim \frac{Zze^2}{mv^2 a} = 0.2\,\text{deg}\,. \tag{2.62}$$

At scattering angles smaller than θ_{pc} deviations from the point-charge model are expected while the limit on the classical treatment of the more realistic collision model is even smaller:

$$\theta_{qm} \sim \frac{\hbar}{mva} = 0.01\,\text{deg}\,. \tag{2.63}$$

Therefore Rutherford's choice of the point-charge model for scattering of heavy alpha particles from atoms of gold was well justified. Especially, since the most important result of his measurements was the observation of large-angle scattering. Therefore the departure from small scattering angles was not noticed since it was constrained to extremely small angles for which reliable measurements are very difficult. In fact the original experiments from 1913 (CITE http://web.ihep.su/dbserv/compas/src/geiger13/eng.pdf) were performed for scattering angles in the range $[5\,\text{deg}, 150\,\text{deg}]$.

The success of Rutherford's model lied in confirmation of the large-angle scattering caused by small impact parameters (i.e. a positively or negatively charged nucleus) thus proving validity of the point charge model of atomic nucleus. Departures from the point-charge model were studied experimentally much later, see e.g. TODO CITE WILLIAMS. That the charge is positively charged was shown in a 1917 experiment which showed that the positive nuclei were knocked forward (not backward) by the alpha particles.

Quantum vs classical regime

Let us make a few simple estimates of the de Brogile wavelength for various collision processes. In atomic units the de Brogile wavelength is

$$\lambda = \frac{2\pi}{p}. \tag{2.64}$$

- Electron scattering from atoms. Let's require $\lambda < a_0$. The condition for the classical scattering regime is then approximately $\frac{2\pi}{p} < 1$ which implies $E = p^2/2 > 2\pi^2$ H, i.e. $E > 550$ eV.

- Molecules CH_3F at room temperature. Their mean velocity is approx. 400 m/s. This implies $\lambda \sim 0.3$ Åwhile the typical range of interaction forces is on the order of units of Angstrom (e.g. in H_2 it is approximately 4 Å). Therefore these collisions can be treated classically.
- Molecules CH_3F at 30 mK. Their mean velocity is approx. 4 m/s implying $\lambda \sim 30$ Å. This is 100 times larger than in the previous case and we're now in the deep quantum regime. Typically at low temperatures molecules/atoms are in their lowest quantum states (including hyperfine) and their reactions become extremelly sensitive to these states. This opens possibilities for control of chemical reactions.

2.3.4 Singularities in classical collisions

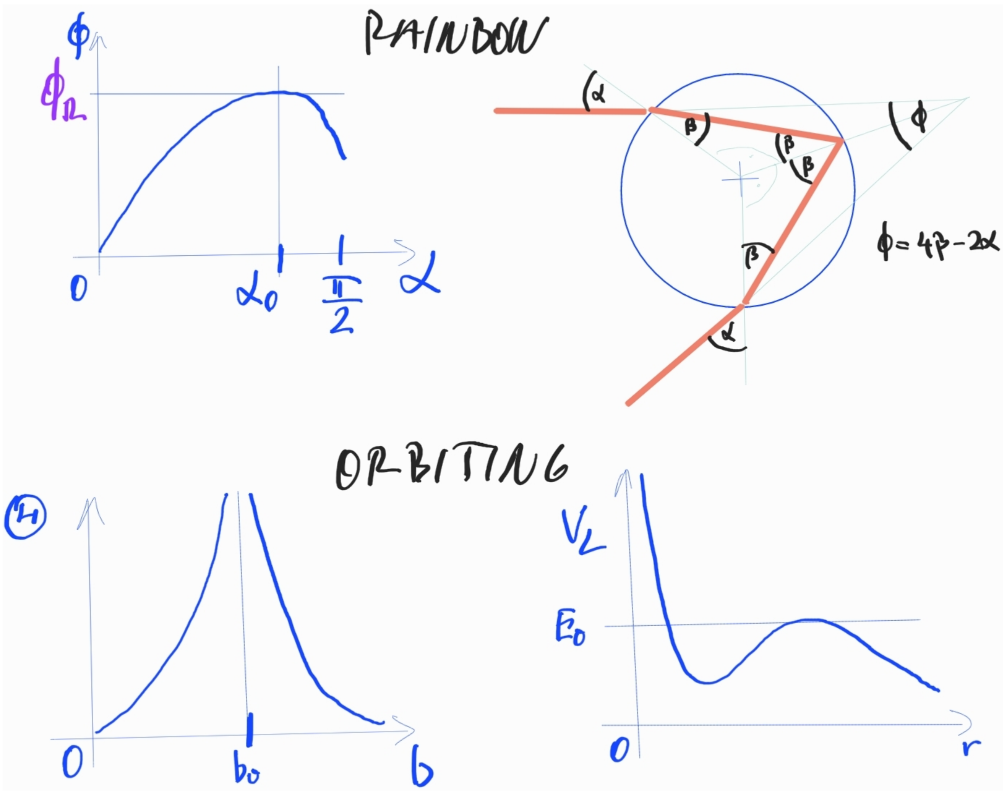

Figure 2.8: Singularities in classical cross sections. Panel A: rainbow singularity appears when the deflection function has a local minimum/maximum. Panel B: orbiting singularity arises when energy of the incoming particle matches a local maximum in the effective potential.

The classical cross section has the general form

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{b}{\sin\theta}\left|\frac{db}{d\theta}\right| = \frac{b}{\sin\theta\left|\frac{d\Theta}{db}\right|}, \tag{2.65}$$

which may be divergent in specific cases illustrated in Fig. 2.8.

- **Glory scattering** This effect may be forward ($\theta = 0$) or backward ($\theta = \pi$) and is due to the $\sin\theta$ term becoming zero. It is caused by the vanishingly small element of the solid angle at these points. Nevertheless, this divergence disappears from Eq (2.65) when it is integrated over a small region of solid angles around these points since the $\sin\theta$ term from $d\Omega$ cancels the divergent part.
- **Rainbow scattering** A divergence of this type arises from disappearance of the derivative $\frac{d\Theta}{db}$ in Eq (2.65). Physically, this corresponds to an infinite density of scattering trajectories at this point. As the name suggests this effect is responsible for the optical rainbow effect, when corrected for the wave nature of light, see below. Rainbow scattering arises in monotonous attractive potentials since $\Theta(0) = \Theta(\infty) = 0$ but $\Theta(b) \neq 0$ for $0 > b < \infty$. This implies that $\Theta(b)$ either has an extremum or diverges for some finite impact parameter leading to orbiting, see below.
- **Orbiting** This effect is observed when energy of the incoming particle exactly matches a local maximum in the effective potential $V_L(r)$. This leads to trapping of the incoming particle in an infinite orbit and to divergence of the deflection function. Precisely, the condition for orbiting are repeated roots of Eq (2.9) for points of the closest approach.

The optical rainbow effect, see Fig. 2.8, is understood as intense scattering under a particular angle α_0. This is calculated from the deflection angle and Snell's law:

$$\phi = 4\beta - 2\alpha, \tag{2.66}$$

$$\sin\alpha = n\sin\beta. \tag{2.67}$$

The last equation allows us to express β, insert it into the preceding expression and take its derivative with respect to the impact parameter (angle)

$$\frac{d\phi}{d\alpha} = 4\frac{d}{d\alpha}\arcsin\left[\frac{\sin\alpha}{n}\right] - 2 = 4\frac{1}{\sqrt{1-\frac{\sin^2\alpha}{n^2}}}\frac{\cos\alpha}{n} - 2. \tag{2.68}$$

The rainbow angle α_0 is found equating the last expression to zero obtaining

$$\cos\alpha_0 = \sqrt{\frac{n^2-1}{3}}. \tag{2.69}$$

2.4 Scattering cross sections and chemical reactions

Real systems (e.g. the atmosphere, plasma, interstellar clouds, etc.) are characterized by temperature which implies a distribution of velocities of the interacting particles and therefore collisions do not happen at a single energy. How do we characterize reactions (collisions) that take place in these systems?

Consider a reaction where reactants A a B are turned into products C and D

$$A + B \to C + D, \tag{2.70}$$

and define an **abundance** of A: [A] as the number of particles per cm^3. Then the rate of loss of reactants A and B is proportional to the product of their abundance (since the reaction requires presence of both reactants) and the **reaction rate coefficient k**

$$\frac{d}{dt}[A] = \frac{d}{dt}[B] = -k[A].[B]. \tag{2.71}$$

We can write a similar equation for the rate of gain of abundance of the products as

$$\frac{d}{dt}[C] = \frac{d}{dt}[D] = +k[A].[B]. \tag{2.72}$$

Solution of this system of equations relies on knowledge of the rate constant k which is thus used to calculate yields of chemical reactions. The reaction rate coefficient for a single energy is related to the cross section for the collision $A + B \to C + D$

$$k(v_r) = \sigma(v_r)v_r, \tag{2.73}$$

where v_r is the relative velocity of the reactants. The reaction rate has dimensions of volume per time. We can rationalize this definition by analyzing the expression for $d[B]$ for example:

$$-d[B] = [A][B]\sigma(v_r)v_r dt. \tag{2.74}$$

In this equation [A] and [B] are measured in cm^{-3} while the cross-section has dimension of cm^2 and therefore the definition of k is justified at least on dimensional grounds.

To calculate the reaction rate corresponding to a given temperature T, we have to average it over the distribution of relative velocities of the reactants. At thermal equilibrium this distribution is described by the Maxwell-Boltzmann distribution

$$f(v_r, T) = 4\pi v_r^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{m v_r^2}{2k_B T}\right], \tag{2.75}$$

$$k(T) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty dv_r \sigma(v_r) v_r^3 \exp\left[-\frac{m v_r^2}{2k_B T}\right], \tag{2.76}$$

where m is the reduced mass of the collision complex. To make estimates it is useful to remember that

$$\langle v_r \rangle = \sqrt{\frac{8k_B T}{\pi m}}, \tag{2.77}$$

$$k_B = 8.617 \times 10^{-5} eV/K. \tag{2.78}$$

The last equation shows that reaching e.g. electronically excited states in atoms and molecules, with energies on the order of eV, requires heating the reaction complex to very large temperatures of the order 10^5 K.

Nevertheless, there are many types of collision experiments where projectiles with specific energies are generated, e.g. by accelerating electrons in an electrostatic field, where averaging over energies (velocities) does not take place. In all cases the primary quantity of interest is the scattering (reaction) cross section for a given energy.