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THE THEORY OF ELASTIC SCATTERING IN A CENTRAL FORCE FIELD

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In this chapter we discuss the theory of mutual elastic scattering of particles interacting through a central force,* that is, a force that acts along the line of centers of the particles and whose magnitude depends only on the distance of separation. Only binary nonrelativistic collisions are treated. The classical theory is presented first and is followed by the quantum mechanical treatment. Experimental studies of elastic scattering are described in Chapter 4, which also contains results of theoretical calculations on a number of specific systems.

PART A. THE TWO-BODY CENTRAL FORCE PROBLEM IN CLASSICAL MECHANICS

3-1. SEPARATION OF THE CENTER-OF-MASS MOTION FROM THE TOTAL MOTION

Consider two particles of masses m and M which interact with one another through a potential $V(r)$, which is a function only of the length of the vector \mathbf{r} separating them. Let \mathbf{R}_m and \mathbf{R}_M denote the position vectors

* A reference on scattering in noncentral force fields, such as those described in Section 1-7, is J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.

of the two particles in the Lab system of coordinates, so that $\mathbf{r} = \mathbf{R}_m - \mathbf{R}_M$. If no external forces are applied, Newton's second and third laws of motion for this system may be expressed as

$$\mathbf{f}_m = m \frac{d^2 \mathbf{R}_m}{dt^2} \quad (3-1-1)$$

$$\mathbf{f}_M = M \frac{d^2 \mathbf{R}_M}{dt^2} = -\mathbf{f}_m \quad (3-1-2)$$

The forces \mathbf{f}_m and \mathbf{f}_M , derivable from the potential $V(r)$, act on m and M , respectively. Now introduce the vector \mathbf{R} , which locates the center of mass of the two particles with respect to the origin of the Lab coordinates:

$$\mathbf{R} = \frac{m\mathbf{R}_m + M\mathbf{R}_M}{m + M} \quad (3-1-3)$$

(cf. Section 1-2). If we differentiate (3-1-3) twice with respect to the time, we obtain

$$\ddot{\mathbf{R}} = \frac{m\ddot{\mathbf{R}}_m + M\ddot{\mathbf{R}}_M}{m + M} = \frac{\mathbf{f}_m + \mathbf{f}_M}{m + M} = 0 \quad (3-1-4)$$

Thus we see that the center of mass travels with a uniform rectilinear velocity.

Now we multiply (3-1-1) by M and (3-1-2) by m and subtract the second from the first. The result is

$$\mathbf{f}_m = M_r \frac{d^2}{dt^2} (\mathbf{R}_m - \mathbf{R}_M) \quad (3-1-5)$$

where M_r is the reduced mass of the pair of particles, defined by the equation

$$M_r = \frac{mM}{m + M} \quad (1-2-6)$$

Since \mathbf{f}_m is in the direction of the vector $\mathbf{r} = \mathbf{R}_m - \mathbf{R}_M$, (3-1-5) for the relative motion has the same form as the equation of motion of a single particle of mass M_r in a central force field.

3-2. REDUCTION TO A TWO-BODY PROBLEM IN TWO DIMENSIONS

Let us now take the cross product of the vector $(\mathbf{R}_m - \mathbf{R}_M)$ with both sides of (3-1-5). The left side will vanish because of the central force assumption. Therefore

$$(\mathbf{R}_m - \mathbf{R}_M) \times \frac{d^2}{dt^2} (\mathbf{R}_m - \mathbf{R}_M) = 0$$

or

$$\frac{d}{dt} \left[(\mathbf{R}_m - \mathbf{R}_M) \times \frac{d}{dt} (\mathbf{R}_m - \mathbf{R}_M) \right] - \left[\frac{d}{dt} (\mathbf{R}_m - \mathbf{R}_M) \times \frac{d}{dt} (\mathbf{R}_m - \mathbf{R}_M) \right] = 0$$

The second term on the left side of this equation obviously equals zero. If we integrate the first term with respect to the time, we obtain

$$(\mathbf{R}_m - \mathbf{R}_M) \times \frac{d}{dt} (\mathbf{R}_m - \mathbf{R}_M) = (\mathbf{R}_m - \mathbf{R}_M) \times (\mathbf{v}_m - \mathbf{v}_M) = \mathbf{r} \times \mathbf{v}_r = \mathbf{K} \quad (3-2-1)$$

where \mathbf{v}_m and \mathbf{v}_M are the velocities of m and M , respectively, in the Lab system, \mathbf{v}_r is their relative velocity,* and \mathbf{r} is the directed distance from M

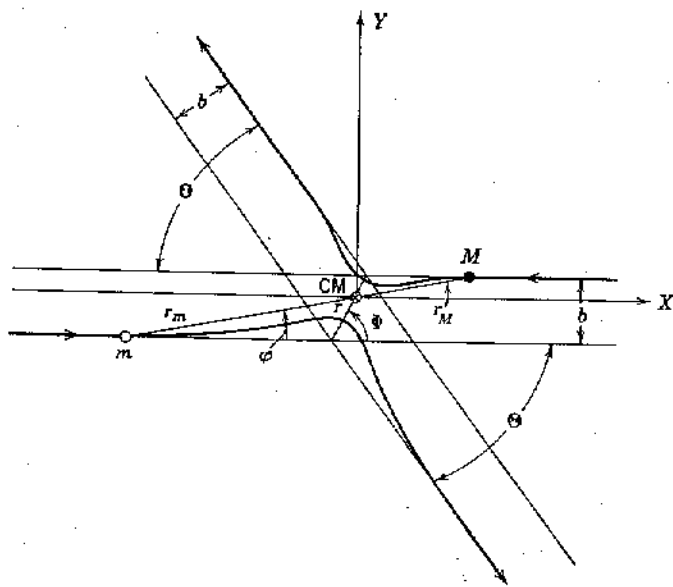


FIG. 3-2-1. The mutual elastic scattering of particles m and M as viewed in the center-of-mass system, in which the motion is two-dimensional. The motion pictured here occurs in the plane of the paper, which is perpendicular to the vectors \mathbf{K} and \mathbf{J} . An interaction potential consisting of an attractive component and a shorter range repulsion is assumed.

to m ; \mathbf{K} is a vector whose magnitude and direction are constant in time. Evidently \mathbf{K} is perpendicular to the plane defined by \mathbf{r} and \mathbf{v}_r . The two particles and their center of mass thus remain in a plane perpendicular to

* The relative velocity of the collision partners at any arbitrary time is denoted by \mathbf{v}_r ; \mathbf{v}_0 has been used to represent their relative velocity of approach at large r before their interaction becomes appreciable.

the vector \mathbf{K} throughout the collision. Since the collision takes place in a fixed plane containing the center of mass and the motion of the center of mass is known to be uniform, only a two-dimensional problem remains to be considered.

Figure 3-2-1 shows the collision in the plane perpendicular to \mathbf{K} . The impact parameter is b , and φ is the angle specifying the instantaneous orientation of the vector \mathbf{r} . The particles are separated by a distance r , and r_m and r_M , the distances of m and M , respectively, from the center of mass, are in the ratio M/m . The value Φ is assumed by φ at the distance of closest approach, and Θ is the angle of scattering in the CM system. The CM trajectories of both m and M are symmetrical about the line of closest approach (the "line of apses") at the angle Φ . Proof of this statement is deferred until Section 3-5.

Let us now calculate the total kinetic energy of the particles T_{CM} in the center-of-mass system. Establish a rectangular Cartesian coordinate system X, Y, Z whose origin moves with the center of mass and whose Z axis points in the direction of the vector \mathbf{K} . The X axis corresponds to $\varphi = 0$. It is evident that

$$T_{CM} = \frac{1}{2}m(\dot{x}_m^2 + \dot{y}_m^2) + \frac{1}{2}M(\dot{x}_M^2 + \dot{y}_M^2) \quad (3-2-2)$$

The rectangular and polar coordinates are related by the equations

$$x_m = -\frac{M}{m+M}r \cos \varphi \quad (3-2-3)$$

$$y_m = -\frac{M}{m+M}r \sin \varphi \quad (3-2-4)$$

$$x_M = \frac{m}{m+M}r \cos \varphi \quad (3-2-5)$$

$$y_M = \frac{m}{m+M}r \sin \varphi \quad (3-2-6)$$

By substituting these relationships into (3-2-2), we may express the kinetic energy in the CM system as

$$T_{CM} = \frac{1}{2}M_r(\dot{r}^2 + r^2\dot{\varphi}^2) \quad (3-2-7)$$

The angular momentum of the pair of particles about the center of mass is

$$\mathbf{J}_{CM} = (\mathbf{r}_m \times \mathbf{p}_m) + (\mathbf{r}_M \times \mathbf{p}_M) \quad (3-2-8)$$

where \mathbf{p}_m and \mathbf{p}_M are the linear momenta of m and M , respectively, in the CM system. The component of \mathbf{p}_m which is perpendicular to \mathbf{r}_m is $m r_m \dot{\varphi}$, and a similar expression applies for M . Consequently,

$$J_{CM} = r_m m r_m \dot{\varphi} + r_M M r_M \dot{\varphi} = M_r r^2 \dot{\varphi} \quad (3-2-9)$$

Now the quantity $r \times v$, was shown in (3-2-1) to be a constant. The magnitude of this quantity equals $r(r\dot{\varphi}) = r^2\dot{\varphi}$, and the angular momentum is seen to be a constant of the motion, as is the total energy.

Let v_0 be the initial relative velocity of the particles, that is, the relative velocity outside the region in which the interaction becomes appreciable.

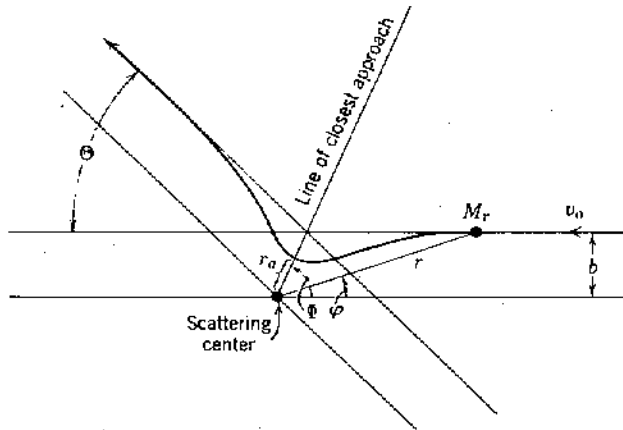


FIG. 3-2-2. The one-body problem which is dynamically equivalent to the two-body problem illustrated in Fig. 3-2-1. The center-of-mass motion of two particles m and M interacting through a potential $V(r)$ can be obtained as follows: a single hypothetical particle of mass $M_r = mM/(m+M)$ is considered to be scattered by a center of force fixed in the CM frame. The potential describing this force field is $V(r)$, where r is the separation distance between m and M . The CM velocity of M_r is considered to be equal to v_0 , where v_0 is the initial relative velocity of m and M . The hypothetical particle M_r is moving toward the stationary scattering center with impact parameter b . The instantaneous distance of M_r from the scattering center is r , and M_r is scattered through an angle Θ , whose value can be calculated by (3-4-5). This angle is also the scattering angle of both m and M in the CM frame.

At some time before the collision occurs the angle $\varphi \rightarrow b/r$ and $\dot{\varphi} \rightarrow -b\dot{r}/r^2$. Then (3-2-7) and (3-2-9) show that the initial kinetic energy is $M_r v_0^2/2$ and the angular momentum is $M_r b v_0$ (cf. Section 1-2). Utilizing the constancy of the total energy and angular momentum of the system, we may then write, for any point along the trajectory,

$$\frac{1}{2} M_r v_0^2 = \frac{1}{2} M_r (\dot{r}^2 + r^2 \dot{\varphi}^2) + V(r) \quad (3-2-10)$$

$$J = M_r b v_0 = M_r r^2 \dot{\varphi} \quad (3-2-11)$$

Equations 3-2-10 and 3-2-11, which are the equations of motion in the CM system, furnish a complete description of the motion in terms of the interaction potential, the initial relative velocity, and the impact parameter.

If we are given the potential, a particular trajectory may be specified by assigning values to the parameters v_0 and b or, alternatively, to the constants of motion (i.e., the total energy and the angular momentum).

Figure 3-2-2 describes the one-body problem which is dynamically equivalent to the two-body problem under discussion (cf. Equation 3-1-5). We have already shown that the equivalent single-body motion is planar and can be drawn in two dimensions. The quantities b , r , φ , Φ , and Θ are given so that their significance in the one- and two-body problems may be compared.

3-3. REDUCTION TO THE EQUIVALENT ONE-BODY PROBLEM IN ONE DIMENSION

A further conceptual reduction of the problem is possible. If we substitute the value of $\dot{\varphi}$ from (3-2-11) into (3-2-10), we may write the following expression for r as a function of time:

$$\frac{1}{2} M_r v_0^2 = \frac{1}{2} M_r \dot{r}^2 + V_{\text{eff}}(r) \quad (3-3-1)$$

where $V_{\text{eff}}(r)$ is the "effective potential" defined by

$$V_{\text{eff}}(r) = V(r) + \frac{M_r v_0^2 b^2}{2r^2} \quad (3-3-2)$$

Equation 3-3-1 contains no terms in φ . It can be regarded as describing the one-dimensional motion (along the r axis) of a particle of mass M_r with total energy $M_r v_0^2/2$ in an effective potential field described by $V_{\text{eff}}(r)$. The second term on the right in the expression for $V_{\text{eff}}(r)$ is equal to $J^2/2M_r r^2$ and represents the rotational kinetic energy of the system. Note that this term is a positive monotonic decreasing function of r . It can therefore be considered the source of a fictitious outwardly directed force, the "centrifugal force," and for this reason the second term on the right side of (3-3-2) is termed the "centrifugal potential." We use the symbol V_c to denote this quantity.

3-4. THE SCATTERING ANGLE IN THE CENTER-OF-MASS SYSTEM

Perhaps the most important feature of an elastic collision, from our point of view, is the angle of scattering in the center-of-mass system (see Fig. 3-2-1.) Since the CM trajectories are symmetrical about the line of closest approach, the scattering angle Θ is related to the angle Φ by the equation

$$\Theta = \pi - 2\Phi \quad (3-4-1)$$

The value, Φ , of the orientation angle φ , corresponding to the distance of closest approach, is easily calculated: dr/dt is given by (3-3-1) and $d\varphi/dt$ by (3-2-11). Hence

$$\frac{dr}{d\varphi} = \frac{dr/dt}{d\varphi/dt} = \pm \frac{r^2}{b} \left[1 - \frac{V(r)}{M_r v_0^2/2} - \frac{b^2}{r^2} \right]^{1/2} \quad (3-4-2)$$

The negative sign applies for the incoming branch of the trajectory and the positive sign for the outgoing branch. At the angle of closest approach Φ we have

$$1 - \frac{V(r_a)}{M_r v_0^2/2} - \frac{b^2}{r_a^2} = 0 \quad (3-4-3)$$

The largest real root of this equation is the distance of closest approach r_a .

We should note that a real solution of (3-4-3) does not always exist. If we assume an attractive potential of the form $V(r) \sim -r^{-n}$ and further assume $n \geq 2$, there are values of the initial velocity and impact parameter for which no solution exists (see Section 3-6). The particle spirals inward until it is stopped by some repulsive force and then spirals back out. A solution always exists for a repulsive potential, however.

If a solution exists

$$\Phi = - \int_{\infty}^{r_a} \frac{d\varphi}{dr} dr = - \int_{\infty}^{r_a} \frac{(b/r^2) dr}{\left[1 - \frac{V(r)}{M_r v_0^2/2} - \frac{b^2}{r^2} \right]^{1/2}} \quad (3-4-4)$$

Equation 3-4-4 then shows Θ to be

$$\Theta(v_0, b) = \pi - 2b \int_{r_a}^{\infty} \frac{dr/r^2}{\left[1 - \frac{V(r)}{M_r v_0^2/2} - \frac{b^2}{r^2} \right]^{1/2}} \quad (3-4-5)$$

Equation 3-4-5 is of particular importance to us, since the angle of scattering is the only aspect of an elastic collision that enters into the formulas for the transport coefficients.¹ The foregoing integral has been evaluated for several potentials used to describe neutral nonpolar gases, and the results applied to the calculation of transport properties, by Hirschfelder, Curtiss and Bird.²

The solution of 3-4-5 for integrable power-law potentials is treated by Whittaker³ and Goldstein,⁴ among others. If the potential is assumed to be of the form $V(r) \sim \pm r^{-n}$, a solution in terms of circular functions is obtainable for $n = +2, +1$, and -2 . The integral exponents $n = -6, -4, -1, +3, +4$, and $+6$ lead to solutions in terms of elliptic integrals. The fractional exponents $n = +\frac{1}{2}, +\frac{3}{2}, -\frac{3}{2}, +\frac{5}{2}$, and $+\frac{7}{2}$ also lead to elliptic functions.

3-5. THE SYMMETRY OF THE TRAJECTORIES IN THE CENTER-OF-MASS SYSTEM

Having obtained the differential equation of the orbit in the CM system, we may now show that the trajectory of each of the particles is symmetrical about the line of closest approach, for which $\varphi = \Phi$. To do this, let us square both sides of (3-4-2) and make the substitution $\varphi = \alpha + \Phi$. The introduction of the angle α is equivalent to counter-clockwise rotation of our polar coordinate system about the Z axis through the angle Φ , so that the line of closest approach now corresponds to $\alpha = 0$. The resulting equation is

$$\left(\frac{dr}{d\alpha} \right)^2 = \frac{r^4}{b^2} \left[1 - \frac{V(r)}{M_r v_0^2/2} - \frac{b^2}{r^2} \right] \quad (3-5-1)$$

The trajectory of each particle will be symmetrical about the line of closest approach if reflection about this line produces no change. Mathematically, this reflection is accomplished by substitution of $-\alpha$ for α . Equation 3-5-1 is obviously invariant under this substitution.

3-6. CLASSIFICATION OF THE ORBITS; ION-MOLECULE REACTIONS

A. PHYSICAL BASIS. In Section 3-4 it was stated that a solution of (3-4-3) always exists for a repulsive potential, but not always for an attractive potential of the form $V(r) \sim -r^{-n}$, if $n \geq 2$. This statement is easily understood in terms of the effective one-dimensional motion and the centrifugal potential.

First let us consider motion in a typical repulsive potential field such as that described by the potential function $V(r)$ in Fig. 3-6-1. It has already been pointed out that if we wish to analyze the scattering problem in the single dimension r we must add to the real potential, $V(r)$, a fictitious centrifugal potential, $V_c(r)$, given in terms of the angular momentum, J , of the system by the equation

$$V_c(r) = \frac{J^2}{2M_r r^2} \quad (3-6-1)$$

This potential is plotted in Fig. 3-6-1 for some arbitrary but nonzero value of J . The total effective potential, $V_{\text{eff}}(r) = V(r) + V_c(r)$, is also shown in the figure. It is apparent that in this case the only significant effect of the centrifugal potential will be to supplement the real potential. If $V(r)$ decreases monotonically with increasing r , the effective potential will likewise, regardless of the value of the angular momentum. Hence in this one-dimensional formulation of the scattering problem a particle of total

energy E will approach the scattering center and be reflected at the distance of closest approach, r_a , given by the intersection of the horizontal line at height E and the curve $V_{\text{eff}}(r)$. The radial velocity \dot{r} at any point is given by the equation

$$E = \frac{1}{2}M\dot{r}^2 + V_{\text{eff}}(r) \quad (3-6-2)$$

whereas the angular motion must, of course, be such that the angular momentum is conserved throughout the scattering.

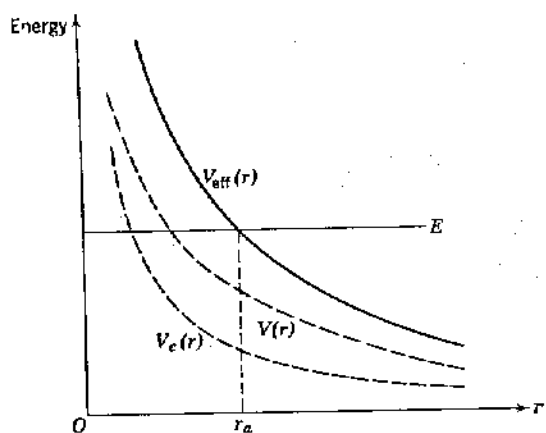


FIG. 3-6-1. The potential functions used for analysis of elastic scattering in a typical repulsive potential field.

The shape of the effective potential curve is quite different if an attractive potential is assumed. However, if $V(r) \sim -r^{-n}$ with $n < 2$, the effective potential again decreases monotonically with increasing r , at sufficiently small r , and the one-dimensional motion is similar to that in the repulsive case in regard to reflection along the r axis at some finite distance of closest approach. (This situation is illustrated in Fig. 3-6-2, in which an attractive inverse-first-power potential is assumed.) Stable orbits* are possible only for $n < 2$, and for values of E lying in the well.

If, on the other hand, the attractive potential falls off with increasing r faster than r^{-2} , the attractive potential must dominate the centrifugal potential at small r , and an effective potential of the form shown in Fig. 3-6-3 results.† (An inverse-third-power attractive potential is assumed in this illustration.) Let us consider the motion for several different values of

* A particle is said to be in a *stable orbit* if the application of a small perturbation produces a small bounded excursion from the original orbit.

† The limiting case in which $n = 2$ must be treated separately. Here the shape of $V_{\text{eff}}(r)$ is determined by the relative magnitudes of J and the coefficient of r^{-3} in the expression for $V(r)$.

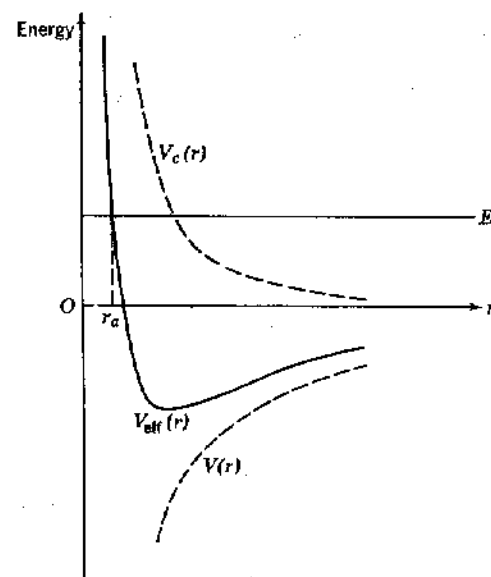


FIG. 3-6-2. The potential functions used for analysis of elastic scattering in an attractive inverse-first-power potential field.

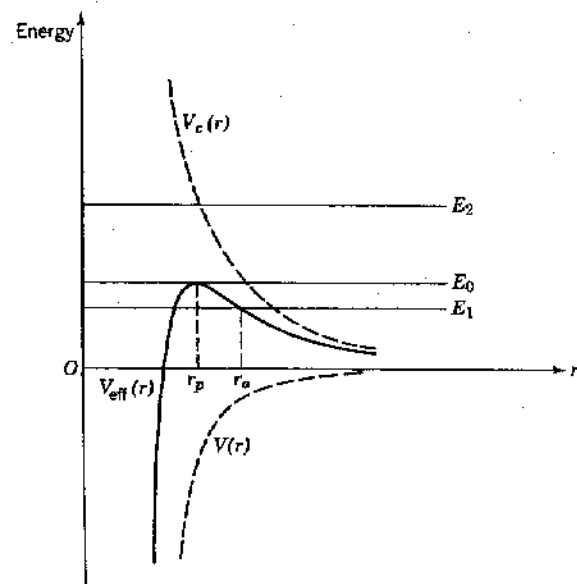


FIG. 3-6-3. The potential functions used for analysis of elastic scattering in an attractive inverse-third-power potential field.

the total energy. A particle of energy $E_1 < E_0$ starting at large r and moving toward the center of attraction will evidently be reflected at $r = r_a$ by the potential barrier shown. If, however, the total energy is $E_2 > E_0$, the particle will be able to pass over the potential barrier. It will experience a repulsion only for $r > r_p$ and will sense an attraction thereafter, as its radial distance from the scattering center decreases. When $E > E_0$, the particle actually passes through the center of attraction, which is assumed

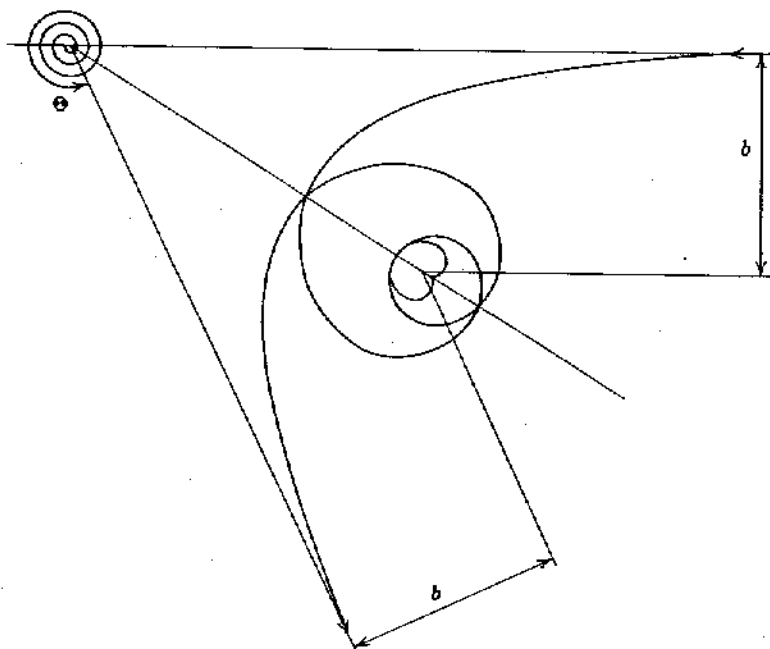


FIG. 3-6-4. An orbiting collision for which the scattering angle Θ has a large value.

to be a mathematical point in the model under consideration here.⁶ A particularly interesting situation develops when the total energy just exceeds E_0 , the value of $V_{\text{eff}}(r)$ at the peak of the potential curve. In this case the particle will spend a considerable time at a radial distance near the peak, where r is small by assumption, while spiraling inward toward the center. The particle is then said to "orbit" about the scattering center.* The angular motion speeds up as r decreases in order to conserve angular

* This type of collision is sometimes referred to as a "sticky collision." As a rule, however, the term *sticky collision* means an impact in which the colliding particles temporarily form a complex structure with an appreciable amount of internal excitation energy. This structure then flies apart after a lifetime which is long compared to usual collision times.

momentum, and a large number of revolutions may be made. (This is an unstable orbit, unlike those for which $n < 2$.) Under certain conditions the scattering angle may approach $-\infty$.⁶ Figure 3-6-4 illustrates an orbiting collision for which Θ has a value between 6π and 7π . In this figure a long-range attractive potential and a short range, hard-core repulsive potential are assumed. A cusp appears in the trajectory when the particle is reflected from the hard core.

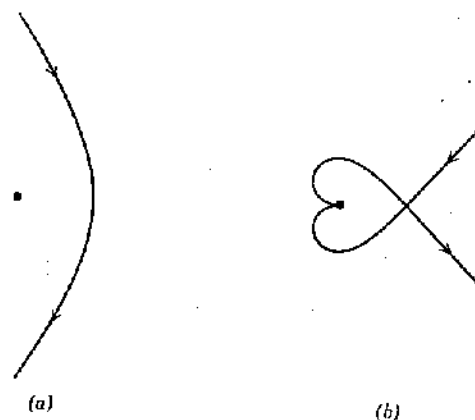


FIG. 3-6-5. Types of orbit of a particle moving in the attractive inverse-fourth-power polarization potential field:¹² (a) large angular momentum, nonspiraling orbit; (b) small angular momentum, spiraling orbit.

We see that the orbits may thus be meaningfully classified as *spiraling* or *nonspiraling*, and this distinction is frequently encountered in the literature. We shall illustrate the classification of orbits by discussing the important case of the attractive inverse-fourth-power polarization potential. The original treatment of this case by Langevin is reproduced in detail in Appendix II. The Lennard-Jones (6-12) potential has been treated similarly by Hirschfelder, Bird, and Spotz,⁷ and the Buckingham (6-exp) potential, by Mason.⁸

B. CLASSIFICATION OF THE ORBITS IN THE POLARIZATION POTENTIAL FIELD. The inverse-fourth-power polarization potential has the form

$$V(r) = -\frac{\alpha e^2}{2r^4} \quad (3-6-3)$$

where e is the ionic charge and α is the electric polarizability of the molecule. Two types of orbit are possible in this potential field. The orbits corresponding to large angular momentum resemble hyperbolas (Fig. 3-6-5a), whereas for small angular momentum an inward spiraling motion takes place until some repulsive force reverses the trend (Fig. 3-6-5b).

The scattering angle for the polarization potential may be expressed as

$$\Theta = \pi - 2\Phi = \pi - 2 \int_0^{\rho_0} \frac{d\rho}{\sqrt{1 - \rho^2 + e^2 \alpha \rho^4 / M_r v_0^2 b^4}} \quad (3-6-4)$$

in which $\rho = b/r$ and ρ_0 is the lower of the two positive roots of the polynomial in the denominator if such roots exist. If this polynomial has no real root, the integration goes from 0 to ∞ . The existence of a real root is related to the nature of the orbit. If b is large enough for given v_0 , a root exists, and an orbit of the type shown in Fig. 3-6-5a will result. For b less than a certain critical value b_0 , no root exists, and the orbit is of the type presented in Fig. 3-6-5b. For b_0 , the limiting value of b , the particles spiral into a circular orbit; b_0 is found by setting the discriminant of the square root in (3-6-4) equal to zero:

$$b_0 = \left(\frac{4e^2 \alpha}{M_r v_0^2} \right)^{1/4} \quad (3-6-5)$$

Orbits for which $b < b_0$ pass through the origin if no repulsive core is present, whereas those orbits for which $b \geq b_0$ come no closer than $r_0 = b_0/\sqrt{2}$.* Several orbits of each type are accurately plotted in Fig. 3-6-6, which is a modified version of a drawing prepared by Langevin.⁹ In this figure only the incoming branch of each spiraling trajectory is shown, the subsequent portion being omitted for clarity. The complete drawing appears in Fig. 4 of Appendix II.

Now let us suppose that there exists a certain critical radius r_c such that a given type of reaction between the two particles under consideration is impossible if the distance of closest approach is greater than r_c and almost certain to occur if it is less than r_c . Then, if r_c lies between 0 and $b_0/\sqrt{2}$, all collisions for which $b < b_0$ must lead to this reaction. We may therefore assume that the cross section for the reaction is the same as the *cross section for orbiting collisions*, namely

$$q_0(v_0) = \pi b_0^2 = \frac{2\pi}{v_0} \left(\frac{e^2 \alpha}{M_r} \right)^{1/2} \quad (3-6-6)$$

This type of analysis has been used by Gioumousis and Stevenson,⁹ and others, in calculating the rates of ion-molecule reactions.† Since b_0 for the polarization potential varies inversely as the square root of v_0 , there must be some collisions at the higher velocities for which it is not true that $r_c < b_0/\sqrt{2}$. Thus this model is not realistic when applied to the calculation of the reaction cross section at high energies—it predicts that this

* For a short proof of this statement see K. Yang and T. Ree, *J. Chem. Phys.* **35**, 588 (1961).

† For further discussion of such reactions see Sections 6-3, 9-6, and 9-9.

cross section should fall to zero, whereas it should actually drop to πr_c^2 . We may easily derive an alternative expression for the reaction cross section which is valid at high energies and holds for attractive or repulsive potentials of arbitrary form. Our starting point is the orbit equation (3-4-2). At the distance of closest approach r_c we have $dr/d\varphi = 0$. Thus

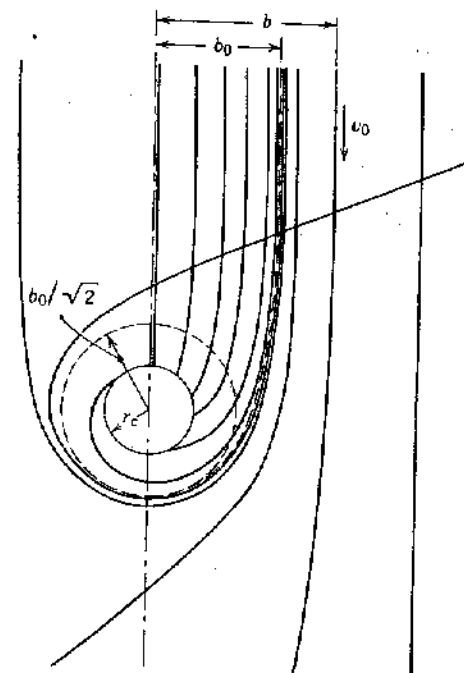


FIG. 3-6-6. Representative trajectories for the inverse-fourth-power polarization potential as a function of the impact parameter b for a given relative velocity v_0 . For clarity only the incoming branch of each spiraling trajectory is shown.

(3-4-3), which is obtained from (3-4-2) by setting $dr/d\varphi = 0$, gives a relationship between the impact parameter and the distance of closest approach if we assume that the potential function and initial velocity are specified. Now let us suppose that an ion-molecule reaction is inevitable if r decreases to a value as small as r_c . The critical impact parameter b_0 , which corresponds to the trajectory for which $dr/d\varphi = 0$ at $r = r_c$, is obtained by replacing r_a by r_c and b by b_0 in (3-4-3). Thus

$$1 - \frac{V(r_c)}{M_r v_0^2 / 2} - \frac{b_0^2}{r_c^2} = 0 \quad (3-6-7)$$

The reaction cross section is then equal to πb_0^2 , as is apparent from Fig. 3-6-7, and we obtain

$$q_r(v_0) = \pi r_c^2 \left[1 - \frac{V(r_c)}{M_r v_0^2 / 2} \right] \quad (3-6-8)$$

We now have the cross section for the reaction in terms of only one parameter, $V(r_c)$, if $V(r)$ is known. Equation 3-6-8 applies at all energies

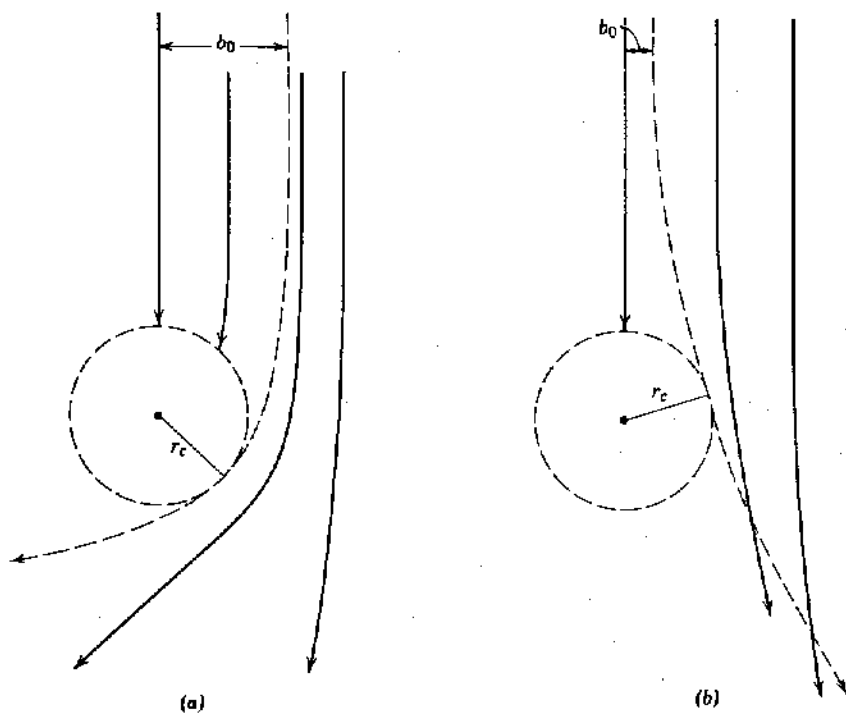


FIG. 3-6-7. (a) Attractive potential; (b) repulsive potential. Trajectories for typical attractive and repulsive potentials corresponding to a given relative velocity of approach and various impact parameters. The interparticle separation distance decreases to a value less than the critical value r_c for any trajectory whose impact parameter is less than b_0 . Each of these trajectories is assumed to lead to an ion-molecule reaction so that the reaction cross section is equal to πb_0^2 .

for attractive potentials which cannot produce orbiting and predicts a monotonic decrease from a high value at low energy toward a limiting value of πr_c^2 at high energies. For an attractive potential which can lead to orbiting, (3-6-8) is valid only at high energies. Equation 3-6-6 should be used for the polarization potential at low energies. Equation 3-6-8 applies in repulsive potentials only to energies above a certain threshold

value, which is equal to the potential energy evaluated at the radius r_c . For repulsive potentials there is a hyperbolic increase in the reaction cross section from zero at the threshold toward a limiting value of πr_c^2 at high energies. This model was developed by Present¹⁰ and has been applied by him and by Mason and Vanderslice¹¹ to the solution of specific problems.

The cross section expressed by (3-6-6) is a good approximation to the diffusion cross section for the polarization potential, the accurate value of which is given in (9-3-13). The reason¹² for this is that the final directions of the spiraling orbits are very nearly random (see Fig. 4, Appendix II), whereas the deflections associated with the nonspiraling orbits are so small that they make a negligible contribution to an integral of the type

$$q_D = \int (1 - \cos \Theta) I_s(\Theta) d\Omega_{CM} \quad (1-6-1)$$

Vogt and Wannier¹³ have also shown that the quantum mechanical description of the polarization potential is in many respects similar to the classical description.

3-7. EVALUATION OF THE SCATTERING CROSS SECTION

Let us now calculate the differential cross section $I_s(\Theta) d\Omega_{CM}$ for scattering into the element $d\Theta$ between the angles Θ and $\Theta + d\Theta$. The necessary and sufficient condition for scattering particles of initial relative velocity v_0 into the element of solid angle $d\Omega_{CM} = 2\pi \sin \Theta d\Theta$ is that the particles be incident in the annular impact ring of area $2\pi b db$ formed by circles of radius b and $b + db$, where b is related to Θ by (3-4-5). Hence

$$|2\pi b db| = |I_s(\Theta) 2\pi \sin \Theta d\Theta| \quad (3-7-1)$$

or

$$I_s(\Theta) d\Omega_{CM} = \left| \frac{b}{\sin \Theta} \frac{db}{d\Theta} \right| d\Omega_{CM} \quad (3-7-2)$$

The differential cross section in the laboratory system, $I_s(\theta) d\Omega_{Lab}$, is given in terms of $I_s(\Theta) d\Omega_{CM}$ by (1-4-16), and the total scattering cross section is obtained by integrating the differential cross section over the complete solid angle:

$$q_s = \int_0^{2\pi} \int_0^\pi I_s(\Theta) d\Omega_{CM} = \int_0^{2\pi} \int_0^\pi I_s(\theta) d\Omega_{Lab} \quad (3-7-3)$$

These integrals diverge for potentials of infinite range, such as $V(r) \sim \pm r^{-n}$, because of a pole in the differential cross section in the forward direction, $\Theta = 0$. For potentials of this type, some deflection of the interacting

particles occurs, no matter how large the impact parameter may be. Thus the effective cross sectional area of the particles appears to be infinite. This paradox is resolved in Section 3-11 by quantum mechanical considerations.

It can be seen from (3-7-2) that $I_s(\Theta)$ will become infinite if $\Theta = n\pi$ ($n = 0, 1, 2, \dots$) for $b \neq 0$ because of the $\sin \Theta$ term in the denominator; it will also become infinite if $d\Theta/db = 0$. Both are possible for potentials that are attractive at large distances and repulsive at small distances.* Both classical scattering phenomena have optical analogues which become apparent in the quantum theory of scattering when the wave nature of the particles is explicitly introduced. The first effect is called a "glory" and the second, a "rainbow." For molecules and ions the forward and backward glories are lost in the unscattered beam, but the rainbow is observable under certain conditions (see Section 4-7-B).

3-8. COULOMB SCATTERING†

We now illustrate the use of the techniques developed above by deriving the differential cross section for *Coulomb scattering*. The potential that applies here is

$$V(r) = \frac{Zze^2}{r} \quad (3-8-1)$$

It expresses the electrostatic interaction between particles of charge Ze and ze , separated by a distance r . Either charge may be positive or negative.

Again we introduce the variable $\rho = b/r$ and define a quantity α by the equation

$$\frac{V}{M_r v_0^2/2} = \alpha\rho \quad (3-8-2)$$

so that

$$\alpha = \frac{2Zze^2}{M_r v_0^2 b} \quad (3-8-3)$$

Equation 3-4-5 then becomes

$$\Theta = \pi - 2 \int_0^{\rho_0} \frac{d\rho}{\sqrt{1 - \alpha\rho - \rho^2}} \quad (3-8-4)$$

where ρ_0 is one of the roots of the equation

$$\rho^2 + \alpha\rho - 1 = 0 \quad (3-8-5)$$

* See W. L. Fite and S. Datz, "Chemical Research with Molecular Beams," *Ann. Rev. Phys. Chem.* 14 (1963), Annual Reviews, Inc., Palo Alto, Cal.

† As the reader is doubtless aware, scattering by a Coulomb field is usually referred to as *Rutherford scattering* in nuclear physics. A clear and comprehensive treatment of Rutherford scattering appears in R. D. Evans, *The Atomic Nucleus*, McGraw-Hill, New York, 1955, Appendix B.

The two roots of (3-8-5) are

$$\rho = -\frac{\alpha}{2} \pm \left(\frac{\alpha^2}{4} + 1\right)^{1/2} \quad (3-8-6)$$

and since $\rho = b/r$ it is evident that the solution containing the positive square root must be chosen.

Integrating (3-8-4), we obtain

$$\Theta = \pi - 2 \cos^{-1} \frac{\alpha}{\sqrt{\alpha^2 + 4}} \quad (3-8-7)$$

so that

$$\frac{\alpha}{\sqrt{\alpha^2 + 4}} = \cos \left(\frac{\pi - \Theta}{2} \right) = \sin \frac{\Theta}{2}$$

Thus

$$\alpha = 2 \tan \frac{\Theta}{2} = \frac{2Zze^2}{M_r v_0^2 b}$$

and

$$b = \frac{Zze^2}{M_r v_0^2 \tan(\Theta/2)} \quad (3-8-8)$$

The use of (3-7-2) then gives

$$I_s(\Theta) d\Omega_{CM} = \left| \frac{b}{\sin \Theta} \frac{db}{d\Theta} \right| d\Omega_{CM} = \frac{Z^2 z^2 e^4}{4M_r^2 v_0^4 \sin^4(\Theta/2)} d\Omega_{CM} \quad (3-8-9)$$

which is the desired result. It is interesting to note that precisely the same expression is obtained in the quantum mechanical treatment of Coulomb scattering (cf. Section 3-17). By dimensional analysis it can be shown¹⁴ that if the interaction potential varies as $1/r^n$ the total scattering cross section varies as h^{2-2n} , where h is Planck's constant. Only for an inverse-first-power scattering potential does the cross section have no dependence on h , and therefore only in this case can the quantal description agree exactly with the classical description.

Because of the $\sin^4(\Theta/2)$ term in the denominator, the differential cross section expressed in (3-8-9) leads to infinite values for both the total scattering and momentum transfer cross sections. The physical basis for the divergence of the integrals expressing these quantities is the infinite range of the Coulomb potential. This difficulty is circumvented in calculations of the properties of plasmas by the use of a "shielded" Coulomb potential, a stratagem that is not only mathematically essential but also physically realistic. This matter is discussed further in Section 3-17, in Appendix I, and in all books on plasmas. The shielded Coulomb potential also accurately represents the interaction between atoms colliding at high impact energies (see Section 4-10). The differential, momentum transfer,

and total collision cross sections for scattering of atomic projectiles by a Coulomb potential with exponential screening have been calculated by Everhart and his coworkers.¹⁵

3-9. VARIATION OF THE DIFFERENTIAL SCATTERING CROSS SECTION WITH VELOCITY

It was stated in Section 1-8 that if the interaction potential between two colliding particles varies as $V(r) \sim r^{-n}$ the variation of the center-of-mass differential scattering cross section with velocity is given classically by the expression

$$I_s(\Theta) \sim v_0^{-4/n} \quad (3-9-1)$$

where v_0 is the initial relative velocity of approach.* This statement is easily verified by dimensional considerations.

Our starting point is (3-4-2), which now assumes the form

$$\frac{dr}{d\varphi} = \pm \frac{r^2}{b} \left(1 - \frac{k}{v_0^2 r^n} - \frac{b^2}{r^2} \right)^{1/2} \quad (3-9-2)$$

All of the constants appearing in the middle term under the radical have been lumped into the single constant k . If b , v_0 , and k are specified, the trajectories of the particles are determined. Let us now scale the velocity v_0 by a factor c and then scale the distances b and r appropriately to recover an orbit equation that is formally identical to the original equation (3-9-2). Evidently, if v_0 is scaled to give a new velocity $v_0^* = cv_0$, b and r must be replaced by b^* and r^* , defined by the equations $b^* = c^{-2/n}b$ and $r^* = c^{-2/n}r$. The new orbit equation is then

$$\frac{dr^*}{d\varphi} = \pm \frac{r^{*2}}{b^*} \left(1 - \frac{k}{v_0^{*2} r^{*n}} - \frac{b^{*2}}{r^{*2}} \right)^{1/2} \quad (3-9-3)$$

and is seen to be formally identical to (3-9-2) so that the scattering angle Θ is the same as before. Since (3-7-2) shows that $I_s(\Theta)$ is proportional to b^2 , it follows that

$$I_s(\Theta, cv_0) = c^{-4/n} I_s(\Theta, v_0) \quad (3-9-4)$$

Our proof is thus completed. Other proofs of the same result are given by Present and by Yang and Ree.¹⁶

As pointed out in Section 1-8, (3-9-1) yields the result that with elastic spheres, for which $n = \infty$, the scattering cross section is independent of the velocity. Hence the elastic sphere model is one of constant mean free path.

* The variation with scattering angle is also of interest. For a potential of the form $V(r) \sim r^{-n}$ classical theory predicts that $I_s(\Theta) \sim [\Theta^{1+2/n} \sin \Theta]^{-1}$ for small Θ . See E. H. Kennard, *Kinetic Theory of Gases*, McGraw-Hill, New York, 1938, pp. 119-120.

On the other hand, $n = 4$ for particles interacting through the point charge-induced dipole polarization potential, and here the differential scattering cross section varies inversely with the velocity. The collision frequency, which is proportional to $I_s(\Theta)v_0$, is then independent of v_0 , and we have a constant mean free time situation. According to (3-9-1), the differential cross section is inversely proportional to v_0^4 for Coulomb scattering, in agreement with the result derived in Section 3-8.

As we shall see in Section 3-11, classical theory does not properly describe scattering at small angles in the CM system, and thus (3-9-1) cannot be used to obtain the velocity dependence of the total scattering cross section q_s .* Quantum mechanics must be used for this purpose. Massey and Mohr¹⁷ have obtained an approximate quantal solution for an interaction potential of the form $V(r) = -Cr^{-n}$. Their result, which is derived in Section 4-7, is

$$q_s = B \left(\frac{C}{v_0} \right)^{2/(n-1)} \quad (3-9-5)$$

where B is a known constant.

PART B. THE QUANTUM THEORY OF ELASTIC SCATTERING

We now turn to the quantal view of elastic scattering. As in Part A of this chapter we shall consider only nonrelativistic scattering in a spherically symmetric force field. After suitable preliminary discussion, we shall formulate the problem of elastic scattering in quantum mechanical terms and then develop methods for calculating the cross section for the case in which the collision partners are dissimilar. The mutual scattering of identical particles is then considered. The results of calculations on specific systems are discussed in Chapter 4. The material presented here is based largely on the treatments of the subject by Massey and Burhop, Mott and Massey, Schiff, Burhop, and Massey.¹⁸ Other excellent sources of information are listed in Ref. 19.

3-10. THE INADEQUACY OF THE CLASSICAL TREATMENT OF SCATTERING

We may invoke the Heisenberg uncertainty principle to show how the classical theory fails, in general, to give an accurate description of collision processes. This principle applies to any pair of canonically conjugate

* It does, however, give the correct dependence of the diffusion cross section on v_0 because the small-angle contributions are suppressed by the weighting factor $(1 - \cos \Theta)$ in the integral expressing q_D .