Cross Sections and Rate Constants

Introduction

In order to describe in a quantitative way the phenomena discussed in the previous chapter, we need to be able to calculate or measure the required cross sections or rate constants. To begin the discussion, we divide collisions into two classes: elastic collisions (scattering) during which the particles interact (collide) with each other but only their directions of motion and speeds change, and inelastic collisions in which both the motion and the internal energies of the particles are changed. In Table 2.1 are given examples of inelastic collisions which we will consider in this text. Although inelastic collisions are clearly more interesting, we start by discussing experiments which only determine whether or not a particle was deflected.

Experiments that only reproduce the phenomena discussed in Chapter 1 often do not give much information about which individual atomic or molecular-level events are occurring or which of these play a controlling role. Therefore, experiments are concocted which isolate particular events, in this case collisions between atoms. In lieu of observing a single collision between atoms, beams of presumably identical atoms are made to impinge on a target containing a large number of identical atoms generally, though not necessarily, different from those in the beam. By observing a large number of similar events one can deduce information about individual events, at least in an average or statistical sense. In the following section we obtain an operational definition of cross section based on this type of experiment.

Total Cross Sections

Cross section, as the name implies, is an effective area, a physical size associated with the colliding particles. To measure effective areas associated
Table 2.1. Examples of Important Collision Processes

<table>
<thead>
<tr>
<th>Collision (reaction)</th>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) A + B → A + B</td>
<td>$\sigma_{AB \rightarrow AB}$</td>
<td>$\sigma$, Elastic collision</td>
</tr>
<tr>
<td>(2) A + B → all possible results</td>
<td>$\sigma_{AB}$</td>
<td>$\sigma_T$, Total cross section</td>
</tr>
<tr>
<td>(3) A + B → A + B*</td>
<td>$\sigma_{AB \rightarrow AB^*}$</td>
<td>$\sigma_{Q^*}$, Excitation</td>
</tr>
<tr>
<td>(4) A* + B → A + B</td>
<td>$\sigma_{A^*B \rightarrow AB}$</td>
<td>$\sigma_{I^*}$, De-excitation</td>
</tr>
<tr>
<td>(5) A + B → A + B* + e</td>
<td>$\sigma_{AB \rightarrow AB^*}$</td>
<td>$\sigma_{e^*}$, Ionization</td>
</tr>
<tr>
<td>(6) A* + B → A + B</td>
<td>$\sigma_{A^*B \rightarrow AB}$</td>
<td>$\sigma_{et^*}$, Charge transfer</td>
</tr>
<tr>
<td>(7) A + B* → A* + B</td>
<td>$\sigma_{AB^* \rightarrow A^*B}$</td>
<td>$\sigma_{R^*}$, Excitation transfer</td>
</tr>
<tr>
<td>(8) A + BC → AB + C</td>
<td>$\sigma_{A, BC \rightarrow AB, C}$</td>
<td>$\sigma_{R}$, Rearrangement</td>
</tr>
<tr>
<td>(9) A + B + C → AB + C</td>
<td>$\sigma_{A, B, C \rightarrow AB, C}$</td>
<td>$\sigma_{R}$, Reaction</td>
</tr>
</tbody>
</table>

* The species indicated by A, B, and C can imply a simple atom or ion, or a complex molecular species. The asterisk implies the species is not in the lowest state. It may be in a higher electronic state or, for molecules, a higher rotational or vibrational state. The superscript plus implies the species is ionized.

with a simple collision between two atoms or molecules, or between an electron and a molecule, the experimental setup in Figure 2.1 can be employed. A beam of particles, all assumed to have approximately the same speed and direction of motion, is incident on a target made up of atoms or molecules. The target particles may be in a liquid, gaseous, or solid state, and the speeds of the target particles are assumed negligible compared to the incident particle speeds; that is, the temperature of the target is kept low. In traversing the target we allow, for the present discussion, two possible results: (a) particles pass through the target with their directions and speeds essentially unchanged; (b) particles are deflected and slowed (scat-

![Figure 2.1](image)

**Figure 2.1.** Beam experiment to obtain total scattering cross section.
tered) or stopped in the target. Internal energy changes, if they occur, are ignored. Clearly, if the target is very “thick,” i.e., dense or long or both, the likelihood of case (b) occurring for any incident particle increases. It may appear remarkable at first that even for the thinnest targets a beam particle can pass through an apparently solid material of atoms with negligible deflection. However, before Rutherford’s experiments, in which he irradiated a gold target with a beam of α-particles (He⁺⁺), it was thought that few, if any, particles would be deflected significantly, and the effect of the material would be to slow the particles.

Employing the experimental setup in Figure 2.1, we obtain the attenuation of the beam of unscattered particles by measuring the transmitted beam intensity, \( I \), at the detector as a function of target thickness, \( X \).

* The intensity or flow is the rate at which particles strike the detector divided by the detector area. If the target thickness is increased from \( X \) to \( X + \Delta X \), the change in beam intensity at the detector, \( \Delta I \), is proportional to the change in thickness, \( \Delta X \), the intensity, \( I(X) \), of particles entering \( \Delta X \), and the density of atomic targets in the target material, \( n_B \). That is,

\[
\Delta I = -\sigma_{AB} n_B I(X) \Delta X
\]

(2.1)

where the proportionality constant, \( \sigma_{AB} \), inserted into Eq. (2.1) has the dimensions of area and is referred to as the total collision cross section for A and B.† In the limit of small \( \Delta X \), the above equation has the solution

\[
I(X) = I(0) \exp \left[ -\sigma_{AB} n_B X \right]
\]

(2.2)

Using Eq. (2.2), the cross section can be determined by plotting the measured intensity as a function of \((n_B X)\) on semilog paper and noting the slope at low values of \((n_B X)\).† The quantity \( \sigma_{AB} \) is a measure of the ability of the target particles, B, to deflect the beam particles, A. That is, if \( \sigma_{AB} \) is large, the particles are deflected easily and appear large to each other; the opposite is true if \( \sigma_{AB} \) is small. As the quantity \((n_B X)^{-1}\) is the average cross-sectional area of the target material occupied by each target atom looking in the direction of the beam, then \((\sigma_{AB} n_B X)\) in Eq. (2.2) is the probability of a deflection by any atom.

As atoms and molecules are not hard spheres with well-defined boundaries, one of the first results revealed by measurements like those described above is that \( \sigma_{AB} \) depends on the relative speeds of approach of the incident and target particles, as is seen in Figure 2.2. This also indicates the size of the cross sections that will be considered \((\sim 10^{-16} - 10^{-15}\text{cm}^2)\). Because

* For gaseous targets the gas density instead of \( X \) may be varied.
† In the experiment described care must be taken to discriminate against particles which have been scattered a number of times and end up moving in the incident-beam direction by keeping the target thin or by also measuring final velocities.
Figure 2.2. Cross section, $\sigma_{AB}$, vs incident particle energy: (a) $e + H$: circles and solid lines—experiment; dashed lines—calculations [from R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo Phys Rev. 124, 135 (1961)]; (b) He + He: detector apertures: A, 0.57°; B, 0.26°; C, 0.11°; D, 0.056° [from W. J. Savola, Jr., F. J. Eriksen, and E. Pollack, Phys. Rev A 7, 932 (1973)]. For units see Appendix J.

the detector has finite width, as does the beam, it cannot distinguish between particles which are unscattered or particles which are deflected only slightly. In fact, since atoms have diffuse boundaries, the distinction may be meaningless if the angle in question is very small, a point we will return to in Chapter 5. Therefore, the measured cross sections $\sigma_{AB}$ are often labeled by the effective angular aperture (opening) of the detector, shown in Figure 2.1, particularly in heavy particle collisions, viz., Figure 2.2.
Instead of cross section one often discusses, especially in thermodynamics, the mean free path, $\bar{\lambda}$, of the atoms traversing the material. This is the quantity

$$\bar{\lambda}^{-1} = n_B \sigma_{AB}$$  \hspace{1cm} (2.3)

occurring in the exponent of Eq. (2.2). The mean free path $\bar{\lambda}$ indicates the average distance atoms A travel before colliding with a target atom; or $\bar{\lambda}^{-1}$ is the probability of a collision per unit path length traveled. A target is considered thin, as stated above, if its thickness, $X$, is much less than $\bar{\lambda}$. A closely related quantity is the total collision frequency

$$v \equiv v\bar{\lambda}^{-1}$$  \hspace{1cm} (2.4)

where $v$, the relative collision velocity, equals the velocity of incident atoms A ($v_A$ in these experiments).

In defining the cross section, via the experiment in Figure 2.1, we have also shown that the intensity of a beam of radiant energy incident on a material (atmosphere, reactor wall, etc.) decreases exponentially with depth and/or number density. If cross sections have been measured in the laboratory, then Eq. (2.2) can be used to estimate the amount of radiant energy transmitted through a material of given thickness. Equation (2.1) is simply an extension of Eq. (1.2) to the case of perpendicular incidence and in which only loss of incident particles is considered.

Inelastic Cross Sections

Attenuation measurements of the undeflected and unchanged particles, like those described above, will lead to a determination of $\sigma_{AB}$, where $\sigma_{AB}$ accounts for all scatterings, with and without internal changes. To obtain information about the likelihood of a particular inelastic event, the changed species have to be distinguished one from the other directly, by collection, or indirectly, via electrons (ionization) or photons (excitations) produced. The experiments to be described, therefore, require detection of the scattered incident or target particles, or their collision products, often involving a distinct detection scheme for each type of inelastic effect.

As we are interested in what takes place, statistically, in a single collision, the target thickness must be kept small enough that most of the beam particles are not scattered.* This ensures that, if a particle is scattered out of the beam, it is, with high probability, due to a single collision between the beam particle and a single target particle. Multiple scattering experiments are more difficult to interpret but are sometimes unavoidable.

* In all beam experiments, the beam density should be small enough that the effect of the beam particles on one another is negligible.
We also will require that the number of targets affected at any time be small compared to the number of targets available, so the number density of targets \( n_B \) is nearly constant. For this type of experiment sensitive detectors must be employed as the experimenter is generally counting a small number of events. Considering, as an example, the charge transfer reaction, \( A^+ + B \rightarrow A + B^+ \), measurements may be made of the rate of production of target ions \( B^+ \), \( dN_{B^+}/dt \), for a given target thickness. This may be accomplished by applying a very small electric field across the target to sweep out and count the number of ions produced.

The rate of production of target ions \( B^+ \) is proportional to the target area, \( \mathcal{A} \), irradiated by the beam, the thickness \( \Delta X \), the number density of targets, and the beam intensity \( I_{A^+} \) (the number of ions crossing a unit area per unit time), which we assume here is practically constant over the target length. This can be written quantitatively as

\[
\frac{dN_{B^+}}{dt} = \sigma_{A^+ B \rightarrow AB^+} n_B I_{A^+} \Delta X \mathcal{A}
\]

where the proportionally constant, written \( \sigma_{A^+ B \rightarrow AB^+} \), again has the dimension of area. The quantity \( n_B \Delta X \mathcal{A} \) is the number of atoms in the target material, and therefore the cross section is defined, per target atom, as

\[
\sigma_{A^+ B \rightarrow AB^+} = \frac{\text{Number of collisions per unit time resulting in an electron capture}}{\text{Incident intensity}}
\]

Writing the number of ions produced, \( N_{B^-} \), in terms of the density of species \( B^+ \) produced, \( N_{B^+} = n_B \Delta X \mathcal{A} \), we see that the rate of increase of the product species density, \( n_{B^-} \),

\[
\frac{dn_{B^-}}{dt} = \sigma_{A^+ B \rightarrow AB^+} n_B I_{A^+}
\]

is independent of the size of the target volume irradiated by the beam.

The experiment as described cannot distinguish between ionizations, \( A^+ + B \rightarrow A^+ + B^- + e \), and charge exchanges, \( A^+ + B \rightarrow A + B^+ \). This distinction can be made by also counting the electrons produced by ionization or by detecting the scattered beam particle in coincidence with the production of \( B^+ \). In some cases the experimenter may be interested only in the number of ionized targets produced by either charge exchange or ionization, in which case the measured cross section is a sum of \( \sigma_{A^+ B \rightarrow AB^+} + \sigma_{A^+ B \rightarrow A^- B^-} \).

The meaning of the quantity \( \sigma_{A^+ B \rightarrow AB^+} \) is not as clear as the cross section defined earlier. Recalling that if all the inelastic events are monitored for \( A^+ \) incident on B, as well as the elastic scatterings, \( \sigma_{A^+ B \rightarrow A^+ B} \), then of course all the scattering events are accounted for. Now the total rate
of scattering of particles \( d\mathcal{N}_s/dt \) is the sum of the rates for the individual events, each of which has the form of Eq. (2.5), yielding

\[
\frac{d\mathcal{N}_s}{dt} = \left( \sum_j \sigma_{A^+ B^{-} \rightarrow j} \right) n_B I_{A^+} \Delta X \omega
\]

(2.8)

where \( j \) labels the possible results: elastic collision, ionization, change transfer, etc. The total scattering rate is related to the decrease in beam intensity for a thin target, \( d\mathcal{N}_s/dt = -\Delta I \omega \). Using Eqs. (2.1) and (2.8), we find that the total scattering cross section from the attenuation experiment is the sum of the individual cross sections:

\[
\sigma_{A^+ B^-} = \sum_j \sigma_{A^+ B^- \rightarrow j}
\]

(2.9)

Now the probability, \( P_{A^+ B^- \rightarrow AB^+} \), of a charge-transfer collision occurring when \( A^+ \) collides with \( B \) is the ratio of the scattering rate leading to charge transfer, Eq. (2.5), to the total scattering rate, Eq. (2.8), or

\[
P_{A^+ B^- \rightarrow AB^+} = \frac{\sigma_{A^+ B^- \rightarrow AB^+}}{\sigma_{A^+ B^-}}
\]

(2.10)

Therefore, the inelastic cross section indicates not only the effective sizes of the colliding particles, but also the likelihood, or probability, of a given inelastic event occurring. It is often useful to think of an inelastic cross section as proportional to the particle size, indicated by the total cross section, and the probability of the particular inelastic event,

\[
\sigma_{A^+ B^- \rightarrow AB^+} = P_{A^+ B^- \rightarrow AB^+} \sigma_{A^+ B^-}
\]

(2.11)

Both \( \sigma_{A^+ B^-} \) and \( P_{A^+ B^- \rightarrow AB^+} \) generally depend on the relative velocity of approach of the beam and target particles.

Lastly, if an inelastic process is thought of as "damaging" the target molecule \( B \), then, integrating Eq. (2.7), we obtain the fraction of the target molecules which remain unaffected after a time \( t \):

\[
f = \exp \left[ -\sigma_D I t \right]
\]

(2.12)

where \( \sigma_D \) is the inelastic cross section (e.g., ionization, dissociation, etc.). This expression will be employed in Chapter 6 when discussing radiation effects.

**Rate Constants**

In Eq. (2.7), the intensity of the beam, \( I_{A^+} \) (ions/cm\(^2\)/sec), can also be written as the beam density, \( n_{A^+} \) (ions/cm\(^3\)), times the particle velocity \( v_{A^+} \). For our example, \( v_{A^+} \) is also equal to the relative velocity between \( A^+ \) and \( B \) and, therefore, we have used instead the symbol \( v \). Now, the production
of ions can be explicitly written as being proportional to both the target and incident atom densities,
\[
\frac{dn_{B^+}}{dt} = \sigma_{A^+ \rightarrow AB^+} v n_{A^+} n_B
\]  
(2.13a)

and the formal distinction between target and incident particle disappears. That is, the experiment with B moving and A\(^+\) standing still will yield the same result as long as the relative speed of approach is the same! This is a general property of collisions occurring in a region where there are no outside effects, like strong electric fields. This type of equation can be applied also to an experiment in which two sets of beams are crossed, as long as \(v, n_{A^+},\) and \(n_B\) are calculated carefully. Changing the angle between the crossed beams changes \(v,\) allowing one to study the velocity dependence of the cross section. One can further relax the constraint that either set of atoms colliding is in the form of a monoenergetic beam. That is, thermal beams can be used where there is a distribution of velocities, for which case one writes
\[
\frac{dn_{B^+}}{dt} = \overline{(\sigma_{A^+ B \rightarrow AB^+} v)n_{A^+} n_B}
\]  
(2.13b)

where the bar means the product \(v\) and the cross section are averaged over the velocities occurring in the thermal beam. (Note: This is not usually equal to \(\bar{\sigma} \cdot \bar{v}.\)) If such an experiment is used to measure the cross section at a single velocity, then a procedure has to be developed for unfolding the average, which usually requires some knowledge of the general behavior of \(\sigma\) with velocity.

A very important class of experiments is carried out for studying chemical reactions in which the gases are simply mixed. For a particular reaction, for example reaction (8) in Table 2.1, which is known to be a result of a binary collision (a bimolecular reaction), one combines known densities of the two species A and BC together at a given temperature and monitors as a function of time the production of C or AB. The production of C clearly depends on the density (availability) of the two initial species and, therefore, we write
\[
\frac{dn_C}{dt} = k_{A, BC \rightarrow AB, C}(T)n_A n_{BC}
\]  
(2.14)

which is the continuity equation of Chapter 1 without flow, e.g., Eqs. (1.5) and (1.14). In Eq. (2.14), the proportionality constant \(k_{A, BC \rightarrow AB, C}(T)\) is referred to as the rate constant of the reaction and is dependent on the temperature of the mixture. If the above experiment is performed for a period of time which is very short, so that the changes in the densities \(n_A\) and \(n_{BC}\) are negligible but the amount of C produced is detectable, then
extracting \( k_{A, BC\rightarrow AB, C}(T) \) is simple and direct. The number density of \( C \) as a function of time is

\[
n_C(t) \simeq k_{A, BC\rightarrow AB, C}(T) n_A n_{BC} t
\]

(2.15)

where \( t \) is the time at which the measurement is taken, and the densities \( n_A \) and \( n_{BC} \) are assumed to be the initial densities.

Comparing Eq. (2.14) to Eq. (2.13b), it is at once evident that in a binary reaction the rate constant is related to the inelastic (here reactive) cross section via

\[
k_{A, BC\rightarrow AB, C}(T) = \frac{\sigma_{A, BC\rightarrow AB, C} v}{T}
\]

(2.16)

where, again, the bar implies an average, which, for the example considered here, is over the thermal distribution of collision velocities in the gas, as indicated by the subscript \( T \). It is clear that rate constants contain less detailed information than cross sections obtained from a beam experiment because of the averaging over relative velocities. However, there are many instances for which beam experiments are not required and/or not practical. It is often difficult to produce monoenergetic beams with low velocities, though recently, crossed beam techniques have been used to create low relative velocities of approach as well as nozzle beams.

The above method is particularly well suited to reactions involving more than two bodies for which beam experiments would be extremely difficult. For the three-body reactions \( A + B + C \rightarrow AB + C \), we can generalize Eq. (2.14):

\[
\frac{dn_{AB}}{dt} = k_{A, B\rightarrow AB, C}(T)n_A n_B n_C
\]

(2.17)

In this particular reaction, particle \( C \) acts as a catalyst and, as its density does not change, the time dependence of the production of \( n_{AB} \) is similar to that for the two-body reaction. This three-body reaction requires that species \( A \) and \( B \) be both close enough to \( C \) for the reaction to proceed. Therefore, the effective cross-sectional area of the catalyst \( C \) will determine the size of the three-body rate constant. Many three-body chemical reactions can be thought of for which particle \( C \) does not play a passive role. That is, its structure is important in determining the size of the reaction rate, and the state of \( C \) may change during the reaction.

Another quantity of interest in collisions is the average energy-loss rate of the incident particle, which was invoked in our discussion of random collision cascades. The energy-loss rate associated with a particular inelastic process, \( AB \rightarrow j \), can be written

\[
- \frac{dE}{dt} \bigg|_{AB \rightarrow j} = v_A \Delta E_j \sigma_{AB\rightarrow j} n_B
\]
by the arguments used to obtain Eq. (2.13a). The quantity $\Delta E_j$ is the average energy loss of incident particle A in a collision during which the process $AB \rightarrow j$ occurs. Summing over all possible processes, as in Eq. (2.8), one obtains the total energy-loss rate or the more frequently used quantity, the energy loss per unit path length,

$$-\frac{dE}{ds} = n_B \sum_j \Delta E_j \sigma_{AB \rightarrow j} \equiv n_B S_{AB}$$

(2.18)

where we used $dE/dt = v_A (dE/ds)$. The coefficient of $n_B$ in Eq. (2.18) is often referred to as the stopping cross section, $S_{AB}$, and $dE/ds$ the stopping power of the material, a quantity directly measurable with an experimental arrangement like that in Figure 2.1. Instead of counting the number of particles deflected out of the incident beam in that experiment, one monitors the loss of kinetic energy of all the exiting particles as a function of material thickness and then averages. The net energy loss for any particle is conceptually broken into two categories, that involved in the deflection of A by B, due primarily to the nuclei, and that transferred to the electrons of the material. These are referred to separately as the elastic-nuclear energy, loss and the inelastic energy loss, and can be separated because of the large mass differences between electrons and nuclei. These ideas were implicit in our construction of Eqs. (1.2) and (1.3) as we separated collisions which changed the momentum of the particle from the electronic drag on the incident particle.

The energy-loss rate is of interest in other than beam experiments. If a small amount of a "hot" gas, A, is mixed into a dense background gas B, then the rate at which A equilibrates in B is determined by $dE/dt$ averaged over the velocity distribution of the mixture. Atoms A can be "heated" selectively using a laser of the appropriate frequency, where we assume B is dense enough that collision processes are faster than radiative processes. Another example is a weakly ionized plasma in which one heats the electrons and ions, as for example solar ultraviolet (UV) radiation heating of the ionospheric plasma discussed in Chapter 1. The subsequent equilibration of the electrons and ions is determined by $dE/dt$.

Cross Section Calculations

The concept of a cross section, as discussed earlier, involves an effective size and an average probability of a particular event. We imagine a moving particle A approaching an initially stationary particle B (Figure 2.3), the situation occurring in the experiment discussed earlier. Clearly, if a large number of atoms are incident on a large number of targets as in Figure 2.1, some will approach rather closely, even head-on, and others will pass quite
far away. As the likelihood of a collision will clearly depend upon the
closeness of approach, it is customary to introduce the concept of an impact
parameter, \( b \). For the beam experiment (Figure 2.3), \( b \) is the perpendicular
distance from the center of the target to the path the incident particle would
take it if were not deflected—the dashed line. The impact parameter, along
with the velocity of approach, is sufficient to characterize the initial condi-
tions for objects which are spherically symmetric. For nonspherical objects,
as in collisions involving most molecular species, the relative orientations of
the colliding particles need to be specified as well as \( b \) and \( v \). Initially, we
will discuss spherically symmetric systems.

On each trajectory, labeled \( b \), there is a probability, \( P_{AB}(b) \), that a
deflection will occur resulting in either an elastic or inelastic scattering of
the two particles. This depends, obviously, on how closely the objects ap-
proach as in the collision between two spheres represented in Figure 2.4. As
we have already stated, the concept of cross section is statistical. Therefore,

Figure 2.4 Collision of spheres. All incident particles \( A \) passing through the ring experience a
similar impulse. Dotted area of radius \( r_A + r_B \) indicates cross section for the collision.
we assume it is equally likely, when large numbers of beam and target particles are involved, that \( A \) approaches \( B \) with any impact parameter, \( b \). As the objects are spherically symmetric, it does not matter on which side \( A \) approaches \( B \) as long as the value of \( b \) is the same. Imagining a thin ring of width \( db \), circumference \( 2\pi b \), and area \( 2\pi b \, db \) in the plane perpendicular to \( v_A \), through which the center of \( A \) passes; then, in the limit that \( db \) is small, trajectories for all particles passing through the ring are similar. For the collision in Figure 2.4, if \( b \leq r_A + r_B \), the two objects will collide and be scattered, whereas for \( b > r_A + r_B \) they miss. Therefore, any particle passing through a circle of radius \( r_A + r_B \) in Figure 2.4 will be scattered, implying that the effective cross-sectional area the two objects present to each other is \( \sigma_{AB} = \pi(r_A + r_B)^2 \).

This area also can be thought of as being made up of a sum of the areas of those rings, discussed above, for which a collision will occur. That is,

\[
\sigma_{AB} = \int_0^{r_A + r_B} 2\pi b \, db
\]  

(2.19)

or, more generally, noting that the collision probabilities are

\[
P_{AB}(b) = 1, \quad b \leq r_A + r_B
\]

\[
= 0, \quad b > (r_A + r_B)
\]

we write

\[
\sigma_{AB} = 2\pi \int_0^\infty P_{AB}(b) \, db
\]  

(2.20)

In this expression the nature or size of the particles is contained in the quantity \( P_{AB}(b) \). For particles which behave deterministically, such as classical particles, \( P_{AB} \) is either zero or one, as above. Therefore, for forces of infinite range, this calculation yields an infinite cross section! For particles that interact non-deterministically, such as quantum-mechanical particles, \( P_{AB} \) depends on \( b \) and \( \sigma_{AB} \) may be finite even for such forces (viz. Fig. 2.2). In any particular calculation, for comparison with experiment, the integral cannot be carried out to infinity as there are always neighboring target atoms which may be closer to \( A \) than the target of interest. Therefore, an upper limit, \( d \), related to the average distance between the target atoms (e.g., \( n_b \Delta X^{-1} = \pi d^2 \)) should be imposed on the integral in Eq. (2.20). At this distance the collision ceases to be binary. For the thin-target experiments described earlier, an alternative upper limit is \( b_m \), the impact parameter beyond which all deflections are smaller than the angular resolution of the detector. Computationally, the ideal situation is that the upper limit is large
enough for $P_{AB}$ to be zero for all $b$ greater than either $d$ or $b_m$. Now one can integrate out to $b_m$, $d$, or infinity and obtain the same result.

The concept of an impact parameter is obviously a very classical concept, in which it is assumed that the path of the incident particle can be determined. A closely related quantity, the angular momentum, $L$, is often used as this is a quantity which can be discussed in both classical and quantum-mechanical descriptions of collisions. For the collision in Figure 2.3, the angular momentum of A about the initial center of B is

$$L_A = M_A \cdot v_A \times R$$  \hspace{1cm} (2.21)

where $M_A$ is the mass of the moving object A and $R$ is the vector distance between the particles. It is easily seen that the impact parameter is now equal to

$$b = \frac{L_A}{M_A v_A}$$  \hspace{1cm} (2.22)

Therefore, in all the expressions above, $L_A$ can be used to replace $b$.

For a large number of incident and target particles, the probability of scattering per unit time per scattering center is the probability per unit time that a particle A will pass within an impact parameter $b \leq (r_A + r_B)^2$ of a target B. This can be written as $\frac{\pi}{4} (r_A + r_B)^2$ or $I \sigma_{AB}$. Now the density of scattered particles per unit time, for a target number density $n_B$, is

$$\frac{dn_s}{dt} = \sigma_{AB} n_B$$  \hspace{1cm} (2.23)

hence $\sigma_{AB}$ calculated above is consistent with the total cross section in Eq. (2.8). To determine cross sections for separate inelastic or elastic events, we note that, for particles entering at any impact parameter (or with any angular momentum), there is a probability of a given inelastic event occurring. Therefore, a particle passing through the element of area $2\pi b \, db$ about a target will cause, for example, an ionization with a probability $P_{AB \rightarrow AB^+}(b)$, implying that

$$\sigma_{AB \rightarrow AB^+} = 2\pi \int_0^\infty P_{AB \rightarrow AB^+} \, b \, db$$  \hspace{1cm} (2.24)

The sum of probabilities of all possible scattering events, elastic and inelastic, caused by particles passing at an impact parameter $b$ equals the total probability of a scattering in Eq. (2.20),

$$P_{AB}(b) = \sum_j P_{AB \rightarrow j}(b)$$  \hspace{1cm} (2.25)

maintaining the relationship established earlier between the total cross section and the separate inelastic cross sections.
In many chemical reactions due to binary collisions, for instance reaction (8) in Table 2.1, it is known that the reaction will take place with a given probability \( P_{A,BC\rightarrow AB,C} \) if the particles pass within a certain critical distance of each other, i.e., approach each other within a given impact parameter \( b_R \). When this is the case the reaction probability is written as

\[
P_{A,BC\rightarrow AB,C} = \begin{cases} 
P_R, & b \leq b_R \\ 0, & b \geq b_R. \end{cases}
\]

Now the reaction cross section becomes, using Eq. (2.24),

\[
\sigma_R = P_R \pi b_R^2
\]

This has the general form described in Eq. (2.11), as \( \pi b_R^2 \) is often the geometric total cross section.

The usefulness of Eq. (2.26) is that physical arguments may be used frequently to obtain either \( P_R \) or \( b_R \), allowing one to avoid a detailed calculation of \( \sigma_R \). We will refer to this form frequently when we discuss applications of cross-section calculations later.

In calculating cross sections in the manner described above, the problem reduces to a determination of impact-parameter probabilities for inelastic and elastic scattering. We can generalize the above results to consider nonspherically symmetric particles by introducing a set of relative orientation angles \( \Omega_M = (\theta_M, \phi_M) \). If the outside fields are imposed to select a single orientation, then \( P_{AB}(b) \) is replaced by \( P_{AB}(b, \Omega_M) \) and a cross section is obtained for each orientation. Generally all orientations are equally likely, in which case the quantity \( P_{AB}(b) \) which we have been discussing is an average over all orientations. Similar considerations apply to inelastic cross sections.

Before leaving this section we estimate some characteristic sizes of the quantities we have been describing. For atoms and molecules, quantities like \( (r_A + r_B) \) and \( b_R \) discussed above are of the order of \( 10^{-8} \) cm. For example, the mean radius of a ground-state hydrogen atom is \( 0.53 \times 10^{-8} \) cm and the mean separation of the nuclei in a hydrogen molecule is \( 0.74 \times 10^{-8} \) cm. Such characteristic sizes imply total cross sections of the order of \( 10^{-15} \) to \( 10^{-16} \) cm\(^2\) (viz. Figure 2.2). On the other hand, the probability of a reaction or an inelastic effect, \( P_R \), will depend on the ratio \( \tau_R/\tau_c \), where \( \tau_c \) is the length of time the particles are close together (the collision time), and \( \tau_R \) is a characteristic reaction time. Characteristic reaction times are related to natural periods of motion of the composite particles in the targets. For ionization collisions, the orbital period of the outer-shell electrons, \( \tau \sim 10^{-16} \) sec, determines the reaction times. For chemical reactions, the vibrational period, \( \tau \sim 10^{-13} \) sec, or rotational period, \( \tau \sim 10^{-11} \) sec, is the important characteristic times. When the natural periods match the collision time, \( \tau_R/\tau_c \sim 1 \), one expects that the reaction
probability would be optimum. Based on this notion, ionizing collisions would occur efficiently for atoms and molecules with keV (10^3 eV, 1 electron volt = 1.602 × 10^{-12} ergs) to MeV (10^6 eV) energies depending on the masses of the particles involved and ionization energies; i.e., inner-shell ionization requires higher energies. For incident electrons the range would be of the order of 5 to 50 eV. Chemical reactions, on the other hand, are generally efficient at meV (10^{-3} eV) to eV energies. Extending this, we note that the mean kinetic energy of a molecule at room temperature is about \( \frac{1}{27} \) eV, suggesting a bimolecular reaction rate, \( k(T) \sim \left( \sigma_R \frac{v}{v_T} \right) \) of the order of \( 10^{-11} \) to \( 10^{-12} \) cm^3/sec, depending on the masses of the reactants, if \( \bar{P}_R \) is near unity. For an inefficient bimolecular reaction \( k(T) \) may be considerably smaller. On the other hand, in reactions involving electrons (e.g., \( e + O_2^+ \)), \( k(T) \) would be larger as the electron speeds are larger. A three-body reaction [e.g., Eq. (2.17)] can be thought of as two separate encounters (reactions) of A and B with C during the collision time \( \tau_c \); \( k_{A,B,C} \sim k_{AC}k_{BC} \tau_c \sim 10^{-33} \) cm^6/sec. Such estimates are very useful in designing experiments or making preliminary models of collision phenomena and will be used at various points in the text.

Angular Differential Cross Sections

In our previous discussion we only needed to know if an incident particle was deflected. For any net force between the two particles along a given trajectory the incident particle will be scattered. However, to describe the probability of being scattered into a particular angle, it is not sufficient to know there is a force, but the details of interaction have to be known. Conversely, knowing the angular distribution of scattered particles, one should be able to learn something about the details of the interaction and not just the extent of the particles.

The cross sections defined previously, which do not differentiate between particles scattered into different angles, are referred to as integrated cross sections, implying that all scattered particles are counted. Sometimes the word total is used, though here we use total when referring to the sum of all integrated cross sections. Employing an experimental setup like the schematic diagram in Figure 2.5, one can measure the number of particles scattered into a particular angular region. For this arrangement, the distance between the target and the detector, \( R \), is assumed to be large compared to the dimensions of the target volume, and the angular position of the detector is labeled by \( \theta \) and \( \phi \) shown. The detector spans an angular region (solid angle) about \( \theta \) and \( \phi \) indicated by the angles \( \Delta \theta \) and \( \Delta \phi \) in Figure 2.5. The element of solid angle, \( \Delta \Omega = \Delta a/R^2 \), \( \Delta a \) being the detector area and \( R \) the distance to the detector, is \( \Delta \Omega = \sin \theta \Delta \theta \Delta \phi \). By moving the
detector to all angular positions for a fixed $R$, all the scattered particles can be counted, and the detector will have covered an area $4\pi R^2$ or a total solid angle of $4\pi$.

Returning to Eq. (2.8), we measure the number of particles scattered per unit time. Now, however, we consider only those scattered into a given solid angle, $\Delta \Omega_A$, where the subscript indicates that we are collecting particles of type A. Based on the previous discussion, the angular differential cross section, $d\sigma/d\Omega|_{AB}$ for the scattering of A on B is defined by

$$
\frac{d\sigma}{d\Omega}|_{AB} \Delta \Omega_A = \frac{\text{Number of particles per unit time scattered into } \Delta \Omega_A}{\text{Incident intensity}}
$$

(2.27)

By summing over all angular regions, the integrated cross section is recovered:

$$
\sigma_{AB} = \int d\Omega \int_0^{2\pi} d\varphi_A \int_0^\pi \sin \theta_A d\theta_A \left. \frac{d\sigma}{d\Omega} \right|_{AB}
$$

(2.28)

When there are no outside fields the orientation of the $x$, $y$ axis is arbitrary, and therefore $d\sigma/d\Omega|_{AB}$ is independent of $\varphi_A$. Consequently, one often writes, using $d\cos \theta_A = -\sin \theta_A d\theta_A$,

$$
\sigma_{AB} = 2\pi \int_{-1}^1 d\cos \theta_A \sigma_{AB}(\theta_A)
$$

(2.29)

where $\sigma_{AB}(\theta_A)$ and $(d\sigma/d\Omega)|_{AB}$ are identical for this case. We use these symbols interchangeably in the following, unless there is an explicit dependence on the azimuthal angle. It should be emphasized that the absence of the azimuthal angle for this quantity occurs when there is no outside field or structure and has nothing to do with the shape of the target particles. If there are no forces or lattices orienting the target molecules, then we
assume their orientations are random and, on the average, all azimuthal angles are equivalent.

If, in addition to collecting scattered atoms, the detecting apparatus can differentiate between atoms which have experienced or caused an internal change, then an angular differential cross section for each inelastic process can be defined. The sum of these cross sections will, of course, equal \( d\sigma/d\Omega \mid_{AB} \). Extending the definition in Eq. (2.6), we define an angular differential cross section for charge transfer (per target atom):

\[
\frac{d\sigma}{d\Omega}_{A^{-}B^{+} \rightarrow AB^{+}} \equiv \frac{\text{Number of particles per unit time scattered into } \Delta\Omega_{A} \text{ having captured an electron}}{\text{Incident intensity}} \tag{2.30}
\]

If the internal change of interest is a change in the state of the struck target particle, the experimenter may choose to measure the distribution of scattered targets or note a property of A which can be associated with the event of interest in B, as for example an additional loss of kinetic energy beyond that associated with a simple deflection.

**Calculation of Angular Differential Cross Sections**

To calculate an angular differential cross section, we imagine that a particle which entered the collision region as part of a beam, and was detected as being scattered into some angle, followed a particular trajectory in response to the forces between it and a target particle (Figure 2.6). This

![Figure 2.6](image-url)  
*Figure 2.6. Collision of particles A and B. All particles A passing through the ring have similar trajectories and experience very nearly the same deflection \( \Theta_{A} \). The angle \( \Theta_{B} \), not indicated, is the angle \( \Theta_{b} \) makes with the axis.*
could be a force, either repulsive or attractive, which acted gradually over the full trajectory, as in Figure 2.6, or an abrupt collision, as in Figure 2.4. For simplicity we again consider collisions between spherically symmetric particles.

For each impact parameter $b$ with azimuthal angle $\phi$, there is a probability of being scattered into an angular region $d\Omega$ about $\theta$ and $\varphi$ which we write as $p_{AB}(b, \theta) d\Omega$. For spherical particles, the azimuthal angle $\varphi$ equals the incident azimuthal angle $\phi$ as there are no torques, and the labels on $\theta$ are dropped, as we can consider either the scattered incident or target particles. The probability of being scattered into any angle, $P_{AB}(b)$, which we discussed earlier, is a sum of these probabilities:

$$P_{AB}(b) = \int \int p_{AB}(b, \theta) d\Omega$$

$$= 2\pi \int_{-1}^{1} p_{AB}(b, \theta) d\cos \theta$$

(2.31)

From the probability per unit solid angle of a scattering, $p_{AB}(b, \theta)$, we can write an expression for the angular differential cross section. Using Eqs. (2.31) in Eq. (2.20) and comparing it to Eq. (2.29), we find

$$\sigma_{AB}(\theta) = 2\pi \int_{0}^{\infty} p_{AB}(b, \theta) b \, db$$

(2.32)

This expression merely states that the scattering into an angular region about $\theta$ is a sum of contributions from all impact parameters for which a scattering into the angle $\theta$ is likely, as indicated by $p_{AB}$. Again we have only postponed the basic problem of obtaining the probability density $p_{AB}$ from the details of the interaction. Carrying the above one step further, if we are able to distinguish in our calculation between inelastic and elastic events, we can write, for the ionization cross section,

$$\sigma_{\text{AB}\rightarrow\text{AB}}(\theta) = 2\pi \int_{0}^{\infty} p_{\text{AB}\rightarrow\text{AB}}(b, \theta) b \, db$$

(2.33)

Equation (2.32) simplifies further when the interaction is a purely repulsive or attractive force which at any instant during the collision depends only on the distance between the two particles. Now, each impact will result in a scattering into a particular angle $\theta$. A relationship between the scattering angle and impact parameter, referred to as the deflection function, $\Theta(b)$, can be calculated from the forces of interaction using Newton’s laws. In such a deterministic model $\Theta(b)$ has a single value for each impact parameter, $b$, and it is clear that $p_{AB}$ is zero for this example except when $\cos \theta = \cos \Theta(b)$. This type of density function is called a delta function, and, in Appendix A, we discuss the behavior of such functions. Before com-
Completing this approach, we return to the defining equation for the differential cross section.

We note that the number of beam particles per unit time entering a ring of area $2\pi b \, db$ about the center of a given target atom (see Figure 2.4 or 2.6) is $12\pi b \, db$. For our example, this is also the rate of scattering into the solid angular region associated with $\cos \theta = \cos \Theta(b)$. Using Eq. (2.27), we obtain the calculated differential cross section from the expression

$$\sigma_{AB}(\Theta) 2\pi \sin \Theta \, d\Theta = \frac{(2\pi b \, dB \, I)}{I}$$

Simplifying and rewriting we have

$$\sigma_{AB}(\Theta) = \left| \frac{b}{\sin \Theta} \frac{db}{d\Theta} \right|$$ (2.34)

where the absolute value signs are included to assure that the cross section is positive. We stated that $\Theta(b)$ was single valued. If, in addition, at each measuring angle, $\cos \theta$, there is only one $b$ for which $\cos \theta = \cos \Theta(b)$, then the differential cross section $\sigma_{AB}(\theta)$ will be the calculated classical cross section $\sigma_{AB}(\Theta)$ in Eq. (2.34). However, not infrequently the calculated deflection function, $\Theta(b)$, will have both positive and negative values and there may be more than one value of $b$ for which $\cos \theta = \cos \Theta(b)$. That is, experimentally we cannot distinguish between negative and positive deflections as we cannot see on which side of the target atom a particular incident particle approaches a particular target particle. The measured cross section should, therefore, be estimated as a sum of contributions from all $b$ yielding the same deflection cosine

$$\sigma_{AB}(\theta) = \sum \{ \sigma_{AB}[\Theta(b)] \}_{\cos \theta = \cos \Theta(b)} \quad (2.35)$$

where $\sigma_{AB}(\Theta)$ is calculated as in Eq. (2.34) when the deflection function $\Theta(b)$ is known. In the following sections, we review classical kinematics and obtain cross sections for some simple examples using Eqs. (2.34) and (2.35).

Before ending this discussion, we return to our earlier approach, that of a deterministic collision for which $p_{AB}$ is a delta function,

$$p_{AB}(b, \theta) = \frac{1}{2\pi} \delta[\cos \theta - \cos \Theta(b)]. \quad (2.36)$$

Substituting this expression into Eq. (2.31) and using the properties of a delta function discussed in Appendix A, we find that the impact parameter probability of a collision is unity, $P_{AB}(b) = 1$, as discussed earlier. Substituting Eq. (2.36) into the expression for the differential cross section, Eq. (2.32), we obtain the result in Eq. (2.35). This is left as a problem for the reader. Based on this approach to the problem, statistical models can be immediately envisaged. As a simple example, we note that when an atom collides
with a molecule, the molecular orientations are random. For any particular orientation, the deflection function \( \Theta(b, \phi, \Omega_M) \) and corresponding azimuthal deflection function \( \varphi(b, \phi, \Omega_M) \) are determined from classical mechanics, where \( \Omega_M \) indicates the molecular orientation. After integrating over all azimuthal scattering angles \( \varphi \), the classical density function for the molecular collision becomes

\[
p_{AB}(b, \Theta) = \frac{1}{2\pi} \langle \delta[\cos \beta - \cos \Theta(b, \phi, \Omega_M)] \rangle_{\Omega_M, \phi}
\]

(2.37)

where the brackets indicate averaging over the random orientations of the molecule and the azimuthal impact angle \( \phi \). One can also imagine models for which the density function will not be a delta function but will have a width associated with the fact that the impact parameter cannot be precisely defined. Extending this notion, then, at larger impact parameters, \( p_{AB} \) will not generally integrate to unity because the boundaries of the atom are diffuse. Such a model, though nondeterministic, would still be classical in form and is an attempt to incorporate quantum-mechanical effects. In Chapter 3 we will discuss the quantum mechanical solution of the problem.

**Collision Kinematics: Elastic Collisions**

Here we apply two conservation laws, the conservation of energy and momentum, derived from Newton’s equations of motion, to the collision of two bodies A and B, shown in Figure 2.6, with masses \( M_A \) and \( M_B \). The velocities before the collision are \( v_A \) and \( v_B \), with \( v_B = 0 \), and, after they have separated by a large distance, they are \( v'_A \) and \( v'_B \). The conservation laws are independent of the details of the forces and apply to all trajectories which produce the same deflection. We define the deflection angles of A and B, \( \Theta_A \) and \( \Theta_B \), as the angles the final velocity vector make with the incident velocity vector. With these definitions, conserving energy, \( \mathcal{E} \), yields

\[
\mathcal{E} = \frac{1}{2} M_A v_A^2 = \frac{1}{2} M_A v'_A^2 + \frac{1}{2} M_B v'_B^2
\]

(2.38)

The conservation of momentum tells us that the vectors \( v_A, v'_A, \) and \( v'_B \) all lie in the same plane, and that in that plane,

\[
M_A v_A = M_A v'_A \cos \Theta_A + M_B v'_B \cos \Theta_B
\]

\[
0 = M_A v'_A \sin \Theta_A - M_B v'_B \sin \Theta_B
\]

(2.39)

If we take the \( M_A, M_B, \) and \( v_A \) as given initial quantities, the three equations above relate the four quantities \( v'_A, v'_B, \Theta_A, \) and \( \Theta_B \). Therefore, conservation laws alone cannot describe the collision; we require a force equation involving the interaction. However, some simple relationships can be obtained first.
Table 2.2. Angular Range of $\Theta_A$

<table>
<thead>
<tr>
<th>Condition</th>
<th>Relation</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy target</td>
<td>$M_B \gg M_A$</td>
<td>$\mu \gg 1$</td>
</tr>
<tr>
<td>Equal masses</td>
<td>$M_B = M_A$</td>
<td>$\mu = 1$</td>
</tr>
<tr>
<td>Light target</td>
<td>$M_B \ll M_A$</td>
<td>$\mu \ll 1$</td>
</tr>
</tbody>
</table>

Using Eqs. (2.38) and (2.39), we see that the final scattering angles are related by the expression

$$\tan \Theta_A = \frac{\mu \sin 2\Theta_B}{1 - \mu \cos 2\Theta_B}$$  \hspace{1cm} (2.40)

where $\mu = M_B/M_A$ is the mass ratio. It is clear from the collision of spheres, shown in Figure 2.4, that in collisions for which orbiting of the particles does not occur, $0 < |\Theta_B| < \pi/2$. Orbiting will be treated later. Equation (2.40) now places restrictions on the angular range of $\Theta_A$, expressed in Table 2.2. For angles outside the kinematically allowed range, $\sigma(\Theta_A) = 0$. It is seen from Table 2.2 that forward scattering is generally preferred and backscattering can occur only in those collisions for which $\mu \to \infty$. Measuring the angular range of elastically scattered particles $A$ is therefore, a means of estimating the mass of the target particles $B$.

Postponing the discussion of realistic forces between atoms we note that in the example of hard-sphere collisions (Figure 2.4) the impulse is along the axis connecting their centers at contact. This implies that the

![Figure 2.7](image)

**Figure 2.7.** Cross sections, $\sigma(\Theta_A)$, and deflection functions, $\Theta_A$, for the collision of hard spheres of radius $r_A$ and $r_B$, where $\mu = M_B/M_A$ and $r_A + r_B = d$. 
scattered target moves off at an angle of $\Theta_B$ such that $\sin \Theta_B = b/(r_A + r_B)$. Using Eq. (2.40), we can determine the deflection function for the incident particle, $\Theta_A(b)$. As $\Theta_A$ depends on the relative masses of the incident and target particles, so will the elastic cross calculated using Eq. (2.34). Writing $d = (r_A + r_B)$, the collision diameter, the differential cross sections for the collision of spheres are plotted in Figure 2.7 for three limiting cases. The angular dependence of the cross section is shown to be strongly dependent on the mass ratio $\mu$. For light particles incident on heavy target particles the differential cross section is isotropic, a rather special result for an impulsive collision, which is employed, too often, in making macroscopic calculations. It should also be noted that $\sigma(\Theta)$ is nonzero at $\Theta = 0$. This may at first seem surprising on recalling the experimental measurements of the cross section in which we excluded transmitted beam particles. However, $\sigma(\Theta)$ is the cross section per unit solid angle and, therefore, must account for those small-angle collisions in an angular region about $\Theta = 0$. Using Eq. (2.27), we see that the number of particles scattered per unit time into a given angular region is proportional to $\sigma(\theta) \sin \theta \Delta \theta$, where $\Delta \theta$ is the aperture. As $\theta$ goes to zero the number of scattered particles decreases, in this example, even though, for the case $\mu \ll 1$, the differential cross section may be quite large. It is common to plot the quantity $\rho(\theta) = \theta \sin \theta \sigma(\theta)$ to account roughly for these angular factors.

From the conservation laws, a relationship between the elastic energy loss, $T = \frac{1}{2}M_B v_B^2$, and the scattering angles can be obtained. Using Eq. (2.38) and (2.39), we find

$$\cos \Theta_B = (T/\gamma E_A)^{1/2}$$

$$\cos \Theta_A = \frac{1 - [(1 + \mu/2)T/E_A]}{[(1 - T)/E_A]^{1/2}}$$

(2.41)

where $\gamma = 4M_A M_B/(M_A + M_B)^2$, $E_A = \frac{1}{2}M_A v_A^2$, and the maximum energy transfer is $T_M = \gamma E_A$. For the equal-mass case, $\gamma = 1$, all the energy may be transferred, whereas, for a large mismatch in particle masses, either $\mu \gg 1$ or $\mu \ll 1$; then $\gamma \ll 1$, and only a fraction of the energy may be transferred in an elastic collision. Table 2.2 also contains estimates of $T$ for the cases being considered. Because the energy transfer is of considerable interest and is simply related to $\Theta_A$, it is often useful to discuss a cross-section differential in elastic energy transfer. Defining $d\sigma/dT$ via

$$\frac{d\sigma}{dT} \Delta T \equiv \frac{\text{Number of particles scattered per unit time with elastic energy transfer between } T \text{ and } T + \Delta T}{\text{Incident intensity}}$$

we can relate $d\sigma/dT$ and $\sigma(\Theta_A)$:

$$\frac{d\sigma}{dT} = \sigma(\Theta_A) \left| \frac{d \cos \Theta_A}{dT} \right|$$

(2.42)
This yields, for the elastic collisions of spheres, the simple result \( \frac{d\sigma}{dT} = \frac{1}{\gamma E_A} \pi d^2 \), which is independent of \( T \). In the following section we will reconsider the kinematics in a coordinate system for which the mass factors play a less important role as in the energy transfer cross section.

**Center of Mass System**

The kinematics of the collision were shown to play an important role in determining the angular differential cross section. Thus far we have concentrated on the collision between a moving atom, A, and a stopped particle, B. However, it was pointed out that the integrated cross sections and the rate constants depended only on the relative speed between the particles if there were no outside fields, and therefore the ratio of the masses \( M_A \) and \( M_B \) was not important. It would be useful, therefore, to discuss the collision in a reference system for which the kinematics could be described using only the relative velocity.

The center of mass of the colliding particles, a distance \( R_C \) from some fixed origin, is located on a line connecting A and B, as shown in Figure 2.8. The quantities \( r_A \) and \( r_B \) in Figure 2.8 are the positions of A and B as measured from the center of mass, \( C \). The usefulness of using \( C \) as an alternate origin is immediately apparent as the velocities of A and B, \( v_A \) and \( v_B \), are both proportional to \( v \), the relative velocity. The coordinate system centered on \( C \) is referred to as the center-of-mass (CM) coordinate system, and that with the fixed origin, the laboratory coordinate system. Relationships between CM and laboratory variables are summarized in Table 2.3 and the derivations are left as a problem for the reader. From Table 2.3 it is seen that in the CM system quantities of physical interest are given in terms of \( v \) and a quantity \( m = M_A M_B / (M_A + M_B) \), the reduced mass. In the CM system the momenta of A and B are equal and opposite, or the total momentum is zero, hence it is also referred to as the zero-momentum system. For the case we are considering, there are no outside fields and the

![Figure 2.8](image_url)
Table 2.3. Relationships between Laboratory and CM Variables

<table>
<thead>
<tr>
<th>Positions</th>
<th>Velocities</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_c = (M_A R_A + M_B R_B)/(M_A + M_B) )</td>
<td>( V_c = \dot{R}_c = (M_A v_A + M_B v_B)/(M_A + M_B) )</td>
</tr>
<tr>
<td>( R = R_A - R_B = r_A - r_B )</td>
<td>( v = R = v_A - v_B = \dot{r}_A - \dot{r}_B )</td>
</tr>
<tr>
<td>( r_A = R_A - R_c, r_B = R_B - R_c )</td>
<td>( M_A \ddot{r}_A = -M_B \ddot{r}_B = \mathcal{N} \dot{v} )</td>
</tr>
</tbody>
</table>

Laboratory quantities

- \( M = M_A + M_B \)
- \( \delta = \frac{1}{2} M_A v_A^2 + M_B v_B^2 = \frac{1}{2} M v_c^2 + E \)
- \( \mathcal{P} = M_A v_A + M_B v_B = M v_c \)
- \( \mathcal{L}^l = M_A R_A \times v_A + M_B R_B \times v_B = m M R_c \times V_c + \mathcal{L} \)

CM quantities

- \( m = \frac{M_A M_B}{M_A + M_B} \)
- \( E = \frac{1}{2} M_A \ddot{r}_A^2 + \frac{1}{2} M_B \ddot{r}_B^2 = \frac{1}{2} m \dot{v}^2 \)
- \( P = M_A \ddot{r}_A + M_B \ddot{r}_B = 0 \)
- \( L = M_A r_A \times \dot{r}_A + M_B r_B \times \dot{r}_B = m R \times \dot{v} \)

Forces between the two bodies must be equal and opposite, or \( \dot{R}_c \) is a constant. Since the laboratory and the CM coordinates move relative to each other at constant velocity, as we know from classical mechanics, examining the motion in the CM system does not affect the forces.

The kinematics of the collision in the CM system are indicated in Figure 2.9 using the momentum vectors of the particles. Since the net momentum is zero before the collision, it is also zero after the collision. If, in addition, the collision is elastic, the magnitudes of the momenta remain the same. For the case \( v_B = 0 \), \( v \) and \( V_c \) are in the same direction, which simplifies the transformation between the laboratory and CM coordinates after the collision. For this case the final and initial velocities all lie in the same plane, the collision plane, as shown in Figure 2.9. When \( v_B \neq 0 \), the transformation back to the final laboratory velocities is also straightforward. In general, we will deal with the \( v_B = 0 \) case.

![Figure 2.9](image)

**Figure 2.9.** Kinematics of collision indicated in the CM system. To obtain laboratory momentum and angles the velocity of the center of mass, \( V_c \), is added to the CM motion of each particle. Here we assume \( v_A = v \) and \( v_B = 0 \) initially.
Cross Sections and Rate Constants

When the colliding systems are spherically symmetric, only the CM deflection angle, $\chi$, is needed to describe the collision, and it is clear from Figure 2.9 that $\chi$ takes on all values between 0 and $\pi$. The relationships between the laboratory quantities and the CM angle, from Fig. 2.9, are

$$\Theta_B = \frac{1}{2}(\pi - \chi)$$

$$\tan \Theta_A = \frac{\mu \sin \chi}{1 + \mu \cos \chi}$$

$$T = \frac{\gamma E_A \sin^2 \chi / 2}{E_A} = \frac{1}{2} M_A v_A^2, \quad v_B = 0$$

Equations (2.43) are equivalent to Eqs. (2.40) and (2.41). From Figure 2.9 it is apparent that particles A and B follow equivalent trajectories in the CM system. Further, from Eq. (2.43) it is seen that if $\mu \gg 1$, $\Theta_A = \chi$. Therefore, in the CM system the collision can be treated as if a particle of mass $m$, the reduced mass of the two particles, and velocity, $v$, the relative velocity, collides with an infinitely heavy, hence stationary, target. This will be exploited in subsequent discussions.

The forces and the equations of motion are used to obtain a CM deflection function, $\chi(b)$, for a reduced-mass particle and, hence, an angular differential cross section, in the CM system:

$$\sigma(\chi) = \left| \frac{b}{\sin \chi} \frac{db}{d\chi} \right|$$

(2.44)

The calculated CM cross section can be changed to the laboratory system, Eq. (2.34), by the transformation

$$\sigma(\Theta_A) = \sigma(\chi) \left| \frac{d \cos \chi}{d \cos \Theta_A} \right| = \sigma(\chi) \frac{(\mu^2 + 2\mu \cos \chi + 1)^{3/2}}{\mu^2 |\mu + \cos \chi|}$$

(2.45)

if the collision is between spherically symmetric particles. By using the relationships in Eq. (2.43) the elastic-energy-transfer cross section and the CM cross section are simply related,

$$\frac{d\sigma}{dT} = 2\pi \sigma(\chi) \left| \frac{d \cos \chi}{dT} \right| = \frac{4\pi}{\gamma E_A} \sigma(\chi)$$

(2.46)

For the impulsive collision of spheres considered earlier, $\sigma(\chi) = d^2/4$. That is, the CM cross section is isotropic for this example regardless of the particle masses. The nonisotropic laboratory cross sections shown in Figure 2.7, therefore, are a result only of the particle kinematics. This is the essence of the CM calculation—to separate the calculation of the kinematical factors from the details of the interaction, the later determining the CM cross section.
Kinematics of Inelastic Collisions

The kinematics of an inelastic collision are shown in Figure 2.10 using the CM system, and the results are summarized in Table 2.4. During the collision we allow the internal energies of each particle, \( \varepsilon_A \) and \( \varepsilon_B \), to change as well as their masses. For nonrelativistic collisions the energy and mass are conserved separately. Defining \( Q \) as the net change in internal energy (see Table 2.4), we specify the type of inelastic collision as follows: \( Q > 0 \), an endothermic collision; \( Q = 0 \), an elastic collision if no internal changes have occurred, or resonant if the net internal changes in A and B yield \( Q = 0 \); \( Q < 0 \), an exothermic collision; and \( M_A \neq M'_A \) and \( M_B \neq M'_B \), a rearrangement collision. The change in internal energy \( Q \) is essentially a CM quantity, as can be seen in Table 2.4. That is, it effects a corresponding change in the center-of-mass kinetic energy. Conversely, in order for an endothermic reaction to occur, the kinetic energy in the CM system must exceed the threshold energy for a given reaction. Below this energy the inelastic cross section is zero.

The relationship between \( \Theta_A \) and \( \chi \), the CM scattering angle, has the same form as that found for elastic collisions, except the internal energy change modifies the mass ratio. For instance, a large increase in the internal energy to a higher or more loosely bound state (\( Q \) positive, endothermic) restricts the laboratory scattering to the forward direction. A large decrease in the internal energy to a more tightly bound state, that is, internal energy converted to kinetic energy (\( Q \) negative, exothermic), may permit significant backscattering. The latter is like an explosion occurring when the particles collide. For the collision of two soft spheres, that is, spheres which dissipate an amount of energy \( Q \), the center-of-mass cross section is \( \sigma_Q(\chi) = \frac{1}{4} d^2 \), as in the elastic case. Again the CM cross section only indicates the nature of the

* The convention for the sign on \( Q \) is often the opposite to that used here. We prefer \( Q \), like \( T \), to be positive when the initial kinetic energy is lost or transferred. Minus \( Q \), as used here, is often referred to as the energy defect of the collision.
Table 2.4. Inelastic Collision Kinematics

<table>
<thead>
<tr>
<th>Laboratory system</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta = \frac{1}{2} M_A v^2_A + \frac{1}{2} M_B v^2_B + \epsilon_A + \epsilon_B = \frac{1}{2} M_A v^2_A + \frac{1}{2} M_B v^2_B + \epsilon_A + \epsilon_B$</td>
</tr>
<tr>
<td>$M = M_A + M_B = M_A' + M_B'$</td>
</tr>
<tr>
<td>$\varepsilon = M_A v_A + M_B v_B = M_A' v_A + M_B' v_B = M V_c$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CM system</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E = \frac{1}{2} m v^2 = \frac{1}{2} m v^2 + Q$</td>
</tr>
<tr>
<td>$Q = (\epsilon_A' + \epsilon_B') - (\epsilon_A + \epsilon_B)$</td>
</tr>
<tr>
<td>$m = M_A M_B / M$, $m' = M_A' M_B' / M$</td>
</tr>
<tr>
<td>$P = 0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transformations for $\epsilon_B = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tan \Theta_A = \frac{(\mu \mu')^{1/2} \sin \chi}{1 + (\mu \mu')^{1/2} \cos \chi}$; $g = 1 - Q/E$</td>
</tr>
<tr>
<td>$T = \frac{\gamma E_A}{4 M_B} \left[ 1 + \frac{\mu}{\mu'} g - 2 \left( \frac{\mu}{\mu'} g \right)^{1/2} \cos \chi \right]$; $E_A = \frac{1}{2} M_A v^2_A$</td>
</tr>
<tr>
<td>$\cos \Theta_A = \frac{(M_A'/M_A)^{1/2} (1 + M_A/M_A') - (1 + \mu')/2 (T/E_A) - \frac{1}{2} Q/E_A}{[1 - (T + Q/E_A)^{1/2}]^{1/2}}$</td>
</tr>
</tbody>
</table>

Interaction, and the kinematics are determined by $Q$ and the mass ratio using the relationships in Table 2.4.

It is seen in Table 2.4 that $\cos \Theta_A$ depends on both $T$ and $Q$, the amount of elastic energy transfer to particle $B$ and the net internal energy change. This suggests a simple scheme for measuring the inelastic cross sections. At each scattering angle the net change in kinetic energy of the beam particle, $\Delta E = T + Q$, can be measured, as we discussed earlier when considering the energy loss rates. Such a procedure is straightforward using the apparatus in Figure 2.11 if the scattered particle is an ion. In atomic and molecular systems, a large number of $Q$ values are possible for any particular collision, and, therefore, one measures, at each angle, an energy spectrum of scattered particles. For very fast collision, for which $Q/E \ll 1$, $T$ and $\cos \Theta_A$ have the same relationship we found for elastic collisions. Therefore, at each scattering angle, $T$ can be calculated independent of $Q$ and the spectrum $\Delta E$ can be converted directly to a spectrum in $Q$. For low-energy collisions, the extraction of $Q$ at each angle and $E$ is only slightly more complicated. The measured energy spectrum, therefore, yields
Figure 2.11. Diagram of apparatus for measuring cross sections differential in angle and energy. Pivot allows change in acceptance angle and bending magnet is used for energy analysis of scattered particle. [From R. E. Johnson and J. W. Boring, Charge Transfer in Atomic Systems, in Collision Spectroscopy, ed. R. G. Cooks, Plenum Press (1978)]
a double-differential cross section, one differential in angle and inelastic energy loss, defined, per target atom B, as

\[ \frac{d^2\sigma_{AB}}{d\Omega dQ} \Delta\Omega \Delta Q = \frac{\text{Number of particles scattered per unit time between } \Omega \text{ and } \Omega + \Delta\Omega \text{ and with energy loss between } Q \text{ and } Q + \Delta Q}{\text{Incident intensity}} \]  

(2.47)

Clearly, summing over all angles and energy losses, one recovers the total cross section \(\sigma_{AB}\). In atomic systems the internal energy changes are often discrete, except for the ionization process. However, as the instrument has finite apertures, both in angle and energy, the spectrum will be broadened and can generally be treated as a continuum, as suggested by the definition in Eq. (2.47). In Figure 2.12 is shown, as an example, results of an energy-analyzed scattering equipment for the reaction \(\text{He}^{++} + \text{Ne} \rightarrow \text{He}^+ + \text{Ne}^+\), where the scattered \(\text{He}^+\) is monitored. The scale for \(Q\) has been identified, and the plot is the scattering count rate, which is proportional to the double-differential cross section. There are seen to be groups of closely spaced discrete states which are populated with varying probabilities as a function of changing scattering angle and, hence, impact parameter. For the harder collisions shown in Figure 2.12, which correspond to large deflections, not only will more elastic energy, \(T\), be transferred, but it becomes increasingly likely that higher states are excited. That is, larger amounts of internal energy tend to be absorbed in hard collisions—a general characteristic of inelastic collisions. For the collision in Figure 2.12, at small scattering angles exothermic collisions are favored. This is not a general feature of inelastic collisions; rather, it is determined by the detailed nature of the atomic interaction, i.e., \(p_{i \rightarrow j}(b, \theta)\) of Eq. (2.33). These topics will be reconsidered later. In the following we use the laws of classical mechanics to calculate the deflection function \(\chi(b)\).

**The Classical Deflection Function**

To obtain the relationship between \(\chi\), the CM scattering angle, and \(b\), the impact parameter, we will consider a collision between a particle of mass \(m\), the reduced mass of the system, and a fixed target. The initial relative velocity, \(v\), changes as a function of time in response to the force between the particles. This force depends on the separation of the particles, their orientations and relative velocities, and is an appropriate CM quantity. We will treat the case of a velocity-independent force which can be expressed in terms of an interaction potential, \(V(R)\), such that \(F = -\nabla V\). As with the earlier discussion, we will initially consider spherically sym-
Figure 2.12. Energy spectra of scattered He\(^+\) ions from He\(^{++}\) + Ne \rightarrow He\(^+\) + Ne\(^+\) collisions. Laboratory scattering angle indicated on right. [From R. E. Johnson and J. W. Boring, Charge Transfer in Atomic Systems, in Collision Spectroscopy, ed. R. G. Cooks, Plenum Press (1978), p. 126.]

metric incident and target particles, so that \( V \) is a function of the separation, \( R \), only.

For this case, the collision takes place in a plane, and it is useful to express the relative velocity at any time in terms of radial and angular components,

\[
v \equiv \dot{\mathbf{R}}(t) = \dot{R}\hat{\mathbf{R}} + R\dot{\mathbf{\omega}}
\]

(2.48)
Figure 2.13. Trajectory for reduced-mass particle with velocity $v$ and impact parameter $b$ subject to a central attractive force. The quantity $\chi$ is the CM scattering angle, $R$ the distance to the fixed center, $\alpha$ the angular position of the particle along the trajectory, and $R_0$ the distance of the closest approach. Dashed line, tangent at $R_0$, indicates symmetry of the first and second halves of the collision.

where $\alpha$ is the angle between $\vec{R}$ and the collision axis in Figure 2.13. The CM angular momentum, from Table 2.3, is written as

$$L = mR^2\dot{\alpha} = m\dot{b}$$

(2.49)

and the energy as

$$E = \frac{1}{2}m\dot{R}^2 + \frac{1}{2}mR^2\dot{\alpha}^2 + V(R) = \frac{1}{2}mv^2$$

(2.50)

where $m\dot{b}$ and $\frac{1}{2}mv^2$ are the initial values for these conserved quantities. This collision can be characterized by an initial energy or velocity ($E$ or $v$) and by an initial angular momentum or impact parameter ($L$ or $b$). The potential energy in Eq. (2.50) is assumed to be zero at large separations. We will also have occasion in future sections to write the energy in terms of a radial momentum $p(R) = m\dot{R}$ and the angular momentum $L$.

$$E = \frac{1}{2} \frac{p^2(R)}{m} + \frac{1}{2} \frac{L^2}{mR^2} + V(R)$$

(2.51)

As $L$ and $E$ are conserved quantities, Eq. (2.51) explicitly shows that the radial momentum or radial velocity is only a function of the separation $R$ during the collision. That is, rearranging Eq. (2.51), one obtains

$$p(R) = m\dot{R} = \pm p_0 \left[ 1 - \left( \frac{b}{R} \right)^2 - \frac{V(R)}{E} \right]^{1/2}$$

(2.52)

where Eq. (2.49) was used to replace $L$ by the impact parameter and $p_0 = mv$ is the initial momentum of the reduced-mass particle.

Equation (2.52) can be integrated to obtain the radial position as a function of time during the collision. In the experiments described, however, this information is not obtainable. The quantity of interest is the net deflection, the CM scattering angle, $\chi(b)$, which is calculated by integrating $\alpha$ in Eq. (2.49) to obtain the angular excursion of $R$. Based on the relationship between $\alpha$ and $\chi$ indicated in Figure 2.13, the CM deflection function is:
\[ \chi = \pi - \int_{-\infty}^{\infty} \dot{\chi} \, dt \]

where \( R \) is a function of time and \( v \) and \( b \) are constants. From Eq. (2.52), it is seen that the radial velocity (or momentum) decreases as the particles approach, becoming zero at the distance of closest approach, and then increases as the particles recede. The distance of closest approach, \( R_0 \), for each impact parameter occurs when \( \dot{R} = 0 \), implying

\[ 1 - \left( \frac{b}{R_0} \right)^2 - \frac{V(R_0)}{E} = 0 \]  

(2.54)

Changing variables in Eq. (2.53) and using Eq. (2.52), we calculate the CM deflection angle as

\[ \chi(b) = \pi - 2b \int_{R_0}^{\infty} \frac{dR}{R^2} \frac{1}{\left[ 1 - \left( \frac{b}{R} \right)^2 - \frac{V}{E} \right]^{1/2}} \]  

(2.55)

where the contributions to \( \chi \) before and after \( R = R_0 \) are equal, as indicated in Figure 2.13. Specifying the potential energy and performing the integration in Eq. (2.55), we see that \( \chi(b) \), the CM deflection function, depends on the initial relative velocity \( v \) (or \( E \)) and \( b \) (or \( L \)), as stated earlier. The deflection function can now be used to obtain the CM cross section \( \sigma(\chi) \) using Eq. (2.44).

For a number of potential functions (cf. Problem 2.10), the above expression for \( \chi(b) \) can be integrated analytically. This is the case for the simple coulomb interaction between charged particles. However, for most realistic potentials a numerical scheme, like that described in Appendix B, must be employed. Examination of Eq. (2.55) shows that the relationship between \( \chi(b) \) and the potential \( V \) is not very transparent. However, it is clear that the major contributions to the integral come from values of \( R \) near \( R_0 \). Here the denominator in the integral approaches zero, implying that the behavior of \( V(R) \) near \( R_0 \) determines the size of the deflection. This fact will prove useful in estimating the deflection functions and hence cross sections.

To further examine the relationship between \( V \) and \( \chi \), it is instructive to consider collisions in which \( V/E \) is small throughout the collision, that is, large \( b \) collisions which lead to small-angle scatterings. This can be handled directly by expanding the denominator in Eq. (2.55), which we leave as a problem for the reader. Alternatively, a small deflection can be thought of as being due to a small net impulse, \( \Delta mv \), roughly perpendicular to the direction of motion. Now \( \chi \) has the form

\[ \chi \sim \frac{\Delta mv}{mv} = \int_{-\infty}^{\infty} F_{\perp} \, dt \]  

(2.56)
where $F_\perp$ is the component of force perpendicular to the direction of motion. For large impact parameters the path can be closely approximated by a straight line, allowing us to write $R^2 = R_0^2 + Z^2$, where $Z$ is along the trajectory. Further, the speed can be assumed to be nearly constant, so $Z \approx vt$. On substitution into Eq. (2.56), $\chi(b)$ can be written as

$$\chi(b) \sim -\frac{d}{dR_0} \frac{1}{2E} \int_{-\infty}^{\infty} V dZ$$  \hspace{1cm} (2.57a)$$

Changing the integration variable yields

$$\chi(b) \sim -\frac{1}{E} \int_{0}^{\infty} \frac{(dV)}{(dR)} \frac{R_0 dR}{R[1 - (R_0/R)^2]^{1/2}}$$  \hspace{1cm} (2.57b)$$

This result is often referred to as the classical impulse approximation or the momentum approximation to the deflection function. For small-angle scattering the penetration is small and one generally replaces $R_0$ by $b$ in the above expressions.

In Appendix B, the expression in Eq. (2.57a) is evaluated for a number of potential functions. For the inverse power law potentials, $V(R) = C/R^n$, using Eq. (2.57a), we obtain the deflection function as

$$\chi(b) \simeq a_n [(V(R_0)/E)]$$  \hspace{1cm} (2.58)$$

with

$$a_n = n \int_{0}^{\pi/2} \sin^n \alpha d\alpha = (\pi)^{1/2} \frac{\Gamma[(n + 1)/2]}{\Gamma(n/2)}$$

where $\Gamma(\cdot)$ is the gamma function (see Appendix B). For $n = 1$, $a_n = 1$; for $n = 2$, $a_n = \pi/2$; etc., with $a_n \rightarrow (\pi n/2)^{1/2}$. This class of potentials is particularly useful since realistic atomic and molecular interaction potentials, which we will describe in Chapter 4, can be written in terms of inverse power laws at large $R$. For the simplest case, the interaction between two charged particles (the coulomb potential), $n = 1$ for all $R$ and $C_1 = q_A q_B$, where $q_A$ and $q_B$ are the charges of the colliding particles. Even when a potential does not have the power-law form, it often can be fitted locally to a power law near the distance of closest approach. Employing this notion, Lindhard suggested a generally useful expression for estimating the classical deflection function in the impulse approximation. The so-called “magic” formula for $\chi(b)$ for an arbitrary, monotonically increasing or decreasing potential is

$$\chi^2(b) \simeq -\frac{3}{4E^2} b^{1/3} \frac{d}{db} [V^2(b) b^{2/3}]$$  \hspace{1cm} (2.59)$$

which for power laws implies $a_n \sim [(3n - 1)/2]^{1/2}$ in Eq. (2.58).
The velocity dependence of $\gamma(b)$ in Eq. (2.57) is quite simple and explicit. The quantity $\tau \equiv \gamma(b)E$ calculated in the impulse approximation can be seen to depend only on the impact parameter and is independent of the coordinate system. That is, using Eq. (2.43), $\tau$ also can be written in terms of laboratory quantities if the scattering angles are small, $\tau \sim E \theta$. The reduced cross section, defined as $\rho = \chi \sin \chi \sigma(\chi)$, is written, using Eq. (2.44), as

$$\rho \sim \frac{1}{2} \frac{db^2}{d \ln \tau}$$ (2.60)

for small $\chi$. The quantity $\rho$ now depends only on $\tau$, and hence $b$, and is also independent of the coordinate system when $\chi$ is small, being equal to the reduced cross section $\rho \sim \Theta \sin \Theta \sigma_{AB}(\Theta)$ defined earlier. Therefore a $\rho$ vs $\tau$ plot of experimental data, like that shown in Figure 2.14, should be very nearly energy independent and directly related to the form of the interaction potential. For the power-law potentials, using Eq. (2.58) in Eq. (2.60) and setting $R_0 = b$, we obtain $\rho$ as

$$\rho \sim \frac{1}{n} \left( \frac{a_n C_n}{\tau} \right)^{2/n}$$ (2.61a)

For the data in Fig. 2.14, $n$ is seen to increase with decreasing $\tau$ (increasing $b$).

![Figure 2.14 Plot of $\rho$ vs $\tau$ from experimental data for three values of $E$: ---, 25 keV; ---, 50 keV; ---, 100 keV. For $\rho$, $\theta_A$ is in radians. Approximate power laws are indicated by $n$. The reader should replot this using CM angles and energies. [From E. N. Fuls, P. R. Jones, F. P. Ziembka, and E. Everhart, Phys. Rev. 107, 704 (1957).]
Using Eq. (2.46), the equivalent energy transfer cross section is

$$
\frac{d\sigma}{dT} \sim \frac{\sigma_n}{E^{1/n}} \frac{1}{T^{1+1/n}}
$$

(2.61b)

$$
\sigma_n = \frac{\pi}{n} \left( \frac{M_A}{M_A + M_B} \frac{C_n^2 a_n^2}{C_n^2 a_n^2} \right)^{1/n}
$$

If a potential is thought to be monotonically increasing or decreasing, Eq. (2.61) provides a scheme for extracting the behavior of $V(R)$ directly from experimental data! Plotting $\rho$ on a log-log scale, like the data in Figure 2.14, and using Eq. (2.61), we can determine the power law dependence, $n$, and $C_n$ for $V(R)$ at the point of closest approach, $b$ in this example. The value of $b$ is then obtained from Eq. (2.58) or (2.59). More sophisticated analytic inversion methods are available but have very limited usefulness. The general approach for $\chi$ not small or $V$ not well approximated by power laws is to parametrize a potential and adjust the parameters via some numerical scheme, like a least-squares fit to the cross section or $\rho$ vs $\tau$ data. Picking the most physically, appropriate potential form, the one with the fewest parameters and best fit, is part of the art of atomic physics. When nonclassical effects are involved, like interference, which we will discuss in the next chapter, other potential extraction techniques become available.

In Figure 2.15 two simple interaction potentials are characterized, allowing us to examine explicitly the relationship between potential, deflection function, and cross section. For a potential yielding a purely repulsive force between atoms, $\chi(b)$ is always positive and has a maximum value $\pi$.

**Figure 2.15.** Deflection function ($\chi$ vs $b$) and angular differential cross section (as $\rho = \chi \sin \chi \sigma(\chi)$ vs $\tau = E\chi$) for two interaction potentials: repulsive potential on left and long-range attractive plus short-range repulsive on right. Rainbow angle is indicated is $\chi_r$. Three impact parameters, $b_1$, $b_2$, and $b_3$, contributing to same $|Z|$ for $|X| < |Z|$. Results for high-energy (solid line) and low energy (dashed line) are indicated.
corresponding to backscattering in the CM system. At each value of \( \cos \chi \) one impact parameter contributes to the cross-section calculation. The differential cross section, as is evident in Eq. (2.61), is singular at \( \chi = 0 \), which is a characteristic of classical cross sections derived from potentials with infinite range. (The hard-sphere example discussed earlier had a finite range and no singularity at \( \chi = 0 \).) It was of course clear from the discussion of total cross section that if \( P_{AB}(b) = 1 \) out to infinity, the angular differential cross section must be singular at \( \chi = 0 \).

For the case of a purely attractive potential (not shown) there is also a singularity at \( \chi = 0 \). However, there is no restriction on the maximum scattering angle as the particles may orbit each other before receding. For the long-range attractive and short-range repulsive potential, shown in Figure 2.15, which is a typical intermolecular potential, the shape of the deflection function, \( \chi \), at large \( b \) is that predicted by Eq. (2.58) or (2.59). At smaller \( b \), because of the change in slope of the potential, the deflection function passes through a minimum value, \( \chi_r \), at the impact parameter labeled \( b_r \). At this angle the classical cross section, defined in Eq. (2.44), is also singular as \( d\chi/db = 0 \). The quantity \( \chi_r \) is called the rainbow angle, as this enhancement in the cross section is similar to the effect that produces rainbows in light scattering. When \( \chi_r < \pi \), then, for angles larger than \( \chi_r \), only one impact parameter contributes to the classical deflection function, as in the previous example. For angles smaller than \( \chi_r \), three impact parameters are associated with the same value of \( \cos \chi \), as indicated in Figure 2.15. Trajectories for this potential are shown in Figure 2.16. For high energies, when the impulse approximation applies, the rainbow angle can be obtained from Eq. (2.58). Using a potential of the Lennard-Jones form,

\[
V = \frac{C_{2n}}{R^{2n}} - \frac{C_n}{R^n}
\]  

(2.62)

\[ \text{Figure 2.16.} \text{ Classical trajectories corresponding to a collision of a reduced-mass particle with a fixed force center. Interaction is a long-range attractive and short-range repulsive potential. Deflection function } \chi \text{ vs } b \text{ is shown on the right. [From H. Pauly, in } \text{Atom-Molecule Collision Theory}, \text{ ed. R. B. Bernstein, Plenum Press, New York (1979), p. 127.]} \]
one finds that $b_r > R_m$, the position of the minimum in $V$, and

$$
\tau_r = E_{\chi_r} \simeq \frac{1}{4} \frac{(a_n C_n)^2}{a_{2n} C_{2n}}
$$

which depends on the relative strengths of the repulsive and attractive interactions. As $E$ decreases significantly, although Eq. (2.63) is not valid, it is clear that $\chi_r$ eventually becomes greater than $\pi$ and additional impact parameters will contribute to the calculation of cross section at all angles. At still lower energies, values of $\chi$ less than $-2\pi$ occur, implying the particles orbit each other during the collision. Therefore, backscattering in the laboratory system becomes a very likely process, and many impact parameters contribute to all scattering angles.

If the attractive part of the potential decreases faster than $1/R^2$, then at very low energies there will be an impact parameter, $b_0$, at which the particle can be classically trapped. That is, the radial acceleration is zero: $\ddot{R} = 0$, at the distance of closest approach, i.e., $\dot{R} = 0$. The effective potential is plotted in Figure 2.17 for three impact parameters at a low energy: $b > b_0$, $b = b_0$, and $b < b_0$. When the attractive part of the potential dominates, $b_0$ is easily estimated for power laws:

$$
b_0 \simeq \left(\frac{n C_n}{\frac{2}{2} E}\right)^{1/n} \left(\frac{n - 2}{n}\right)^{(n-2)/2n}
$$

(2.64)
e.g., for $n = 4$,

$$
b_0 \simeq \left(4 \frac{C_4}{E}\right)^{1/4}
$$

![Figure 2.17. Effective potential, $V_{\text{eff}} = V(R) + \frac{L^2}{2mR^2} = V(R) + \frac{Eb^2}{R^2}$, for three impact parameters (or angular momenta), with CM energy $E$: $b = 0, V_{\text{eff}} = V(R); b = b_0$, orbiting occurs at distance of closest approach; $b > b_0$. Distances of closest approach indicated by dots. The quantity $R$ is the internuclear separation.](image)
This expression is quite useful for estimating ion–molecule reaction cross sections for which the long-range interaction goes as $R^{-4}$. As can be seen from Figure 2.17, if $b < b_0$, the particles will not only orbit at low energies, but will have a small value of $R_0$. Since the two molecules spend a relatively long time at close proximity, a reaction is likely for $b < b_0$, whereas for $b > b_0$ they never approach closely and the collision time is relatively short. The reaction cross section from Eq. (2.26) is therefore $\sigma_R = \pi P_R b_0^2$, where $P_R$ is the reaction probability, often called the steric factor. Employing Eq. (2.64), we obtain the energy dependence of the cross section, $\sigma_R \propto E^{-2/n}$, the oft-used Langevin result for determining molecular reaction rates which we will consider further in Chapters 5 and 6. From Eq. (2.16) and Problem 2.3 the temperature dependence of the molecular reaction rate is found to be $k_R \propto T^{1-2/n+1/2}$, which is temperature independent for $n = 4$.

The impulse approximation discussed above is easily extended to molecular targets, i.e., multiple impulses. For the collision $A + BC$, an atom colliding with a diatomic molecule, atom $A$ receives impulses from each of the target atoms during its passage. If the effect of molecular binding between $B$ and $C$ can be ignored during the collision, the magnitude of the net laboratory deflection is obtained from a binary encounter between $A$ and each target atom, as in Eq. (2.56):

$$\Theta^2_A (b, \Omega_M) \sim \left[ \frac{(\Delta M_A v_{A})_{AB} + (\Delta M_A v_{A})_{AC}}{M_A v_A} \right]^2$$  \hspace{1cm} (2.65)

The deflection therefore depends not only on $b$ and $v$ but also on the molecular orientation, $\Omega_M$. It is tempting now to average $\Theta_A$ over the random orientations of the molecule. However, the quantity that should be averaged is the cross section, or the scattering probability into each angular region, which was described in Eq. (2.37). For many collisions it is useful to look at two limiting cases. For $b$ large compared to the separation of the molecular atoms the impulses are very nearly in the same direction and the molecular target becomes like an atomic target of mass $M_A + M_B$. Now the earlier results apply directly. On the other hand, at very high energies, measurable deflections only occur if $A$ makes a close encounter with either $B$ or $C$. Therefore $\Theta_A$ is essentially due to a single impulse from one of the target atoms, again allowing the use of the previous results. In this limit the molecular gas is equivalent to a gas mixture of unbounded atoms $A$ and $B$. That is, their separations can be assumed to be large and random. The two limiting cases, referred to respectively as the united atom and binary-encounter approximations, have been extensively used to avoid the difficulties inherent in treating a true molecular target, and they apply over a broad range of energies and impact parameters.

The classical deflection function for inelastic collisions requires a knowledge of the energy loss mechanism, which of course is quantum mech-
anical. If it is assumed that the inelastic energy transfer or transition occurs at a single point or a series of points along the classical trajectory, then the equations of motion can be integrated between these points with the CM energy changing in steps at each transition point. For instance, an assumption consistent with the impulse approximation is to describe the transition as a single change in energy occurring at the distance of closest approach, where \( R = 0 \), i.e., the relative motion is the slowest. The net CM deflection is now a sum of two deflections, one on the approach and another as the particles recede. However, for fast heavy-particle collisions, the only transitions occurring with significant probability are those for which \( E \gg Q \). In this case, as the change in energy due to a transition is negligible, the transition probability \( P_{AB-j}(b) \) and the cross section \( \sigma_{AB}(\theta) \) can be determined separately, the latter generally via classical mechanics, as described above, and the probabilities via quantum mechanics (Chapter 4).

Before leaving this section, we note that there exists an alternative starting point for deriving the equations of motion and the classical deflection function. Defining a quantity called the classical action, \( S_c \), as

\[
S_c = \int_{\text{path}} \left[ \frac{1}{2m} p^2 - V(R) \right] dt
\]

where the integral is carried out over the path of the particle, we obtain the equations of motion by assuming that the classical trajectory is that path for which \( S_c \) is a minimum. This approach is referred to as the principle of least action and is discussed in standard texts on classical mechanics. The action, therefore, is a property of a moving classical particle and, in fact, is unusual in that it is an accumulative property for which the history of the path plays a role. This property is important in wave mechanics, and we only note here that \( S_c \) can also be written in the form

\[
S_c = \int_{\text{path}} \left[ \mathbf{p} \cdot d\mathbf{R} - E dt \right]
\]

(2.66)
a form we will encounter in the following chapter.

**Classical Inelastic Cross Sections**

Before considering the wave-mechanical description of collisions, we can employ the classical kinematics developed above to approximate the inelastic collision cross sections. In an inelastic collision, the component particles of the target molecule acquire or lose energy and momentum in addition to that required for them to follow the overall motion of the target. The appropriate classical calculation involves solving the equations of motion during the collision for the interaction between the incident particle
and all the particles, (electrons and nuclei) that make up the target atom or molecule. This formidable, many-body problem has been considered by a number of people, but more useful information often comes from analyzing two limiting cases. These are the same limits considered above when analyzing the deflections by molecules. One such limit applies to very large impact parameters for which the target electrons and nuclei appear and behave as an aggregate during the collision. Here one immediately runs into difficulties trying to describe the aggregate effects classically. An approach developed in early quantum mechanics was to consider the individual target particles as oscillating classically, about the CM of the target. The collision between an incident ion and such a target is described in Appendix C.

In the other limit, appropriate when the impact parameter is small, one considers the interaction between each component of the target and the incident particle separately. During the collision, the interaction times are assumed short enough that the effect of the particles of the target on one another is small, that is, all aggregate effects in the target are ignored. This case is referred to as the classical binary encounter approximation (BEA), as the many-body problem is reduced to two-particle collisions. This is merely an extension of our definition of a binary cross section in the beginning of the chapter where we ignored the effect of neighboring particles when describing collisions in gaseous or solid targets. In a gas one has the option of varying the mean distance between the target particles. However, for the present problem, as for solid targets, these distances cannot be controlled, implying the BEA will be valid only when the distance of closest approach between the target component in question and the incident particle is small compared to the mean separation of target particles during the collision. In this method the net effect of the collision is a sum of the effects for each component of the target, as in Eq. (2.65); here, however, we are concerned with energy transfer to the target.

A binary cross section can be constructed as in Eq. (2.34) with the exception that the target particles, like the electrons in an atom, are not stationary but will have a distribution of velocities. Rather than develop the general case, we assume the incident particle is moving at a speed large compared to the speed of the target particle of interest. That is, the target particles are assumed to be at rest and our previous results apply directly. The energy-transfer cross section between the incident particle A and particle i in target B is, from Eq. (2.46),

$$\frac{d\sigma}{dQ} = \frac{4\pi}{\gamma_i E_A} \sigma(\chi_i)$$

where $Q = \gamma_i E_A \sin^2 (\chi_i/2)$, with $\chi_i$ the CM angle for this collision, and $\gamma_i = 4M_A M_i/(M_A + M_i)^2$. We use the symbol $Q$ to remind the reader that the energy transferred to the electrons results in inelastic energy loss.
Considering any electron which changes energy by an amount greater than the ionization limit, \( I_B \), as ionized, we write the inelastic cross section for ionization approximately as

\[
\sigma_{AB \rightarrow AB} \approx N_B \int_{Q_B}^{Q_{\max}} \frac{dQ}{dQ} dQ
\]  

(2.68)

Here \( Q_{\max} = 2m_e v_A^2 \), where \( m_e \), the electron mass, is small compared to \( M_A \), and \( N_B \) is the number of electrons on B. If the incident particle is a bare ion, \( \Lambda^+ \), then the force between the ion and electron is obtained from the coulomb potential, \( V(R) = -Z_A e^2/R \), where the charge on A is \( q_A = Z_A e \), with \( e \) the magnitude of the electronic charge. The CM cross section for this potential is \( \sigma(\chi) = (Z_A e^2/2m_e v^2)(1/\sin^4 \chi/2) \) [cf. Problem 2.10 or Eq. (2.61 b)], which is equivalent to Eq. (2.61a) if \( \chi \) is small. Assume, further, that atom B has electrons in a number of shells, where \( N_{Bi} \) and \( I_{Bi} \) are the number of electrons and the ionization energy for shell \( i \). Using the above in Eqs. (2.67) and (2.68), we obtain the simple Thomson cross section for ionization of B by ion \( \Lambda^+ \)

\[
\sigma_{A^+ B \rightarrow A^+ B} \sim 2\pi \frac{(Z_A e^2)^2}{m_e v_A^2} \sum_{i, \text{shells}} N_{Bi} \left( \frac{1}{I_{Bi}} - \frac{1}{2m_e v_A^2} \right)
\]  

(2.69)

This result has the basic behavior of an inelastic cross section involving electronic processes. It decreases at high energies and goes through a maximum when the velocity of the incident particle is comparable to some mean speed of the electrons in the atom. That is,

\[
v_A^{-2} = \frac{2}{N_B} \sum N_{Bi} \left( \frac{2I_{Bi}}{m_e} \right)^{-1}
\]

at the maximum, where the quantity in brackets is roughly the mean-square speed of the electrons in the ith shell. Further, the cross section becomes small well above the threshold energy (the threshold energy for the ith shell is \( E = I_{Bi} \)), which is a result of the large difference in mass between \( A \) and the electrons.

Of course at low and intermediate energies the above result is suspect as we cannot assume the electrons are stationary, unless, of course, the energy transfer required for an ionization is "large". Large energy transfers require a small distance of closest approach, favoring a binary encounter approach. The above method applies quite well for a screened interaction. For instance, when \( A \) is a neutral atom, the long-range force is weak and significant energy transfer occurs only in close collisions. It is also applicable to the treatment of molecular dissociation as the heavy particles generally behave in a classical manner. For the reaction
$A + BC \rightarrow A + B + C$ the BEA cross section would be written

$$
\sigma_{A, BC \rightarrow A, B, C} \sim \left[ \gamma_{AB} E_A \right]_{[(M_B + M_C)/M_C]} D_{BC} \left( \frac{d\sigma}{dT} \right)_{AB} dT
+ \left[ \gamma_{AC} E_A \right]_{[(M_B + M_C)/M_B]} D_{BC} \left( \frac{d\sigma}{dT} \right)_{AC} dT
$$

(2.70)

where, for instance, the power law expressions for $d\sigma/dT$ of Eq. (2.61b) can be used to evaluate the integrals. In Eq. (2.70) $D_{BC}$ is the dissociation energy of $BC$, and the mass factors indicate that the energy in the CM system of the molecule must be greater than $D_{BC}$ for dissociation to occur. For comparison with our earlier result, note that if $C$ is an electron, $B$ a nucleus, and $D_{BC}$ the ionization potential, it is, of course, very difficult to ionize an atom via energy transfer to the nucleus.

Another useful quantity defined in Eq. (2.18), the stopping power, is also easily evaluated in the BEA approximation. In this approximation the inelastic energy loss to the electron, $Q$, as well as the energy transferred elastically to the atom, $T$, are continuous and, therefore, the sum in Eq. (2.18) is replaced by an integral. Treating these energy transfers separately, one obtains a stopping power for target material $B$ of the form

$$
- \frac{dE}{dx} \simeq n_B \left( N_B \int_{Q_{\min}}^{Q_{\max}} Q \frac{d\sigma}{dQ} dQ + \int_{T_{\min}}^{T_{\max}} T \frac{d\sigma}{dT} dT \right) \equiv n_B S_{AB}
$$

(2.71)

where $Q_{\min}$ is the minimum excitation energy of the target electrons and $T_{\min}$ is generally zero. The two contributions in Eq. (2.71) are referred to as the electronic and nuclear stopping powers, and the terms in brackets the stopping cross sections. The stopping cross sections for the target constituents, calculated from the coulomb potential as in Eq. (2.69), have the form

$$
S_{\text{coul}} = 4\pi \left( \frac{Z_A e^2}{\Delta E_{\text{max}}} \right)^2 \ln \frac{\Delta E_{\text{max}}}{\Delta E_{\text{min}}}
$$

(2.72)

where $\Delta E$ is either $Q$ or $T$. Because of the large differences in masses, the electronic stopping power dominates at high energies. This may seem strange at first as $T_{\max} \gg Q_{\max}$. However, the maximum energy transfer occurs only in close collisions. The result in Eq. (2.72) implies that the larger impact parameter collisions, in which the electrons receive energy more efficiently, dominate.

Before leaving this example, we note that a certain ambiguity exists in the classical calculation which can be exploited. In the ionization calculation, $Q_{\max}$ and $Q_{\min}$ correspond to energy transfer for the smallest and largest distances of closest approach leading to an ionization. If the smallest distance of closest approach $(R_{\phi})_{\min} = 2(Z_A e^2/m_e V_A^2)$ for the coulomb collision becomes less than the uncertainty in the separation between $A$ and $B$,
as determined by the Heisenberg uncertainty principle, then the collision in this region is nonclassical. The BEA approximation, therefore, should be cut off at a $Q$ smaller than $Q_{\text{max}}$. Also, if the largest distance of closest approach exceeds the screening length of the neighboring particles in the target, then the BEA does not apply and $Q$ should be cut off at a value larger than $Q_{\text{min}} = I_B$. Two different screening lengths can be of importance in determining this cutoff. The most obvious, a static screening, involves the mean distance to the neighboring particles. The other, a dynamic screening, is obtained by requiring that the collision time be short compared to the characteristic periods of the particle in the target for the BEA to apply. That is, if this condition is not met, the target particles should be treated as an aggregate. If $\omega_c$ is a characteristic angular frequency, defining the collision time roughly as $R_0/v_A$, this screening length for slow or distant collisions is $v_A/\omega_c$, often called the adiabatic screening length. When considering an ionization of a small atom, $\omega_c$ is the binding frequency of the electrons, as the nucleus screens the interaction between the target electron and $A$ for slow collisions. In the dissociation of a molecule, $\omega_c$ is the molecular binding frequency, as the screening is due to the other atoms bound in the target. For ionization of heavy atoms or molecules involving many electrons the most important screening is due to the neighboring electrons. This has been shown by Lindhard and others to be characterized by the so-called plasma frequency, which depends on the electron density. The origin of these effects will become clear from the discussion in the following sections in which we consider the wave-mechanical treatment of collisions. However, it should be evident that carefully choosing the upper and lower limits on the integral in Eq. (2.68) allows one to extend the usefulness of the classical BEA method.

**Exercises**

2.1. What is the order of magnitude of the geometric cross section for an atom incident on each of the following targets: atom, benzene ring, RNase molecule, DNA molecule, cell.

2.2. The rate equation, Eq. (2.14), for a species $n_c$ depends on the changing densities $n_A$ and $n_{BC}$ in the reaction $A + BC \to AB + C$. Solve the equation in general and obtain the limiting case in Eq. (2.15).

2.3. For a reaction cross section of the form $\sigma_R = \Pi \pi b_R^2$, where the cutoff impact parameter, $b_R$, is $b_R = C/E^2$, show that the temperature dependence for the reaction cross section of Eq. (2.16) is $k_B T^{1-2\alpha+1/2}$. Assume both the reacting particles have Maxwell–Boltzmann velocity distributions:

$$f(v_i) = \left(\frac{m_i}{2\pi k T}\right)^{3/2} \exp\left(-\frac{m_i v_i^2}{2k T}\right)$$
2.4. Assume the reaction $A + BC \rightarrow AB + C$ proceeds with a 50% probability if the centers of the particles approach each other with a radius less than $0.5 \times 10^{-8}$ cm. If the masses are $M_A = 10$, $M_B = 5$, and $M_C = 20$, in atomic mass units, calculate and plot the temperature dependence of the reaction rate for $Q = 0.01$ eV, $Q = 0.1$ eV, and $Q = 1$ eV using Eqs. (2.16) and (2.26).

2.5. For a deterministic collision with $\rho_{AB}$ a delta function, as in Eq. (2.36), derive the expression for the angular differential cross section in Eq. (2.34).

2.6. Obtain an expression for the laboratory differential cross section for the collision of hard spheres using the CM cross section $\sigma(\chi) = \frac{1}{3}d^2$ for the three limiting cases $\mu \gg 1$, $\mu = 1$, $\mu \ll 1$ shown in Figure 2.7 i.e., Eq. (2.45).

2.7. Derive the relationships between the laboratory quantities $E$, $\rho$, $\mathcal{L}$ and CM quantities $E$, $\rho$, $\mathcal{L}$ in Table 2.3.

2.8. Derive the relationship between the laboratory angle $\Theta_A$ and the CM angle $\chi$ for the general inelastic collision in Table 2.4. Express $\Theta_B$ in terms of $\chi$ also.

2.9. For an ionization of a stationary argon atom, which requires about 15.8 eV, estimate the laboratory threshold energy for an incident proton, argon ion, and a uranium ion. Estimate the “threshold” energy for the Thomson cross section, Eq. (2.69).

2.10. Derive the exact classical deflection function and the CM cross section for the coulomb interaction potential $V(E) = q_A q_B/R$, i.e., $\sigma(\chi) = (q_A q_B/4E)^2/\sin^4(\chi/2)$ using Eq. (2.55).

2.11. Using the Gauss–Mehler quadrature for $\chi(b)$ given in Appendix B, for 5, 10, and 20 integration points, calculate $\chi(b)$ and compare it to the exact and impulse results for power-law potentials $n = 1, 2, 4$.

2.12. Use the data in Figure 2.14 along with Eqs. (2.58) and (2.61a) to extract approximate potentials for the $He^+ + Ar$ and $Ne^+ + Ar$ systems; plot result.

2.13. For a Lennard-Jones form of the potential, Eq. (2.62), relate the measured rainbow angle to the position and depth of the potential minimum.

Suggested Reading

Much of the content of this chapter is well presented in many texts on atomic and molecular collisions or classical mechanics, a few of which are listed below. Additional specific references are also given on some topics.

General


Cross Sections and Rate Constants


**Effects of Neighboring Atoms in Molecules or Solids**


**Classical Deflection Function Expressions**


**Classical Stopping Power Calculation**
