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Charge Transfer in Atomic Systems

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1. Introduction

In considering the topic of collisions between atomic and molecular particles, one must pay particular attention to the processes that involve the transfer of an electron from one of the colliding partners to the other, since frequently this is one of the most probable processes. This process plays a predominant role in a considerable body of physical phenomena. For instance, in the charge balance in the ionosphere, as well as in laboratory plasmas, the charge-transfer process is an important and often dominant intermediate step. The process has also been experimentally useful for obtaining neutral beams with known distributions of states which can be used then to study other phenomena. Here we are also interested in charge transfer both as a means for obtaining certain atomic spectra and for understanding interatomic forces. We are concerned in this chapter with events in which the participants in the collisions are atomic systems, i.e., atoms and ions, and in which a single electron is transferred. The following equations indicate the events to be considered:

\[ A^+ + B \rightarrow A + B^+ \]
\[ A^{2+} + B \rightarrow A^+ + B^+ \]  

(1.1)
It is seen that we have limited ourselves to a consideration of only singly and doubly charged ions. Although the subject of charge transfer for highly charged ions is interesting, there is relatively little information available for these processes. We have also limited ourselves to considerations of events in which the target particle [B in Eq. (1.1)] is a neutral atom, but even with these limitations we are left with a large range of possible processes, particularly when one considers that each of the reactants shown in Eq. (1.1) may be in any one of a number of internal electronic states. Although for simplicity in notation we have not specifically indicated by symbols in Eq. (1.1) that the colliding partners may be in electronically excited states, we certainly intend to consider these possibilities, since some of the more interesting features of charge transfer come about because of the existence of these states.

In discussing charge transfer it is important to consider the electronic states of the reactants before and after the collision takes place. In a general consideration of charge-transfer processes an important parameter is the total change in internal energy that takes place during the collision, \( Q \) (sometimes called the energy defect in the collision). The energy \( Q \) can either be positive (a decrease in internal energy during the collision, with a corresponding increase in kinetic energy) or negative (an increase in internal energy and a decrease in kinetic energy). The former is called an exothermic reaction and the latter an endothermic one. The energy \( Q \) can also be zero as is seen in the discussion that follows.

For the processes indicated by Eq. (1.1) there are some special cases that are worthy of note. If A and B are of the same species, then electron transfer for the singly charged incident ion becomes

\[
A^+ + A \rightarrow A + A^+
\]  

(1.2)

This process is called symmetrical charge transfer, and if the reactants are all in their ground electronic states such that the total internal energy before the collision is the same as that after the collision \((Q = 0)\), the event is also called resonant charge transfer because of the generally high probability of these processes (especially at low kinetic energies). It is also possible for the asymmetrical case to be resonant or nearly resonant if there are appropriate electronic states available so that \( Q \) is nearly zero, and these processes are called accidentally resonant.

Having discussed the processes to be considered here, let us proceed to ask what aspects of these collisions are of interest to us. In collisions between heavy particles it is generally meaningful to speak in terms of the classical trajectories of the nuclei involved, although we must usually resort to quantum mechanics to describe the motion of the electrons during the collision. This is referred to as a semiclassical treatment. Thus, we may represent a typical collision as shown in Fig. 1. In this figure we have chosen
the reference frame in which the target particle B is initially at rest (closely approximating many laboratory conditions when the velocity $v_A$ of the incident ion is reasonably large and B is a thermal gas). The incident particle has a velocity $v'_A$ after the collision and the target particle has a velocity $v'_B$. The classical impact parameter is $b$ and the laboratory scattering angle of the incident particle is $\theta$. The state of $A^+$ before the collision is indicated by $\alpha$ and that of $A$ after the collision by $\alpha'$; correspondingly, the internal state of $B$ before the collision is $\beta$ and that of $B^+$ after the collision is denoted by $\beta'$.

Ideally, one would like to know for any desired species and initial states, $A^+ (\alpha)$ and $B (\beta)$, what the probability is of the collision resulting in any possible combination of final states, as a function of $v_A$ and $b$. It is also desired that the relationship between $b$ and $\theta$ be known. This information is far from being realized at the present time. In looking at the problem from the theoretical point of view, one must consider the interaction potentials that represent the transient molecular ion states formed during the collision and possible electronic transitions between these states in order to be able to obtain the desired probabilities. Except in special cases such calculations are severely hampered by a lack of information about the appropriate potentials as well as the quantum mechanical difficulties in calculating accurate transition probabilities between the potential curves. From the experimental point of view, it is difficult to obtain the kind of detailed information one would like to have for comparison with available calculations. Most experiments have involved measurements that either sum over the final states or effectively integrate over $\theta$ (i.e., $b$), or do both (total cross sections). It is clear that it is desirable to have experiments performed that give as much detail as possible, but this can, of course, only be achieved at the expense of greater experimental complexity.
We will discuss here general topics having to do with the experimental study of charge-transfer events such as those indicated by Eq. (1.1). We will consider the most general requirements for such measurements and the major difficulties we expect to encounter in making them. A somewhat more detailed discussion of experimental techniques is given in Section 3.

Charge-transfer measurements are normally performed by forming a beam of the appropriate ions and allowing these ions to collide with the desired target atoms. When the source of target atoms is simply a gas at room temperature, then there is no question that the great majority of the target atoms are in their ground electronic states, moving with thermal kinetic energies. The electronic state of the incident ions is a somewhat more difficult question since it has been shown that with conventional ion sources some care is required to be assured that the beam does not have an unknown mixture of ions in various long-lived excited states. If one desires to study collisions in which the incident ions are in known excited electronic states, rather than in their ground states, then the experimental difficulties of establishing that the beam has the desired composition are greatly increased. If one wants to study collisions in which the incident ion is multiply charged, there is generally no particular difficulty in producing doubly charged ions in the conventional ion sources (although the intensity obtained is usually much less than that for singly charged ions), but creating ions with charges greater than 2 in sufficient quantity is generally quite difficult, requiring that special ionization techniques be used. Most charge-transfer measurements have been performed at incident-ion energies greater than around 10 eV, since in the use of the usual techniques at lower energies one encounters serious experimental difficulties due to space charge spreading of the ion beam and the effects produced by surface charges within the apparatus.

In considering the general difficulties that arise when attempting to detect the results of collisions in which charge transfer has taken place, a great deal depends on the amount of information one seeks concerning the details of the collisions. If total cross sections are to be measured by collecting the positive ions produced in a gas when a beam of ions passes through the gas, then the principal task is to be assured that the ions collected result from the desired events rather than other possible processes such as ionization. If one wishes to obtain the greater detail given by differential cross sections, then the angular distribution of the incident particles after receiving an electron from the target atoms is to be measured. The principal problems associated with this type of measurement occur when the incident ions are singly charged, resulting in neutral particles whose number must be detected in an absolute manner. Neutral atoms in their ground state can be successfully detected by electron-multiplier detectors when their kinetic energy exceeds 1 keV, but even at these energies it is not a simple task to determine the absolute efficiency of the detector, which
is required in order to obtain absolute differential cross sections. When the kinetic energy of the neutral products of a charge transfer process is less than 1 keV the difficulty is compounded because of the lack of sensitive detectors for low-energy neutral particles. When the charge transfer process to be studied involves the use of doubly charged incident ions which receive a single electron from the target atom, then the detection problems are considerably simplified since it is much easier to detect the singly charged ions that result than it is to detect neutral atoms.

For information concerning the final internal states of the collision products, some study of the energetics of the interaction must be made. When doubly charged incident ions are used the single charge on the ion that results after charge transfer allows one to measure its kinetic energy by the usual techniques, such as electrostatic analysis. For neutral product particles it is usually necessary to use pulsed beam and time-of-flight techniques to obtain their kinetic energy. Another possibility for studying the energetics of charge-transfer processes is to observe the photons that result from transitions between electronic states either during the collision or shortly after. One significant advantage of the observation of the light emitted is that much greater energy resolution can be obtained than is usually possible for kinetic energy measurements. The greatest disadvantage to studies of the light emitted is the necessity of being assured that the light observed is coming from the events in which one is interested. This difficulty can be greatly relieved by studying coincidences between photons emitted and particles scattered through a known angle. This latter type of experiment allows the possibility of relating scattering angle to impact parameter, while at the same time retaining the good energy resolution of optical spectroscopy. These advantages, of course, come at the expense of much more complex apparatus compared to that required for the measurement of the total cross sections and are limited to the study of optically allowed transitions. In all experimental studies of absolute charge-transfer cross sections one of the most difficult quantities to measure accurately is the number density of the target particles. When the target particles are gas atoms within a gas cell this amounts to requiring an accurate determination of the pressure within the cell, a procedure that in many cases requires a great deal of care in order to obtain cross sections that are accurate to a few percent. If the charge-transfer events are studied in a crossed-beam configuration, then the determination of the target number density is even more difficult than it is for the gas cell, and more indirect methods must be employed to make this measurement.

In considering theoretical studies of charge transfer one is concerned with transitions between the electronic states before the collision to some final states. In calculating differential cross sections one requires a knowledge of interaction potentials corresponding to the states that participate in
the collision, as well as the probabilities of transitions between these states. For most systems it is difficult to obtain both the interatomic forces and the transition probabilities, making the theoretical difficulties in obtaining accurate cross sections comparable to those encountered in attempting experimental studies of reasonably complex systems. In essence one is reduced to making approximations except for the simplest processes. In an approximate calculation done for comparison with experiment, numerical accuracy is often much less important than the physical insight which is brought to bear on the collision process, since those collision partners that are easily studied in the laboratory are often not the most important species involved in physical phenomena for which atomic cross sections play a role.

If, instead of desiring to compute differential cross sections, one is interested in cross sections integrated over angle (or impact parameter $b$), the difficulties are reduced considerably. One often obtains sufficient information from knowledge of the maximum interatomic separation for which a given reaction will take place and an average transition probability within the reaction region. A considerable body of literature exists describing such methods in the fields of nuclear collisions, electron–atom collisions, as well as ion–atom and molecular collisions. For the latter cases one of the most widely used methods is the so-called Landau–Zener–Stueckelberg approximation which we will consider later.

In the following sections we will describe in more detail some of the theoretical and experimental methods that we feel are most useful for these charge-transfer cross sections. The state of the art of the theory of atomic collisions is considerably advanced as compared, for instance, to that for molecular collisions, and we spend in the next section considerable time describing some of the more important aspects of ion–atom collisions in the energy range of interest.

2. Theory

2.1. Introduction

As stated earlier, in the application of quantum mechanics to charge transfer collisions severe approximations need to be made to obtain results for all but the simplest systems. A complete discussion of many of the most important methods is contained in a recent text by Mapleton on charge transfer as well as other texts on the general field of atomic collisions. It is seen that the appropriate method for a particular collision depends primarily on the relative velocity of motion of the colliding particles. In this section, we restrict ourselves to a brief discussion of some of the concepts involved in
charge transfer problems, paying particularly close attention to the semiclassical method since this description provides a useful conceptual interpretation of experimental observations, as well as a good starting point for a reasonably accurate calculation.

The primary quantities of interest are cross sections differential in angle and energy for a given collision. These provide the most direct connection between experiment and theory, and the most rigorous test of approximate methods and interpretations. Closely related to this quantity is the energy-loss spectrum as a function of angle (or impact parameter) which shows the relative importance of the various channels at each scattering angle. The probability of observing an energy loss, associated with a given reaction and angle of scattering, is proportional to the differential cross section for that reaction. Also of interest, although they often allow a variety of interpretations, are such summed quantities as the cross section integrated over angle and reaction rates, or total differential cross sections, i.e., summed over energy loss or final states.

For incident-ion energies such that the relative velocity of the colliding particles is of the same order of magnitude or smaller than the velocity of the outer-shell electrons (generally around one atomic unit,* 1 a.u., of velocity for a proton ~25 keV), reactions can best be viewed as transitions between a set of quasi-molecular electronic states formed by the collision partners (cf. Chapter 3, Section 2). Associated with each state is an interaction potential which depends on the internuclear separation $R$, and which is represented as a potential curve that is a sum of the nuclear–nuclear repulsion and the average electronic binding energy. These potential curves determine the nuclear motion, which is often treated classically because of the large mass, hence small de Broglie wavelength, associated with the nuclei. For charge-transfer reactions, transitions between the quasi-molecular states often occur at internuclear separations on the order of 2–5 a.u. and this is generally the region where envisioning the system as composed of separate atomic and ionic species breaks down. For smaller $R$ the outer electrons, at these collision velocities, must be treated as moving in the combined field of the two charge centers. Therefore, in a collision in which the colliding particles penetrate to smaller $R$, their outer electrons will have a probability of following either nucleus out subject to constraints on changes in energy, momentum, and angular momentum.

At considerably higher velocities of relative motion the charge-transfer reaction can be pictured as a two-step process and is best described by the second Born approximation.* This involves an energy transfer from the incident ion to the target electron followed by a “second collision” involving

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*In atomic units $\hbar = 1, m_e = 1,$ and $\epsilon = 1.$ Therefore, 1 a.u. of energy is twice the binding energy of the hydrogen atom, 27.2 eV, and 1 a.u. of length is the radius of the Bohr orbit for ground state hydrogen, etc.
the target nucleus which allows the electron to have the correct momentum to be carried off by the incident ion. This is clearly a complementary view to the previous one and generally involves considerably smaller internuclear separations for the transition.

In the following we will discuss the charge-transfer process from the first point of view, i.e., as a transition between quasi-molecular electronic states, since our primary interest is in collision velocities where this approximation is valid, and even at higher velocities the concept of such states can often prove useful. In implementing this scheme one first chooses a set of electronic wave functions to describe the quasi-molecular states associated with each set of atomic states $\alpha\beta$ at $R \to \infty$, as described earlier. A possible and unique choice for this set are the adiabatic wave functions, solutions to the electronic Hamiltonian with fixed nuclei at each value of $R$. One uses this set at very low velocities and transitions are induced by the nuclear motion (i.e., the Born–Oppenheimer approximation breaks down). For velocities of interest here other sets, called diabatic wave functions, are more appropriate for describing a collision (cf. Chapter 3, Section 2). One such set of states is constructed of molecular orbitals for which the electron–electron interactions are averaged. Because the diabatic states are not exact solutions of the electronic Hamiltonian, the energy levels or potential curves associated with states of the same symmetry may cross (i.e., become degenerate for some $R$) and transitions are attributed to an interaction potential coupling any two states. For the charge-transfer reaction the coupling is related to the exchange interaction, the sharing of the electron by the two centers, which has an exponential dependence on $R$. If a crossing occurs at a separation $R_x$, as in Fig. 2, transitions generally occur with high likelihood in the vicinity of $R_x$ depending on the strength of the coupling.

![Diagram](image-url)

**Fig. 2.** Crossing of diabatic potential energy curves at internuclear separation $R_x$. 
Quite often the general behavior of the diabatic potential curves and the approximate crossing points can be estimated from simple considerations of the molecular orbitals without solving for the wave function,\textsuperscript{10,11} and hence the usefulness of this procedure.

Using a set of wave functions one can solve for the nuclear motion quantum mechanically or classically. In the latter case, elastic scattering trajectories and hence cross sections are easily obtained for each potential associated with a given state. However, when transitions occur the classical trajectory considerations become ambiguous. This is not too important for integrated cross sections, but for angular differential results it is very important. The method described in the following section attempts to deal with this.

2.2. Semiclassical Cross Sections Differential in Angle and Energy

In this section we will discuss a semiclassical method for describing cross sections which are differential in angle and energy of the scattered particle, which is that, where the final state of the scattered particle is analyzed. We describe the result in one form that is intuitively appealing and useful for determining the principal features of the differential cross sections. In wave mechanics we imagine that the scattering intensity at a given angle is the sum of contributing partial waves (wavelets) originating at all parts of the incident wave front which we often parametrize with an impact parameter (the perpendicular component of the distance from the point in the wave front to the scattering center). In this sum constructive interference (a region of stationary phase) for each scattering angle is found to occur for a few regions of impact parameter.\textsuperscript{12} Each of these impact parameters can be associated with a classical trajectory, leading to scattering at the angle of interest. For a given transition, $\alpha \beta \rightarrow \alpha' \beta'$, the contributing classical trajectories can be deduced from the diagram of potential energy curves if switching between curves (states) is considered to occur for well-defined regions of $R$ where the coupling is optimum\textsuperscript{13} (e.g., at a curve crossing). Associated with each trajectory ($j$) and corresponding impact parameter $b^{(j)}$ is a classical action $A^{(j)} = \int [p^{(j)} \cdot dR - \int p \cdot dR]$ (where $p^{(j)}$ is the center-of-mass momentum along the trajectory and $p$ is the incident momentum) and a classical, elastic scattering cross section $\sigma^{(j)}(\theta)$ (where $\theta$ is the center-of-mass scattering angle) determined from the potential energy curves.\textsuperscript{9} The differential cross section at any angle is a sum of interfering amplitudes associated with each classical trajectory:

$$\sigma_{\alpha \beta \rightarrow \alpha' \beta'}(\theta) = \sum_{j} |P_{\alpha \beta, \alpha' \beta'}^{(j)} \cdot \sigma^{(j)}(\theta)|^{1/2} \exp \left[ \frac{iA^{(j)}}{\hbar} - i\gamma^{(j)} \right]^{2} \tag{2.1}$$

In this expression $P_{\alpha \beta, \alpha' \beta'}^{(j)}$ is the total transition probability for $\alpha \beta \rightarrow \alpha' \beta'$ on
the trajectory \( (j) \) (a number of transitions between intermediate states may occur), \( \gamma^{(1)} \) is an additional constant phase factor, generally \( \pm \pi/4, \) \(^{12,13} \) and only differences in the classical action between any two trajectories are evaluated. For other interference effects, such as rainbow scattering, where for a singe potential more than one impact parameter may contribute to a given scattering angle, e.g., a potential which is attractive for large \( R \) and repulsive at small \( R, \) simple modifications to Eq. (2.1) can be made. \(^{12} \) Beyond this the validity of Eq. (2.1) depends on the transition regions being well localized in \( R. \) The transformation to laboratory angles and differential cross section when the internal energy is changed by \( Q \) is straightforward, involving a multiplicative kinematic factor.

To help elucidate the trajectory consideration in Eq. (2.1), we consider two familiar examples involving only two states throughout the collision. First, for curve crossing (Fig. 2), these two trajectories will result in a transition described by the potential functions given in Fig. 3 if the distance of closest approach during the collision is smaller than \( R_s. \) The differential cross section for a transition then becomes, using Eq. (2.1),

\[
\sigma_{\alpha \beta \rightarrow \alpha' \beta'}(\theta) = P_{\alpha \beta, \alpha' \beta'} \left[ \frac{\sigma^{(1)}(\theta) + \sigma^{(2)}(\theta)}{2} \left( \frac{A^{(1)} - A^{(2)}}{h} - \frac{1}{\gamma^{(1)} + \gamma^{(2)}} \right) \right] \]

(2.2)

where we have assumed that the transition probability \( P^{(1)}_{\alpha \beta, \alpha' \beta'} = P^{(2)}_{\alpha \beta, \alpha' \beta'} \). This reduces to the standard curve crossing expression when the cross sections for the two trajectories are about equal. \(^{6} \) A closely related example is symmetric resonance-charge transfer:

\[
\Lambda^2+ + A \rightarrow A + \Lambda^2+, \quad \Lambda^+ + A \rightarrow A + \Lambda^+ \]

Now the two states involved are the gerade (g), symmetric with respect to inversion, and ungerade (u), unsymmetric, states of the molecule which are

![Fig. 3. Potential curves from Fig. 2 associated with the two trajectories leading to a transition \( \alpha \beta \rightarrow \alpha' \beta' \). Arrows indicate relative motion of the colliding particles during the collision.](image-url)
degenerate at large $R$. There is a probability of $\frac{1}{2}$ for being in either state. On exiting these states can lead to either elastic scattering or charge transfer:

$$
\sigma_+ (\theta) \approx \frac{1}{2} \left[ \sigma^{(\epsilon)}(\theta) + \sigma^{(\nu)}(\theta) \pm 2 \sigma^{(\epsilon)}(\theta) \cdot \sigma^{(\nu)}(\theta) \right]^{1/2} \cos \left( \frac{A^{(\epsilon)} - A^{(\nu)}}{\hbar} \right)
$$

(2.3)

where the $+$ implies elastic scattering and $-$ charge transfer. At very low energies, because the nuclei are identical, contributions from angles $(\pi - \theta)$ must be included.\(^1\text{e}\) If in this expression $\sigma^{(\epsilon)}(\theta) = \sigma^{(\nu)}(\theta)$, then one obtains the well-known expression for the charge transfer probability:

$$
P \approx \sin^2 \left( \frac{A^{(\epsilon)} - A^{(\nu)}}{2\hbar} \right)
$$

(2.4)

In both of these examples the characteristic oscillatory structure of differential cross sections is seen to be due to the differences in action for the two trajectories.

### 2.3. Transition Probabilities and Energy-Loss Spectra

At those scattering angles and energies\(^*\) for which the deflections associated with the different trajectories are all roughly the same, a single average trajectory and elastic scattering cross section $\bar{\sigma}(\theta)$ may be used. This occurs, for instance, when the deflections are primarily determined by the repulsive core. For these cases the internuclear separation may be treated as a simple function of time and the motion of the nuclei can be thought of as creating a time-dependent field for the electrons. This results in the impact parameter equations for the transition probabilities. The differential cross section becomes

$$
\sigma_{\alpha\beta \rightarrow \alpha'\beta'} (\theta) \approx P_{\alpha\beta,\alpha'\beta'} \bar{\sigma}(\theta)
$$

(2.5)

with $P_{\alpha\beta,\alpha'\beta'}$ a sum of transition probabilities $P^{(i)}_{\alpha\beta,\alpha'\beta'}$ and phase factors in Eq. (2.1). In this method the action becomes $\int_{-\infty}^{\infty} \frac{V(t)}{\hbar} dt$, where $V(t)$ is the interaction energy along a trajectory. One solves the time-dependent Schrödinger equation to obtain the transition probabilities

$$
\left[ H_e (\vec{r}|\vec{R}) - i\hbar \frac{\partial}{\partial t} \right] \phi(t) = 0
$$

(2.6)

where $H_e$ is the electronic Hamiltonian and $R$ is a function of time.\(^8\) At high energies it is important to include the momentum change of the active electron.\(^8\)

\(^*\)Expressed conveniently in terms of the reduced scattering angle $\tau = E\theta$, which for small-angle scattering depends only on the impact parameter.\(^1\text{e}\)
As the sum of the transition probabilities $P_{ab',\alpha',\beta'}$ over all final states is unity for any set of initial states $ab$ the quantity $\tilde{\sigma}(\theta)$ is the total differential cross section, i.e., the angular differential cross section summed over all final states or energy transfers. Therefore, the quantity $P_{ab,\alpha',\beta'}$ can also be described as the transition spectrum at angle $\theta$ or the energy-loss spectrum at that scattering angle if the state labels are translated into the corresponding change in internal energy of the colliding system. That is, $P_{ab,\alpha',\beta'}$ is the probability of an energy loss (or gain) associated with the difference in internal energy between the $ab$ and $\alpha'\beta'$ states. More precisely the probability as described here should be multiplied by the density of states. This description is only valid, of course, at those $\tau$ values at which the impact parameter method is valid. The converse of this is that for many regions of $\tau$ energy-loss spectra provide a direct measure of the impact parameter probabilities provided the relationship between $b$ and $\theta$ can be established.

At other values of $\tau$ where the different trajectories have significantly different $\theta$, $b$ relationships, the two-state impact parameter equation can be solved locally to obtain $P^{(\tau)}_{ab,\alpha',\beta'}$ using an average trajectory in the transition region for the time dependence in Eq. (2.6). Here we consider some approximations to that solution for three classes of coupling: weak coupling and strong coupling, with or without a curve crossing. For weak coupling, with coupling matrix element $V_{0f}(R)$, one has

$$P^{(i)}_{0f} = \left| \int_{\infty}^{\infty} V_{0f} \exp \left[ \frac{i}{\hbar} \int_{-\infty}^{t'} \left( V_f - V_0 \right) dt' \right] dt \right|^2$$  \hspace{1cm} (2.7)

where to simplify notation the subscripts 0 and $f$ are used for the initial and final state labels, respectively, and $V_0$, $V_f$ are the corresponding interaction potentials. In the calculation of $A^{(i)}$ the transition can be treated as occurring at the distance of closest approach, i.e., follow $V_0$ on the way in and $V_f$ on exiting. This is the impact parameter version of the widely applicable distorted wave approximation. The distorted wave approximation has been shown to describe the threshold dependence at a curve crossing reasonably accurately. In Eq. (2.7) it has become customary for simplicity to treat the time dependence by a straight-line trajectory, $R^2 = b^2 + v^2 t^2$, in which case analytic expressions for $P^{(i)}_{0f}$ can often be obtained.

When the distance of closest approach in a collision is such that a curve crossing has been passed, the LZS (Landau-Zener-Stueckleberg) expression for transition probabilities has proven to be a useful approximate solution to the local two-state impact parameter equations. In ion-atom collisions one often finds a series of crossings, as when the initial diabatic state correlates with a doubly excited state of the united atom.
Fig. 4. Diabatic correlation of singlet gerade states in He$^{2+}$,\(^{177}\).

\((R = 0)\); see Fig. 4 for He$^{2+}$ + He. Each successive crossing can be treated separately if the transition regions, which have extent

\[
\delta R_s = \left| \frac{V_{0f}}{\epsilon_s R_s} \left[ \frac{\partial}{\partial R_s} (V_f - V_0) \right] \right|_{R_s = R_s}, \tag{2.8}
\]

do not overlap. The total transition probability is then the product of the individual ones. Each time a crossing point \(R_s\) is passed on a trajectory \((j)\), the probability of staying on the same diabatic curve has the form \(P_i^{(j)} = \exp(-\Omega^{(j)})\), where

\[
\Omega^{(j)} = \frac{2\pi}{\hbar} \left| \frac{V_{0f}}{P_i^{(j)}} \right|_{R_s = R_s}. \tag{2.9}
\]
with $\mu$ the reduced mass, and $p_R^{(i)}$ the radial component of momentum. The term in parentheses is essentially the time it takes to pass through the transition region, $\delta R_s$. From Fig. 3, for a collision involving a single crossing region the transition probability becomes $2p_1^{(i)}(1 - p_2^{(i)})$; however, more complicated cases may be considered. For instance, if two crossings are encountered on a trajectory, as in Fig. 5, the total transition probability for that trajectory would be written

$$P_{0,i}^{(i)} \approx p_1^{(i)}(p_2^{(i)})^2(1 - p_1^{(i)})$$ (2.10)

The LZS approximation breaks down in the threshold region where the distance of closest approach is approximately equal to $R_s$. Here one might use Eq. (2.7), Bates and Delos et al. have discussed other limitations on Eq. (2.9).

If the initial state is close in energy to a continuum of states, as in the He$^{2+} +$ Ar collision, "crossings" may occur in the continuum since there are often well-defined states of the quasi molecule which correlate at large $R$ to autoionizing states of the separated ion. For this case the dominant effect is caused by transitions between the initial state and these well-defined molecular states at the crossing, with the remainder of the continuum treated as a perturbation.

For cases in which the curves do not cross, localized regions of strong coupling may still occur especially at large separations. This is particularly important for charge transfer, as in the H$^+$ + Ar $\rightarrow$ Ar$^+$ + H reaction. At large $R$ the energy defect is small. As the exchange interaction $V_{ij}$ increases with decreasing $R$ and the adiabatic potentials therefore diverge, a point $R_s$ is reached at which the coupling is optimum. This can be shown by a numerical integration of the two-state impact parameter equations (Fig. 6). Here the probability of being in the excited $^1\Sigma^+$ state of ArH$^+$ that leads to charge transfer changes essentially once on the way in and again on the way out at well-defined internuclear separations. If $V_0$, $V_f$ are the diabatic

![Fig. 5. A trajectory involving two curve crossings.](image)
Fig. 6. The probability of being in the excited 'S' molecular ion state of ArH during the course of a collision with impact parameter \( b = 2 \) a.u. Results were obtained from integrating the two-state impact parameter equations for the \( \text{H}^+ + \text{Ar} \) collision. \( R_x \) indicates region of strong coupling. 24

potentials of the initial and final states, then \( R_x \) is roughly defined by the relation

\[
V_{of}(R_x) = \frac{1}{2} |V_f - V_0|_{R_x} \tag{2.11}
\]

i.e., when the coupling is comparable to the splitting. This is the region discussed earlier where the outer electron orbitals of the \( \text{ArH}^+ \) molecular ion change from a system of separated atomic orbitals to molecular orbitals.

A useful estimate of the transition probabilities can be deduced in this case from the Rosen–Zener model solution to the two-state equations. 24, 25 For distances of closest approach much smaller than \( R_x \), the deflections do not depend significantly on contributions from \( R > R_x \). Therefore, the adiabatic potentials, which include the effect of the interaction potential between the states, are used to obtain \( \alpha^{(i)}(\theta) \) and \( A^{(i)} \) in Eq. (2.1). Then, by analogy with the LZS method, the transition probabilities \( P^{(i)}_f \) for each crossing of the transition region \( R_x \) can be obtained from 24, 25

\[
4P^{(i)}_f(1 - P^{(i)}_e) = \left| \int_{-\infty}^{\infty} V_{of} \cdot \exp\left( \frac{(i\pi/4)\int_{-\infty}^{\infty} (V_f - V_0) dt'}{\int_{-\infty}^{\infty} V_{of} dt'} \right) dt \right|^2 \tag{2.12}
\]

For exponential coupling, \( V_{of} = Ae^{-\alpha R} \), if the phase in Eq. (2.12) is approximated by \( Qt/\hbar \), and a straight-line trajectory is used for the integration, one obtains

\[
4P^{(i)}_f(1 - P^{(i)}_e) = \left| \frac{K_1(b^{(i)} \alpha')}{K_1(b^{(i)} \alpha)} \right|^2 \cdot \left( \frac{\alpha}{\alpha'} \right)^2 \tag{2.13}
\]

where \( \alpha' = [\alpha^2 + \left( Q/\nu h \right)^2]^{1/2} \) and the \( K_1 \) are modified Bessel functions. A similar result can obviously be obtained for the weak coupling case Eq. (2.7). These expressions provide useful approximations to the transition probabilities (or energy-loss spectra in the appropriate \( \tau \) regions) and they are written explicitly in terms of the energy change \( Q \). It should be emphasized
that in applying Eq. (2.13) to the type of collisions discussed here, for \( Q \) one should use the energy difference between the states in the transition region. For charge transfer transitions occurring at large \( R \) with incident doubly charged ions exothermic processes will therefore be favored because of the \( 1/R \) potential in the final state. For transitions occurring at small \( R \) the effect of the \( 1/R \) potential is negligible. Equation (2.13) is intended to be used when only two states are involved in a transition. When many final states are involved a corresponding integration of Eq. (2.7) is useful. In Eq. (2.13) it can be seen that, unlike the curve-crossing case, as \( v \to \infty \), \( P^0_{ij} \to \frac{1}{2} \). That is, the states behave as if they are effectively degenerate (resonant) at large \( R \). A case of particular interest in charge-transfer collisions is where the atomic or ionic spin-orbit splittings are large\(^{26,27} \) as in

\[
\text{H}^+ + \text{Xe} \to \text{H}(1s) + \text{Xe}^+(\ell P \ell) \quad \text{or} \quad \text{Xe}^+(\ell P \ell) + \text{Xe} \to \text{Xe} + \text{Xe}^+(\ell P \ell)
\]

collisions. At some value of \( R \) the exchange interaction becomes equivalent to the spin-orbit coupling, and in this region transitions among the spin states may occur with high likelihood depending on the relative velocity.

One can also exploit this to create, for instance, a neutral beam of polarized atoms at the appropriate scattering angle.\(^{26} \) For the systems under consideration in this chapter one may have both strong coupling regions and curve crossings, as in Fig. 7.

The approximate methods discussed here have proved useful in estimating and understanding the behavior of measured angular differential and integrated cross sections as will be discussed in Section 4. Needless to say there are many additional approximate methods which we have not discussed. The reader is referred to standard texts for a review of these other methods as well as accurate numerical methods for obtaining cross sections.\(^6 \)

![Fig. 7. Examples of transitions occurring at both a curve-crossing and non-curve-crossing region.](image-url)
2.4. General Considerations

It is seen from the expressions for approximate transition probabilities [e.g., Eq. (2.13)] that the probability of a transition depends on the separation in energy of the quasi-molecular states and the rate of change of the coupling matrix. Therefore, at low collision energies, calculations of transition probabilities indicate that charge exchange occurs preferably between states of small energy defect, if the potentials do not diverge. Except at the very lowest velocities, where orbiting occurs, there is no general preference between exothermic and endothermic transitions; one has to consider the behavior of the potential curves in each case. The impact parameter formalism for transition probabilities essentially considers as coupling the two largest corrections to the Born–Oppenheimer approximation.\(^5\,^8\). These two corrections have separate selection rules on the change of electronic angular momentum along the internuclear axis, \(M_L\), when spin–orbit coupling is weak. Radial coupling, due to the rate of change in the radial coordinates, which in diabatic expressions is replaced by a potential, obeys the selection rule \(|\Delta M_L| = 0\), e.g., \(\Sigma \rightarrow \Sigma, \Pi \rightarrow \Pi\). Rotational coupling, due to the angular rate of change of the internuclear axis, occurs with greatest probability near the distance of closest approach in the collision, where the rate of rotation of the axis is greatest, and obeys the selection rule \(|\Delta M_L| = 1\), e.g., \(\Sigma \rightarrow \Pi\). The rotational coupling operator, which we have not treated, comes from the angular contribution to the time derivative in Eq. (2.6).\(^6\) It also plays an important role at large \(R\) where spin–orbit coupling is important.\(^7\)

Additional rules apply: \(g \rightarrow u\) and \(\Sigma^+ \rightarrow \Sigma^-\). In the impact parameter formalism it is assumed that any change in total electronic angular momentum of the separated ion–atom system can be compensated for by a corresponding change in the angular momentum of the nuclear motion, conserving angular momentum. When the impact parameters are large and coupling between the nuclear and electronic motion is weak, the total electronic angular momentum may be conserved separately. It is clear that these selection rules are very different from those for optical transitions encountered in spectroscopy. Therefore in collision spectroscopy one may observe, depending on impact parameter, transitions between states of the colliding atoms and ions which may be difficult to observe by optical spectroscopy. It is also clear from Eq. (2.1) that the differential cross sections will have considerable structure due to the interference between the contributions from different classical trajectories. For this reason, the observation, for instance, of energy loss at a single angle may lead to an erroneous interpretation of the overall relative likelihood of a given process. It also means that the differential cross sections do not frequently lend themselves to simple interpretations and care must be taken in analyzing data.
Our discussion of transitions has involved an exchange of energy between electronic and nuclear motions. Because the lifetimes for spontaneous emissions of photons are generally large compared to the collision times, optical transitions are not usually observed during the collision. However, in very fast collisions which affect inner-shell electrons, transitions between quasi-molecular states due to induced emission have been seen recently. For the collisions of interest here it may be possible to observe transitions involving autoionization during the collision since the lifetimes for this process are often comparable to the collision times involved in the kiloelectron volt region.

In the collision of a doubly charged ion with a neutral atom, double-charge transfer (see also Chapter 4) is the process which competes most efficiently with single-charge transfer at low collision energies. Therefore, a discussion of this process must be included in any complete description of collisions of the type \( \Lambda^{2+} + B \rightarrow \Lambda^+ + B^+ \). In fact, as can be seen from Fig. 4, single-charge transfer into excited states of \( \Lambda^+ \), in the collision of \( \Lambda^{2+} \) with \( \Lambda \), will most likely occur via crossings with one of the "elastic" scattering potentials, which in this case can lead to either elastic scattering or resonant double-charge transfer. This is discussed further in Section 4. At large collision energies the probability for double-charge transfer can be considered as roughly the square of the probability for capture of one electron and it is therefore a second-order process having a small cross section. In the low energy region where the quasi-molecular potential curves describe the collision, Komarov and Yanov have obtained an expression for the two-electron exchange splitting for symmetric systems. In general, the exponential screening constant at large \( R \) is the sum of the screening constants for each electron determined by the overlap of the electron orbitals on one center with those for the electron on the other center of charge. Since the molecular states leading to double-charge transfer have no long-range repulsive force associated with them, they are often crossed by the single-charge-transfer states, making transitions likely. For symmetric systems such as \( \Lambda^{2+} \) + \( \Lambda \), resonant double-charge transfer to the ground state dominates. However, in very nonsymmetric systems double charge exchange leaving either the projectile or target in an excited state may also be a very important process. In general, this process requires a change in two molecular orbitals. However, single-charge transfer leaving the target in an excited state is also a two-orbital process and therefore the cross sections are comparable. Further, at low energies the energy defect is as important as the coupling matrix elements in determining which states have the largest cross sections. At long range the primary difference between these processes for nonsymmetric systems is that \( \Lambda^{2+} + B \rightarrow \Lambda^+ + B^+ \) goes by curve crossing to exothermic states and \( \Lambda^{2+} + B \rightarrow \Lambda + B^{2+} \) will go preferentially to near-resonant states.
3. Experimental Methods

3.1. Introduction

The purpose of this section is to provide a general survey of the several experimental arrangements for studying charge transfer events. We do not intend to discuss the details of these techniques since these have been summarized elsewhere.\textsuperscript{30-32}

The discussion considers both measurement of total cross sections, where no information is gained concerning the angular distribution of the product particles, and measurement of cross sections that are differential in the angle of at least one of the product particles. Within each of these two main categories, there are subdivisions according to which characteristics of the collision are studied, e.g., the kinetic energies of the products or their internal states.

Before proceeding to a discussion of the methods used for making charge-transfer measurements, we will discuss briefly some general considerations that apply to all studies of the results of atomic collisions. Although the principles for performing these experiments are quite simple, a good deal of effort has been expended in the last few decades in developing reliable methods for measuring the quantities necessary for the determination of collision cross sections.

In general the experimental study of charge transfer involves the production of an ion beam which is allowed either to pass through a gas cell or in the cross-beam arrangement to intersect a second beam of neutral particles. Probably the simplest measurement to make is the total charge-transfer cross section, performed by observing the number of ions that have picked up an electron or by collecting all the slow ions produced. This of course provides one with the least detailed information. Another possibility is to observe the fast neutral particles as a function of their angular deflection. This gives a greater amount of information since it may be possible to relate the angular deflection to the corresponding impact parameter for the collision process. If one makes measurements of both the angular deflection and kinetic energy of the fast particle, then one can use energy- and momentum-conservation principles to infer the total change in internal energy of the system. This latter type of measurement is made difficult by the fact that there is no easy way to determine the kinetic energy of neutral particles, unless one resorts to time-of-flight techniques. We see from the foregoing that it is possible to learn something about the internal states of the reactants by measuring the kinetic energy of either of the final products. This method has its limitations in that energy resolution would be limited and one still has only information concerning the total change in internal energy of the states. Additional information could be obtained by
observing whatever light may be produced in the collision process. This would add complexity to the experimental problem but would yield greater energy resolution and add some information about the internal states of the final products.

Our attention will also be given to some of the most salient points to be considered in measuring the density of target particles and to the devices used for detecting the collision products, since these are usually the critical factors in determining the amount of information that can be obtained and the accuracy of the results. A few brief remarks will also be made concerning the production of a beam of the desired characteristics.

It should be noted that over the years a large number of measurements of charge-transfer cross sections have been made, some of which disagree markedly from others for what is supposedly the same cross section. It has been found that many of these discrepancies can be explained on the basis of an unknown excited state population in the beam (and sometimes even an unknown species), unknown contaminants in the target gas, and errors in the measurement of the pressure of the target gas. Since in many experiments the measurement of the pressure of the target gas is the crucial factor in determining the target gas density, we will give in the following section a brief discussion of the methods used and the difficulties encountered in such studies.

3.2. Pressure Measurement

In making absolute cross-section measurements where the target particles are contained in a gas cell, it is essential that one be able to measure absolute gas pressures in the range $10^{-3}-10^{-5}$ torr accurately. For many years the standard method of measuring pressure in this range has been by the use of the McLeod gauge, and considerable attention has been given to the construction and operation of these gauges. In normal use in collision experiments, a cold trap is placed between the McLeod gauge and the target gas cell to prevent mercury vapor from contaminating the target gas. The streaming of mercury vapor from the gauge to the trap causes a difference between the desired and the measured pressure. This fact seems to have been ignored for many years until it was pointed out in 1961 by Ishii and Nakayama, and has undoubtedly led to many of the inconsistencies in cross-section measurements.

One of the more promising alternatives to the McLeod gauge for the absolute measurement of pressures is the capacitance manometer. Since the gas to be measured does not come into contact with a liquid, this device creates much less of a contamination hazard than instruments based on liquid manometer principles. Capacitance manometers have been shown to agree with McLeod gauges to within 2% in the pressure range $10^{-3}-10$ torr.
under conditions in which the mercury-streaming error is expected to be negligible.\textsuperscript{37}

3.3. \textit{Detectors}

In performing charge-transfer measurements, it is necessary to obtain information concerning the nature of the collisions that result in charge transfer, thereby requiring the use of detectors that will enable one to measure the particular aspects of the collisions that are of interest. The ideal detector of particles would be one that would be able to detect single particles, and determine their mass, velocity, charge, and internal energy state with no limitations on the ranges of these quantities that can be studied. Real detectors fall far short of this ideal and the amount of information one can obtain about collision processes depends primarily on one’s ability to develop a suitable system of detectors. Most detectors can be categorized according to the basic processes that underlie their ability to detect particles. We will briefly discuss detectors that use the following four basic processes:

1. Collection of the charge of the particles.
2. Detection of the temperature rise of a solid due to the absorption of the kinetic energy of the particles (thermal).
3. The emission of secondary electrons from the surface of a solid.
4. The production of free electrons in gases and semiconductors.

For details concerning the use of specific detectors, the reader is referred to texts on experimental methods.\textsuperscript{35}

3.3.1. \textit{Charge Collection}

Obviously, this method of particle detection is useful only when the particles to be detected have a net electrical charge. The most troublesome aspects of this type of detector are its relatively low sensitivity and the necessity to be assured that the reflection of the particles to be measured and the effects of secondary electron emission produce negligible errors in the measurement of particle fluxes. A widely used version of this type of collector is the Faraday cup.\textsuperscript{39}

3.3.2. \textit{Thermal Detectors}

In these detectors, the particles deposit nearly all (it is assumed) of their kinetic energy in a solid, creating a temperature rise that can be detected by arrangements that utilize thermocouple junctions,\textsuperscript{40} thermistors,\textsuperscript{41} or superconducting films.\textsuperscript{42} These detectors have the advantage of being sensitive to both neutral and charged particles, but as a group they have a relatively low
sensitivity compared to detectors such as electron multipliers. It should be pointed out, though, that superconducting films have been found to be capable of detecting single α particles provided enough energy is deposited in the film, and that this type of detector has also been shown to be capable of detecting single He and Ar neutral atoms with energies above 150 eV.  

3.3.3. Secondary Electron Emission

In this detector the particle to be detected strikes a solid surface and emits one or more secondary electrons. These secondary electrons can be detected directly or their number increased by having the electrons strike other surfaces, thereby emitting more electrons. This latter technique forms the basis for the operation of electron multipliers. Electron multipliers can be operated in the dc mode where one measures the amplified electron current, or in the counting mode where a single incident particle produces a pulse of electrons at the output. The latter method offers a sensitive means of detecting low fluxes of particles. Electron multipliers are limited by being unable to tolerate very large particle fluxes (but for these cases some of the previously mentioned detectors may be suitable), and by being unable to detect with good efficiency neutral particles whose kinetic energy is less than 500 eV (unless they happen to be in a metastable electronic state).

Scintillators are widely used as detectors in nuclear physics, but are generally of little use as detectors of heavy particles whose energy is less than ~10 keV. However, it is possible to make use of a combination of secondary electron emission and a scintillator to produce a sensitive detector, whereby the particle to be detected ejects secondary electrons from a surface and the electrons are accelerated to an energy of 10–50 keV and then allowed to strike a scintillator to produce a light pulse which is detected by a photomultiplier.

A detector which is similar to the ones based on the emission of secondary electrons is the surface ionization detector. In this device the particle to be detected (usually an alkali metal atom) is ionized upon its approach to a hot metal surface and the resultant positive ions are detected. This type of detector is quite useful for detecting particles of low (thermal) energy, but the fact that it is limited to only a few species of particles is a serious disadvantage.

3.3.4. Ionization in Gases and Solids

Detectors that utilize the ionization produced by the particle to be detected in gases and semiconductors have frequently been used for the
detection of both ions and neutral particles. When the medium of the
detector is a gas, one generally achieves the amplification desired by
operating the detector as a proportional counter. When the medium is a
semiconducting solid, the most common detectors are silicon-surface barrier
and lithium-drifted germanium detectors. The advantages of these detectors
are high gain, low noise, and under some circumstances the ability to
measure the energy of the detected particle with good resolution. The main
disadvantage of these detectors is that they are limited to the detection of
particles that have a kinetic energy in excess of 1 keV for light particles
such as protons, and energies greater than ~10 keV for particles as heavy
as Ar. Even when these detectors are capable of detecting particles at
the low energy end of their range, statistical fluctuations in the number
of primary ions formed reduce the usefulness of the detector for energy
analysis.

3.4. Beam Production

In general the production of an appropriate beam for performing
collision studies is a relatively simple matter. An ion source is used which
utilizes an arc or electron bombardment to produce positive ions which are
then extracted from the ion source by an electric field and accelerated to the
desired energy. As is frequently the case, there may be a number of different
species of ions coming from the ion source, so one usually uses magnetic
analysis to select the desired species.

One of the difficulties often encountered in producing ion beams is the
possibility that there will be an unknown mixture of electronically excited
states, and in many cases considerable care must be exercised to ensure
that only a single electronic state is present in the beam. This difficulty has
led to many of the discrepancies observed in the results of charge-transfer
measurements.

In considering measurements with ion beams at low energies, the
maximum beam flux available may be limited by the space charge spreading
of the beam due to the mutual repulsion of the positive ions. It is for this
reason that it is difficult to make measurements at energies lower than
~10 eV, unless the cross section of interest is large enough that a low-
intensity beam can be tolerated. In recent years this difficulty has been
somewhat avoided by going to what are called merged-beam techniques in
which both of the reactant particles are a part of a beam, with these two
beam components traveling with very nearly the same velocity, such that the
relative velocity and the relative kinetic energy between the two types of
particles are rather small. These techniques can be used to perform collision
studies down to several tenths of an electron volt.
3.5. Cross-Section Measurements

3.5.1. Total Cross Sections

Experiments that measure total cross sections\textsuperscript{51–53} are in one way or another integrated over the scattering angles of the products. One can detect either the relatively fast incident particles after they have picked up an electron from the target particle or the slow ions produced from the target particles. We discuss these separately below.

3.5.1.1. Detecting Fast Particles. In measuring total cross sections by detecting the fast products one assumes that the great majority of charge-transfer events result in only a small deflection of the incident particle during the collision, so that measuring the number of these products at angles near 0° (the incident beam direction) will effectively include nearly all the events that occur. This assumption would in general be expected to be valid only for rather large incident energies (say, >10 keV), and so most such experiments are performed at these higher energies.

(a) Growth Curve Method. If one passes a beam of particles through a chamber or cell that initially contains no gas, then the beam is unchanged in its passage through the cell. If gas is then introduced into the cell, it is found that charge components other than that of the primary beam leave the cell, and these can be separated by the application of appropriate electric or magnetic fields transverse to their direction of motion. If the intensity of each of these components is found to depend linearly on the gas pressure in the cell, then it is implied that the charge changes that have occurred are the result of single collisions within the cell and one can therefore deduce cross sections directly from such data. If the dependence of the charge components on pressure is not linear, then it is concluded that multiple collisions have occurred and the extraction of cross sections from the results is made more complex, especially for systems in which a number of different charge states are produced. This method has been used extensively to determine cross sections for charge-changing collisions both for single-collision conditions and for multiple collisions.\textsuperscript{51}

(b) Beam Attenuation in Transverse Fields. A second method for studying charge transfer is similar to the growth curve method, but it involves placing a transverse electric or magnetic field within the scattering region in the gas cell. Any collision events that result in a change of charge for the beam particles will result in their departure from the path followed by those particles that do not change their charge state, with a corresponding attenuation of the number of particles that leave a slit in the gas cell positioned so as to permit only the particles that did not undergo a change of charge to pass through.\textsuperscript{52}
(c) **Beam-Equilibrium Method.** A third method involves the use of higher gas pressures within the collision region, resulting in multiple collisions before the particles leave the cell. In this technique, one observes the fraction $F_i$ of the total number of particles leaving a gas cell that are in a particular charge state $i$, and then observes how these fractions vary as the gas density in the cell is increased. In particular, when the fraction no longer changes with increased gas density, the beam is said to have come to an equilibrium charge state, with components $F_{i\rightarrow}$. For simple systems such as H$^+$ incident on a gas at energies where it is expected that double electron transfer is negligible, one expects only two possible charge states to be present after the beam has passed through the cell, namely H$^+$ and H. For this situation one can determine the cross sections for electron capture $\sigma_{10}$ and loss $\sigma_{01}$ from the equations

$$F_{1\rightarrow\infty} = \frac{\sigma_{01}}{\sigma_{01} + \sigma_{10}} \quad \text{and} \quad F_{0\rightarrow\infty} = \frac{\sigma_{10}}{\sigma_{10} + \sigma_{01}}$$

This method has frequently been used to obtain information about charge transfer, but its usefulness is generally limited to situations in which one can have no more than three charge components leaving the gas cell.

3.5.1.2. **Detecting Slow Ions.** In addition to the methods just described where the charge transfer events are observed by detecting the fast particles that have picked up an electron in the collision, one can also observe the relatively slow ions produced when the target atoms lose an electron. This method is best applied at rather low energies where the probability of ionization is small, since the ionization events also produce slow positive ions which makes the measurement of charge-transfer cross sections less straightforward. In this method, the beam passes through a gas cell where positive ions are produced with small kinetic energy and then collected by applying a small transverse electric field created by a pair of parallel plates, with the ions being collected on the negative plate. Care must be exercised that the measured current is not significantly influenced by secondary electron emission from the collecting plate caused by either photons, electrons, or the positive ions striking the plate. This method has been widely used with a variety of configurations for producing the collecting electric field.

As a variation on this technique the slow ions can be extracted from the collision region and subsequently mass analyzed. The advantages of this method are most apparent when the target gas is composed of molecules so that a number of different species of positive ions might be produced.

3.5.2. **Differential Cross-Section Measurements**

Experimental studies of the charge-transfer process in which the angular distribution of one of the collision products is measured generally
provide more information about the nature of the process than does the measurement of total cross sections. Still more detail is obtained if some information can be gathered concerning the internal electronic-energy states that participate in the collision. As stated earlier, most of the incident ions that pick up an electron during the collision undergo only a small change in direction if the incident energy is high (e.g., >10 keV), making an experimental study of the angular distribution difficult. For this reason most of the differential cross-section measurements discussed in this section were performed at energies less than 10 keV (with a few exceptions where at the higher energies the small number of events that do result in angular deflections of several degrees were observed). One of the principal advantages to be gained from differential measurements is the fact that it may be possible to relate scattering angle to classical impact parameter and thus provide a firmer basis for comparing experiment with theory. The ability to relate angle to impact parameter depends on one's knowledge of the potential curves that participate in the collision and the positions at which transitions between these curves take place.

Let us now consider the charge-transfer process

\[ A^+ + B \rightarrow A + B^- \]  \hspace{1cm} (3.2)

One possibility for obtaining differential information about this process is to observe the angular distribution of the neutral product A. The detection of these products is usually accomplished by the use of an electron multiplier, but if A is in its ground electronic state, then it must have enough kinetic energy to produce a significant number of secondary electrons in the detector, thereby producing a lower limit on the energies for which such studies may be carried out. If A happens to be in a metastable state, then it is quite possible that sufficient secondary emission can be obtained even at low kinetic energies, but this of course limits the type of processes that can be studied to those events in which the electron is transferred to a metastable state. It should be emphasized that a critical factor in any study of differential charge transfer by observing the neutral products is a knowledge of the absolute efficiency of the detector for detecting neutral particles, whether ground state or not. Another possibility for detecting the results of charge transfer to metastable states is by quenching the atoms in these states by an electric field and observing the photons produced. This has the added advantage of providing information about the states in which the charge transfer has left the neutral product.

In addition to the methods described in which the relatively fast neutral atom is observed, it is also possible to observe the angular distribution of the slow B^- ions formed in process (3.2), since these charged particles are easily detected even though they have small kinetic energies.
Let us now consider the charge-transfer process

$$A^{2+} + B \rightarrow A^+ + B^+ \quad (3.3)$$

This type of collision has a large experimental advantage over those already discussed since both products are charged. Since $A^+$ usually has the larger kinetic energy, it is more common to detect it rather than $B^-$. As in any experiment in which one is detecting charged products, when these products have a kinetic energy which is not sufficiently large to produce secondary electrons at the entrance of an electron multiplier, it is a simple matter to accelerate them with an appropriate potential difference before allowing them to strike the electron multiplier. The existence of the charged product $A^+$ provides the opportunity to use electrostatic analysis of its kinetic energy spectrum to provide information on the internal energy states to which the charge transfer has taken place.$^{66,67}$

The measurements described by Siegel et al.$^{67}$ were performed with the system shown in Fig. 8. They were differential in angle and the kinetic energy of the products $A^+$ was measured with a cylindrical electrostatic analyzer. Thus, at different values of impact parameter, corresponding to different scattering angles, the relative population of the final intermediate states could to a large extent be determined by observing these energy spectra, since in many cases only one of the product ions was in an excited electronic state after the collision. A disadvantage to this method of observing the final internal states of the products is the limited energy resolution possible for electrostatic analyzers operated without deceleration of the ions before analysis. Values of $\delta E/E$ in the range 0.001–0.01 are commonly used, which corresponded in the experiments of Ref. 67 to peak widths of a few electron volts. If one achieves improved energy resolution by decelerating the ions before analyzing them, then the problem of losing ions in the region of deceleration creates difficulties in making measurements of absolute cross sections. One could achieve a greatly improved energy resolution by just looking at the optical spectra from transitions that follow the charge-transfer events, but at the expense of not being able to correlate observed transitions with a given impact parameter. This difficulty could in principle be obviated by observing coincidence between charged particles scattered through a known angle and the photons produced from the scattering event, but low-intensity experiments of this type are quite difficult.

For the system

$$\text{He}^{2+} + B \rightarrow \text{He}^+ + B^+$$

where $B$ is a rare-gas atom, it is especially easy to assign internal states for all the participants in the collision since there is no question concerning the states of the incident and target particles, and one of the products, $\text{He}^+$, has a set of hydrogenic states with rather large and well-known separations.
Fig. 8. Apparatus used for single-charge-transfer measurements differential in angle and energy. 77
4. Experimental Data and Interpretation

4.1. Introduction

In this section we will present some characteristic experimental results and discuss them in light of the theoretical discussion given earlier. More extensive collections of experimental data and comparisons of that data with theoretical calculations are available elsewhere.\textsuperscript{6,8,30,31,67} Since quantum mechanics can presumably be used to describe ion–atom collisions as accurately as one likes, the primary role of theory in this field is the interpretation of the experimental phenomena to gain an understanding of the physical processes at work. For this reason simple model descriptions which indicate the mechanism involved are still often preferred to detailed calculations since they can be used for predictive calculations on other systems. Here we hope to indicate how potential energy information, interaction mechanisms, and spectroscopic data may be obtained from cross-sectional data.

4.2. Integrated Cross Sections

Integrated cross sections for charge transfer with incident singly and doubly charged ions have well-known general characteristics. For strong coupling, the cross terms in Eq. (2.1) which depend on the difference in action generally go through many oscillations as a function of $b$ (or $\tau$) at intermediate and low velocities. These terms are often assumed to be self-canceling (the random phase approximation) out to some impact parameters $b^*$ where the phase differences and/or the transition probabilities become very small. Using this, the integrated cross section is written in a form that lends itself to direct comparison with experiment:

$$\sigma(v) \approx |\tilde{P}_{0,f} \cdot \pi b^{*2}|$$ (4.1)

where $\tilde{P}_{0,f}$ is the transition probability in Eq. (2.5) averaged over the impact parameter from $b = 0$ to $b = b^*$. In the two-state approximation, $b^*$ is chosen to be the largest value of impact parameter for which the phase differences are equal to some small value (Firsov\textsuperscript{68} used $2/\pi$ for this value). The velocity dependence of the cross section may be determined by either $\tilde{P}_{0,f}$ or $b^*$.

For symmetric resonant charge transfer, the phase difference between the $g$ and $u$ states is related to the exchange energy, which falls off exponentially at large $R$. Therefore, $b^{*} = \alpha -1[\beta - \ln(v)]$, where $\beta$ depends on the potential parameters, and $\alpha$ is the screening constant indicating the overlap of the atomic wave functions.\textsuperscript{6,30} As $\tilde{P}_{0,f} \approx \frac{1}{2}$, this cross section increases monotonically with decreasing velocity at low and intermediate
velocities (Fig. 9). The experimental cross section can therefore be used to obtain the parameters $\beta$ and $\alpha$. This procedure fails at high energies since the cosine of phase differences does not go through a number of oscillations, and, also, the excited states become important. At very low velocities $b^*$ may be determined by the orbiting radius.¹

For charge transfer due to a curve crossing, a reasonable approximation is obtained by setting $b^* \approx R_s$. Then using the LZS transition probabilities of Eq. (2.9), one has

$$\bar{\varphi}_{0,1} \approx \int_0^1 2P_s(1-P_s)\left(\frac{b}{R_s}\right) d\left(\frac{b}{R_s}\right)$$

which is velocity dependent. This expression has been applied to a large variety of charge exchange collisions involving curve crossings, particularly single charge transfer with incident doubly charged ions.² The general velocity dependence given by this prescription is characteristic of the observed velocity dependence for nonresonant charge-transfer collisions (Fig. 10). The cross sections usually go through a single broad maximum, falling off rapidly at low energies, and becoming orders of magnitude smaller than the maximum value of the cross section.

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![Graph](image-url)

Fig. 9. Charge-transfer cross section (atomic units) as a function of incident-ion energy ($E$) for $Ar^{+} + Ar$ collision showing dependence on $\ln(E)$ predicted by a simple model [Eq. (4.1)]. Solid lines are experiments; dashed line gives detailed impact parameter calculation.³
The two-state, nonresonant charge-transfer reactions which do not involve a curve crossing, also go through a single broad maximum.\textsuperscript{70-72} At low velocities, $\tilde{P}_{ij}$, obtained from averaging over the transition probability in Eq. (2.12), has the dominant velocity dependence, and therefore, as in the curve-crossing case, one chooses $b_0 = R_c$, the region of strong coupling. However, at higher energies, $\tilde{P}_{ij} \rightarrow \frac{1}{2}$ and $b_0$ has a velocity dependence similar to the symmetric resonant case\textsuperscript{71} (Fig. 11). For nonresonant charge transfer, two broad maxima have been found for some collisions for which the reaction may proceed by either crossing or noncrossing mechanisms.\textsuperscript{71}

Using these prescriptions, potential energy information may be obtained directly from the measured cross sections.\textsuperscript{67} The size of the maximum in the cross section is determined by the position of the transition region $R_c$, and the position of the maximum by the coupling strength. Obviously more information can be obtained with a more detailed parametrization of the problem. The position of the maximum $v_{\text{max}}$ can be estimated
from an argument based on the uncertainty principle, yielding the equation

\[ l = \frac{\Delta_{0f} \cdot \delta R_x}{\hbar v_{\text{max}}} \]  \hspace{1cm} (4.3)

where \( \Delta_{0f} \) is the separation of the adiabatic potentials in the transition region and \( \delta R_x \) is the width of this region. For the noncrossing case where the distortion of the potentials is not important, one often estimates \( \Delta_{0f} \) as \( Q \), the energy defect as in Eq. (2.13), and \( \delta R_x \) of the order of a few Bohr radii, obtaining the so-called adiabatic criterion of Massey.

For resonant or near-resonant charge transfer between unlike species, a common occurrence when the target is a molecule or when a number of close lying spin states are involved, e.g.,

\[ \text{H}^+ + \text{O}(^3P) \rightarrow \text{H} (^2S_{1/2}) + \text{O} (^4S_{3/2}) \]

similar concepts can be applied. However, the behavior of the long-range forces critically affects the position of the maximum as they split the
degenerate or nearly degenerate initial and final states of the collision system. In many cases, there is significant spin–orbit splitting in the final state multiplet. As the exchange interaction increases exponentially with decreasing $R$, it eventually dominates the spin–orbit interaction at some value of $R$. The concepts developed here are useful for determining the relative populations of products among the final state multiplet. If $b^*$ is less than that internuclear separation where the spin–orbit and exchange interactions are approximately equal, the fraction of products in a given atomic $J$ state of the multiplet can be determined from a statistical

Fig. 12. Cross sections for Xe$^+$ + Xe → Xe$^+$ + Xe$^*$. Solid lines are theoretical curves: $\sigma(\frac{1}{2})$, $J = \frac{1}{2} \rightarrow J = \frac{1}{2}$; $\sigma(\frac{3}{2})$, $J = \frac{3}{2} \rightarrow J = \frac{3}{2}$; C.T., inelastic charge transfer; D, inelastic, no charge transfer. Dashed lines are experimental charge-transfer cross sections.
weighting. If $b^*$ is much greater than that internuclear separation, the different $J$ states should be treated as distinct final states (Fig. 12).

Deviations from the general behavior described herein occur for a variety of reasons. For instance, if the difference in the potential functions and corresponding actions for two trajectories go through a maximum, the random phase approximation would break down in the vicinity of the maximum. Accounting for the constructive (or destructive) interference in this region will modify the cross section by superimposing an oscillatory structure on the general behavior already described. For instance, for the symmetric resonant two-state example discussed earlier, if a stationary point exists, Eq. (4.1) becomes

$$\sigma (v) = \left\{ \frac{\pi}{2} b^* \right\} \left[ \frac{\pi^{3/2} b}{\left( \frac{\partial^2}{\partial b^2} (A^{(e)} - A^{(u)}) \right)^{1/2} \cos \left( \frac{A^{(e)} - A^{(u)}}{\hbar} + \frac{\pi}{4} \right) b - b_0} \right]$$

where $b_0$ is the position of the stationary point. A similar modification can be applied to the inelastic cases. The spacing and magnitude of the oscillatory structure (Fig. 13) can be used to determine the behavior of the potential differences in the vicinity of the extremum.

4.3. Energy-Loss Spectra with Doubly Charged Ions

In the collision processes

$$A^{2+} + B \rightarrow A^+ + B'$$

either product may be formed in an excited state. Since the kinetic energy of the scattered ions can be accurately determined, this provides a means for observing the states of the ions, as well as the mechanisms for charge transfer. Work with incident He$^{2+}$ colliding on the rare gases and measuring the energy loss as a function of scattering angle has been carried out by Chen, Boring, and Siegel$^{17,18}$ and Cooks et al.$^{16}$ Because the states of the He$^+$ ion are well known a straightforward interpretation of the collision in terms of the excited states of the rare-gas ion can be made. The important parameter is the energy defect $Q$ between the electronic binding energies of the particles in the incident and exit channels. Since the binding energies of the target atoms may differ considerably, each collision system must be interpreted separately according to its peculiar arrangement of ionic states.
In Fig. 14, we give the energy-loss spectra for He$^{2+}$ + Ne as a function of laboratory angle for 200 eV laboratory energy from the data of Chen. Because $\tau$ at small angles is roughly related to an impact parameter (Section 2.3), it can be seen in Fig. 14 that for distant collisions only one peak occurs, and this can be associated with Ne$^+$-excited states which are exothermic by 5–6 eV. There is another group of states with exothermicity of the order of 1.2–2.2 eV. Transitions to these states only occur at smaller impact parameters and the thresholds are easily observable. If the exothermic states
discussed are treated as having a $1/R$ long-range repulsive force and the incident channel as having a polarization attractive force, then the crossings with the incident state can be deduced for both groups. For the state He$^+$ Ne$^-[2s2p^2, 2S]$ with $Q = 5.94$ eV, this implies $R_c = 4.77a_0$, whereas for He$^+$ Ne$^-[2p^42s, ^2D]$ with $Q = 2.2$ eV, $R_c = 12.3a_0$. The transition probability at a crossing depends on the strength of the coupling [Eq. (2.9)], which falls off exponentially for the charge-transfer reaction. For this reason, transitions to states with higher exothermicity dominate at small scattering angle, and the channel with small exothermicity has an angular
dependence similar to the noncrossing endothermic channels. Because of the finite angular resolution in the experiments, impact parameters equal to and greater than $R_s = 4.77$ are included in the 0° measurement, and the threshold for the $Q = 5.94$ eV channel is not seen. Further, no transitions to the exit channel with exothermicity of 32.8 eV are observed because the large energy defect at these collision energies results in rapid oscillations of the phase factors in the transition probabilities [Eq. (2.13)]. The quantity of importance is $Q/v$.

The incident channel He$^{2+} + \text{Ne}[2p^6, 1S]$ leads to a single molecular state of symmetry '1$\Sigma^+$'. According to the coupling mechanisms discussed in Section 2, one would imagine that '1$\Sigma^+$' $\rightarrow$ '1$\Sigma^+$' and '1$\Sigma^+$' $\rightarrow$ '1$\Pi$' transitions would be allowed. Using the Wigner–Witmer coupling scheme$^{50}$ for the exit channels of exothermicity between 5 and 6 eV, He$^[1S] + \text{Ne}[2s(2p)^n, 1S]$ leads to '1$\Sigma^+$' molecular states and He$^[1S] + \text{Ne}[3P_3, 2S]$ leads to '1$\Pi$' and '1$\Pi$'. However, at small angles the peak has been identified$^{67,77}$ with the Ne$^[2s(2p)^n, 2S]$ state. The fact that the other state is not observed is consistent with the fact that rotational coupling is weak for slow collisions at large internuclear separation.$^6$

The spacing of the first and second peaks as a function of $\tau$ is shown in Fig. 15. It is clear that the position of the peak changes with $\tau$ or impact parameter. For small $\tau$, i.e., large impact parameters, the second peak appears to be associated with the Ne$^[3P_3, 2S^o]$ state, a transition conserving electronic orbital angular momentum. However, this leads to '1$\Sigma^+$' quasi-molecular states or transitions which are forbidden under the rules described earlier. This implies that spin–orbit coupling of the outer electron with the open shell of Ne$^+$ most likely plays a role, for there is a close-lying Ne$^[3P_3, 2P^o]$ state which leads to a '1$\Sigma^+$' state, among others. For larger $\tau$, i.e., smaller impact parameter, the peak appears to be a varying mixture of the two final state channels with exothermicity between 1.2 and 2.2 eV associated with '1$\Sigma^+$' molecular states. The oscillations for each energy appear to have some regularity. Neutral helium atoms associated with a double-charge transfer were not observed in these experiments. However, the molecular states associated with this reaction are felt to play an important role here. That is, the repulsive final states may be populated by crossings with the double-charge-transfer states. The results of Fig. 15 illustrate how measurements differential in energy and in scattering angle can identify reaction channels which could not be resolved by kinetic energy measurements alone.

The He$^{2+} + \text{Ar}$ system has very different energy characteristics. The entrance channel lies in the continuum of the Ar$^+$ ion for charge transfer to the He$^+$ ground state. As in the previous case, the possible endothermic channels at large $R$ diverge in energy from the incident '1$\Sigma^+$' state. Therefore, for large impact parameters exothermic reactions are preferred. Three
broad peaks, i.e., broader than the elastic peaks, are distinguishable\textsuperscript{27} (Fig. 16). The largest is associated with the closely spaced Ar\textsuperscript{+} single excited states. The next peak may be associated with doubly excited autoionizing states in the continuum of Ar\textsuperscript{+}. It is known that these doubly excited states may lead to well-defined quasi-molecular potentials.\textsuperscript{24} Autoionizing states of doubly excited Ar\textsuperscript{+} have been identified at 0.3 and 1.8 eV into the continuum.\textsuperscript{26} The last peak is associated with single charge transfer into the continuum of states associated with He\textsuperscript{+}(1s) + Ar\textsuperscript{2+} + e and those other bound states that lie in the continuum, e.g., He\textsuperscript{+}(2s) + Ar\textsuperscript{+}. This peak grows and broadens with increasing $\tau$ (decreasing impact parameter; see Fig. 17). Further, the maximum shifts toward the endothermic energy transfers as $\tau$ increases, as the transitions are taking place at smaller values of $R$ where the
biasing effect of the $1/R$ long-range potential has diminished. The peak can be roughly described by the weak coupling probability equation (2.7), modified to account for the density of states. Such a peak can be thought of as arising from the system relaxing into some statistical distribution of final states after the disturbing particle has passed and, in this case, removed an

Fig. 16.  Energy-change spectra of single-electron capture in He$^{2+} +$ Ar.
electron. For closer collisions the disturbance, and hence the spread in final states, is greater. In contrast, the maximum of the peak due to coupling at large \( R \) remains very nearly fixed in energy transfer over a broad range of \( \tau \). This peak at \( Q = 12 \text{ eV} \) is broader than the elastic peak, indicating that a
number of close-lying states are involved. For the \( \text{He}^{2+} + \text{Kr} \) collision, Cooks \emph{et al.}\textsuperscript{76} find a sharp peak near the incident channel associated with \( \text{He}^+(n = 2) + \text{Kr}^+ \) which is nearly resonant, and a broad, weak peak associated with the excited states and continuum of \( \text{Kr}^+ \) with \( \text{He}^- \) in the ground state.

4.4. Angular Differential Cross Sections

Angular differential cross-section data yield information not only on the relative likelihood of the possible transition but also on the interaction potentials, through the angular dependence. For purely elastic scattering on a monotonically decreasing potential with increasing \( R \), straightforward mathematical schemes are available for inverting the data to obtain the potential.\textsuperscript{80} For large \( \tau \) values where there is a common repulsive potential for all processes such procedures have often been used to calculate an average, total differential cross section.\textsuperscript{80} This is defined as the sum of all the elastic and inelastic cross sections, including charge transfer [see Eq. (2.5)]. For more complicated situations, the procedure is one of trial and error, based on an understanding of the physical phenomena. The theoretical procedure described in Section 2.2 has been employed with success by Smith and co-workers\textsuperscript{16,19,81} to a number of collisions involving charge transfer. They find that even though the procedure has severe limitations near the angular threshold region, it gives an excellent starting point for interpreting the angular dependence and interference oscillations in inelastic and elastic cross sections. The quantities one wishes to find are the differences between potential energy curves, the position of transition regions, and the coupling strength.

The semiclassical relationship

\[
\frac{\partial A^{(j)}}{\partial \theta} = L^{(j)} \tag{4.5}
\]

where \( L^{(j)} = p b^{(j)} \), can be used to relate the oscillations in the differential cross sections, when they can be resolved, to the spacing between the potential curves for the different trajectories.

If the energy defect in the transition is small compared with the incident particle energy \( E \), then using Eq. (4.5), the spacing between the maxima is related to the difference in impact parameters for two trajectories associated with the scattering into a given angle \( \theta \), by

\[
\Delta b(\theta, E) = 2\pi \left( \frac{E}{2\mu} \right)^{1/2} \frac{\partial n}{\partial \tau} \tag{4.6}
\]

where \( n \) is an indexing number for the maxima.\textsuperscript{81} Therefore, a first step is to choose potentials which yield deflection functions producing the correct spacing. This does not uniquely determine the potential curves unless one
knows the value of the potentials at some $R$ from an accurate calculation or
the trial potentials also yield good absolute values of the cross section. Since
absolute differential cross-section measurements often have large errors
associated with them, the latter check is sometimes difficult. For the unsymmetric
charge transfer collision $\text{He}^+ + \text{Ar} \rightarrow \text{He} + \text{Ar}^+(3s, 3p^\pi)$, which
takes place via curve crossing, Smith et al. have plotted the position of the
maxima in the charge transfer cross section as a function of $\tau$ (Fig. 18) for
incident ion energies of 45–300 eV. It is seen that the slope of this plot is very
nearly a constant, $\Delta b = 0.51a_o$, implying that the deflection functions are
separated in $b$ by a constant. This suggests that the potentials for the
appropriate internuclear separations are nearly exponential functions of $R$
with approximately the same screening constant but different multiplicative
constants.

This procedure has been applied most successfully for high-energy,
small-angle collisions, where the trajectories are simply approximated by
straight lines and the phase differences have the form

$$\frac{1}{\hbar} |A^{(1)} - A^{(2)}| = \frac{1}{h} \left| \int_{-\infty}^{\infty} [V_1(R) - V_2(R)] dZ \right|$$

(4.7)
where $R^2 = h^2 + Z^2$ and $\tau$, a function of $h$, is determined from some average interaction potential. In this limit, the oscillations have a simple $v^{-1}$ dependence (Fig. 19). Everhart and collaborators\textsuperscript{58,59,62} applied this concept to the symmetric resonant single-charge-transfer collisions $H^+ + H$ and $H^+ + He$ to obtain values for the exchange energy $V_g - V_a$ as a function of internuclear separation. At lower energies, the expression given in Eq. (2.3) should be used to account for the different trajectories on the gerade and ungerade states.\textsuperscript{15} Here, if one of the states has a minimum, the oscillations may be superimposed on a rainbow structure.\textsuperscript{15,83} At low energies, additional oscillations may occur if the nuclei are identical;\textsuperscript{84} at both high and low energies, an effective shift in phase from this expression may occur due to coupling to close-lying excited states.\textsuperscript{15} Equation (2.1) is the starting point for interpreting these phenomena.

Nonresonant capture cross sections at intermediate and high energies show a similar $v^{-1}$ dependence in the charge-transfer probability. However, as can be seen for the $H^+ + He$ collision (Fig. 20), the oscillations are heavily

![Graph showing electron-capture probability versus ion energy for $H^+ + H$ collision showing the reciprocal velocity dependence of the oscillatory structure.](image-url)
damped, the damping being related to the collision time. This is an example of a non-curve-crossing, strong-coupling collision in the energy range shown. The damping has been shown to proceed roughly as $e^{-\nu_0 t}$, where $\nu_0$ is a constant, for both crossing and noncrossing cases. This is easily deduced from Eqs. (2.9) and (2.13) for the transition probabilities. Here again the spacings between the oscillations are a measure of the separation of the two lowest $\Sigma$ molecule–ion interaction potentials of HeH$^+$.\textsuperscript{13}

The position of a curve crossing can be experimentally estimated from either perturbations on the elastic scattering curves or the onset of the inelastic differential cross section. For the elastic scattering cross section for
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Fig. 21. Elastic scattering of He\(^{2+}\) + He at 200-eV incident ion energy from Ref. 27. Solid curve. Calculation based on Eq. (2.3) using potentials chosen to fit oscillatory structure and approximate the absolute value of experiment,\(^{30}\) dashed curve.

He\(^{2+}\) + He at 200 eV (Fig. 21), the competing double-charge-transfer reaction is evident from the oscillatory structure.\(^{44}\) At 3400 and 4500-eV deg., two perturbations appear which can be associated with crossing of the incident channel \(^1\Sigma^+_g\) state, with higher states of the same symmetry leading to

\[
\text{He}^{2+} + \text{He} \rightarrow \text{He}'(1s) + \text{He}'(n = 2)
\]

(Fig. 4). This type of perturbation has been described by Smith and coworkers for a number of ion-atom collisions.\(^{20,85}\) In Fig. 22, we represent hypothetical classical deflection functions corresponding to the two elastic

Fig. 22. Hypothetical classical deflection functions corresponding to the two elastic scattering trajectories involved in a curve crossing: \(b_x\) indicates impact parameter for which the distance of closest approach is \(R_a\). Corresponding classical deflection functions exist for inelastic trajectories, Fig. 3. See Ref. 20.
Fig. 23. Probabilities of single-electron capture as a function of scattering angle for C^{2+}, N^{2+}, O^{2+} on He, Ne, Ar at impact energies of 1 and 3 keV.
scattering trajectories, where the crossing region is indicated by $b_c$. When the lower trajectory is smoothed over the region about $b_c$, it can be seen that it goes through two extrema which will result in the perturbations occurring between $\theta_0$ and $\theta_1$ as indicated. Using potential functions in Eq. (2.3) which reproduce the oscillatory behavior of the elastic differential cross section, the crossing is estimated\textsuperscript{80} to occur at $R_c \approx 0.97a_0$. These perturbations will be followed, at larger $\tau$, by a drop due to the inelastic process; however, the perturbations are often not resolved in an experiment.

In Fig. 23 are shown charge-transfer probabilities as measured by Hasted\textit{et al.}\textsuperscript{85} for a number of collisions of the type $A^{2+} + B \rightarrow A^+ + B^-$. The oscillations in angle are clearly observed since the data were deconvoluted to enhance the oscillatory structure. In some cases, the data indicate that more distant curve crossings contribute to charge transfer at small angles. On a $\tau$ plot, it is clear that the threshold regions seen here are very energy dependent. A calculation by Bates\textit{et al.}\textsuperscript{85} in the impact parameter approximation of the transition probability for $\text{Be}^{2+} + \text{H} \rightarrow \text{Be}^+ + \text{H}^+$ is illustrated in Fig. 24, and this energy dependence is apparent. Using the long-range interaction potential of the incident channel to describe the collision, Hasted\textit{et al.}\textsuperscript{85} have plotted transition probabilities versus impact parameter. In Fig. 25 we give the results for $\text{C}^{2+} + \text{Ne}$ collision where the dashed line indicates the crossing point. The values of $b$ should not be taken too seriously, since in the threshold region a deflection function which is the average of the deflection functions for the incident and outgoing channel should be used. However, the general energy dependence exhibited in the sample calculation by Bates is evident. These figures also indicate one of the major flaws in the LZS transition probabilities. When the distance of closest approach equals $R_c$, the LZS transition probability is zero. Therefore, it should only be applied for impact parameters much smaller than $R_c$, as stated earlier. The problem is clearly that the transition region is finite in size. Recently the LZS transition region probabilities were employed in a partial wave calculation yielding improved agreement in this region, though not as good as the distorted wave approximation.\textsuperscript{19} The energy dependence seen in Fig. 24 is much less than in Fig. 25, indicating that the crossing region may be better defined or narrower for the first case.

From the average value of the transition probability one can attempt to estimate the magnitude of the coupling matrix element based on the LZS approximation. It is found that coupling matrix elements determined from experiment may differ significantly from theoretically determined matrix elements for some single-charge-transfer collisions.\textsuperscript{31} This has been attributed to coupling to excited states and the fact that the active electron does not start and finish in an $s$ orbital,\textsuperscript{22} upon which criteria the LZS approximation is derived. However, conceptually the LZS approximation continues to be useful.
4.5. Cross Sections Differential in Angle and Energy

A most valuable result is to obtain differential cross sections with final state analysis as discussed earlier. Cross sections differential in angle and energy obtained by analyzing the kinetic energy of the scattered particles provide such a result. Much of the preceding discussion applies to this case since in the analysis it was always presumed that the final state was known, and that only one final state was involved. In fact, calculations involving two states have been used for years for comparison with experiments in which
the products were not state analyzed. In many of these cases the predominant final state of the products can be deduced, but this is not always reliable, and in other cases there is no single predominant final state.

The angular threshold for the charge-transfer differential cross sections, when it can be seen, yields information about the transition region and the coupling strength. At low energies for He$^{2+} +$ He, the threshold in $\tau$ on the elastic channel, located as described earlier, may be shifted considerably

Fig. 25. Probabilities of single-charge transfer in C$^{2+} +$ Ne as a function of impact parameter $b$.\textsuperscript{e\textdagger}
from that on the inelastic channel (Fig. 26) because the differences in the potentials of the final states are important. Since the outgoing potential for the reaction

\[ \text{He}^{3+} + \text{He} \rightarrow \text{He}^+(1s) + \text{He}^+(n = 2) \]

is much less repulsive for \( R \) near the transition region (Fig. 4), the threshold in Fig. 26 seems to be consistent with the elastic perturbations discussed in the preceding section. Analysis of this cross section based on the LZS approximation yields a coupling strength of 0.17 a.u. and a value of 3.7 a.u. for the quantity \( \frac{\partial}{\partial R} (V_f - V_0) \big|_{R_c} \). However, the two peaks in the cross section have been established to be associated with the separate crossing of the incoming channel \( ^3\Sigma_u^+ \) state with the two \( ^3\Sigma_u^+ \) states leading to the \( \text{He}^+(1S) + \text{He}(n = 2) \) final states (Fig. 4). Using the half-height of the peaks and the elastic potentials discussed earlier, the second crossing occurs at about \( R_c = 0.85a_0 \). The cross section \( \rho_3 \) in Fig. 26 is the sum of all
unresolved higher single-charge-transfer processes. The onset of transitions to these higher states is about $R_e \approx 0.8a_0$.

The single-charge-transfer spectra shown earlier (Fig. 14) lead to the differential cross sections for $\text{He}^+ + \text{Ne} \rightarrow \text{He}^+ + \text{Ne}^+$ shown in Fig. 27. Also shown is the elastic cross section and a theoretical average cross section obtained from a screened Coulomb potential with the screening constant chosen to be the same as used for $\text{He}^+ + \text{Ne}$ collisions. The impact parameters at the top of the figure are determined from this average potential and are useful only as a rough reference. The cross section represented by $\rho_1$ is that leading to the $\text{He}^+(1S) + \text{Ne}^+(2S, 2p^6)$, as discussed earlier, which is populated by transitions at a curve crossing. This threshold is not observed. However, thresholds for the higher-lying blocks of states are evident. Further, on $\rho_1$ and $\rho_e$, the elastic cross section, the interference pattern due to the first transition is evident prior to the onset of the higher transitions.

Fig. 27. Differential elastic scattering ($\rho_e$) and single-electron capture cross sections for $\text{He}^+ + \text{Ne}$ at 200 and 300 eV. Impact parameter is in atomic units.\(^{27}\)
Using $R_s \approx 4.77a_0$ as discussed earlier, and $(\partial/\partial R)(V_f - V_0)|_{R_s}$ determined from a Coulomb and polarization attractive potential, the coupling strength at $R_s$ is estimated to be 0.14 eV. Even though the long-range force for the exit channels associated with $\rho_2$, $\rho_3$, and $\rho_4$ is stronger than that for elastic scattering, the threshold for these processes as observed on the elastic channel is displaced to larger scattering angle than on the inelastic cross sections. This indicates that the potential associated with the elastic channel is more deeply repulsive near the distance of closest approach, which is roughly the transition region for these energy transfers. It is quite clear also that the threshold for $\rho_2$ changes with energy, possibly implying a rotational coupling effect, while the half-heights of the $\rho_3$ and $\rho_4$ curves are roughly at 1450 and 2000 eV-deg for these energies.

It is clear from these figures that the energy loss cross sections for these single charge transfer processes are complex since only in very isolated circumstances can one reduce the problem to the simple two-state form. In all cases the analysis presented here is only useful in describing general features and as a first attempt to obtain values for potential parameters. Clearly if a very accurate understanding of the experimental results is needed, it can only be achieved through detailed calculations.

5. Summary

In the present chapter we have considered the principal experimental and theoretical methods for describing the charge-transfer reaction.

To summarize the analytical concepts—charge transfer, like other inelastic ion–atom collisions, can be described as transitions between diabatic molecular states, taking place at well-defined internuclear separations in most instances. The transitions can be grouped roughly into weak coupling, where the transition region is at the distance of closest approach, and strong coupling, where it is not. Simple methods exist for predicting the behavior or for making preliminary analyses of experimental data. Two useful methods are the LZS and Rosen–Zener methods when the coupling is strong. These involve obtaining a transition probability based on some interaction potential. For low-velocity charge-transfer collisions, this potential generally has an exponential behavior related to the overlap of the electron clouds on the two centers. The transition probabilities are also determined by the differences in the behavior of the diabatic potential curves associated with the incoming and outgoing states of the colliding particles, as well as the energy defect $Q$. The principal selection rule is that transitions take place between diabatic states which involve no change in the component of electronic angular momentum along the internuclear axis. By changing the angle of observation of the scattered particles at fixed energy, or the incident-particle
kinetic energy with fixed scattering angle, one changes the distance of closest approach and therefore scans the interaction potentials of the colliding particles. This procedure allows one to determine the transition regions for charge transfer. Since charge transfer results from a sharing of the electrons by the two centers, the region where the molecular states are formed, 3–5 a.u., is a region of considerable interest. Therefore, for single-electron transfer with incident doubly charged ions, the outgoing repulsive states, with the exothermicity appropriate to result in a crossing in this region, will have large transition probabilities when the distance of closest approach is comparable with or smaller than these values.

It has been pointed out in this chapter that in investigating charge transfer processes experimentally one must produce an ion beam, allow it to collide with some target atoms (usually in a gas cell), and detect the result of the events of interest. It is in this last category of detection that the experimenter's greatest ingenuity is required to achieve the maximum amount of information.

References

1. Sec, for example, A. Dalgaro, Rev. Mod. Phys. 39, 858 (1967).
80. G. H. Lane and E. Everhart, Phys. Rev. 120, 2064 (1960).