HEAVY PARTICLE COLLISIONS

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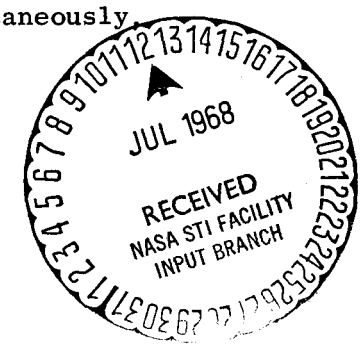
The whole field of the physics of heavy particle collisions is currently in a rapid and exhilarating phase of growth. The greatest advances are being made on the experimental side, but they are stimulating a lot of thought about interpretations and are providing the incentive for new theoretical developments.

I propose to limit the coverage of this survey in several ways. First, it will be limited to diatomic collisions and second, its focus will be on the energy range above the thermal one, and principally from a few eV upwards. These limitations are justified not only by the avowed aim of this Conference, but also by the fact that recent developments in molecular collision studies and in the whole field of collision processes at thermal energies have been well covered in a number of recent reviews.[1] This means that I shall not discuss effects involving molecular rotation, vibration, or dissociation, nor those of chemical reaction or of ion-molecule reactions. The principal processes that remain are elastic scattering and inelastic processes involving electronic excitation, ionization, and electronic energy or charge transfer. In this limited domain, I shall try to give a survey of the types of phenomena that are now being measured and an indication of the information that these measurements provide about interatomic interactions. No full coverage of the literature is aimed at, but rather a selection of illustrative examples.

For many years it has been customary, both in experiment and in theory, to focus attention principally on total cross sections and to ignore the details of angular distributions. The most striking features of experimental developments in recent years have been: (a) a trend to monitoring more variables simultaneously,



In this survey I shall not be able to say much about recent developments in the purely theoretical approach to these collision problems. Instead I wish to concentrate on some of the experimental developments and on the simple theoretical concepts that can be used for their interpretation.

The first question is, What can be observed? In the most detailed atomic scattering experiments one can observe the cross section for a given event as a function of the scattering angle, the initial kinetic energy, and the energy change (if any),

$$\sigma(\theta, E, \Delta E) \quad (\Delta E = E - E_f) \ . \tag{1}$$

It is obviously convenient to think of these quantities as defined in the moving barycentric frame and not in the laboratory one. The energy change ΔE may be observed in several ways:

(a) by analyzing the energy of the projectile before and after scattering as well as the angle of scattering (particularly convenient if the projectile is an ion)

(b) by simultaneous measurement of the scattering angles of the projectile and the target (the coincidence method)

(c) by spectroscopic observation of the radiation emitted from the excited projectile or target (preferably in coincidence with an angular measurement of the projectile motion)

(d) by observing an electron from one of the atoms, preferably with analysis of its energy, as well as measuring the projectile's angle of scattering,

(e) by determining the charges of the atoms after the collision (which provides at least a lower bound for the energy lost to ionization), as well as a scattering angle.

Analysis for mass is also useful in distinguishing the scattered or recoiling particles.

In addition to measurements of the full differential cross section of Eq. (1) it is possible to measure instead various total or average cross sections which contain less information. In particular we have the ordinary total cross section which involves the summation over all angles of scattering θ,

$$Q\ (E, \Delta E) = \int \sigma \sin\theta d\theta \ . \tag{2}$$

particularly to the study of differential scattering, (b) the effort to achieve improved resolution in energy and in other variables, and (c) an increase in the interest in processes at lower energies and especially at energies comparable to the energetic threshold for various inelastic processes of interest. These developments have had the immediate consequence of revealing a great deal of interesting structure in the cross sections for various collision processes which was previously unexpected and unsought for, and especially of showing that many inelastic processes remain important down to surprising low energies, close to the threshold in question. A striking example is shown in Fig. 1.[2] As a result of these developments there is coming into being a collision spectroscopy of diatomic systems that is quite comparable to optical spectroscopy in the richness of structure and variety of features that can be observed and that has similar potentialities for revealing information about the electronic structure and interactions of the transient molecular system formed in the course of the collision. One of the theoretical tasks for the next few years is to develop enough understanding of these features and of the underlying principles so that the empirical evidence that can be obtained from experiments may be converted into reliable information on interatomic potentials and other interaction parameters which can reliably be used for a variety of predictive purposes. This development of an empirical and phenomenological theoretical framework will obviously be closely interwoven with the continued development of methods for the complete ab initio calculation of a variety of collision processes, but the latter approach will necessarily continue to be confined largely to the smaller and simpler colliding systems. It is through a combination of these three approaches, experimental, semiempirical and purely theoretical, that even more rapid progress can be expected in the next few years.

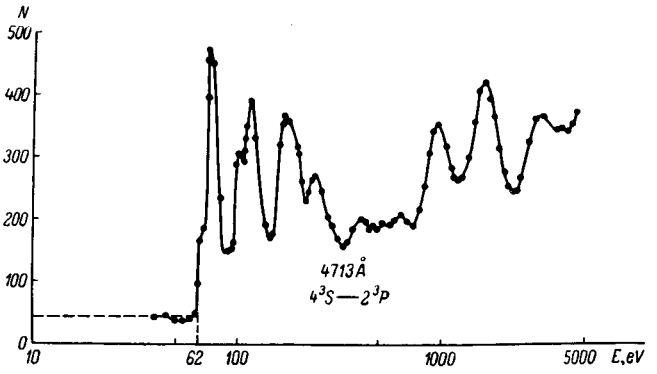


Figure 1. Excitation of He 4^3S in the collision He^+ + He as a function of energy. (ref. 2b)

In some cases the energy loss ΔE is not known or is known with very poor resolution, in which case an energy-averaged (or energy-summed) cross section is measured,

$$\sigma_g(\theta,E) = \Sigma_{\Delta E}\sigma(\theta,E,\Delta E) \ ; \qquad (3)$$

in the case of collisions at high energies (above 10 keV, for instance), where the ratio $\Delta E/E$ is probably small, this sum is called the quasielastic differential cross section (it has sometimes, confusingly, also been called a "total cross section"). Obviously then we also have a quasielastic total cross section by summing over both angle and energy loss.

Closely related to these observable experimental parameters is a quantity of fundamental importance for most models of the atomic collision processes, namely the impact parameter b. This is not directly observable but it is closely related to the observables because of a relationship which is usually valid to a high degree of accuracy in the semiclassical limit,

$$\theta \simeq \theta\ (b,E,\Delta E), \quad b \cong b\ (\theta,E,\Delta E)\ . \qquad (4)$$

For the purposes of calculating cross sections classically and semiclassically the problem usually involves no more than the three variables b, E, and ΔE, and exactly the same information is contained in the cross section if it is known as a function of the three variables of Eq. (1). Consequently, studies of differential scattering of atoms with energy analysis provide an enviably complete amount of information on the collision processes, particularly if a wide angular range can be covered, and if any further parameters of the collision could be measured they would, in principle, provide no further information but only a consistency check. This kind of information therefore makes possible the most searching test of any theoretical predictions. On the other hand, since the information available involves no averages or summations it also provides the best possible raw material for an analysis to determine interaction parameters empirically from the experimental data.

In recent years it has been widely recognized that relations like Eq. (4) can be used in the analysis of experimental data in order to correlate various observed processes with the impact parameter at which they appear to occur. Such correlations are often highly illuminating. In making them, however, it has often been necessary to assume a potential form in order to obtain the connection between b and θ. Unfortunately, some authors have adopted the practice of reporting experimentally measured quantities such as cross sections or transition probabilities directly as functions of an assumed impact parameter and have too often neglected to report also the true experimentally measured parameter, namely the angle of scattering. Since the assumed impact

parameter sometimes depends rather sensitively on the assumed potential, it is very important, if the data is to be used by others, that the experimental parameters be reported as a routine matter. It should also be pointed out that many cases are known in which the scattering at a single angle does not strictly arise from a single impact parameter, but represents a superposition of or interference between processes occurring at several more or less separated impact parameters. Nevertheless, when applied circumspectly the connection represented by Eq. (4) is extraordinarily fruitful.

Closely related to Eq. (4) are certain scaling laws or principles of similarity which have proved very valuable in the comparison and analysis of experiments. A fact which has long been known and which was effectively exploited by Everhart at an early date,[3] is that the product of collision energy and angle of scattering is a function predominantly of the impact parameter and more or less independent of the energy, at least in simple elastic scattering at small and moderate angles. This is a consequence of the existence of an expansion,[4]

$$\tau = E\theta(b,E) = \tau_0(b) + E^{-1}\tau_1(b) + E^{-2}\rho_2(\tau)\ldots, \qquad (5)$$

as a consequence of which the impact parameter can be expressed as a function of τ with correction terms as an expansion in the angle,

$$b = b_0(\tau) + \theta b_1(\tau) + \theta^2 b_2(\tau)\ldots. \qquad (6)$$

It has recently been observed that some other experimental observables can be expanded in the same way.[5] In particular, in simple elastic scattering a reduced cross section can be defined in terms of experimental observables and expanded as follows:

$$\rho = \theta\sin\theta\sigma(\theta,E) = \rho_0(\tau) + \theta\,\rho_1(\tau) + \theta^2\rho_2(\tau)\ldots. \qquad (7)$$

When plotted in terms of ρ vs. τ, experimental data in small angle scattering can be effectively compared from energy to energy. Furthermore, features which occur in a limited range of τ can be recognized as being associated with a given impact parameter and distance of closest approach even if the actual value of the impact parameter concerned is not known.

Equations (5) through (7) are valid for simple elastic scattering uncomplicated by interference effects. Often, however, the scattering process shows a more complicated pattern arising from the interference of two or more terms in the scattering amplitude, both of which are important at the same angle of scattering. In that event it is usually possible to write the differential cross section in the form

$$\sigma(\theta,E) = \left|\Sigma_i f_i(\theta,E)\right|^2 , \qquad (8)$$

where each of the component amplitudes can be written as

$$f_i = \sigma_i^{1/2} e^{i\alpha_i/\hbar v} , \qquad (9)$$

where v is the velocity, σ_i is related to a ρ_i that can be expanded as in Eq. (7) and α_i has the expansion

$$\alpha_i(\tau,\theta) = \alpha_{i0}(\tau) + \theta\alpha_{i1}(\tau) + \ldots \qquad (10)$$

Inelastic processes can be handled in substantially the same way but the functions $\rho_{im}(\tau,\Delta E)$, $\alpha_{im}(\tau,\Delta E)$ depend on ΔE as well as τ, and certain transition probabilities may also be needed which depend on the collision velocity.

By their nature these scaling laws are limited to small angle scattering, but this is experimentally one of the most important and accessible regions. Other forms are available to deal with the other limiting case in the region near back scattering.[4,5] Another procedure has been given by Lindhard, Nielsen and Scharff which appears to be valuable for higher energy collisions and to cover in an approximate way the entire range of angles.[6]

Let us now turn to the experimental field and survey briefly some of the features that are observed and some of the quantities that can be measured. We can begin by looking at elastic scattering. First let us consider the simplest case of elastic scattering in the absence of any special symmetry, particularly the scattering of two different atoms A + B in S states, which can form only one molecular state without promoting an electron. In this case data from differential scattering can be treated by the simple scaling law of Eq. (7). This has been shown to be valid over a very wide energy range: Greene and Ross have used it successfully at thermal energies[7] and we have applied it to data in the systems He^+ + Ne and He^+ + Ar at energies running from 10 eV to 100 keV;[8] an example is given in Fig. 2. Such data can be used to deduce potential parameters, and if the experimental data cover a wide enough span in the variables they can be used to determine the whole potential of a corresponding wide range in r. Methodical inversion processes for doing this have been developed by Hoyt,[9] Firsov[10] and others.[5] From such information one can then associate a particular distance of closest approach r_o with each value of the reduced scattering angle τ according to the general scheme

$$\rho_o(\tau) \rightarrow \tau_o(b) \rightarrow V(r) ,$$

$$\tau \longleftrightarrow b \cong r_o \ (\theta \text{ small}) . \qquad (11)$$

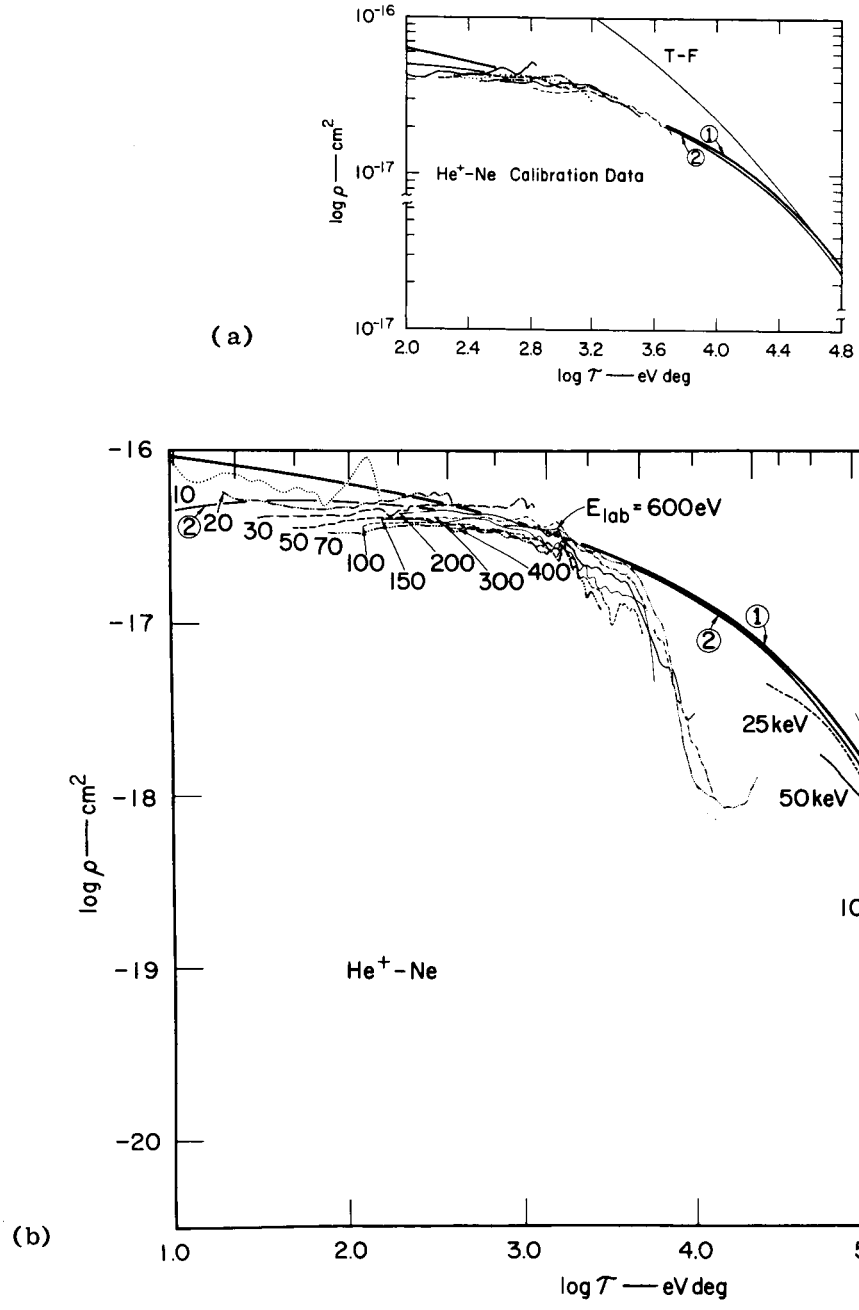


Figure 2. Scaling of elastic scattering cross sections for He^+ + Ne. (ref. 8)

(a) Absolute measurements.

(b) Pure elastic data from 100 to 600 eV, quasielastic data from 25 to 100 keV.

When the interaction potential has both attractive and repulsive parts and consequently a minimum (or sometimes a maximum), the differential scattering shows a localized peak in a fixed range of τ and, under high resolution, one or more sets of interference peaks. These features result from rainbow and glory scattering.[1,11] Such effects have been studied most thoroughly in the thermal energy range but they have also been seen at energies above 10 eV.

In symmetric systems at least two types of oscillations are observed that arise from the general symmetries of the diatomic system. Departing from the historical order, I shall consider first the nuclear symmetry effect which arises from the general requirement of symmetry of the wave function with respect to exchange of atomic particles. As a consequence in a given electron state the angular momentum quantum number ℓ for the motion of the heavy particles is limited to either even or odd values, from which there results a symmetry in the scattering amplitude,

$$\ell \text{ even}, \quad f(\theta) = f(\pi - \theta) = \frac{1}{2}\left[f(\theta) + f(\pi - \theta)\right] ,$$

$$\ell \text{ odd}, \quad f(\theta) = -f(\pi - \theta) = \frac{1}{2}\left[f(\theta) - f(\pi - \theta)\right] . \qquad (12)$$

From this when ℓ is large there arises an oscillating pattern that is equivalent to the interference between direct scattering of the projectile through the angle θ and knock-on scattering of the target through $\pi - \theta$. This oscillation disappears if the nuclear symmetry is removed. An example is shown in Fig. 3, where it is superimposed on another oscillation due to the electronic symmetry. The nuclear symmetry effect was predicted in the early '30's[12] but has only recently been seen;[13] it is to be expected equally in cases where only a single electronic state is accessible, for example in the scattering of He by He. An example of the types of curves to be expected will be found in Fig. 4, taken from an article by Olson and Mueller.[14]

The nuclear symmetry effect may also be expected to be observable in some cases of inelastic scattering, but ordinarily it will be much less pronounced because of the fact that inelastic cross sections usually depend very strongly on the angle θ. The nuclear symmetry oscillations will only be pronounced in special cases where $f(\theta)$ and $f(\pi - \theta)$ happen to be comparable in magnitude. This condition is bound to be satisfied if the inelastic cross section is sizable near $\theta = \frac{\pi}{2}$.

It is often the case that two or more electronic states are available which are distinguished by having different symmetry properties. In symmetric systems we may have both g and u states depending upon their properties under reflection in the internuclear plane. This is the case in such combinations as $H^+ + H$ and

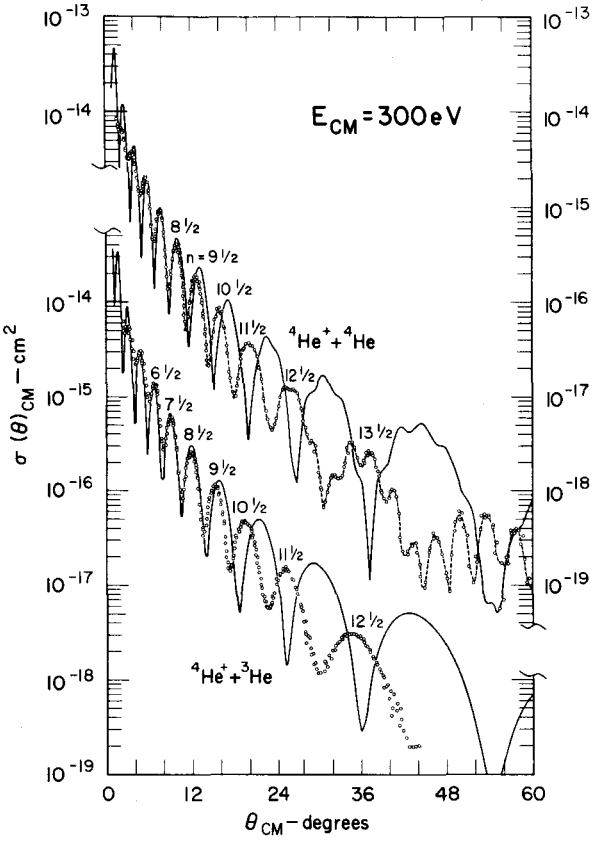


Figure 3. Nuclear and Electronic Symmetry Oscillations in Scattering of He^+ by He. The electronic (g-u) interference peaks are numbered. The nuclear symmetry oscillations appear on the right in the collisions $^4He^+ + ^4He$, and are absent for $^4He^+ + ^3He$. Circles are experimental points, solid lines are theoretical using approximate potentials $V_g(r)$, $V_u(r)$. (ref. 13).

He^++He. In that case the g and u states lead to two separate potentials and to two scattering amplitudes which are combined to give the cross sections for either direct (+) or charge exchange (-) scattering:

$$V_g(r) \rightarrow f_g(\theta,E), \quad V_u(r) \rightarrow f_u(\theta,E) \ ,$$

$$\sigma_\pm = \left| f_g \pm f_u \right|^2 = A(\theta,E) \pm B(\theta,E) \cos\left[2\pi N(\theta,E) + \alpha\right]. \qquad (13)$$

The resulting electronic symmetry oscillations were first seen by Ziemba and Everhart.[15] Fig. 3 gives an example of these

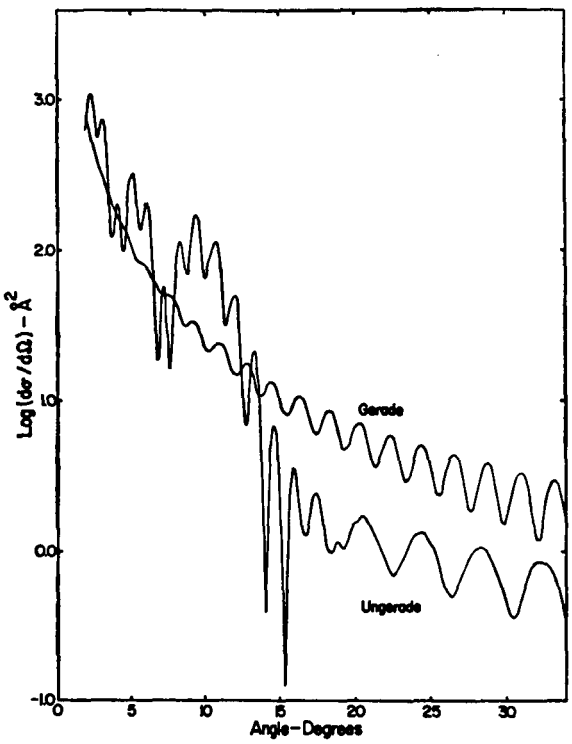


Figure 4. Nuclear Symmetry Oscillations in One-State Scattering. $|f_g(\theta)|^2, |f_u(\theta)|^2$ calculated from the potentials $V_g(r)$, $V_u(r)$ of the system He_2^+. The ungerade curve shows rainbow oscillations on the left. (ref. 14)

oscillations as well as of the nuclear symmetry ones. Comparing this with Eqs. (9) and (10) we see that the index number N when multiplied by the velocity can be expanded as follows:

$$vhN = \Delta a(\tau, \theta) = \Delta a_o(\tau) + \theta \Delta a_1(\tau) + \ldots, \qquad (14)$$

which gives a scaling law that can be applied to the experimental data. The positions of the peaks are then related to the potentials; since they can be located with great precision they often provide a more sensitive test of potentials than the magnitude of the cross section, which ordinarily is much harder to measure precisely.

At high energies it has been observed empirically that the product vN is a constant independent of both energy and angle, except for very small values of the scattering angle.[3] This product is a characteristic velocity which is related to the integral of the difference between the two potentials[16]

$$2\pi vN \rightarrow v^{*} = 2\hbar^{-1}\int_{o}^{\infty} \Delta V(R)dr \quad (E \rightarrow \infty,\ b \rightarrow 0) \ . \tag{15}$$

This implies that in the high energy limit the maxima and minima are independent of the scattering angle (except at very small angles where the impact parameter b is large). Fig. 5 shows an example from the system He^{+} + He,[17] where the locations of maxima and minima are plotted as functions of E and θ, showing the expected horizontal trend at high E. As a consequence of this behavior the total cross section given by Eq. (2) oscillates in just the same way as a function of the energy, and the characteristic velocity v^{*} can be evaluated from total cross section data. Such measurements have been made in the case of ion-atom scattering in symmetric systems of the alkali metals; an example from the work of Perel[18] is shown in Fig. 6.

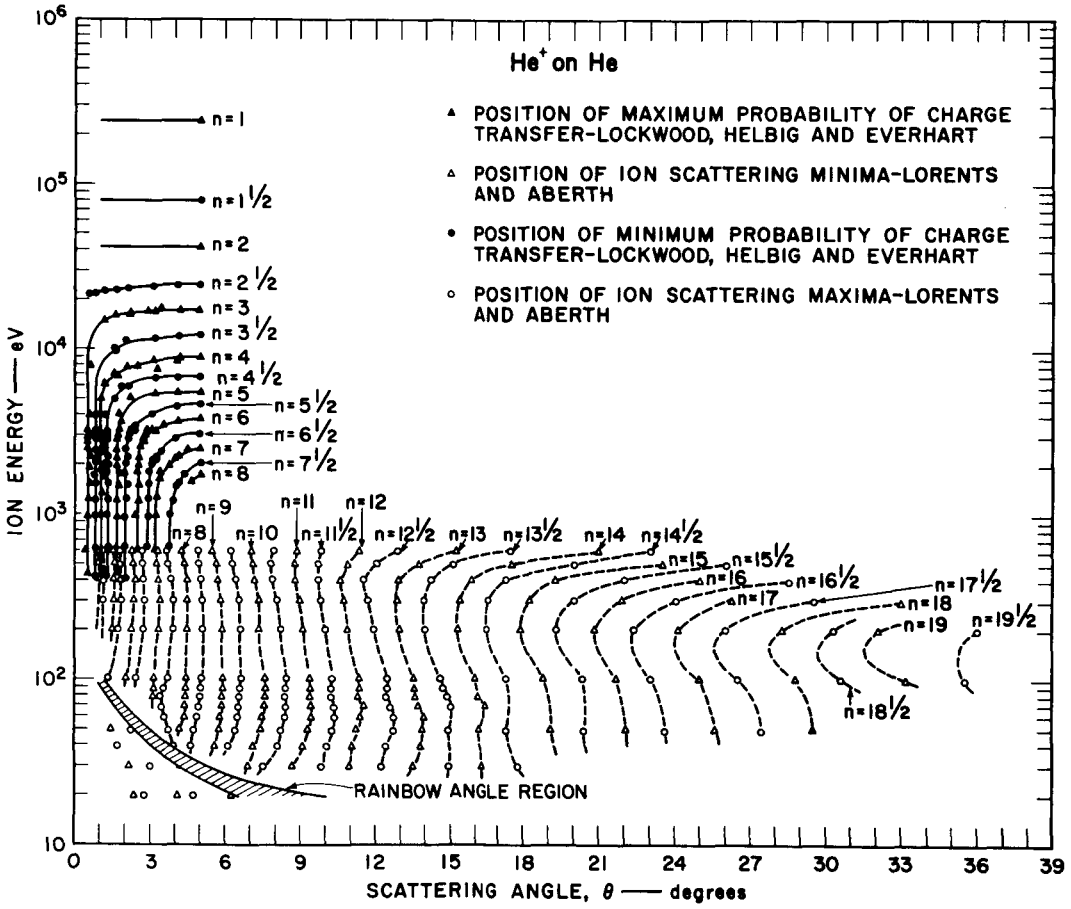


Figure 5. Locations of maxima and minima in the scattering of He^{+} + He. Charge-transfer maxima and scattering minima coincide. At high E the loci become horizontal (independent of θ) except for very small angles. (ref.17)

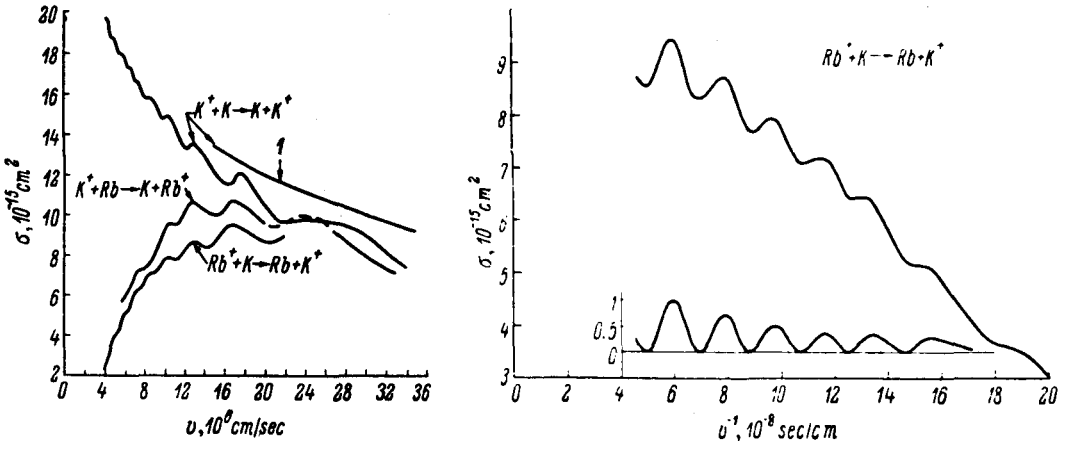


Figure 6. Alkali Ion-Atom Charge Transfer Oscillations: Symmetric and Asymmetric Cases. (ref. 18)
(a) $K^+ + K$, $K^+ + Rb$, $Rb^+ + K$. Total cross section versus velocity.
(b) $Rb^+ + K$, the total cross section and its oscillatory component plotted against reciprocal velocity.

Fig. 6 also shows very similar oscillations in total charge exchange cross sections for asymmetric systems. This involves an inelastic process but it obviously has considerable similarity to the elastic one in symmetric systems. As Lichten pointed out,[19] even in asymmetric systems when the nuclei are close together the electronic wave functions have an approximate g or u symmetry which becomes exact in the united atom limit. This symmetry breaks down more and more at larger distances but it is believed that one can at least approximately identify a characteristic distance R_x at which the united atom approximation should be abandoned and replaced by a description in terms of separated atomic systems. In this case the characteristic velocity is defined by an equation very similar to (15) but with a finite limit to the integral,

$$v^* = 2\hbar^{-1}\int_0^{R_x} \Delta V(r)\,dr \ . \qquad (16)$$

In contrast to the symmetric case the asymmetric charge transfer cross sections show an overall trend with a broad maximum at some velocity v_m. This is a second important characteristic velocity that depends on parameters of the interaction.

In many cases inelastic processes are fruitfully discussed in terms of a curve crossing model, the principal results of which were deduced by Landau, Zener and Stueckelberg in 1932.[20] If the crossing occurs at R_x the probability of remaining in a state with

the same electronic configuration at a single transition past the crossing is

$$p \cong \exp\left[-\pi v_o / v_r(R_x)\right] , \tag{17}$$

where the characteristic velocity v_o is

$$v_o = \frac{2U_{12}(R_x)\Delta R}{\hbar} = \frac{\Delta U(R_x)\Delta R}{\hbar} , \tag{18}$$

and where

$$\Delta R = \frac{U_{12}(R_x)}{\left|\frac{d}{dR}(U_{11}-U_{22})\right|_{R_x}} . \tag{19}$$

v_r is the radial velocity associated with the nuclear motion. The last formula represents a characteristic range of the interaction at the crossing. A maximum in the differential cross section occurs when

$$v_{max} \cong \frac{\pi v_o}{\ell n 2} . \tag{20}$$

When the last form of Eq. (18) is combined with (20) there results an expression identical in form with Massey's adiabatic criterion,[21] provided we identify ΔR as the characteristic range of the interaction instead of using some atomic diameter R.[22] There seems to be little justification for the common assumption (for which Massey is not fully responsible) that the energy separation ΔU at infinite separation should be used in his formula, and recent experimental data also contradict the simplified criterion.[2]

In Fig. 7 I show some inelastic differential scattering patterns for the system $He^+ + He$.[23] Here two features are evident. First, the absence of inelastic scattering in the forward direction and a sharp rise toward a first maximum at a finite angle and second, a series of oscillations of considerable regularity. The sharp rise to a peak with a more or less broad maximum in the overall envelope is to be expected on the Landau-Zener model or from more refined variations of the curve crossing mechanism. The oscillations are an interference pattern arising from the fact that two trajectories are available that are particularly favorable for the inelastic process, one where the transition occurs at R_x on the inbound passage and a second where it occurs on the outbound passage. An interference pattern between scattering amplitudes for each of the processes explains the observed oscillations; such a pattern of oscillations was predicted by Stueckelberg in his comprehensive analysis in 1932.[20(c)] These Stueckelberg oscillations have now been seen in a number of cases of inelastic scattering

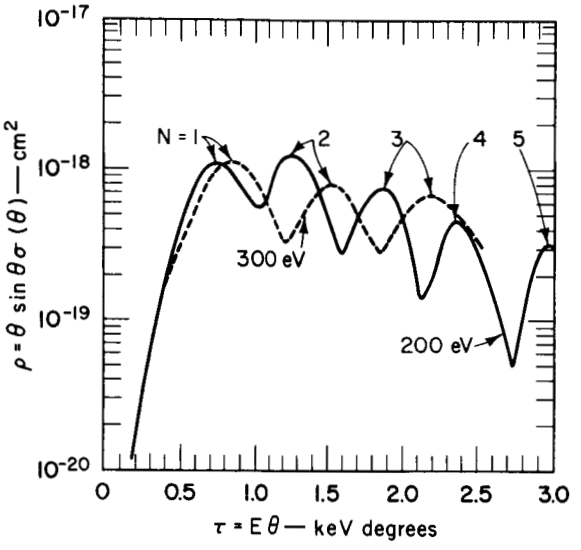


Figure 7. Inelastic scattering of $He^+ + He$ producing $He(2^3S)$. Reduced cross section plotted against reduced angle. (ref. 23)

and they are also observable in elastic scattering where it is perturbed by a curve crossing, because again there are two trajectories, one in which no transition occurs and one on which transitions occur at both passages past the crossing.

At low energies the Stueckelberg oscillations, like other interference oscillations, depart severely from the limiting case represented by Eqs. (15) and (16). Instead, they depend strongly on angle, often with the property that the product of velocity and spacing in angle $v\Delta\theta$ is almost constant or slowly varying. It is a consequence of the scaling laws given earlier that the reciprocal of this product in many cases measures the difference in impact parameters between the two trajectories that conspire to interfere at the same angle of scattering

$$\Delta b(\tau) = \frac{\partial \Delta a}{\partial \tau} = \frac{2\pi}{k} \frac{\partial N}{\partial \theta} . \qquad (2))$$

This difference is one of the measurable quantities in the observations and has an indirect connection with the potentials. There is no obvious reason to expect it to be a constant, but empirically it seems often to vary only slowly with τ.

Empirically it is also found that the first maximum in such an oscillating pattern usually occurs at an approximately constant value of τ_x, independent of energy. This value of τ_x is connected with the location of the crossing R_x. In elastic scattering, when

the potential is known, the location τ_x of a perturbation due to a curve crossing allows one to determine the location R_x of that crossing;[24] in Table I are data on a few such crossings which we have observed and their comparison with theory[25] where possible. These crossings appear to be of two types: isolated crossings producing an interference pattern but without much change in the absolute magnitude of the elastic cross section, and a perturbation followed by a rapid drop in the elastic scattering which appears to be due to the rapid opening up of many competing inelastic channels through a series of crossings following close upon each other.[8]

In inelastic collisions it is easy to measure τ_x but harder to use that information to deduce a value of R_x, because this entails a knowledge of the relationship between τ and b in both the initial and the final states, and thus of both. However, it is possible to learn something about the shapes of the potentials from the location of τ_x. For example, Fig. 8 shows for the charge transfer reaction $H^+ + Kr \rightarrow H + Kr^+$. The inelastic process occurs even in directly forward scattering, which implies that at least one of the curves is attractive. When, as in Fig. 7, inelastic scattering is absent in the forward direction (θ=0), we can deduce that at least one of the curves is repulsive and that the other one is not very strongly attractive. In this case the elastic perturbation is around 1700 eV-degrees and the first maximum of the inelastic cross section occurs at about 780 eV-degrees. Since the inelastic τ_x is a little less than half the elastic one, the implication is that the net effect of the potential for the excited state is a very weak attraction.

In addition to measuring τ_x, inelastic cross sections may also allow us to measure the energy V_x at the crossing point. An example of such a measurement, which can be obtained from the effective energetic threshold for the process to be observed, is given in a paper submitted to this meeting.[27]

In some cases a curve crossing may lead to an excited molecular state which has the possibility of dissociating in more than one way. For example, in the case of $He^+ + He$ the ground state curve of symmetry $^2\Sigma_g^+$ crosses an excited curve of the same symmetry which may dissociate and leave the neutral atom in either of the two states 2^3S or 2^1S; a slow oscillation from one to the other might be expected in the differential cross sections as a function of angle and energy. Similarly excited states of systems like $HeNe^+$ may dissociate by two competing routes leaving the charge on one or the other of the atoms. Indirect evidence of such effects has recently been found.[28]

As we have seen, semiclassical methods are very useful in

Table I

Curve Crossings Located from Elastic Perturbations

System	$\frac{\tau_x}{\text{eV-deg}}$	$\frac{r_x}{a_o}$	Evidence	Probable Symmetry Type	$\frac{r_x}{a_o}$ (Theory) (ref. 25)
$He^+ + He$	1600	1.7	Oscillations (g symmetry)	$^2\Sigma_g^+ - {}^2\Sigma_g^+$	1.5
$He^+ + Ne$	1950	1.9	Oscillations	$^2\Sigma - {}^2\pi$	1.75
	2500 to 9500	1.4 to 1.1	Loss from Elastic Channel	$^2\Sigma - {}^2\Sigma$, etc.	
$He^+ + Ar$	870	2.9	Oscillations	$^2\Sigma - {}^2\pi$	
	1000 to 3000	2.4 to 1.9	Loss from Elastic Channel	$^2\Sigma - {}^2\Sigma$, etc.	

correlating much of the experimental observations that are becoming available and in connecting them with interaction parameters. However, there are important classes of information that are becoming available experimentally for the interpretation of which such approximation methods do not suffice. This is notably true for data close to the threshold in angle or energy or both. In such regions a fuller study of the coupled equations of the quantum

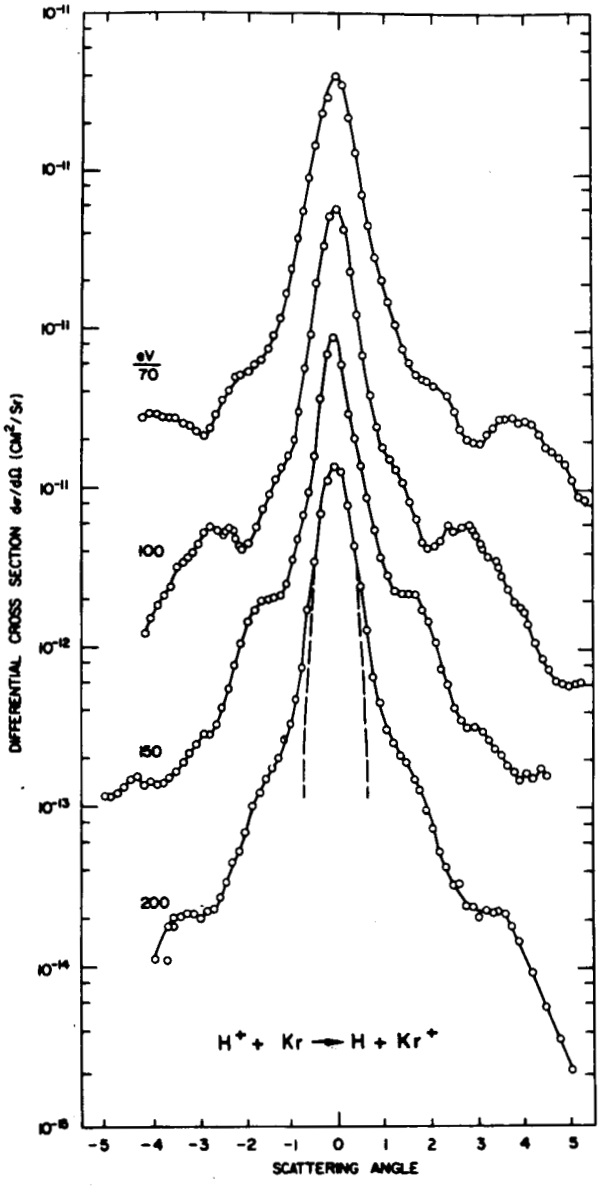


Figure 8. Differential charge transfer cross sections for the process $H^+ + Kr \rightarrow H + Kr^+$. (ref. 26)

mechanical problem is required.[12,29] These equations I shall briefly describe here in a somewhat new form.

Let us take $\underset{\sim}{R}$ to represent the internuclear vector and $\underset{\sim}{r}$ to represent collectively all the electron coordinates. Let us write the Hamiltonian and the Schrödinger equation in a time-independent form as

$$H = T^{nu} + H' , \quad (H-E)\Omega(\underset{\sim}{R},\underset{\sim}{r}) = 0 , \tag{22}$$

and assume that the wave function can be expanded as products of nuclear functions depending only on $\underset{\sim}{R}$ and electronic functions in which the vector $\underset{\sim}{R}$ is considered merely as a parameter,

$$\Omega = \Sigma_k \psi_k(\underset{\sim}{R})\chi_k(\underset{\sim}{R},\underset{\sim}{r}) . \tag{23}$$

At each value of $\underset{\sim}{R}$ the electronic functions are assumed to form an orthonormal complete set,

$$\langle j | k \rangle = \int \chi_j^* \chi_k d\underset{\sim}{r} = \delta_{jk} , \tag{24}$$

from which the following important matrices can be constructed

$$U_{jk}(\underset{\sim}{R}) = \langle j | H' | k \rangle , \tag{25}$$

$$\underset{\sim}{P}_{jk}(R) = \langle j | \underset{\sim}{p}^{nu} | k \rangle . \tag{26}$$

The following identity exists

$$B_{jk} = 2M\langle j | T^{nu} | k \rangle = \left(\underset{\sim}{\mathbb{P}}\cdot\underset{\sim}{\mathbb{P}}\right)_{jk} + \underset{\sim}{p}^{nu}\cdot\underset{\sim}{P}_{jk}(\underset{\sim}{R}) . \tag{27}$$

If we define a generalized nuclear momentum operator

$$\underset{\sim}{\mathcal{P}} = \underset{\sim}{\mathbb{P}}(R) + \mathbb{1}\underset{\sim}{p}^{nu} , \tag{28}$$

and a generalized nuclear kinetic operator

$$2M\mathcal{T} = \underset{\sim}{\mathcal{P}}\cdot\underset{\sim}{\mathcal{P}} = \mathbb{B} + 2\underset{\sim}{\mathbb{P}}\cdot\underset{\sim}{p}^{nu} + \mathbb{1}\underset{\sim}{p}^{nu}\cdot\underset{\sim}{p}^{nu} , \tag{29}$$

the coupled equations arising from

$$\int \chi_j^*(H-E)\Omega d\underset{\sim}{r} = 0 \tag{30}$$

can be put in the matrix form

$$\left(\mathcal{T} + \mathbb{U}(R) - \mathbb{1}E\right)\Psi = 0 . \tag{31}$$

The two matrices $\mathbb{U}$ and $\mathbb{P}$ are of fundamental importance and both

of them may contribute to the coupling responsible for inelastic processes.

Changes may be made from one representation to another through a unitary transformation $\underset{\sim}{\mathbf{C}}(R)$; since invariance of Eq. (31) must be maintained, we must have

$$\underset{\sim}{\mathcal{P}}' = \underset{\sim}{\mathbf{C}}^{-1}(R)\,\underset{\sim}{\mathcal{P}}\,\underset{\sim}{\mathbf{C}}(R) \quad . \tag{32}$$

All these relations have assumed that the electronic coordinates r are measured in a non-rotating frame. However, it is very useful to transform to a molecular frame in which the electronic coordinates $\underset{\sim}{r}'$ are measured in a frame rotating with the nuclear axis. In that case additional angular coupling terms must be introduced[30] into Eq. (31) but the principal radial dependence is contained in two matrices which depend only on the magnitude R, $\mathbf{U}^{mol}(R)$ and $\mathbf{P}_R^{mol}(R)$, where

$$\mathbf{P}_R^{mol}(R)_{jk} = \frac{\hbar}{i}\left\langle j'\left|\frac{\partial}{\partial R}\right|k'\right\rangle \quad . \tag{33}$$

Under transformations from one molecular representation to another the last matrix transforms as follows:

$$\left(\mathbf{P}_R^{mol}(R)\right)' = \mathbf{C}^{-1}(R)\,\mathbf{P}_R^{mol}(R)\,\mathbf{C}(R) + \mathbf{C}^{-1}(R)\,\frac{\hbar}{i}\,\frac{\partial \mathbf{C}(R)}{\partial R} \quad . \tag{34}$$

The usual adiabatic representation is based on the prescription that the matrix $\mathbf{U}^a$ is diagonal, in which case $\mathbf{P}_R^a$ has prominent non-vanishing off-diagonal elements, especially in the neighborhood of an avoided crossing between two adiabatic potentials; such a situation is shown in Fig. 9a.

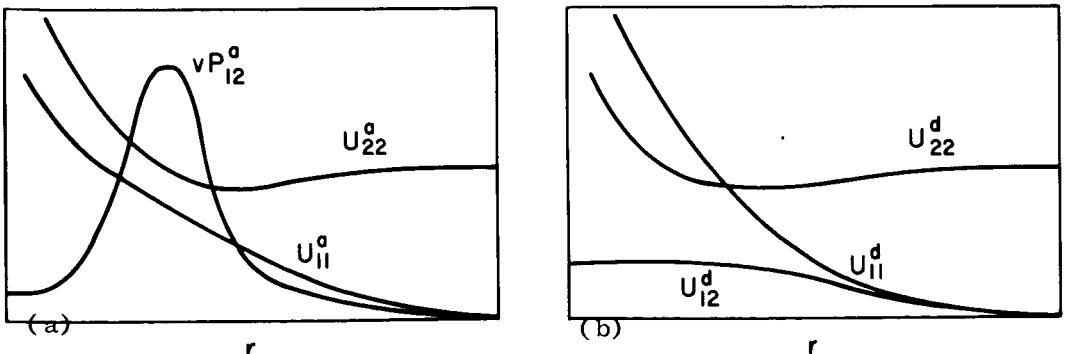


Figure 9. A Curve Crossing in Two Representations.
(a) The Adiabatic Avoided Crossing. $U^a_{12}(R) = 0$, but $P^a_{R,12}(R) \neq 0$.
(b) The Diabatic Crossing. $P^d_{R,12}(R) = 0$, but $U^d_{12}(R) \neq 0$.

The Landau-Zener formula has usually been derived using a non-adiabatic representation in which $\mathbb{U}^{mol}$ is not diagonalized, and Lichten[19] in particular has emphasized the value of such representations for collision problems. He suggested the name "diabatic" and applies it to a representation based on molecular orbitals without configuration interaction.[31] In such a case much of the coupling is removed from the matrix $\mathbb{P}_R^{mol}$ but not all of it, and I wish to suggest that a better definition of the diabatic limiting case can be obtained by requiring that

$$\mathbb{P}_R^d(R) = 0 \quad \text{(all R)}. \tag{35}$$

Such a representation can be obtained from the adiabatic one (or from other molecular representations) by a transformation that satisfies Eq. (34) when set equal to zero, which is equivalent to the integral equation

$$\mathbb{C}(R) = \mathbb{1} + \frac{i}{\hbar}\int_R^\infty \mathbb{P}_R^a(R')\,\mathbb{C}(R')\,dR'$$

$$= \mathbb{1} + \frac{i}{\hbar}\int_R^\infty \mathbb{P}_R^a(R')\,dR' + \left(\frac{i}{\hbar}\right)^2 \int_R^\infty \mathbb{P}_R^a(R')\int_{R'}^\infty \mathbb{P}_R^a(R'')\,dR''dR' + \ldots \tag{36}$$

When this transformation is made an avoided crossing such as that of Fig. 9a becomes a straightforward crossing with potential coupling as shown in Fig. 9b.

There is little doubt that the most important crossings are those with radial coupling of the type we have been considering. However, angular momentum coupling terms are also important, particularly in cases of crossings between states of different symmetry, for example Σ and Π states. These are responsible for at least one of the types of perturbations that have already been seen in elastic scattering, namely the outermost crossing in the $He^+ + Ne$ and $He^+ + Ar$ systems,[25] and also, when the states approach each other R = 0, for a type of rotation-inversion coupling that is responsible for a change in phase of the oscillations in elastic scattering that is seen as one goes from low to high energies in the systems $H^+ + H$ and $He^+ + He$. This effect comes about because swift collisions with very small impact parameters lead to a very rapid reversal of the direction of the internuclear axis, all of which happens well inside most of the electron cloud, whereas the nuclear axis changes direction slowly in collisions with large impact parameters and at lower energies. In the former case a polarized electron cloud does not change its orientation when the internuclear axis flips over, but in the latter case the electron cloud rotates more or less with the nuclear axis. The net effect of the difference between these

two situations is a change in phase in the scattering amplitude for u states as one goes from the low energy to the high energy limit.[32] An illustration taken from the work of Everhart[3] is shown in Fig. 10. This type of coupling can cause inelastic transitions as well.

It is to be expected that the next few years will see a great increase in our understanding of the coupling terms I have been discussing, both from the point of view of semiempirical deductions and from the point of view of their calculation in the molecular orbital framework.

In most of the discussion of inelastic processes I have confined my examples to comparatively low levels of excitation involving only the outer shells of the atoms concerned. As Fano and Lichten pointed out,[33] however, the same considerations apply to inner shell excitations of the type that have been particularly studied at Leningrad[34] and at the University of Connecticut.[35] In this case clearly inner shell electrons are ejected in the course of a violent collision and the subsequent Auger transitions are responsible for the ejection of several electrons from the outer shells leaving both atoms highly ionized. Such processes have been studied both by coincidence techniques and by measuring electron energies; the latter measurements have clearly demonstrated the production of Auger electrons with energies corresponding to these inner shell vacancies.[36] Presently one of the most active current questions in the coincidence measurements is the search

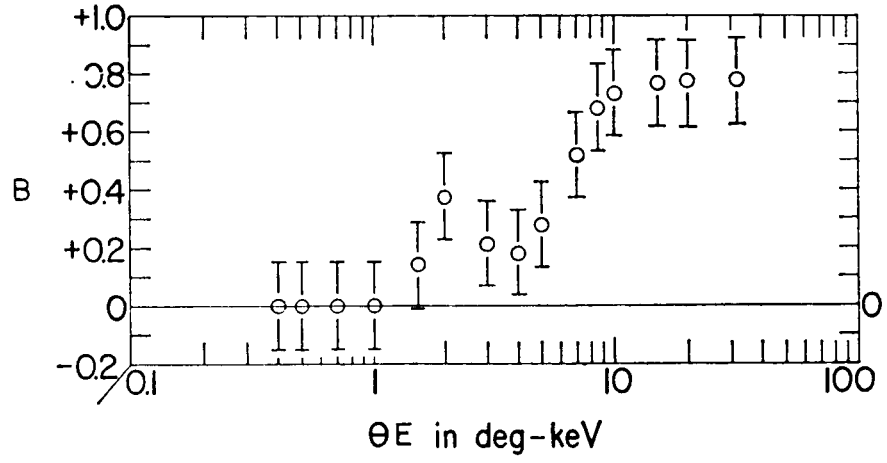


Figure 10. Rotation-Inversion Coupling in He^+ + He. The phase, B, of the high-energy limit of the elastic oscillations is plotted against $\tau = E\theta$; a change of phase occurs between distant collisions ($\tau \to 0$) and close collisions ($\tau \to \infty$). (ref. 3)

for evidence of correlation (or lack of it) between the degrees of ionization in the two atoms leaving the collision region.[35,37] This is connected with the question whether multiple ionization processes occurs quickly while the two atoms are interacting with each other or slowly enough so that the electrons are ejected mainly after the atoms have separated from each other. Other information on inner shell effects has also been obtained from elastic scattering; Fig. 11 shows an example of data from Leningrad showing a strong maximum on an elastic scattering curve corresponding to a process occurring at a distance where the inner shells of the two colliding atoms intersect.[38]

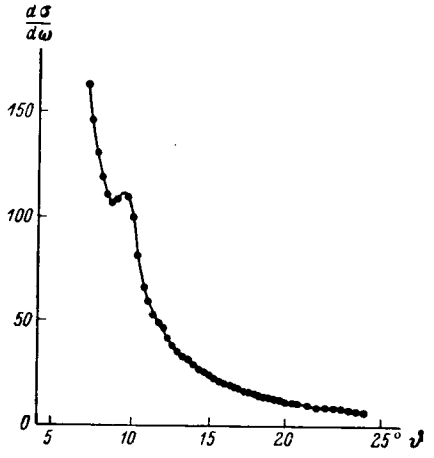


Figure 11. Differential cross section for the scattering of Kr^+ by Kr as a function of angle θ at 25 keV. (ref. 38)

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