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Cross Sections for Energy Transfer in Classical Coulomb Collisions

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The cross section $Q(U)$ for energy transfer of at least U is given for the case where the incident particle is lighter than the target particle. Complete results for $Q(U)$ are represented with the aid of a diagram, the coordinates of which are nondimensionalized mass and nondimensionalized energy of the target particle. Some remarks are made about scaling laws for direct excitation.

I. INTRODUCTION

Classical methods for calculating energy-transfer cross sections have recently found wide application in the estimation of inelastic atomic- and molecular-collision cross sections. The idea of using classical methods for this purpose is due to Thomson.[1] His method consists of calculating the cross section $Q(U)$, for which an incident charged particle transfers an amount of energy of at least U to a stationary electron. This cross section is taken to give the cross section for ionization of an atom or molecule, with the U set equal to the ionization energy of the orbital electron to be removed. Thomson's results were extended by Gryziński,[2-5] who took account of the orbital motion of the atomic electrons, and who emphasized the agreement with experiment which could be obtained by making a number of semiempirical approximations (cf. also, Ref. 6).

A further extension was made by Gerjuoy,[7] who calculated the differential energy cross section $\sigma(U) = -(d/dU)Q(U)$ for an arbitrary mass ratio of the collision partners. The result for $\sigma(U)$ in the special case of an incident particle having a mass m_2 much larger than the mass m_1 of the target particle was also given by Vriens.[8] Expressions for the cross section $Q(U)$ for the special case $m_1 = m_2$ were given in Refs. 9–12 and for the case $m_1 \lesssim m_2$ in Ref. 13.

In the present paper we extend the calculations of Refs. 2–13 by obtaining the results for the cross section $Q(U)$ when $m_1 > m_2$. These results are of interest in view of the equality of the quantum-mechanical and classical Coulomb cross sections. So far, no applications have been found of either the results for $Q(U)$ or the previously given results for $\sigma(U)$ when $m_1 > m_2$.

II. RESULTS FOR $Q(U)$ FOR ARBITRARY RATIO m_1/m_2

The situation considered is sketched in Fig. 1. A target particle (called field particle in Refs. 2–5) of mass m_1 and velocity $\vec{v}_1$ is suffering a collision with an incident particle (called test particle in Refs. 2–5) of mass m_2 and velocity $\vec{v}_2$. That the target particle may be part of an atom is ignored in evaluating the consequences of the collision. The force between the two particles is assumed to be conservative, and derivable from a spherically symmetric potential. It is possible to calculate the amount of energy transferred from the incident particle to the target particle in the laboratory frame of reference as a function of the impact parameter b, and of other variables
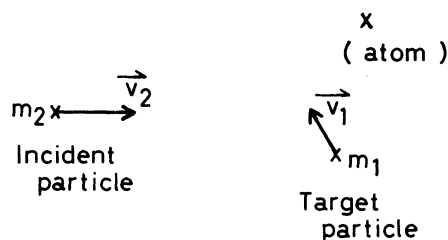

FIG. 1. Particles before collision.

characterizing the collision. Conversely, given a threshold U for the energy to be transferred, one can find the range of impact parameters b for which this is accomplished. Integration over this range yields the cross section for energy transfer of at least U.

In general, both the target particle as well as the incident particle belong to groups, the velocity distribution function of which may be represented by $f_1(\vec{v}_1)$ and $f_2(\vec{v}_2)$, respectively. The energy transfer cross section $Q(U)$ of experimental interest follows by dividing the number of collisions of the type specified occurring per unit time and per unit volume by the flux of incident particles, and by the number density of the target particles $n_1 = \int f_1(\vec{v}_1)\,d\vec{v}_1$:

$$Q(U) = \frac{N_e \int\int\int\int f_1(\vec{v}_1) f_2(\vec{v}_2) \, H(-\Delta E - U) g \, d\vec{v}_1 \, d\vec{v}_2 \, b \, db \, d\epsilon}{n_1 \int f_2(\vec{v}_2) \, v_{2x} \, d\vec{v}_2} .$$

(1)

Here, N_e is the number of equivalent target particles per atom or molecule; H is the Heaviside unit function: $H(x) = 1$ for $x > 0$, $H(x) = 0$ for $x < 0$; and $g = |\vec{v}_2 - \vec{v}_1|$ is the initial relative speed between the colliding particles. The quantity $-\Delta E$ is the amount of energy transferred from the incident particle to the target particle. It is given by

$$-\Delta E = \tfrac{1}{2} m_1(v_1'^2 - v_1^2) = -\tfrac{1}{2} m_2(v_2'^2 - v_2^2) ,$$

where v_1' and v_2' are the speeds after the collision of the target particle and the incident particle, respectively. The angle ϵ is the angle between the fundamental plane, which is defined as the plane containing $\vec{v}_1$ and $\vec{v}_2$, and the orbital plane which by definition contains $\vec{g}$ and the relative velocity after the collision $\vec{g}'$. In the calculations of Refs. 2–5 and 7, the Heaviside unit function was replaced by an integral over a Dirac Δ function, whereas here it is found convenient to keep the unit function.

The problem of evaluating the numerator of (1) is somewhat similar to that of evaluating the collision integral of the Boltzmann equation for the case in which the distribution function is Maxwellian below, and zero above, a cutoff point.[14] It is convenient to carry out the integral over b first. The H function in the integrand is either 1 or 0, and the result of the integration over b simply is $\tfrac{1}{2} b^2$ taken between appropriate limits. In order to evaluate these limits, one can use the expression already given by Gryziński [Eq. (17) of Ref. 3] for the speed v_2' of the incident particle after the collision. The resulting calculation is laborious, but straightforward.[15] Here we only present final results for the case of a Coulomb

force law between the colliding particles:

$$F_{12} = C/r_{12}^2 .$$

(2)

When the particles have electric charges e_1 and e_2, respectively, the constant C is given by

$$C = e_1 e_2 / 4\pi\epsilon_0 ,$$

(3)

where ϵ_0 is the dielectric constant for a vacuum. It is assumed that the energy $E_2 = \tfrac{1}{2} m_2 u_2^2$ of the incident particle is given, so that

$$f_2(\vec{v}_2) = C_2 \delta(v_{2x} - u_2) \delta(v_{2y}) \, \delta(v_{2z}) .$$

(4)

For f_1 the simplest possible choice[2] is taken:

$$f_1(\vec{v}_1) = C_1 \delta(v_1 - u_1) .$$

(5)

As a consequence, the kinetic energy of the target particles is $E_1 = \tfrac{1}{2} m_1 u_1^2$. The normalizing constants C_1 and C_2 cancel in Eq. (1). The results for $Q(U)$ can be presented conveniently with the aid of a diagram in which the quantity $M_1 = m_1/(m_1 + m_2)$ is plotted as a function of the dimensionless variable
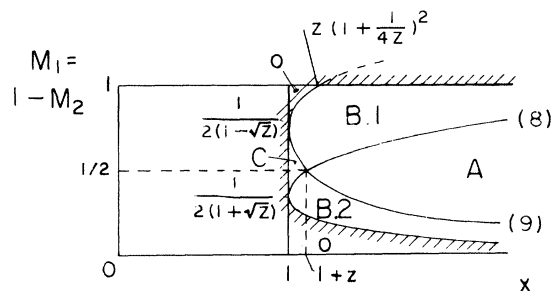
$$x = E_2/U ,$$

(6)

with the dimensionless quantity

$$z = (m_2/m_1)(E_1/U)$$

(7)

as a parameter (See Fig. 2). The region of physical significance of the $M_1 - x$ diagram is $x > 1$,
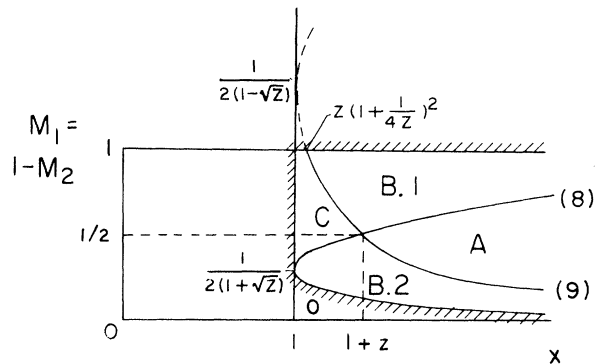
FIG. 2. M_1 versus x diagrams.

$0 < M_1 < 1$. This region is divided into the sub-regions A, B.1, B.2, and C by the curves

$$x^{1/2} = (2M_2)^{-1} \left[(M_1 - M_2) z^{1/2} + (z + M_2/M_1)^{1/2} \right] , \quad (8)$$

$$x^{1/2} = (2M_2)^{-1} \left[(M_2 - M_1) z^{1/2} + (z + M_2/M_1)^{1/2} \right] . \quad (9)$$

The general form of these curves is shown in Figs. 2(a) and 2(b), applicable when $z > \frac{1}{4}$ and $z < \frac{1}{4}$, respectively. The results for $Q(U)$ are, in region A,

$$Q(U) = \frac{\sigma_0}{U^2 x} \left(\frac{2}{3} z + \frac{M_2}{M_1} - \frac{1}{4M_1^2 (x - z)} \right) ; \quad (10)$$

in regions B.1 and B.2

$$Q(U) = \frac{\sigma_0}{U^2 x z^{1/2}} \left[\frac{1}{3}(x-1)^{3/2} \pm \frac{1}{3}\left(z + \frac{M_2}{M_1}\right)^{3/2} \mp \frac{1}{3} x^{3/2} \right.$$
$$\left. + \frac{1}{3} z^{3/2} \pm \frac{1}{2} x^{1/2} + \frac{1}{2}\frac{M_2}{M_1} z^{1/2} + \frac{1}{8M_1^2 (z^{1/2} \mp x^{1/2})} \right] , \quad (11)$$

where the upper signs apply to region B.1, the lower ones to region B.2; and in region C

$$Q(U) = (\sigma_0 / U^2 x z^{1/2}) \frac{2}{3} (x-1)^{3/2} . \quad (12)$$

In these expressions,

$$\sigma_0 = \pi C^2 . \quad (13)$$

The cross section $Q(U)$ differs from zero only in the regions A, B.1, B.2, and C; the boundary of these regions is indicated by cross hatching. On the boundary we have $Q(U) = 0$, except for the line $M_1 = 1$ in region B.1. It can be verified that the expressions given for $Q(U)$ in any two adjacent regions agree on the curve separating those two regions.

For the special case $M_1 = M_2$, the present results (10) and (12) reduce to Eq. (29) of Ref. 4. References 2–5 do not give any analytic results for $Q(U)$ when $M_1 \neq M_2$. The present results (10)–(12) agree with the corresponding results given in Ref. 13 for $M_1 \geq M_2$.

It is useful to compare the results for the differential cross section $\sigma(U) = -(d/dU) Q(U)$ given in Ref. 7 with some of the corresponding results given by Gryziński. In the present notation, the results of Ref. 7 are

$$\sigma(U) = (\sigma_0 / U^3 x) \left(\frac{4}{3} z + M_2/M_1 \right) \quad (14)$$

for region A;

$$\sigma(U) = (\sigma_0 / U^3 x z^{1/2}) [\frac{1}{3}(2x - \frac{1}{2})(x-1)^{1/2} \pm \frac{1}{3}(2z + \frac{1}{2}M_2/M_1)$$
$$\times (z + M_2/M_1)^{1/2} \mp \frac{2}{3} x^{3/2} + \frac{2}{3} z^{3/2}$$
$$\pm \frac{1}{2} x^{1/2} + \frac{1}{2} z^{1/2} M_2/M_1] , \quad (15)$$

with the upper signs applying to region B.1, and **the lower** ones to region B.2; and

$$\sigma(U) = (\sigma_0 / U^3 x z^{1/2}) \frac{2}{3} (2x - \frac{1}{2})(x - 1)^{1/2} \quad (16)$$

for region C. Equation (14) agrees with the first of Eqs. (17) of Ref. 4. The second of Eqs. (17) of Ref. 4 applies to region A, and in addition is subject to the condition $x < z$. However, the latter condition is never satisfied in region A. Consequently, the second of Eqs. (17) of Ref. 4 is without meaning. No result corresponding to (15) was given in Refs. 2–5. Equation (16) agrees with the second of Eqs. (19) of Ref. 4. The first of Eqs. (19) of Ref. 4 is meaningless. It applies to region C, and in addition is subject to the condition $-U > \frac{1}{2} m_1 M_2 (u_1^2 - u_2^2)$, which may be written $x > z + M_1^{-1}$. The latter condition never is satisfied in region C. For the special case $M_1 = M_2$, (14) and (16) reduce to Eqs. (28) of Ref. 4, allowing for misprints which can be corrected by substituting $(\Delta E)^{-2}$ by $|\Delta E|^3$ in both, and $(v_2/v_1)^2$ by v_2/v_1 in the second of the latter equations.[6]

III. REMARKS ABOUT APPLICATION TO INELASTIC ATOMIC AND MOLECULAR COLLISIONS

Application of results of the type obtained to the estimation of cross sections for inelastic atomic and molecular processes was first proposed by Thomson.[1] Interest in this was revived due to the work of Gryziński.[2–5] An excellent review of the present situation with respect to ionization of atoms by electron impact has been given by Rudge (Sec. 4 of Ref. 16). Among other things, he mentions that taking account of the orbital motion of the electrons, which was the main motivation of Gryziński's work, leads to results which are in worse agreement with experiment than are Thomson's. The good agreement of the final expressions given by Gryziński with experiment arises only from making approximations. These approximations are empirical in nature, and Gryziński's results must be viewed as being semiempirical.

In the present section, we wish to make some remarks about the applications of classical energy transfer cross section to direct excitation. Gryziński[2] suggested setting the direct excitation cross section equal to $Q(U_1) - Q(U_2)$, where U_1 is the excitation energy of the state considered, and U_2 the energy of the relevant next-higher state. When $\Delta U = U_2 - U_1 \ll U_1$, as is often the case for atoms and molecules, the cross section becomes approximately equal to $\Delta U \sigma(U_1)$, as noted before. In analogy with the case of ionization, it can be shown that taking account of orbital motion does not improve the over-all agreement with experiment of the direct excitation cross section.[15]

There remains the curious circumstance that the approximate results of Gryziński give rea-

sonably good agreement with experimental results for processes of direct excitation as well as for ionization, while empirical formulas for the ionization cross sections give rather poor agreement when converted to direct excitation cross sections.[6] The reason for this can be understood by writing $Q(U)$ in the form

$$Q(U) = (N_e \sigma_0 / U^2) f(x, y) , \qquad (17)$$

where $y = E_1/U$ and where N_e is the number of equivalent electrons which may participate in the ionization process. This leads to

$$\sigma(U) = N_e \frac{\sigma_0}{U^3} \left[2f(x, y) + x \frac{\partial f}{\partial x}(x, y) + y \frac{\partial f}{\partial y}(x, y) \right]. \qquad (18)$$

If $y \, \partial f / \partial y$ is set equal to zero, as it effectively is in the empirical formulas, the result for $\sigma(U)$ is smaller than when $y(\partial f/\partial y) > 0$. It is only here, in the comparison of experimental data for ionization and for direct excitation, that taking account of orbital motion helps to improve the over-all agreement.

In many investigations concerned with the application of classical energy transfer cross sections, it was found that experimental cross sections for similar processes agree quite well among themselves when plotted in appropriate dimensionless form (see, for example, Refs. 5, 6, 17–20). As a matter of fact, the reduced experimental cross sections tend to agree better among themselves than with any of the theoretical results. This leads to the conclusion that an important result of the classical calculation of energy transfer is the possibility of writing down scaling laws. For example, the scaling law for ionization is [6,13,17]

$$Q = (N_e \sigma_0 / U^2) f_i(x) . \qquad (19)$$

Similarly, the scaling law for direct excitation is

$$Q = (N_e \sigma_0 \Delta U / U^3) f_{ex}(x) . \qquad (20)$$

Analogous formulas can be introduced for other processes. The functions $f_i(x)$ and $f_{ex}(x)$ are related by Eqs. (20) and (18) with f replaced by f_i. Given $f_i(x)$ and $f_{ex}(x)$, these equations essentially determine $y \, \partial f_i / \partial y$. In general, it is not necessary to invoke the relation between f_i and f_{ex}, or even between functions for different elements. Instead, it is better to make use of the similarity
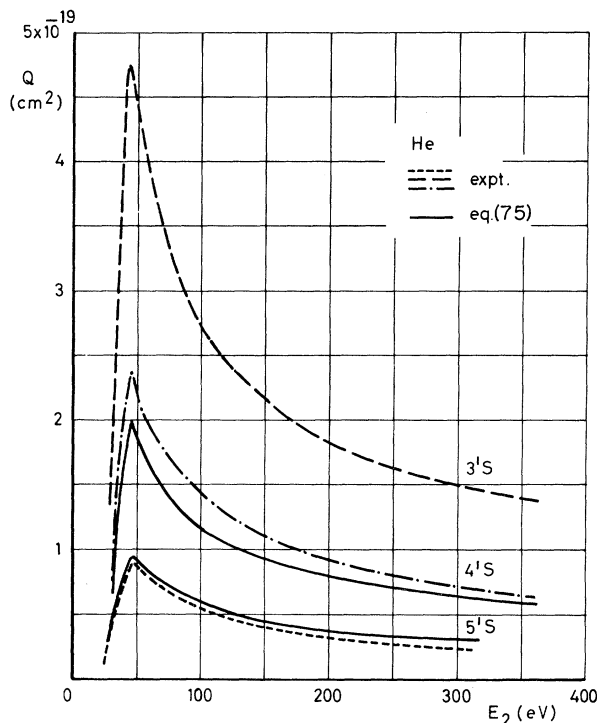

FIG. 3. Excitation cross section for the optically forbidden transitions $1^1S \to n^1S$ of helium by electron collision. Curves labeled Eq. (75) are based on present Eq. (20).

of the functions for one given process. This similarity even holds for many processes which do not lend themselves to calculation by Gryziński's or other methods, such as excitation to optically forbidden lines. An example of this is given in Fig. 3. The experimental $3'S$ result of Ref. 21 was used together with Eq. (20) to calculate cross sections for the processes $1'S \to 4'S$ and $1'S \to 5'S$. The agreement with experiment[21] is quite satisfactory.

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Negative-Ion Reactions in NO-H₂O Mixtures*

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A stationary afterglow system has been utilized to determine rate constants for thermal-energy negative-ion–molecule reactions in photoionized NO-H_2O mixtures. When the decay of the plasma is controlled by ambipolar diffusion of positive and negative ions, quantitative determination of rate constants is shown to be feasible. The plasma transition from electron–positive-ion ambipolar diffusive domination of the transport loss processes to domination by positive-ion–negative-ion ambipolar diffusion is explained by a model which includes the effects of negative-ion trapping. Prominant negative ions in the afterglow include NO_2^-, its hydrates, and clusters involving HNO_2. Reaction-rate constants for the processes $NO_2^- + H_2O + NO \rightarrow NO_2^- \cdot H_2O + NO$ and $Cl^- + H_2O + NO \rightarrow Cl^- \cdot H_2O + NO$ are found to be $1.3 \pm 0.3 \times 10^{-28}$ cm^6/sec and $3.4 \pm 1.3 \times 10^{-29}$ cm^6/sec at 293 K, respectively. Steady glows in NO-H_2O-O_2 mixtures revealed that NO_2^- and the impurity HCO_3^- also formed multiple hydrates and clustered with HNO_2. These results indicate that the terminal negative ions in the D-region of the ionosphere will likely be hydrated.

I. INTRODUCTION

Recently Lineberger and Puckett[1,2] reported stationary-afterglow measurements of NO^+ reactions leading to the formation of $NO^+ \cdot NO$, $NO^+ \cdot n$ (H_2O) and $H_3O^+ \cdot n(H_2O)$ ions in photoionized NO-H_2O mixtures. These investigations elucidated a mechanism by which NO^+ ions can be lost in reactions with atmospheric water vapor. As a consequence of these reactions it is understandable that NO^+ should not be regarded as a terminal positive ion in the D region of the ionosphere.

Ferguson[3] and LeLevier and Branscomb[4] have reviewed D-region negative-ion chemistry and concluded that the "terminal" negative ions are NO_2^- and NO_3^-. This conclusion was based on the observation that these ions are formed through chain-breaking reactions that do not permit the electron to be freed again. Therefore, in their context, "terminal" implies that the ions are indestructible except through ion-ion mutual-neutralization processes. We report results which demonstrate that both NO_2^- and NO_3^- ions do, however, undergo clustering reactions with H_2O and HNO_2 at 293 K.

The negative-ion–molecule reaction rate constants reported in this paper are the first such measurements known to the authors to be made using stationary-afterglow techniques. In order to obtain quantitative negative-ion reaction rate information from a stationary afterglow, it is necessary to make observations subsequent to the disappearance of electrons from the decaying plasma during the interval when positive-ion–negative-ion ambipolar diffusion is the dominant transport-loss mechanism. The transition from positive-ion–electron ambipolar diffusive domination to positive-ion–negative-ion ambipolar diffusive domination is marked by a sudden increase in the negative-ion wall current, and a sudden decrease in the positive-ion wall current. A model is presented which accounts for the features of this transition.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The basic apparatus employed in this experiment is the photoionized stationary-afterglow instrument described previously,[1] and only a brief account of