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CROSS SECTION FOR IMPACT IONIZATION OF H(1s) ATOMS BY H(1s) ATOMS NEAR THRESHOLD

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SUMMARY

Rosen's treatment of impact ionization of neutral atoms is applied to the collision of ground-state hydrogen atoms near the ionization threshold. The singlet interaction potential is approximated by a Morse potential and the triplet interaction potential is approximated by an exponential repulsive potential. The energy-dependent ionization cross section is presented for collision energy between threshold and twice threshold. An implication of the classical path assumption is briefly discussed.

INTRODUCTION

Several years ago an approximate method was introduced by Rosen (ref. 1) for the calculation of atom-atom impact ionization cross sections for collision energies near threshold. At that time it was applied to helium-helium collisions (ref. 1) and argon-argon collisions (ref. 2). The method is used herein to compute the energy-dependent cross section for the interaction

$$H(1s) + H(1s) \rightarrow H(1s) + H^{+} + e^{-} \qquad (1)$$

near threshold.

This calculation has a similar but simpler perturbation matrix element than those considered by Rosen; hence, much of the calculation required to obtain a cross section for process (1) has already been reported (ref. 1).

The only previous calculations (ref. 3) for process (1) made use of the Born approximation and therefore only apply at energies considerably above threshold.

ROSEN'S APPROXIMATION

The method assumes that the two colliding atoms follow classical paths dictated by their interaction potential, but at a time corresponding to their distance of closest approach a perturbation is suddenly turned on. The perturbation matrix element V_{fi} between the initial state i and final state f of the two-atom system decays very slowly because the incident atom has lost most of its kinetic energy and is moving away very slowly. Obviously such conditions will be met only if the kinetic energy of the incident atom is no more than about twice the threshold value. The result of an ionization cross-section calculation under these conditions is obtained from reference 2 as

$$\sigma = \frac{1}{\pi\hbar^3} \int_{p=0}^{\sqrt{2m(\epsilon - I)}} \int_{b=0}^{\infty} \frac{|V_{fi}(R)|^2 p^2 \, dp}{\left(I + \frac{p^2}{2m}\right)^2} \, b \, db \tag{2}$$

where I is the ionization energy, $\epsilon = 1/2(\mu v^2)$ is the relative energy of collision, m is the electron mass, p is the ejected electron's momentum, and $V_{fi}(R)$ is the perturbation matrix element. (All symbols are defined in the appendix.) The relation between the distance of closest approach R and the impact parameter b is given by the classical expression

$$1 = \left(\frac{b}{R}\right)^2 + \frac{U(R)}{\epsilon} \tag{3}$$

where U(R) is the interaction potential between the two atoms.

Perturbation Matrix Element

The perturbation matrix element for the interaction

$$H(1s) + H(1s) \rightarrow H(1s) + H^+ + e^- \tag{1}$$

is written

$$V_{fi} = \int_{\tau} \psi_f^* V \psi_i \, d\tau \tag{4}$$

where V is the perturbation potential, ψ_i is the product of two 1s wave functions and ψ_f is the product of a 1s wave function and a plane wave representing the freed electron.

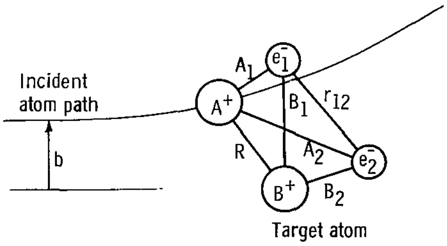

Figure 1. - Coordinate system.

The coordinate system employed in the calculation is shown in figure 1. Atom A is considered to be incident on atom B which is at rest. Electron 1 is initially bound to atom A; electron 2 is initially bound to atom B. The perturbation potential is then given by

$$V = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{A_2} - \frac{e^2}{B_1} \tag{5}$$

The initial and final wave functions are

$$\left.\begin{aligned} \psi_i &= \varphi(A_1)\varphi(B_2) \\ \psi_f &= \varphi(A_1)e^{(i\vec{p}\cdot\vec{B}_2)/\hbar} \end{aligned}\right\} \tag{6}$$

respectively, where φ is the normalized 1s wave function given by

$$\varphi(r) = \left(\frac{z}{a_o}\right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-(z/a_o)r} \tag{7}$$

where a_o is the Bohr radius and z is the effective charge. Combining equations (4) to (6) gives

$$\begin{aligned} V_{fi} = \frac{e^2}{R} \int_{\tau_1,\tau_2} & \varphi(A_1)\varphi(A_1)\varphi(B_2)e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_1 \, d\tau_2 \\ & + e^2 \int_{\tau_1,\tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{r_{12}} e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_1 \, d\tau_2 \\ & - e^2 \int_{\tau_1,\tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{A_2} e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_1 \, d\tau_2 \\ & - e^2 \int_{\tau_1,\tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{B_1} e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_1 \, d\tau_2 \end{aligned} \tag{8}$$

Taking advantage of normalization and the following integrals worked out by Rosen (ref. 1)

$$I_1 \equiv 4 \frac{e^2}{R} \int_{\tau_2} \varphi(B_2)e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_2$$

$$I_2 \equiv e^2 \int_{\tau_1,\tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{r_{12}} e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} \, d\tau_1 \, d\tau_2$$

$$I_5 \equiv e^2 \int_{\tau_2} \frac{\varphi(B_2)}{A_2} e^{(-i\vec{p}\cdot\vec{B}_2)/\hbar} d\tau_2$$

$$I_4 \equiv \int_{\tau_1} \frac{\varphi(A_1)\varphi(A_1)}{B_1} d\tau_1$$

give the perturbation matrix element as

$$V_{fi} = \frac{1}{4} I_1 + I_2 - I_5 - \frac{R}{4} I_1 I_4$$

Rosen (ref. 1) made the approximation, $I_2 - I_5 \simeq 0$. This implies that the atomic separation R is much greater than the electron orbital radius. Using this approximation and the evaluation of I_1 and I_4 in reference 1 gives

$$V_{fi}(R) = \frac{8e^2\sqrt{\pi}\left(\frac{z}{a_o}\right)^{5/2}\left(1 + \frac{z}{a_o} R\right)}{\left[\left(\frac{z}{a_o}\right)^2 + \left(\frac{p}{\hbar}\right)^2\right]^2 R} e^{-2(z/a_o)R} \qquad (9)$$

Substituting equation (9) into equation (2) and defining $X^2 = \frac{p^2}{2mI}$

$$X_m^2 = \frac{\epsilon}{I} - 1$$

$$a^2 = \left(\frac{z}{a_o}\right)^2 \frac{\hbar^2}{2mI} \quad (a^2 = \text{unity for 1s hydrogen})$$

$$\sigma_o = \frac{64e^4\left(\frac{z}{a_o}\right)^5 \hbar^5}{(2mI)^{5/2} I^2} \quad (\sigma_o = 256\ a_o^2 \text{ for 1s hydrogen})$$

$$f(X_m, a) = \int_0^{X_m} \frac{X^2\, dx}{(X^2 + 1)^2 (X^2 + a^2)^4} \qquad (10)$$

and

$$g = \int_0^{\infty} \frac{\left(1 + \frac{z}{a_o} R\right)^2 e^{-4(z/a_o)R}}{R^2} b\, db \tag{11}$$

yields

$$\sigma = \sigma_o f(X_m, 1) g \tag{12}$$

An integral table (ref. 4) was used to obtain the following evaluation of equation (10):

$$f(X_m, 1) = -\frac{X_m}{10\left(X_m^2 + 1\right)^5} + \frac{X_m}{80\left(X_m^2 + 1\right)^4} + \frac{7X_m}{480\left(X_m^2 + 1\right)^3} + \frac{7X_m}{384\left(X_m^2 + 1\right)^2} + \frac{7X_m}{256\left(X_m^2 + 1\right)} + \frac{7}{256} \tan^{-1} X_m$$

Interaction Potential

In order to evaluate g the variable of integration is changed from b to R (ref. 1). Equation (3) can be utilized to write $b\, db$ as

$$b\, db = \left[1 - \frac{U(R)}{\epsilon} - \frac{1}{2} \frac{R}{\epsilon} \frac{dU(R)}{dR}\right] R\, dR \tag{13}$$

The classical collision paths of two hydrogen atoms each in a 1s electronic state can follow one of two well-known potential energy curves corresponding to the $^3\Sigma_u$ and $^1\Sigma_g$ (parallel and antiparallel spins) states of the quasi-molecule (Slater, ref. 5). These potential curves are shown in figure 2 as reported by Dalgarno and Lynn (ref. 6).

Also shown in figure 2 are the convenient approximate forms of the potentials used for computation of g. The $^3\Sigma_u$ state is represented by an exponential repulsive potential

$$U_3(R) = \alpha e^{-\beta R} \tag{14}$$

where $\alpha = 3.6$ Rydbergs and $\beta = 1.48\ a_o^{-1}$. The $^1\Sigma_g$ state is well-approximated by the Morse Potential (Slater, ref. 5).

$$U_1(R) = D\left[e^{-2B(R-\gamma)} - 2e^{-B(R-\gamma)}\right] \tag{15}$$

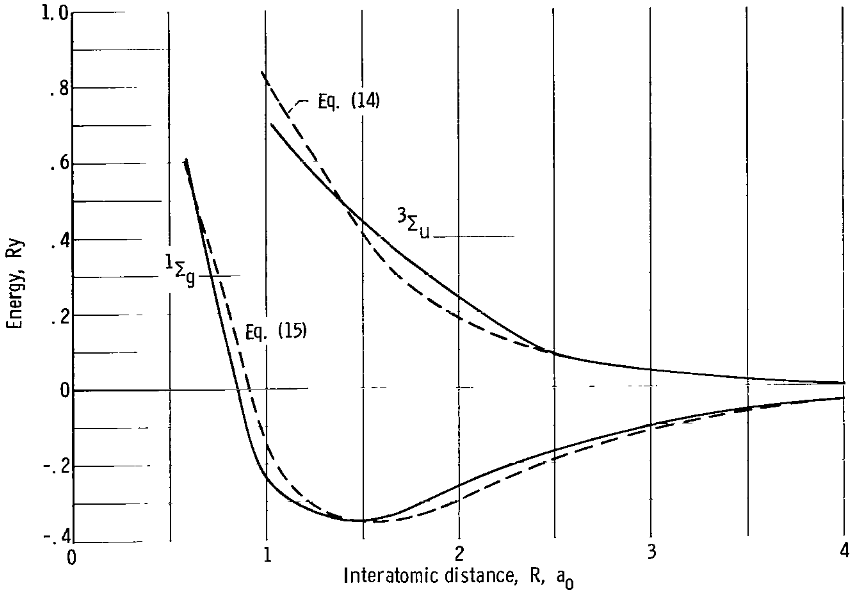

Figure 2. - The interaction energy of H(1s) + H(1s): solid lines (ref. 6). Dashed lines, approximate functions.

where $D = 0.35$ Rydberg, $B = 1.08\ a_0^{-1}$, and $\gamma = 1.5\ a_0$. When the $^3\Sigma_u$ potential (eq. (14)) is used in equations (11) and (13) to compute g the result is designated g_3; when the $^1\Sigma_g$ potential (eq. (15)) is used the result is designated g_1.

Evaluation of g_3 and g_1

Combination of equations (11) and (13) with equations (14) and (15) gives

$$g_3 = \int_{R_{03}}^{\infty} \frac{(1 + R)^2 e^{-4R}}{R} \left[1 - \frac{\alpha}{\epsilon} e^{-\beta R} + \frac{1}{2} \frac{\alpha\beta}{\epsilon} Re^{-\beta R}\right] dR \tag{16a}$$

and

$$g_1 = \int_{R_{01}}^{\infty} \frac{(1 + R)^2 e^{-4R}}{R} \left\{1 - \frac{D}{\epsilon} \left[e^{-2B(R-\gamma)} - 2e^{-B(R-\gamma)}\right] + \frac{D}{\epsilon} BR\left[e^{-2B(R-\gamma)} - e^{-B(R-\gamma)}\right]\right\} dR \tag{17a}$$

respectively, where $z = 1$, $a_0 = 1$ (using atomic units for the case of H(1s)), where from equations (3), (14), and (15)

$$R_{03} = \frac{1}{\beta} \ln \frac{\alpha}{\epsilon}$$

and

$$R_{01} = \gamma - \frac{1}{B} \ln \left(1 + \sqrt{1 + \frac{\epsilon}{D}}\right)$$

The integration indicated in equations (16a) and (17a) may be put in the form

$$g_3 = h(4,R_{03}) - \frac{\alpha}{\epsilon} h(4 + \beta,R_{03}) + \frac{1}{2} \frac{\alpha\beta}{\epsilon} k(4 + \beta,R_{03}) \tag{16b}$$

and

$$g_1 = h(4,R_{01}) - \frac{D}{\epsilon} e^{2B\gamma}h(4 + 2B,R_{01}) + 2 \frac{D}{\epsilon} e^{B\gamma}h(4 + B,R_{01}) + \frac{D}{\epsilon} Be^{2B\gamma}k(4 + 2B,R_{01}) - \frac{D}{\epsilon} Be^{B\gamma}k(4 + B,R_{01}) \tag{17b}$$

where h and k are defined by

$$h(s,t) = \int_t^\infty \frac{(1 + X)^2 e^{-sX}}{X} dX = -Ei(-st) + \frac{2}{s} e^{-st} + \frac{1}{s^2} e^{-st}(st + 1)$$

and

$$k(s,t) = \int_t^\infty (1 + X)^2 e^{-sX} dX = e^{-st}\left[\frac{(t + 1)^2}{s} + 2 \frac{(t + 1)}{s^2} + \frac{2}{s^3}\right]$$

where $-Ei(-X)$ is the exponential integral tabulated by Jahnke and Emde (ref. 7).

Ionization Cross Section

The ionization cross section σ_3 for the interaction along a triplet potential and σ_1 for the interaction along a singlet potential are given by equations (12), (16b), and (17b). These cross sections are presented in figure 3. Also shown in figure 3 is the cross section $\overline{\sigma}$ which would be observed experimentally if there were no mechanism for systematic selection of spin states. This average cross section $\overline{\sigma}$ is given by (ref. 8)

$$\bar{\sigma} = \frac{1}{4}\sigma_1 + \frac{3}{4}\sigma_3 \tag{18}$$

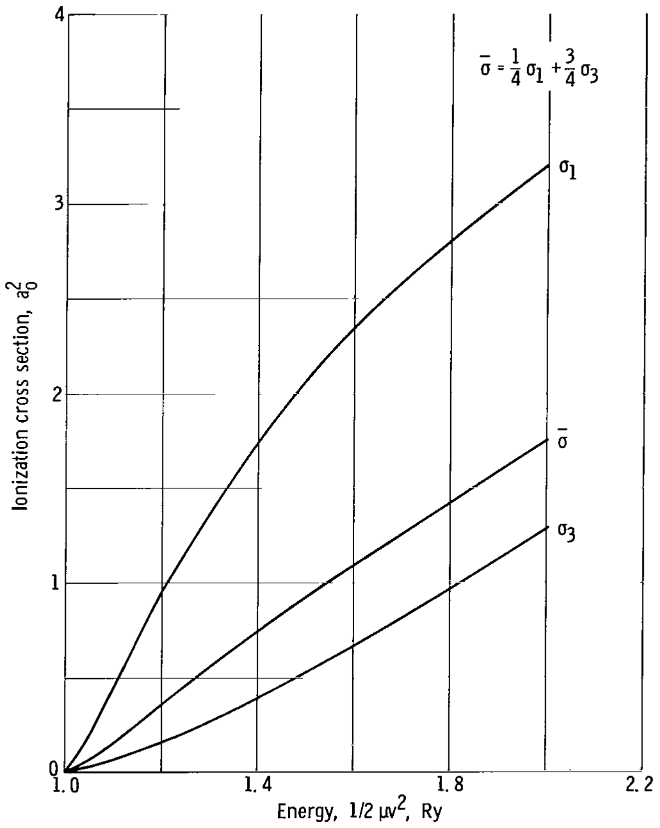

Figure 3. - Cross section of H(1s) + H(1s) impact ionization.

CLASSICAL PATH APPROXIMATION

The classical collision of particles under the influence of certain central potentials (those which decrease faster than $1/r$ as $r \to \infty$) follow paths for which the angular deviation decreases as impact parameter increases. At some critical angle classical mechanics is no longer valid (ref. 9), and there exists a maximum impact parameter b_c, beyond which quantum effects on "particle path" must be considered. Rosen's approximation requires that the particle paths be treated classically; hence, for this approximation to be valid all inelastic transitions must occur at distances of closest approach less than R_c, where R_c corresponds to the impact parameter b_c. Since there is very little deflection of the incident particle at the large values of impact parameter where b_c occurs, the approximation $R_c \simeq b_c$ can be used.

The relation between R_c and the collision parameters for an exponential potential of the form

$$V(r) = C_1 e^{-C_2 r} \tag{19}$$

may be obtained from Mason, Vanderslice, and Raw (ref. 10). Their equations (1) and (69) combine to give

$$-\frac{3}{2}\ln(C_2 R_c) + C_2 R_c = \ln\left[\frac{|C_1|}{\epsilon}\,\frac{k}{C_2}\left(\frac{1}{2\pi}\right)^{1/2}\right] \tag{20}$$

where $k = \mu v/\hbar$ is the wave number of the incident atom.

For the case of H(1s) - H(1s) collisions following the ${}^3\Sigma_u$ interaction potential (eq. (14)) R_c is about 3.5 a_0. The ${}^1\Sigma_g$ interaction potential at long range can be approximated by an exponential attractive potential (eq. (19)

with $C_1 = -2De^{B\gamma}$, $C_2 = B$). This procedure gives a value of about $5a_o$ for R_c.

The effective range of the interaction may be approximated by

$$R_{eff} \simeq \sqrt{\frac{\sigma}{\pi}} \tag{21}$$

where $R_{eff} < 1a_o$ for $\epsilon < 2I$ (fig. 3). Hence $R_c > R_{eff}$ for the H(1s) collisions reported herein.

CONCLUDING REMARKS

It is surprising that more work has not been done with Rosen's approximation, since it applies to the interesting thermal plasma energy regime just above the ionization threshold. This is an energy regime which is difficult to investigate experimentally.

The merit of the method may be judged from a comparison made in references 1 and 2 with the experimental data of Rostagni (ref. 11) for the case of helium-helium and argon-argon collisions. While the experiments were performed at collision energies where the validity of the sudden approximation is questionable, the theoretical and experimental cross sections agreed to within a factor of about two.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 22, 1965.

APPENDIX - SYMBOLS

A_1	distance from electron 1 to nucleus A
A_2	distance from electron 2 to nucleus A
a	atomic parameter, $\frac{z}{a_o} \frac{\hbar}{\sqrt{2mI}}$
a_o	radius of first Bohr orbit, 0.529 Å
B	constant in Morse potential
B_1	distance from electron 1 to nucleus B
B_2	distance from electron 2 to nucleus B
b	impact parameter
b_c	critical impact parameter
C_1, C_2	constants in exponential potential
D	dissociation energy in Morse potential
e	electron charge
f	integral defined by eq. (10)
g_1, g_3	integrals defined by eqs. (16a) and (17a)
$h(s,t)$	$\int_t^\infty \frac{(1 + X)^2 e^{-sX}}{X} dX$
$\hbar$	Planck's constant divided by 2π
I	ionization energy
I_1, I_2, I_3, I_4, I_5	Rosen's integrals evaluating eq. (8)
k	wave number, $\frac{\mu v}{\hbar}$
$k(s,t)$	$\int_t^\infty (1 + X)^2 e^{-sX} dX$
m	electron mass
p	ejected electron momentum

R	interatomic distance of closest approach
R_c	critical distance of closest approach
R_{eff}	effective range of inelastic transition
R_{01}, R_{03}	distance of closest approach corresponding to $b = 0$ for interaction potentials $U_1(R)$ and $U_3(R)$, respectively
r	radial coordinate
r_{12}	distance from electron 1 to electron 2
s	variable in integral functions $h(s,t)$, $k(s,t)$
t	variable in integral functions $h(s,t)$, $k(s,t)$
$U_1(R)$	singlet hydrogen interaction potential
$U_3(R)$	triplet hydrogen interaction potential
V	perturbation potential (eq. (5))
$V(r)$	exponential potential
$V_{fi}(R)$	perturbation matrix element defined by eq. (4)
v	velocity of incident atom
X	dummy variable of integration
X_m	ionization parameter, $\sqrt{\frac{\epsilon}{I} - 1}$
z	effective charge
α	range constant in triplet potential
β	energy constant in triplet potential
γ	radius of energy minimum in Morse potential (singlet potential)
ϵ	collision energy, $\frac{1}{2} \mu v^2$
μ	reduced mass of colliding atoms
σ	ionization cross section
σ_o	constant, $\frac{64e^4\left(\frac{z}{a_o}\right)^5\hbar^5}{(2mI)^{5/2}I^2}$

σ_1	singlet ionization cross section
σ_3	triplet ionization cross section
$\bar{\sigma}$	average ionization cross section defined by eq. (18)
τ	variables of integration representing volume
$\varphi(r)$	normalized hydrogen 1s wave function
ψ_f	wave function for final state of colliding atoms given by product of 1s wave function and plane wave representing ejected electron
ψ_i	wave function for initial state of colliding atoms given by product of two 1s wave functions

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