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

by John W. Sheldon

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION - WASHINGTON, D. C. - DECEMBER 1965
CROSS SECTION FOR IMPACT IONIZATION OF H(1s) ATOMS

BY H(1s) ATOMS NEAR THRESHOLD

By John W. Sheldon

Lewis Research Center
Cleveland, Ohio
CROSS SECTION FOR IMPACT IONIZATION OF H(1s) ATOMS

BY H(1s) ATOMS NEAR THRESHOLD

by John W. Sheldon

Lewis Research Center

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

\[ \text{H}(1s) + \text{H}(1s) \rightarrow \text{H}(1s) + \text{H}^+ + \text{e}^- \] (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

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

(2)

where $I$ is the ionization energy, $\epsilon = 1/2(\nu v^2)$ 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

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

(3)

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

**Perturbation Matrix Element**

The perturbation matrix element for the interaction

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

(1)

is written

$$
V_{fi} = \int \psi_i^* V \psi_i \, d\tau
$$

(4)

where $V$ is the perturbation potential, $\psi_i$ is the product of two $1s$ wave functions and $\psi_f^*$ is the product of a $1s^*$ wave function and a plane wave representing the freed electron.

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
The initial and final wave functions are

$$
\psi_i = \varphi(A_1)\varphi(B_2)
$$

$$
\psi_f = \varphi(A_1)e^{(\mathbf{\vec{p}} \cdot \mathbf{\vec{B}_2})/\hbar}
$$

respectively, where $\varphi$ is the normalized $1s$ wave function given by

$$
\varphi(r) = \left(\frac{z}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-\left(z/a_0\right)r}
$$

where $a_0$ is the Bohr radius and $z$ is the effective charge. Combining equations (4) to (6) gives

$$
V_{fi} = \frac{e^2}{R} \int_{\tau_1, \tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2)e^{(-i\mathbf{\vec{p}} \cdot \mathbf{\vec{B}_2})/\hbar} d\tau_1 d\tau_2
$$

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

$$
- e^2 \int_{\tau_1, \tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{A_2} e^{(-i\mathbf{\vec{p}} \cdot \mathbf{\vec{B}_2})/\hbar} d\tau_1 d\tau_2
$$

$$
- e^2 \int_{\tau_1, \tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{B_1} e^{(-i\mathbf{\vec{p}} \cdot \mathbf{\vec{B}_2})/\hbar} d\tau_1 d\tau_2
$$

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

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

$$
I_2 = e^2 \int_{\tau_1, \tau_2} \varphi(A_1)\varphi(A_1)\varphi(B_2) \frac{1}{r_{12}} e^{(-i\mathbf{\vec{p}} \cdot \mathbf{\vec{B}_2})/\hbar} d\tau_1 d\tau_2
$$
\[ I_5 = e^2 \int_{\tau_2} \frac{\phi(B_2)}{A_2} e^{\frac{-i\vec{p} \cdot \vec{B}_2}{\hbar}} d\tau_2 \]

\[ I_4 = \int_{\tau_1} \frac{\phi(A_1)\phi(A_1)}{B_1} d\tau_1 \]

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, \( I_2 - I_5 \approx 0 \). 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

\[ V_{fi}(R) = \frac{8e^2 \sqrt{\pi} \left( \frac{z}{a_o} \right)^{5/2}}{\left[ \left( \frac{z}{a_o} \right)^2 + \left( \frac{\hbar}{m} \right)^2 \right] R} e^{-2(z/a_0)R} \tag{9} \]

Substituting equation (9) into equation (2) and defining \( \chi^2 = \frac{p^2}{2m\hbar} \)

\[ \chi^2_m = \frac{\epsilon}{I} - 1 \]

\[ a^2 = \left( \frac{z}{a_0} \right)^2 \frac{\hbar^2}{2m} \] (\( a^2 = \) unity for 1s hydrogen)

\[ \sigma_o = \frac{64e^4 \left( \frac{z}{a_0} \right)^5 \hbar^5}{(2m\hbar)^{5/2} I^2} \] (\( \sigma_o = 256 a_0^2 \) for 1s hydrogen)

\[ f(X_m, a) = \int_{0}^{X_m} \frac{\chi^2 dx}{(\chi^2 + 1) (\chi^2 + a^2)^4} \tag{10} \]

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

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

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

\[
b \ dB = \left[ 1 - \frac{U(R)}{\epsilon} - \frac{1}{2} \frac{R}{\epsilon} \frac{dU(R)}{dR} \right] R \ dR \quad (13)
\]

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

\[
U_3(R) = \alpha e^{-\beta R} \quad (14)
\]

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).

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

$$g_3 = \int_{R_03}^{\infty} \frac{(1 + R)^2 e^{-4R}}{R} \left[ 1 - \frac{\alpha}{\epsilon} e^{-\beta R} + \frac{1}{2} \frac{\alpha \beta}{\epsilon} Re^{-\beta R} \right] dR \quad (16a)$$

and

$$g_1 = \int_{R_{01}}^{\infty} \frac{(1 + R)^2 e^{-4R}}{R} \left\{ 1 - \frac{D}{\epsilon} \left[ e^{-2B(R-\gamma)} - e^{-B(R-\gamma)} \right] + \frac{D}{\epsilon} BR \left[ e^{-2B(R-\gamma)} - e^{-B(R-\gamma)} \right] \right\} dR \quad (17a)$$
respectively, where \( z = 1 \), \( a_0 = 1 \) (using atomic units for the case of \( H(1s) \)), where from equations (3), (14), and (15)

\[
R_{03} = \frac{1}{B} \ln \frac{a}{c}
\]

and

\[
R_{01} = r - \frac{1}{B} \ln \left( 1 + \sqrt{1 + \frac{c}{B}} \right)
\]

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

\[
\sigma_3 = h(4, R_{03}) - \frac{\alpha}{c} h(4 + \beta, R_{03}) + \frac{1}{2} \frac{\alpha \beta}{c} k(4 + \beta, R_{03})
\]  

(16b)

and

\[
\sigma_1 = h(4, R_{01}) - \frac{D}{c} e^{2B} h(4 + 2B, R_{01}) + 2 \frac{D}{c} e^{By} h(4 + B, R_{01})
\]

\[
+ \frac{D}{c} Be^{2By} k(4 + 2B, R_{01}) - \frac{D}{c} Be^{By} k(4 + B, R_{01})
\]  

(17b)

where \( h \) and \( k \) are defined by

\[
h(s, t) = \int_t^\infty \frac{(1 + x)^2}{x} e^{-sx} \, dx = -Ei(-st) + \frac{2}{s} e^{-st} + \frac{1}{s^2} e^{-st}(st + 1)
\]

and

\[
k(s, t) = \int_t^\infty (1 + x)^2 e^{-sx} \, dx = e^{-st} \left[ \frac{(t + 1)^2}{s} + \frac{2}{s^2} \frac{(t + 1)}{s} + \frac{2}{s^3} \right]
\]

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

Ionization Cross Section

The ionization cross section \( \sigma_3 \) for the interaction along a triplet potential and \( \sigma_1 \) 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 \( \bar{\sigma} \) which would be observed experimentally if there were no mechanism for systematic selection of spin states. This average cross section \( \bar{\sigma} \) is given by (ref. 8)
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 \(R_c \approx b_c\) can be used.

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

\[
V(r) = C_1 e^{-C_2 r}
\]  

(19)

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

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

(20)

where \(k = \frac{\mu v}{\hbar}\) 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))

\[
\bar{\sigma} = \frac{1}{4} \sigma_1 + \frac{3}{4} \sigma_3
\]

(18)
with \( C_1 = -2De^BY \), \( C_2 = B \). This procedure gives a value of about \( 5a_0 \) for \( R_c \).

The effective range of the interaction may be approximated by

\[
R_{\text{eff}} \approx \sqrt{\frac{C}{\pi}}
\]

where \( R_{\text{eff}} < 1a_0 \) for \( \epsilon < 2I \) (fig. 3). Hence \( R_c > R_{\text{eff}} \) 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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>distance from electron 1 to nucleus A</td>
</tr>
<tr>
<td>$A_2$</td>
<td>distance from electron 2 to nucleus A</td>
</tr>
<tr>
<td>$a$</td>
<td>atomic parameter, $\frac{z}{a_0} \frac{\hbar}{\sqrt{2mI}}$</td>
</tr>
<tr>
<td>$a_0$</td>
<td>radius of first Bohr orbit, 0.529 Å</td>
</tr>
<tr>
<td>$B$</td>
<td>constant in Morse potential</td>
</tr>
<tr>
<td>$B_1$</td>
<td>distance from electron 1 to nucleus B</td>
</tr>
<tr>
<td>$B_2$</td>
<td>distance from electron 2 to nucleus B</td>
</tr>
<tr>
<td>$b$</td>
<td>impact parameter</td>
</tr>
<tr>
<td>$b_c$</td>
<td>critical impact parameter</td>
</tr>
<tr>
<td>$C_1, C_2$</td>
<td>constants in exponential potential</td>
</tr>
<tr>
<td>$D$</td>
<td>dissociation energy in Morse potential</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge</td>
</tr>
<tr>
<td>$f$</td>
<td>integral defined by eq. (10)</td>
</tr>
<tr>
<td>$g_1, g_3$</td>
<td>integrals defined by eqs. (16a) and (17a)</td>
</tr>
<tr>
<td>$h(s,t)$</td>
<td>$\int_t^\infty \frac{(1 + X)^2 e^{-sX}}{X} , dX$</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Planck's constant divided by $2\pi$</td>
</tr>
<tr>
<td>$I$</td>
<td>ionization energy</td>
</tr>
<tr>
<td>$I_1, I_2, I_3, I_4, I_5$</td>
<td>Rosen's integrals evaluating eq. (8)</td>
</tr>
<tr>
<td>$k$</td>
<td>wave number, $\frac{\mu V}{\hbar}$</td>
</tr>
<tr>
<td>$k(s,t)$</td>
<td>$\int_t^\infty (1 + X)^2 e^{-sX} , dX$</td>
</tr>
<tr>
<td>$m$</td>
<td>electron mass</td>
</tr>
<tr>
<td>$p$</td>
<td>ejected electron momentum</td>
</tr>
</tbody>
</table>

...
$R$ interatomic distance of closest approach

$R_c$ critical distance of closest approach

$R_{\text{eff}}$ effective range of inelastic transition

$R_{01}^0, R_{03}^0$ 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, $\sqrt{\frac{E}{I}} - 1$

$z$ effective charge

$\alpha$ range constant in triplet potential

$\beta$ energy constant in triplet potential

$\gamma$ radius of energy minimum in Morse potential (singlet potential)

$\epsilon$ collision energy, $\frac{1}{2} \mu v^2$

$\mu$ reduced mass of colliding atoms

$\sigma$ ionization cross section

$\sigma_o$ constant, $\frac{64e^4 (\frac{Z}{a_0})^5 h^5}{(2\pi\hbar)^{5/2} I^2}$
\( \sigma_1 \) singlet ionization cross section

\( \sigma_3 \) triplet ionization cross section

\( \bar{\sigma} \) average ionization cross section defined by eq. (18)

\( \tau \) variables of integration representing volume

\( \phi(r) \) normalized hydrogen 1s wave function

\( \psi_f \) wave function for final state of colliding atoms given by product of 1s wave function and plane wave representing ejected electron

\( \psi_i \) wave function for initial state of colliding atoms given by product of two 1s wave functions
REFERENCES


"The aeronautical and space activities of the United States shall be conducted so as to contribute... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—National Aeronautics and Space Act of 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

TECHNICAL REPRINTS: Information derived from NASA activities and initially published in the form of journal articles.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546