Classical $S$ Matrix for Linear Reactive Collisions of H+Cl$_2$\footnote{Copyright 1971 by the American Institute of Physics. All rights reserved.}

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Classical trajectories are computed for linear H+Cl$_2$ collisions and used to construct the classical limit of the $S$ matrix for reactive and nonreactive transitions between individual quantum states. An interesting feature of this system is that both "direct" and "complex" mechanisms participate in the collision dynamics. The two mechanisms contribute additively to individual $S$-matrix elements, and within a "random phase approximation" for the complex contribution it is seen that they also contribute additively to the transition probability. The complex contribution to a transition probability is strictly classical, but interference structure may be prominent in the direct contribution. Comparison is made with quantum calculations for the same potential and the agreement is rather poor, even at a fairly coarse level. The reason for this disagreement is not completely clear, but it may be connected with the fact that complex formation is prominent.

I. INTRODUCTION

It is well recognized now that at least the gross features of atomic and molecular collision dynamics are accurately described by classical mechanics. The facility with which classical trajectories can be computed, with averaging over various initial conditions (usually by Monte Carlo methods), and used to generate averaged collision properties (thermal rate constants for chemical reaction, the average energy transferred between internal and translational degrees of freedom, etc.), is evidenced by the large amount of such work currently being reported.\footnote{For the relatively simple atom–diatom and diatom–diatom collision systems this strictly classical approach has almost reached the stage of being a tool for the analysis of experimental results.}

Motivated by the way classical mechanics has been used within a quantum mechanical framework to treat elastic atom–atom scattering,\footnote{We have recently shown how exact classical mechanics (i.e., numerically computed trajectories) for a complex collision system (i.e., one with internal degrees of freedom, such as A+BC) can be used to construct the classical limit of the quantum mechanical $S$ matrix (the "classical $S$ matrix") describing transitions between individual quantum states of the collision partners.\footnote{Use of classical mechanics to construct such transition, or scattering amplitudes (rather than transition probabilities or cross sections directly) means that the quantum principle of superposition is incorporated, and, just as in elastic scattering, the interference features so obtained seem to be the chief contribution of quantum mechanics. It is often possible to analytically continue the interference structure into classically forbidden domains so that transitions which proceed by tunneling can also be treated by classical mechanics (analogous to the WKB treatment of tunneling in one-dimensional problems).}} the notation and results are summarized as they apply to the linear reactive A+BC collision. Figure 1 shows the coordinates, $r_a$ and $R_a$, being the vibrational and center-of-mass translational coordinates for initial arrangement $a$ (A+BC), and $r_e$ and $R_e$ being analogous coordinates for arrangement $e$ (AB+C); we refer to these as the Cartesian coordinates for arrangements $a$ and $e$. A linear transformation relates the Cartesian coordinates of the two arrangements

$$
\begin{pmatrix}
R_e \\
\tau_e
\end{pmatrix} = \begin{pmatrix}
A & B(A+B+C) \\
A+B & (A+B)(B+C)
\end{pmatrix} \begin{pmatrix}
R_a \\
\tau_a
\end{pmatrix},
$$

where $A$, $B$, and $C$ are the masses of the individual atoms.

This paper reports results of the classical $S$-matrix approach applied to a linear reactive atom–diatom collision, H+Cl$_2$→HCl+Cl; the particular potential surface used, collision energies employed, etc., are those for which Miller and Light\footnote{For the relatively simple atom–diatom and diatom–diatom collision systems this strictly classical approach has almost reached the stage of being a tool for the analysis of experimental results.} have recently reported quantum mechanical results. Section II presents the details of the classical $S$-matrix approach as it applies to the linear reactive A+BC system, and Sec. III discusses the numerical results for H+Cl$_2$. The most interesting new feature seen in this system, other than that of reaction itself, is the participation of two distinct collision mechanisms; some trajectories are "direct," whereas others lead to "complex formation" and are thus quite complicated. It is seen in Sec. III how "direct" and "complex" mechanisms contribute to the $S$ matrix and to the net transition probability.

II. CLASSICAL $S$ MATRIX FOR LINEAR REACTIVE A+BC COLLISIONS

The general expressions for the classical $S$ matrix have been given in Ref. 3; here the notation and results are summarized as they apply to the linear reactive A+BC collision. Figure 1 shows the coordinates, $r_a$ and $R_a$, being the vibrational and center-of-mass translational coordinates for initial arrangement $a$ (A+BC), and $r_e$ and $R_e$ being analogous coordinates for arrangement $e$ (AB+C); we refer to these as the Cartesian coordinates for arrangements $a$ and $e$. A linear transformation relates the Cartesian coordinates of the two arrangements

$$
\begin{pmatrix}
R_e \\
\tau_e
\end{pmatrix} = \begin{pmatrix}
A & B(A+B+C) \\
A+B & (A+B)(B+C)
\end{pmatrix} \begin{pmatrix}
R_a \\
\tau_a
\end{pmatrix},
$$

where $A$, $B$, and $C$ are the masses of the individual atoms.
The classical Hamiltonian, in terms of the Cartesian coordinates and momenta of arrangement $a$, is

$$H(P_a, p_a, R_a, v_a) = (P_a^2/2\mu_a) + (p_a^2/2m_a) + V^{tot}(r_a, R_a),$$  

(2)

where the internal and translational reduced masses are

$$m_a = BC/(B+C),$$

$$\mu_a = A(B+C)/(A+B+C);$$

the Hamiltonian can be similarly expressed in terms of the Cartesian coordinates and momenta of arrangement $c$. The internal (vibrational) potentials in arrangements $a$ and $c$ are

$$v_a(r_a) = \lim_{R_a \to 0} V^{tot},$$

$$v_c(r_c) = \lim_{R_c \to 0} V^{tot};$$

the potential surface of Miller and Light$^8$ is such that these vibrational potentials are Morse functions

$$v(r) = D[\exp[-2\alpha(r-r_0)] - 2 \exp[-\alpha(r-r_0)],$$  

(3)

where the Morse parameters $D$, $\alpha$, and $r_0$ correspond to diatomic molecule BC for arrangement $a$ and AB for arrangement $c$.

To effect quantization in the asymptotic regions one carries out a canonical transformation of the internal degree of freedom from Cartesian variables $r$ and $p$ to angle-action variables $q$ and $n$. The generator of this canonical transformation, of the $F_2$ type, is given by

$$f_2(r, n) = \pm \int_{r}^{r_o} \! dr' \bigl[2m_1 [\epsilon(n) - v(r')] \bigr]^{1/2},$$  

(4)

where $r_o$ is the smaller of the two classical turning points; for the Morse potential of Eq. (3) this becomes

$$f_2(r, n) = \pm \frac{1}{2} k [-(z^2 + 2z - \lambda^2)^{1/2}$$

$$+ \cos^{-1} \bigl( (z-1)(1-\lambda^2)^{-1/2} \bigr)$$

$$- \lambda \cos^{-1} \bigl( (z-\lambda^2)(1-\lambda^2)^{-1/2} \bigr)],$$

(5)

where

$$z = \exp[-\alpha(r-r_0)],$$

$$k = 2(2mD)^{1/2}/\alpha;$$

$$\lambda = 1-[(2n+1)/k],$$

$$\pm = \text{sign of } p.$$  

In terms of the angle-action variables the internal Hamiltonian (for either arrangement), $\rho^2/2m + v(r)$, becomes the semiclassical (Bohr–Sommerfeld) eigenvalue function (which, for the Morse oscillator, happens to be identical to the quantum eigenvalue expression)

$$\epsilon(n) = -D[1 - \frac{(2n+1)}{k}],$$

(6)

and the Cartesian variables $r$ and $p$ are given in terms of $q$ and $n$ by

$$r(q, n) = r_0 - \frac{\alpha^{-1} \log[\lambda^{-2} [1 - (1-\lambda^2)^{1/2} \cos q]]}{D},$$

(7)

$$p(q, n) = m \epsilon'(n) \frac{\partial r(q, n)}{\partial q},$$

(8)

where $\lambda$ is given below Eq. (5), and from Eq. (6) one finds

$$\epsilon'(n) = (4D/k)[1 - \frac{(2n+1)}{k}].$$

(9)

All of the expressions in this paragraph apply equally well for either arrangement $a$ or $c$.

It actually turns out to be most convenient$^8$ to carry out the numerical integration of Hamilton’s equations in the Cartesian variables $r$, $p$, $R$, and $P$ rather than the angle-action variables $q$, $n$, $R$, and $P$. Initial conditions, however, are specified in terms of angle-action variables; i.e., one specifies initial conditions in angle-action variables, transforms to Cartesian variables and computes the trajectory, and then transforms back to angle-action variables in the final asymptotic region. At fixed total energy $E$, therefore, one specifies initial values $q^0$ and $n^0$ for the initial arrangement (subscripts 1 and 2 refer to initial and final times $t_1$ and $t_2$, respectively; when it is necessary to specify the time subscript, the arrangement index $\gamma = a, c$ is written as a superscript), and then initial values of all the Cartesian variables are given by

$$R_1^a = \text{large},$$

$$r_1^a = 2\mu_a [E - \epsilon(n_1^a)]^{1/2},$$

$$p_1^a = r(q_1^a, n_1^a),$$

where the functions $\epsilon(n)$, $r(q, n)$ and $p(q, n)$ are given by Eqs. (6)–(8).

With these initial conditions Hamilton’s equations, with the Hamiltonian of Eq. (2), are numerically integrated until one of the asymptotic regions is reached. The final vibrational energy is $\epsilon_f$,

$$\epsilon_f = \frac{p_f^2}{2m_f} + v_f(r_f),$$

(9)

where $\gamma = a$ (nonreactive) or $c$ (reactive); the final vibrational quantum number is found by inverting the eigenvalue function in Eq. (6)

$$n(e) = -\frac{1}{2} \frac{1}{\lambda} [1 - (1-\lambda^2)^{1/2}],$$

(10)
so that $n_2^*$ is given by

$$n_2^* = n_2 (\epsilon_2^*),$$

with $\epsilon_2^*$ given by Eq. (9), and $\gamma = a$ or $c$.

This final vibrational quantum number, as a function of the initial angle-action variables of the internal degree of freedom, $n_2^*(q_1^*, n_1^*)$, is the fundamental classical trajectory function which is required. It plays precisely the same role here as in the case of nonreactive vibrational excitation, except that now there is a reactive and a nonreactive branch; i.e., since a particular trajectory is either reactive or nonreactive, there will be one range of $q_1^*$ which gives nonreactive trajectories and thus determines $n_2^*(q_1^*, n_1^*)$, and another range of $q_1^*$ which give reactive trajectories and thus determines $n_2^*(q_1^*, n_1^*)$.

To construct the classical $S$ matrix for a particular $n_1^* \rightarrow n_2^*$ transition, therefore, one finds all roots of the trajectory relation

$$n_2^*(q_1^*) = n_2^*, \quad (11)$$

where $n_1^*$ is fixed (and not explicitly indicated as an argument of the trajectory function) and where $n_2^*$ on the rhs of Eq. (11) is an integer. The classical $S$ matrix for the $n_1^* \rightarrow n_2^*$ transition is thus

$$S_{n_3^*, n_1^*} = \sum [2\pi (\partial n_2^*/\partial q_1^*)]^{-1/2} \exp \left[ i \phi(n_2^*, n_1^*) \right], \quad (12)$$

where $\gamma = (a$ (nonreactive) or $c$ (reactive)), and where the phase $\phi$ is specified below; the sum is over all the roots of Eq. (11). The transition probability is the square modulus of the $S$-matrix element

$$P_{n_3^*, n_1^*} = | S_{n_3^*, n_1^*} |^2. \quad (13)$$

To construct the phase associated with a particular trajectory, be it reactive or nonreactive, it is useful to take cognizance of the fact that the canonical transformation from Cartesian variables ($r_a, R_a, p_a, P_a$) of arrangement $a$ to Cartesian variables ($r, R, p, P$) of arrangement $c$ is a point canonical transformation—i.e., the coordinates $r_a$ and $R_a$ are expressible in terms of the coordinates $r$ and $R$ alone and do not involve the momenta $p_a$ and $P_a$ [see Eq. (1)]. The $F_1$-type generator for a point canonical transformation, however, is identically zero.\textsuperscript{10} The phase of the $S$ matrix in the coordinate representation of the Cartesian variables is therefore given by

$$\phi(r_2^* R_2^*, r_1^* R_1^*) = \int_{t_1}^{t_2} dt P_a(t) \dot{R}_a(t) + p_a(t) \dot{r}_a(t), \quad (14a)$$

$$= \int_{t_1}^{t_2} dt P_c(t) \dot{R}_c(t) + p_c(t) \dot{r}_c(t), \quad (14b)$$

whether $\gamma = a$ or $c$. The fact that Eqs. (14a) and (14b) are equal is a result of the fact that this “rearrangement transformation” is a point canonical transformation; i.e., according to the general transformation principles established in Ref. 3, Eq. (14b) should have added to it the term $F_1(r_2^* R_2^*, r_1^* R_1^*)$ which results from the rearrangement, but, as noted, this generator is identically zero.

The phase of the classical $S$ matrix in the “quantum number representation” (i.e., the momentum representation of the angle-action variables) is then obtained by carrying out canonical transformations in the initial and final asymptotic regions from the coordinate representation of Cartesian variables to the momentum representation of angle-action variables; the generator for this transformation is

$$F_2(r R, n P) = P R + f_2(r, n), \quad (15)$$

where $f_2$ is given by Eq. (5). Thus the phase $\phi(n_2^*, n_1^*)$ in Eq. (12) is

$$\phi(n_2^*, n_1^*) = P_a \dot{R}_a + f_2(r_2^*, n_1^*) - P_c \dot{R}_c - f_2(r_1^*, n_2^*) + \int_{t_1}^{t_2} dt 2 R, \quad (16)$$

where the integrand of the integral over time is twice the total kinetic energy expressed in the Cartesian variables of either arrangement

$$2T = P_a \dot{R}_a + p_a \dot{r}_a = P_c \dot{R}_c + p_c \dot{r}_c,$$

or the same with $a \rightarrow c$.

The phase is conveniently computed together with $r_a(t), R_a(t), p_a(t), P_a(t)$ by introducing an additional first-order differential equation for the function $\chi(t)$,

$$\dot{x}(t) = P_a \dot{R}_a + p_a \dot{r}_a,$$

with initial condition

$$\chi(t) = P_a \dot{R}_a + f_2(r_1^*, n_1^*);$$

at the end of the trajectory, with $\chi(t), n_2^*, n_1^*$, etc., determined, the phase of the $S$ matrix is given by

$$\phi(n_2^*, n_1^*) = \chi(t) - P_c \dot{R}_c - f_2(r_2^*, n_2^*),$$

for $\gamma = a$ (nonreactive) or $c$ (reactive).

In concluding this Section it should be observed that there are actually no inconveniences or special complications which enter the treatment due to the possibility of rearrangement channels. This is in marked contrast to the purely quantum situation where the complexity is considerably increased due to the fact that the coupled channel Schrödinger equations become integrodifferential equations when rearrangement channels are included.\textsuperscript{11} Classically, on the other hand, reactive trajectories are no more difficult than nonreactive ones, and it has been seen above that construction of the classical $S$ matrix is likewise no more difficult in the case of reaction.

**III. RESULTS FOR H+Cl$_2$**

The potential surface for this system is that which has been devised by Rankin and Light\textsuperscript{15} but with
the potential parameters used by Miller and Light\textsuperscript{8} in their recent quantum mechanical computations; two values for the total energy are considered,\textsuperscript{19} 0.3 and 0.1 eV above the value of the potential at the saddle point. At the higher energy (0.3 eV) vibrational states 0–5 are open in the initial arrangement (Cl\textsubscript{2}), and states 0–7 are open in the final arrangement (HCl); at 0.1 eV total energy states 0–2 and 0–6 are open in the initial and final arrangements, respectively.\textsuperscript{14}

Figure 2 shows a typical classical trajectory function \( n_q^2(q^2, n^2) \) for \( E = 0.3 \) eV, \( n_q^2 = 0 \), and with the potential parameters of Table II, Ref. 6. There is one interval of \( q^2 \) in which the function is quite smooth and well behaved (all of these trajectories being reactive) and another in which it is exceedingly complicated—here the computed points are shown directly, and no attempt is made to draw in the continuous segments. Varying the initial phase \( q^2 \) only slightly in this latter interval causes the trajectory to change from reactive to nonreactive, or vice versa, and causes large changes in the final vibrational quantum number; all energetically accessible vibrational states are reached by trajectories in this interval.

From these features, as well as by direct inspection of the trajectories and the collision times, one concludes that this complicated structure is due to multiple collisions (in classical language), or the formation of a collision complex (in quantum language). This at first seems surprising, for the potential is not “attractive” in the ordinary sense; i.e., if one follows the “reaction path” from H+Cl\textsubscript{2} to HCl+Cl, the potential energy increases monotonically up to the saddle point and then decreases monotonically. Complex trajectories arise because of a “pinch” in the potential surface in the transverse degree of freedom (i.e., the direction perpendicular to the reaction coordinate) near the saddle point, followed by the steep downhill portion (> 2 eV exothermicity) which is essentially flat in the transverse direction but which ends with a sudden narrowing at the bottom of the hill. The situation is analogous to traveling down a steep, but laterally wide canyon with a narrow exit valley at the bottom. If the phase of the transverse vibration is “just right,” therefore, the particle proceeds unhindered through the constricted area; these are the “direct” trajectories, all of which are reactive. Otherwise, the particle strikes the side of the narrow exit valley and is reflected back up the hill. [This is consistent with the fact that in Fig. 2 the boundary between “direct” and “complex” trajectories occurs with “direct” trajectories which have a maximum amount of vibrational excitation in the product.] If reflected, it may return to reactants (a nonreactive trajectory), or it may have lost too much energy along the reaction coordinate to make it back up hill; in the latter case, it returns toward the narrow exit valley and attempts once more to get through. This is the nature of the complex trajectories; whether or not such a potential surface is physically correct, of course, is another matter which we shall not attempt to explore here.

Individual classical \( S \)-matrix elements are constructed by the procedure discussed in Sec. II. For the 0→5 reactive transition, for example, the roots of Eq. (11) are indicated graphically by the intersection of the horizontal dotted line with the reactive branches of the classical trajectory function. It is seen that there are two “direct” trajectories and many “complex” trajectories which contribute to the 0→5 reactive transition, so that the classical \( S \)-matrix element is

\[
S = p_1^{1/2} \exp(i\phi_1) + p_2^{1/2} \exp(i\phi_2) + \sum_{k=3} p_k^{1/2} \exp(i\phi_k) \tag{17}
\]

\[
= S_{\text{direct}} + S_{\text{complex}} \tag{18}
\]

i.e., direct and complex mechanisms contribute additively to the \( S \) matrix. The two phases \( \phi_1 \) and \( \phi_2 \) associated with the direct trajectories are of the same order of magnitude (\( |\phi_1 - \phi_2| \leq \pi \)), but the phases \( \phi_k \) for the complex trajectories all differ from \( \phi_1 \) and \( \phi_2 \), and from each other, on the order of several multiples of 2\( \pi \). (This is due to the extra phase accumulated along the trajectory during the life of the collision complex.) In the transition probability

\[
P = |S|^2, \tag{19}
\]
the complex trajectories) to zero. This gives

$$P = p_1 + p_2 + 2(p_1p_3)^{1/2} \sin(\phi_2 - \phi_1) + \sum_{k=3} p_k \quad (20)$$

$$= P_{\text{direct}} + P_{\text{complex}};$$

i.e., within this “random phase approximation” for the phase of the complex trajectories the contribution of direct and complex mechanisms to the transition probability is also additive. Furthermore, the complex contribution is strictly classical and can be conveniently determined, for example, by Monte Carlo methods (or any other space-filling method of sampling). Even simpler than this, one would expect a statistical approximation to describe the complex contribution adequately.

It is not necessary, therefore, to find the many roots to Eq. (11) which are associated with complex trajectories. Within the “averaged classical” approach used previously, and which is equivalent to a Monte Carlo treatment, one determines the complex contribution to the transition probability as

$$P_{n^a \rightarrow n^a}(\text{complex}) = \frac{(\Delta q_\alpha/2\pi)(m/N)}{(N_e + N_a)} \quad (21)$$

where $\Delta q_\alpha$ is the width of the $q_\alpha$ interval which leads to complex formation, $N$ is a number of trajectories computed at equally spaced $q_\alpha$ values in the interval $\Delta q_\alpha$, and $m$ is the number of such trajectories for which the final vibrational quantum number is in the interval $(n^a_\alpha - \frac{1}{2}, \ n^a_\alpha + \frac{1}{2})$. The statistical approximation to this complex contribution is

$$P_{n^a \rightarrow n^a}(\text{complex}) = \frac{(\Delta q_\alpha/2\pi)/(N_e + N_a)}{N_e + N_a}, \quad (22)$$

where $\Delta q_\alpha$ is as above, and $N_e$ and $N_a$ are the number of reactive and nonreactive states which are classically accessible from the initial state $n^a$. This latter approximation thus assumes that all classically allowed final states are equally likely to be formed from the collision complex.

Figure 3 shows the numerical results for total energy $E = 0.3$ eV and the potential parameters of Table II, Ref. 6. The uniform semiclassical expression was used for the direct part of the transition probability rather than the “primitive” semiclassical form in Eq. (20). Classically forbidden transitions were treated by expanding the trajectory function in a power series about its extrema to sufficiently high order that additional terms did not affect the complex roots thus obtained; in most cases their contribution was actually negligible in comparison to that from complex formation.

For each initial state $n^a = 0, 1,$ and 2, nonreactive transitions occur only via complex formation, and reactive transitions have a contribution from both direct and complex mechanisms. For $n^a = 0$, 100 trajectories were computed at equally spaced points in the interval $\Delta q_\alpha$ which led to complex formation, and the complex contribution to each transition was determined by Eq. (21). The dashed line in Fig. 3 shows the nonreactive transition probabilities which result from this treatment, and it is seen that they are roughly independent of the final quantum number; i.e., the statistical approximation [Eq. (22)], which would give all the nonreactive transition probabilities as $(\Delta q_\alpha/2\pi)/(14\alpha = 0.035)$, is actually not too bad. The actual distribution into final states is seen to favor the smaller and larger quantum numbers somewhat. The complex contribution to reactive transitions is similar.

Since the statistical approximation for the complex contribution is reasonably accurate for $n^a = 0$, it was used for the cases $n^a = 1$ and 2 in Fig. 3; this simplifies matters considerably since only the boundaries of $\Delta q_\alpha$ are thus required. The value of the transition probability to final quantum number 0 in each case shows the value that complex formation contributes to each transition probability, reactive and non-reactive.

For $n^a = 2$ in Fig. 3, one sees prominent interference structure in the reactive transition probabilities similar to that seen in previous studies. A strictly classical treatment of the direct contribution would, of course, miss this feature.

A brief survey was made of the case $E = 0.3$ eV with the potential parameters of Tables I and II.
of Ref. 6. With the parameters of Table III and $n_1^e=0$, all trajectories were direct (i.e., no complex formation) and reactive, and the final vibrational quantum numbers were typically smaller than those for the potential parameters of Table II. With the potential parameters of Table I and $n_1^e=0$, the region of complex formation was greater than that for the parameters of Table II.

Finally, the cases $E=0.1$ eV with the potential parameters of Tables II and III, Ref. 6, were also examined briefly in order to compare some features with the quantum results. The classical trajectory function $n_2^e(q_1^e, n_1^e)$ was computed for $n_1^e=0, 1$, and $2$, and the total reactive probability was determined in a strictly classical approximation,

$$P_{\text{reactive}} \approx \Delta q_{\text{reactive}}/2\pi.$$

For the potential parameters of Table II the classical values were approximately 0.90, 0.75, and 0.80, for $n_1^e=0, 1, 2$, respectively, compared to the corresponding total reactive probability of Miller and Light of 0.81, 0.28, and 0.04. For the parameters of Table III the classical values were 1.00, 0.70, and 0.60, compared to the quantum values 0.87, 0.52, and 0.13. These quantum and classical results are thus in rather poor agreement even at this rather gross level. The reason for the lack of agreement is not completely clear.

One possible factor contributing to the disagreement is the fact that complex formation appears prominently in the classical dynamics. Without the inclusion of a number of closed channels in the quantum calculation, it seems doubtful that a coupled-channel treatment can describe this dynamical feature. It is well known, for example, that Feshbach resonances (a type of complex formation) which appear in the scattering of an electron from a hydrogen atom cannot appear in a coupled-channel description which retains only the open channels.

Before a detailed comparison of individual transition probabilities obtained semiclassically and quantum mechanically could be possible, it would also be necessary to transform the quantum results from the harmonic oscillator basis to the physically meaningful basis of Morse oscillator states. Thus,

$$S_{n_2,n_1} = \sum_{N_1,N_2} \langle N_2 | N_1 \rangle S_{N_2,N_1}(N_1, n_1),$$

where $| N \rangle$ and $| n \rangle$ are harmonic and Morse states, respectively, $S_{N_2,N_1}$ is the $S$ matrix in the harmonic basis obtained in Ref. 6, $S_{n_2,n_1}$ is the physically meaningful $S$ matrix, and $\langle n | N \rangle$ is the overlap between harmonic and Morse states.

IV. SUMMARY AND CONCLUSIONS

With this particular system it has been seen that both "direct" and "complex" collision mechanisms can be operative essentially simultaneously. Furthermore, direct and complex mechanisms contribute additively to the $S$ matrix and, within the "random phase approximation" to the complex contribution, they also contribute additively to the transition probability. The complex contribution to the transition probability is strictly classical, but interference terms between direct trajectories can be quite prominent.

Whether this situation is typical, or an artifact of this particular potential surface, is not known at this time. There are obviously many processes which take place wholly by direct mechanisms and others which proceed wholly by complex formation. Just how often it arises that a process has significant contributions from direct and complex mechanisms is a question that will most likely be answered experimentally before it is theoretically.

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† Alfred P. Sloan Fellow.

# Some of the recent work of this type is (a) J. van de Ree and J. G. R. Okel, J. Chem. Phys. 54, 589 (1971); (b) J. Lorenzen and L. M. Raff, ibid. 54, 674 (1971); (c) J. T. Muckerman, ibid. 54, 1155 (1971); (d) R. L. Thomasson, G. C. Berend, and S. W. Benson, ibid. 54, 1313 (1971); (e) R. L. Jaffe and J. B. Anderson, ibid. 54, 2224 (1971); (f) J. van de Ree, ibid. 54, 3249 (1971).


# This classical $S$-matrix approach may be correctly viewed as an extension of the old quantum theory to the field of scattering. The latter had previously been that "all collision phenomena lie outside the scope of the old quantum theory" [A. Messiah, Quantum Mechanics (Wiley, New York, 1961), p. 40]. The pinnacle of the old quantum theory applied to eigenvalue problems is the treatise by M. Born, The Mechanics of The Atom (Unigar, New York, 1960). Marcus [R. A. Marcus, Chem. Phys. Lett. 7, 525 (1970)], J. Chem. Phys. 54, 3965 (1971)] has made important contributions by a different approach than that in Ref. 3, although many of the physical ideas underlying the independent developments are the same.


# Constructing the generator of the angle-action variable transformation is equivalent to solving the classical equations of motion for the isolated internal degrees of freedom. This is the classical equivalent of the necessity in quantum mechanics of first solving for the eigenstates of the internal Hamiltonian, in terms of which a coupled channel expansion may then be formulated.

# Since the potential surface for the $H+Cl$ system is specified in "natural collision coordinates" (see Ref. 12), it was actually simpler in this special case to carry out the numerical integration directly in these coordinates. In the asymptotic regions these coordinates become the Cartesian coordinates $(r_e, R_a)$ or $(r_e, R)$, so that all the other details of the procedure are just as discussed in this section.


# This fact is implicit in the equations on p. 244 of H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, Mass., 1950).
Dissociative Excitation of $\text{O}_2$ in the Vacuum Ultraviolet by Electron Impact

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The emission cross section of the 1304-Å resonance triplet $({^3}\Sigma^0\rightarrow{^3}P)$ of atomic oxygen produced by dissociative excitation of $\text{O}_2$ by electron impact was measured from threshold to 300 eV. The peak cross section is at 100 eV with a value of $3.00\times10^{-18}$ cm$^2$. The relative emission cross section of the 1386-Å multiplet $({^3}\Sigma^0\rightarrow{^3}P)$ of atomic oxygen was also determined. The peak cross section for the 1386-Å multiplet at 100 eV is at least $1.65\times10^{-18}$ cm$^2$.

INTRODUCTION

The two most intense features of $\text{O}_1$ in the vacuum uv portion of the spectrum in the aurora and in the dayglow are the multiplets at 1304 Å (${^3}\Sigma^0\rightarrow{^3}P$) and at 1356 Å (${^5}\Sigma^0\rightarrow{^3}P$). A substantial amount of these emissions may arise from dissociative excitation of $\text{O}_2$ by electron impact.

The emission cross section of the 1304-Å multiplet produced by dissociative excitation of $\text{O}_2$ by electron impact was measured from threshold to 300 eV. The experimental technique is to measure the cross section in an electron beam optical excitation experiment. The instrumentation, the calibration procedures and the theory have been described previously for this experiment.

By taking account of the fraction of the excited atoms in the $\text{O}({^3}\Sigma^0)$ state that flow out of the field of view of the monochromator, it was possible to estimate a lower limit for the cross section of this multiplet.

Previous measurements of the 1304-Å multiplet of $\text{O}_1$ produced by dissociative excitation of $\text{O}_2$ have been made by Mumma$^7$ and Lawrence.$^4$

EXPERIMENTAL RESULTS

The 1304-Å multiplet of $\text{O}_1$ was produced by dissociative excitation of $\text{O}_2$. The process is:

\[ \text{O}_2 + e^{-} \rightarrow \text{O}_2^{*}, \]
\[ \text{O}_2^{*} \rightarrow \text{O}({^3}\Sigma^0) + \text{O}, \]
\[ \text{O}({^3}\Sigma^0) \rightarrow \text{O}({^3}P) + h\nu_{1304.1 \pm 8} \, \text{Å}. \]

The $\text{O}_2^{*}$ molecule is probably in one of a number of triplet states, either repulsive, predissociating or bound above its dissociation limit. After dissociation the spin correlation rules allow the other $\text{O}_1$ atom to be in any of the singlet, triplet, or quintet states associated with $\text{O}_1$. Thus a possible spectroscopic state for this oxygen atom is the ground state, $^3P$. As the threshold for spectroscopic states higher on the energy level diagram than the $^3P$ term is exceeded, it is also probable these states are excited.

The minimum threshold for excitation of the $^3\Sigma^0$ state can be calculated as

\[ T_{\text{min}} = D_0^0 + E_{1304} \, \text{Å}, \]

where $T_{\text{min}}$ is the minimum excitation energy, $D_0^0$ is the dissociation energy of $\text{O}_2$ into two ground state atoms, and $E_{1304}$ is the excitation energy of the $^3\Sigma^0$ term. The fragments may acquire kinetic energy in the dissociation process.

The emission cross section for the 1304-Å multiplet is shown in Fig. 1. The degree of scatter is about 10%. The peak cross section is at 100 eV with a value of $3.00\times10^{-18}$ cm$^2$. The observed threshold is at $15\pm1$ eV, indicating the dissociation products receive less than 1 eV in excess kinetic energy in the threshold region. The energy dependence also suggests that the intermediate molecular state, $\text{O}_2^{*}$, is a triplet state, although near threshold an electron exchange process is possible. Above threshold, additional triplet states may play a role.

The relative excitation function of the 1356-Å multiplet is shown in Fig. 2. The degree of scatter is about 20%. The observed threshold is at $15\pm1$ eV, which can be compared with a theoretical minimum