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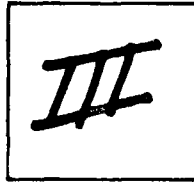4.0   2.0

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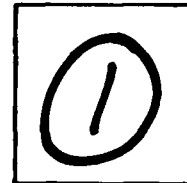NATIONAL BUREAU OF STANDARDS 1963 A

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INVENTORY

THE STUDY OF ATOM-ATOM, ELECTRON-
MOLECULE AND PHOTON MOLECULE PROCESSES

DOCUMENT IDENTIFICATION

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Semi-Annual Report

to the

Office of Naval Research

on

The Study of Atom-Atom, Electron-Molecule

and Photon Molecule Processes

July 1, 1972 – June 30, 1973

Contract No. N00014-67-A-0126-0017
N00014-75-C-0498

Principal Investigator

J. C. Browne

Departments of Computer Sciences and Physics

The University of Texas at Austin

September 30, 1973

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TABLE OF CONTENTS

I. Introduction

The funding on this contract was initiated on February 1, 1972. Thus the period of July 1, 1972 to June 30, 1973, is the first full year of research activity. The personnel working on the research projects covered under this contract are Dr. E. J. Shipsey, Research Associate (12 months), Dr. L. L. Lenamon (2 months), and the principal investigator. The 1972-73 year was a successful one in terms of publication, with six papers representing work sponsored by this contract appearing in the journals and five others accepted for publication (see Section V). An outstanding facet of the research activity has been the establishment of a close working relationship with the experimental and scattering analysis atom-atom collision group at Stanford Research Institute (SRI). R. Olsen of SRI has visited UT-Austin three times during this contract period and I have visited SRI once. This has resulted in the merging of the expertise at UT-Austin in the generation of the necessary molecular basis sets and coupling matrix elements with the experimental problems and the scattering analysis skills of SRI. Some of the results of this collaboration will be discussed in Section II, Atom-Atom Scattering.

II. Atom-Atom Scattering

The primary focus of the atom-atom scattering work has been application of the programs which have been developed for the construction of a molecular basis for low-energy atom-atom scattering. The subsequent paragraphs detail some of this work.

1. $He(2^3S) + He(1^1S) \rightarrow He(2^3P) + He(1^1S)$
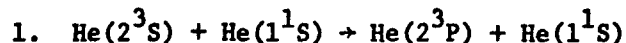
Low-energy (5-100 electron volts) cross sections have been computed for the inelastic scattering of $He(2^3S)$ from $He(1^1S)$ to yield $He(2^3P)$. A preprint of the

paper, which has been accepted by <u>Physical Review</u>, is enclosed with this report.
The inelastic cross-section is a result of close coupling in the molecular basis
between the $c^3\Sigma_g^+$ and $b^3\Pi_g$ potential curves at R = 3.3a$_0$. Reduced plots of the
inelastic differential cross-section show a sharp maximum at a τ (= Eθ) value of
approximately 100 eV·deg. Subsequent to the completion of this work the ex-
perimental group at SRI searched for and found an inelastic process with
characteristics closely approximating that predicted here.[1] The three-state
calculation including the elastic channel has been found to give a rather com-
plete explanation of the total scattering at low energy.

2. $He^+ + Ne \rightarrow Ne^+ + He$

The differential cross-sections for low-energy scattering of He^+ from Ne yielding
the ground states of both systems has contained a set of unexplained oscillatory
behavior. This oscillatory behavior was first attributed to curve
crossing phenomena at small internuclear separations (R ~ 1.7a$_0$ to 2a$_0$). We
have generated as a part of the work under this contract potential curves and
radial-coupling matrix elements for the two low-lying Σ states arising from the
two distinct ionic separated atom limits. The scattering phenomena generated
by these potential curves and this radial coupling has been investigated by R.
Olsen of SRI with the result that oscillatory phenomena is a result of a Demkov-
type process between these two states. This work is, however, not yet complete.

3.
$$Li^+ + He \rightarrow \left\{ \begin{array}{l} Li + He^+ \\ Li^+ + He^* \end{array} \right\}$$

A study of the scattering of Li^+ from He was carried out under this contract in
a four state approximation which includes both the radial couplings hypothesized
by Lorents and Conklin[2] as being the significant mechanism for the production
of charge-transfer states and also the rotational coupling which was hypothesized

by McCarroll and Piacentini[3] as being the dominant mechanism for charge transfer. The work reported here shows that both processes are necessary in order to offer a quantitative explanation of the experimental work. A preprint of this paper (which has been accepted for publication in Physical Review) is enclosed. In the case of this problem the scattering analysis work was done at Austin rather than in collaboration with SRI.

III. Photon Processes

1.   The accurate computation of Rayleigh and Raman scattering photons of frequency less than Lyman-α has been completed and published in the February 1973 Physical Review.[4] Work on the hydrogen molecule has continued with the computation of a set of accurate transition moments for the transition

$$X^1\Sigma_g^+ \leftrightarrow B'^1\Sigma_u^+$$
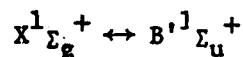
The accuracy of these computations depends to a considerable extent upon the construction of a set of wave functions which satisfies the applicable sum rules so that the few large dominant oscillator strengths must be essentially correct.

2.   The molecular package programs which generate wave functions have been altered to accept as input wave functions which use as an orbital basis functions which arise by constructing total wave functions of the form (e.g.)

$$\Psi(^1\Sigma_u^+) = \Psi(^1\Sigma_u^+) + z \cdot \Psi(^1\Sigma_g^+) + \frac{\partial}{\partial z} \cdot \Psi(^1\Sigma_g^+)$$

Sets of states obtained from the use of such wave function bases satisfy (or clearly approximate) the set of sum rules

$$S(k) = \sum_\ell (E_n - E_\ell)^k f_{n\ell} , \quad k = -1, 0, 1, \text{ and } 2.$$

We have previously only used the terms $\Psi(^1\Sigma_u^+)$ and $z \cdot \Psi(^1\Sigma_g^+)$ which satisfy the sum rules only for $k = -1$ and 0. This extension of capability has allowed the accurate computation for He and H_2 of the mean excitation energies

$$\ln I(k) = \sum_b (E_b - E_n)^k \ln (E_b - E_n) f_{nb}/S(k) \quad \text{for } k = 1 \text{ and } 2.$$

IV. Chemical Reaction Processes

The work discribed here represents a continuation of work begun by Dr. Shipsey several years ago. A paper on this subject appeared in the _Journal of Chemical Physics_ during the contract reference period and two others have been accepted for publication.

In previous work a coordinate system has been developed such that chemically reactive collisions can be studied by means of coupled differential equations rather than coupled integral differential equations. A further transformation has been developed which can be applied to the chemical reaction differential equation resulting in equations which are similar in form and properties to the reference function equations used to describe inelastic collisions. This work casts the chemical reaction problem into the same form as inelastic collisions at the point where approximations are introduced. There has also been developed a description of a locally adiabatic unitary S matrix. This quantity allows a collision to be analyzed as to the region of the potential surface responsible for transitions. The application to inelastic problems has already been made and proved enlightening. The application to reactions is now possible.

There has also been developed a new formalism for application to the area of inelastic collisions. The first and crudest approximation to the equations is the in-out high-frequency decoupling approximation which has proved so useful in high-energetic collisions. This new work shows that old approximation is a special limiting case of the new equations and thus provides the possibility of improved approximations and extension of lower energy. The work shows that an inelastic collision may be described by two matrices. The first we call the phase-derivative matrix satisfies a matrix Ricatti equation and is essentially the transformation matrix of the wave-function matrix to its conjugate momentum

matrix. The second matrix is the unitary representation of the wave function and satisfies a linear, first-order equation with an anti-hermitian coupling matrix. The entire development is in the time-dependent picture so that the anti-hermitian coupling matrix can be regarded as the transition amplitude per unit length. This circumstance allows a rigorous new means of analyzing collisions at an intermediate stage of computation.

V. Contract Related Publications

A. Published Papers--reprints attached

1. "Translational Absorption of HeH", J. Chem. Phys., 57, 2906 (1972), B. J. Ulrich, A. L. Ford and J. C. Browne.

2. "Direct-Resolvent-Operator Computations on the Hydrogen-Molecule: Dynamic Polarizability, Rayleigh and Raman Scattering", Phys. Rev. A 7, 418 (1973), A. L. Ford and J. C. Browne.

3. "Rayleigh and Raman Cross Sections for the Hydrogen Molecule", Atomic Data, 5, 305 (1973), A. L. Ford and J. C. Browne.

4. "Elastic Scattering of Electrons by H_2 in the Born Approximation", Chem. Phys. Lett., 20, 284 (1973). A. L. Ford and J. C. Browne.

5. "Adiabatic Reference Functions and Chemical Reactions", J. Chem. Phys., 58, 5368 (1973), E. J. Shipsey.

6. "Molecular Transitions and Atomic Processes", in Energy Structure and Reactivity, edited by D. Smith and W. B. McRae, (John Wiley and Sons, 1973).

B. Papers Accepted for Publication

1. "Theoretical Low Energy Inelastic Scattering Cross-Sections for $He(2^3s)$ + $He(1^1S) \rightarrow He(2^3P) + He(1^1S)$: Curve Crossing Between the $c^3\Sigma_g^+$ and $b^3\Pi g$ states of He_2" (to appear in Phys. Rev.) L. L. Lenamon, J. C. Browne, and R. E. Olson.

2. "Inelastic Scattering Cross-Sections for Li^+ or He: The Adiabatic Molecular Model" (to appear in <u>Phys. Rev.</u>), B. R. Junker and J. C. Browne.

3. "In-Out Decomposition for Inelastic Collisions as Sub-Dynamics" (to appear in <u>J. Chem. Phys.</u>), E. J. Shipsey.

4. "Comparison of Quantum Mechanical and Transition State Theory Reaction Probabilities for the Reaction $O + HBr \rightarrow OH + Br$" (to appear in <u>J. Chem. Phys.</u>), E. J. Shipsey.

References

1. R. Morgenstern, D. C. Lorents, J. R. Peterson and R. E. Olson (Phys. Rev. A, Submitted).

2. D. C. Lorents and G. M. Conklin, J. Phys. B: Atom. Mole. Phys. 5, 950 (1972).

3. R. McCorroll and R. D. Pracentini, J. Phys. B: Atom. Molec. Phys. 5, 973 (1972).

4. A. L. Ford and J. C. Browne, Phys. Rev. A 7, 418 (1973).

5. E. J. Shipsey, J. Chem. Phys. 58, 5368 (1973).