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FACILITY FORM 602

THEORETICAL STUDY OF ATOMIC AND MOLECULAR GASES

AND THEIR REACTIONS

IN THE UPPER ATMOSPHERE

Submitted to the National Aeronautics and Space Administration, Washington, 25, D. C. The report contains a brief summary of the work done during the period November 1, 1963 to April 30, 1964.

Roop C. Sahni
Project Director

REPORTS CONTROL No. _____

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In the previous reports, it was stated that we were using the computer programs along with the tables of integrals to compute wave functions and energy values of diatomic molecules for calculating potential energy curves and transport properties of the gases of the upper atmosphere. We have also reported in the previous report a number of calculations of the electronic states of O_2, N_2 and NO. In fact this is the first systematic work which has included the ionized and excited states in addition to the usual calculations of the ground state of molecules. We have been very much encouraged in this work as our calculations of the excited and ionized states have the same order of accuracy as the ground state. The reasons for this success were manifold. Firstly, we have been studying the numerical methods and the computation of integrals and special functions for a number of years on the electronic computer, and thus our group has specialized in computation work. Secondly the Institute for Space Studies, 475 Riverside Drive, New York, New York, has provided us ample 7094 computer time for our work. Since we have now developed theory and techniques for computing the electronic states of diatomic molecules using 1s, 2s and 2p functions, we have considered it worthwhile to include 3s and 3p functions. The problem of including 3s and 3p functions is very fundamental to our program of calculating potential energy curves and transport properties of gases. The extended set of orbitals with 3s and 3p functions is bound to give more accurate results and also will enable us to compute some of the excited states which were not possible with the limited set. Therefore, we are describing in the present report the work done in connection with extending the calculations with 3s and 3p orbitals. The complexity of the problem can be judged by the fact that we will be calculating 4398 instead of 528 integrals required for the limited set. Moreover, these integrals are much more complex and tedious to compute. At present these integrals for a single internuclear distance require 30-40 minutes of the 7094 computer's time instead of about 2 minutes for the limited set. We are, therefore, trying to make our programs very efficient to cut down the machine time. The complexity of the problem of using extended set of orbitals is quite large regarding machine time both for integrals and eigenvector-eigenvalue problem but we hope the success will be equally rewarding. We are yet in the middle of different stages of the above problem and hope to report complete results in the coming report.

Roop C. Sahni

Work carried out during the above period can be given under the following headings:

(1) Extension of Integral Programs for Diatomic Molecules to Include 3s and 3p Orbitals.

(2) Extension of the Eigenvector-Eigenvalue Programs to Include the Matrices Involving 3s and 3p orbitals.

(3) Computation of the Wave Functions and Total Energies for the Limited as well as Extended Set of Orbitals for Comparison of the Calculated Data for Ground State of Hydrides of the First Group.

(4) Computation of the Wave Functions and Total Energies for the Limited as well as Extended set of Orbitals for Comparison of the Calculated Data for Ionized and Excited States of Hydrides of the First Group.

(1) EXTENSION OF INTEGRAL PROGRAMS FOR DIATOMIC MOLECULES TO INCLUDE 3s AND 3p ORBITALS

by E. J. De Lorenzo and Franz-Josef Heinen

Our previous programs and the tables of integrals enable us to compute a number of electronic states of N_2, O_2, CO and NO. We have reported in the previous report that the results for the excited and ionized states were of the same order of accuracy as those of the ground state. These results have been rechecked to avoid any errors and the total energies of the different states for N_2 and O_2 along with the observed values and the $^o/o$ accuracy are given in Table I. This accuracy is of the order of 99.2$^o/o$, which is better than reported by other workers for a single determinantal states. The accuracy of these states can be further improved by extending the basic set of functions. We have, therefore, extended the integral programs to include 3s and 3p functions. The results of these computations will be given in the next report.

(2) EXTENSION OF THE EIGENVECTOR-EIGENVALUE PROGRAMS TO INCLUDE THE MATRICES INVOLVING 3s AND 3p ORBITALS

by C. D. La Budde and R. S. Bawa

An automatic program has been built up which can use the integrals as input data and compute wave functions, energy values and total energies for any electronic state of a molecule. This program was originally built up to include only 1s, 2s, $2p_z$, $2p_x$ and $2p_y$ orbitals and involved matrices of the order of 10 x 10. Now another program has been built up to include 3s, $3p_z$, $3p_x$ and $3p_y$ atomic orbitals in addition to the above set. This program involves matrices of the order of 18 x 18. The programs involves the following steps,

1) rearranges integrals in the form of 3 set of column vectors known as H, J and K vectors,

2) multiplies J and K integrals by a_i coefficients, which at the start of the cycle are put as input data,

TABLE 1

TOTAL ENERGIES OF ELECTRONIC STATES * OF N_2 AND O_2

Molecular State	This Calculation	Observed [c]	cal/obs %
N_2, $X\ ^1\Sigma_g^+$	-108.573,572 [a]	-109.618	99.05
$A\ ^3\Sigma_u^+$	-108.309,100	-109.335	99.06
$B\ ^3\pi_g$	-108.298,274	-109.319	99.07
$C\ ^3\pi_u$	-108.108,545	-109.204	99.00
N_2^+, $X\ ^2\Sigma_g^+$	-108.029,387	-109.045	99.07
$B\ ^2\Sigma_u^+$	-107.843,229	-108.932	99.00
O_2, $X\ ^3\Sigma_g^-$	-149.092,076 [b]	-150.40966	99.12
$a\ ^1\Delta_g$	-149.010,520	-150.373	99.09
O_2^+, $X\ ^2\pi_g$	-148.694,117	-149.961	99.16
$a\ ^4\pi_u$	-148.668,197	-149.818	99.23

* All electronic states of N_2 and O_2 are calculated at the internuclear distances R = 2.0675 a.u. and R = 2.28167 a.u., respectively.

a This result compares with the analogous results -108.574 a.u. and -108.57362 a.u. reported by Scherr (4) and Ransil (6), respectively.

b Kotani (16) reported a value of -149.00734 a.u. for a single configuration.

c Computed using the observed ground state energy and observed vertical transition energies

3) rearranges 4 set of matrices of the order of 18 x 18 known as

$\underline{S}$ overlap matrix

$\underline{H}$ bare nuclear Hamiltonian matrix

$\underline{J}^{\alpha}$ and $\underline{J}^{\beta}$ coulomb matrices

$\underline{K}^{\alpha \text{ or } \beta}$ exchange matrix,

4) computes $\underline{F}$ matrix by the following equation

$$\underline{F} = \underline{H} + \underline{J} - \underline{K} \tag{1}$$

5) solves the following eigenvector equations by the Jacobi-Iteration method

$$\underline{F}^{\alpha} = \underline{H} + \underline{J}^{\alpha+\beta} - \underline{K}^{\alpha} \tag{2}$$

$$\underline{F}^{\beta} = \underline{H} + \underline{J}^{\alpha+\beta} - \underline{K}^{\beta} \tag{3}$$

6) after the self-consistency is obtained the program prints in decimal form,

    a) eigenvectors

    b) eigenvalues

    c) total energy.

This program has successfully computed some of the ground state of molecules and at present is being modified to include ionized and excited states.

(3) COMPUTATION OF THE WAVE FUNCTIONS AND TOTAL ENERGIES FOR THE LIMITED AS WELL AS EXTENDED SET OF ORBITALS FOR COMPARISON OF THE CALCULATED DATA FOR GROUND STATE OF HYDRIDES OF THE FIRST GROUP

     by R. C. Sahni and O. P. Anand

The computation of the wave functions and total energies of the ground states of hydrides using the limited set (1s orbital for hydrogen) and the extended set (1s, 2s and 2p orbitals for hydrogen) has been carried out on the IBM 7094 computer. The results of the computed ototal energies for both the sets are compared with those reported by the thers in Table 2. It has been found that the extended set of orbitals gives better results than the limited set of orbitals. Our results of the extended set are better than those reported by the others.

(4) COMPUTATION OF THE WAVE FUNCTIONS AND TOTAL ENERGIES FOR THE LIMITED AS WELL AS EXTENDED SET OF ORBITALS FOR COMPARISON OF THE CALCULATED DATA FOR IONIZED AND EXCITED STATES OF HYDRIDES OF THE FIRST GROUP

     by R. C. Sahni, C. D. La Budde and O. P. Anand

Calculations of the wave functions and the total energies of the ionized and excited states of the hydrides using the limited and extended set of orbitals for hydrogen have been carried out at 7094 IBM computers. The results of the

computations are compared in Table 3 for ionized states and in Table 4 for excited states. For all the ionized and excited states studied, it has been found that the extended set gives better total energies than the limited set. This computation shows that extended set will improve the results of computation and also indirectly shows that the computational procedures followed for ionized and excited states are reliable

TABLE 2

TOTAL ENERGIES (a.u.)

HYDRIDE	CALCULATED		
	Limited Set	Extended Set	Other Works
LiH	- 7.9667	- 7.9688	- 7.9666[1]
BeH	-15.1151	-15.1200	
BH	-25.0621	-25.0747	-25.0621[1]
CH	-38.1640	-38.1877	-38.1640[2]
NH	-54.7828	-54.8213	-54.7850[2]
OH	-75.0630	-75.1338	-75.0620[2]
FH	-99.4785	-99.5822	-99.4750[2]

1. Ransil, B. J., Rev. Mod. Phys., **32**, 245 (1960).

2. Krauss, M., J. Chem. Phys., **28**, 1021 (1958).

TABLE 3

TOTAL ENERGY OF IONIZED STATES OF HYDRIDES
IN ATOMIC UNITS

STATE	LIMITED SET	EXTENDED SET
LiH ($^2\Sigma_u$)	- 7.7050	- 7.7093
BeH ($^1\Sigma$)	-14.7936	-14.8102
BH ($^2\Sigma$)	-24.3796	-24.3919
CH ($^1\Sigma$)	-37.7831	-37.7997
NH ($^2\pi$)	-54.3334	-54.3503
OH ($^1\Sigma$)	-74.5931	-74.6176
FH ($^2\pi$)	-99.1101	-99.1424

TABLE 4

TOTAL ENERGY OF EXCITED STATES OF HYDRIDES
IN ATOMIC UNITS

STATE	LIMITED SET	EXTENDED SET
CH ($^4\Sigma^-$)	-38.1545	-38.1776
CH ($^3\Sigma^+$)	-37.7806	-37.9472
NH ($^1\Sigma^+$)	-54.2598	-54.3674
NH ($^3\pi$)	-54.3806	-54.5204