

NEW YORK UNIVERSITY  
 CHEMISTRY DEPARTMENT  
 UNIVERSITY HEIGHTS  
 Contract No. NSG 76-60  
 Summary of work done in the period  
 May 1, 1965 to October 31, 1965

THEORETICAL STUDY OF ATOMIC AND MOLECULAR GASES  
 AND THEIR REACTIONS  
 IN THE UPPER ATMOSPHERE

FACILITY FORM 802

N 66-14634  
 (ACCESSION NUMBER) (THRU)  
 15 (PAGES) 1 (CODE)  
 OR 69109 (NASA CR OR TRX OR AD NUMBER) 13 (CATEGORY)

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 1.00

Microfiche (MF) .50

N 853 July 65

Submitted to the National Aeronautics and Space Administration, Washington, D. C. The report contains a brief summary of the work done in the period May 1, 1965 to October 31, 1965

Roop C. Sahni

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 Project Director

PERSONNEL

|                       |  |
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22

14634

## INTRODUCTION

In the previous report it was stated that we have successfully extended our computer programs to include 3s and 3p functions in addition to 1s, 2s and 2p functions to calculate the wave functions and total energies of the different states of diatomic molecules. In addition, it was also mentioned that we have succeeded in varying the screening constants of the basic functions to obtain the best LCAO MO's. This best LCAO MO's work was confined to the equilibrium distance only. Extension of this program to a large number of internuclear distances and to a number of ionized and excited states, in addition to the ground state, involved very heavy computation. We have successfully computed the potential energy curves of different states of  $\text{H}_2$  and CO molecules. Some preliminary work has also been done on  $\text{O}_2$ ,  $\text{NF}$ ,  $\text{CN}$  and  $\text{C}_2$  molecules. Some of these results are given in this report. The above work which aims at obtaining limited Hartree-Fock MO's for different states of diatomic molecules involves immense computation due to the optimization of non-linear parameters (screening constants). The above work has involved over 800 hours of IBM 7094 computer at the Institute for Space Studies. We owe the success of the above work to the excellent computing facilities and co-operation of the personnel of the Institute for Space Studies, 475 Riverside Drive, New York, New York.

*Author*

*Roop C. Sahni*

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

- (1) Calculation of the Potential Energy (P.E.) Curves and Molecular Constants of the Ionized States ( $X^2 \Sigma_g^+$ ,  $A^2 \Pi_u$ ,  $A^2 \Sigma_u^+$ ) of  $N_2$  Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions.
- (2) Calculation of the Potential Energy Curves and Molecular Constants of the ground ( $X^1 \Sigma_g^+$ ) and the Excited ( $A^3 \Sigma_u^+$ ,  $A^3 \Pi_g$ ,  $A^3 \Pi_u$ ) States of  $N_2$  Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions.
- (3) Development of the Computer Program to Calculate Best LCAO MO's of Homopolar Molecules Using 3s and 3p Functions in Addition to 1s, 2s and 2p Functions.
- (4) Calculation of the P. E. Curves and Molecular Constants of the Different States of Heteropolar Molecules Using Best LCAO MO's Involving 1s, 2s and 2p Functions.
- (5) Calculation of the P.E. Curves and Molecular Constants of the Ionized States of  $N_2$  Molecules Using Best LCAO MO's with 1s, 2s and 2p Functions

by R. C. Sahni, C. L. La Budde and E. C. Seshney

'Auto vary' programs described in the previous report have been used to calculate the wave functions and total energies of the above states of  $N_2$  at a number of internuclear distances ( $R = 1.5$  (0.025) to 3.0). The programs constructed by P. C. Jain, described in the previous report, have been used to calculate the potential energy curves and molecular constants of the above states. Two different sets of calculations were made. In one set of calculations, (called individually optimized) the MO's and total energy of each of the ionized state was individually optimized at a number of internuclear distances to calculate the P.E. curves and molecular constants. In the second set of calculation: the screening constants of the lowest ionized state ( $X^2 \Sigma_g^+$ ) were used to calculate the MO's and total energies of the different states of  $N_2$ . These energies were then used to calculate the P.E. curves and molecular constants of the ionized states of  $N_2$  molecule. The results of these calculations are reported in Tables I to X.

- (2) Calculation of the P.E. Curves and Molecular Constants of the Ground and the Excited States of  $N_2$  Molecule Using Best LCAO MO's with 1s, 2s and 2p Functions

by R. C. Sahni and E. C. Jain

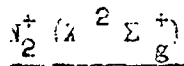
'Auto vary' programs described in the previous report have been used to calculate the ground and excited state of  $N_2$  molecule. Two sets of calculations called 'individually optimized' and 'using optimized ground state ( $X^1 \Sigma_g^+$ ) screening constants' were carried out. From the total energies, P. E. curves and molecular

Molecular Constants for the Potential Energy Curves of  $N_2^+$  Molecule

Obtained from First Principles

The program PSI VIB WKB NP5 SQL WX has been used for deriving the molecular constants for the potential energy curves of various ionized states of  $N_2$  molecule.

The result obtained follows:



|     | <u>Derived</u>     | <u>INDIVIDUALLY OPTIMIZED</u><br><u>Code et al</u> | <u>Experimental</u> |
|-----|--------------------|--|---------------------|
| Re  | 2.11197 a.u.       | 2.0405 a.u.  | 2.10917             |
| T.E | -108.12712193 a.u. |  |                     |

TABLE I

| v  | G(v)     | B <sub>v</sub> |
|----|----------|----------------|
| 0  | 1211.03  | 1.9210         |
| 1  | 3601.94  | 1.9081         |
| 2  | 5970.99  | 1.8948         |
| 3  | 8313.55  | 1.8813         |
| 4  | 10632.84 | 1.8682         |
| 5  | 12937.47 | 1.8550         |
| 6  | 15218.17 | 1.8404         |
| 7  | 17474.46 | 1.8277         |
| 8  | 19710.77 | 1.8149         |
| 9  | 21926.62 | 1.8017         |
| 10 | 24121.75 | 1.7880         |
| 11 | 26295.02 | 1.7745         |

TABLE II  
Derived Values of  $N_2^+ (^2 \Sigma_g^-)$  Individually Optimized

| # of Vibrational Levels Used | $\omega_e$ | $\omega_e x_e$ | $B_e$  | $\alpha_e$ |
|------------------------------|------------|----------------|--------|------------|
| 3                            | 2429.16    | 16.8300        | 1.9276 | 0.0131     |
| 4                            | 2427.40    | 15.3167        | 1.9278 | 0.0133     |
| 5                            | 2426.08    | 14.4400        | 1.9279 | 0.0132     |
| 6                            | 2424.61    | 13.6390        | 1.9278 | 0.0132     |
| 7                            | 2423.38    | 13.0712        | 1.9281 | 0.0134     |
| 8                            | 2422.43    | 12.6895        | 1.9281 | 0.0134     |
| 9                            | 2421.61    | 12.3997        | 1.9280 | 0.0133     |
| 10                           | 2420.87    | 12.1675        | 1.9279 | 0.0133     |
| 11                           | 2420.20    | 11.9767        | 1.9279 | 0.0133     |
| 12                           | 2419.61    | 11.8209        | 1.9279 | 0.0133     |
| Exp. Values                  | 2207.19    | 16.1360        | 1.9322 | 0.0202     |
| Cade et al                   | 2570.5     | 9.809          | 2.065  | 0.0148     |

TABLE III  
INDIVIDUALLY OPTIMIZED

$N_2^+ (A^2 \Pi_u)$

|     |                    |                   |                     |
|-----|--------------------|-------------------|---------------------|
|     | <u>Derived</u>     | <u>Cade et al</u> | <u>Experimental</u> |
| Re  | 2.2284 a.u.        | 2.1344            | 2.2226              |
| T.E | -103.13844013 a.u. |                   |                     |

| v  | G(v)     | $B_v$  |
|----|----------|--------|
| 0  | 1072.35  | 1.7224 |
| 1  | 3170.52  | 1.7089 |
| 2  | 5268.21  | 1.6998 |
| 3  | 7354.17  | 1.6885 |
| 4  | 9420.39  | 1.6773 |
| 5  | 11472.27 | 1.6662 |
| 6  | 13508.30 | 1.6555 |
| 7  | 15529.14 | 1.6444 |
| 8  | 17533.17 | 1.6341 |
| 9  | 19521.59 | 1.6225 |
| 10 | 21494.61 | 1.6116 |
| 11 | 23452.12 | 1.6009 |

TABLE IV

## INDIVIDUALLY OPTIMIZED

Derived Values for A ( ${}^2\Pi_u$ ) State of  $N_2^+$  Molecule

| # of Vibrational Levels Used | $\omega_e$ | $\omega_e x_e$ | $\beta_e$ | $\alpha_e$ |
|------------------------------|------------|----------------|-----------|------------|
| 3                            | 2149.95    | 18.7093        | 1.7273    | 0.0113     |
| 4                            | 2144.50    | 13.6927        | 1.7270    | 0.0111     |
| 5                            | 2140.82    | 11.5052        | 1.7270    | 0.0110     |
| 6                            | 2138.64    | 10.3157        | 1.7270    | 0.0111     |
| 7                            | 2137.10    | 9.6071         | 1.7269    | 0.0110     |
| 8                            | 2135.96    | 9.1436         | 1.7269    | 0.0110     |
| 9                            | 2135.10    | 8.8464         | 1.7268    | 0.0110     |
| 10                           | 2134.44    | 8.6367         | 1.7268    | 0.0110     |
| 11                           | 2133.90    | 8.4842         | 1.7268    | 0.0110     |
| 12                           | 2133.46    | 8.3696         | 1.7268    | 0.0110     |
| Exp. Values                  | 1902.84    | 14.9100        | 1.7400    | 0.0180     |
| Cade et.al.                  | 2312.5     | 6.082          | 1.387     | 0.0175     |

TABLE V

## INDIVIDUALLY OPTIMIZED

B ( ${}^2\Sigma_u^+$ ) StateValues of  $G(v)$  and  $B_v$  for the B ( ${}^2\Sigma_u^+$ ) State of  $N_2^+$ 

|      | Derived      | Cade et.al. | Experimental |
|------|--------------|-------------|--------------|
| Re   | 1.99141      | 1.935       | 2.03139      |
| T.E. | 107.95751572 |             |              |

| v  | $G(v)$   | $B_v$  |
|----|----------|--------|
| 0  | 1465.66  | 2.1616 |
| 1  | 4375.86  | 2.1520 |
| 2  | 7258.96  | 2.1408 |
| 3  | 10129.01 | 2.1300 |
| 4  | 12981.55 | 2.1196 |
| 5  | 15815.36 | 2.1092 |
| 6  | 18634.62 | 2.0981 |
| 7  | 21440.01 | 2.0864 |
| 8  | 24223.52 | 2.0753 |
| 9  | 26984.81 | 2.0644 |
| 10 | 29733.96 | 2.0543 |
| 11 | 32457.21 | 2.0436 |

TABLE VI  
Molecular Constants for the  $\Lambda$  ( $^2 \Sigma^+$ ) State of  $N_2^+$   
(INDIVIDUALLY OPTIMIZED)

| of Vibrational levels Used | $\omega_e$ | $\omega_e x_e$ | $B_e$  | $\alpha_e$ |
|----------------------------|------------|----------------|--------|------------|
| 3                          | 2938.18    | 13.8636        | 2.1671 | 0.0104     |
| 4                          | 2936.65    | 12.5583        | 2.1670 | 0.0106     |
| 5                          | 2935.26    | 11.6285        | 2.1673 | 0.0106     |
| 6                          | 2934.15    | 11.0257        | 2.1673 | 0.0106     |
| 7                          | 2933.14    | 10.5566        | 2.1674 | 0.0106     |
| 8                          | 2932.16    | 10.1544        | 2.1675 | 0.0107     |
| 9                          | 2931.39    | 9.8932         | 2.1678 | 0.0106     |
| 10                         | 2930.85    | 9.7239         | 2.1680 | 0.0108     |
| 11                         | 2930.37    | 9.5850         | 2.1679 | 0.0108     |
| 12                         | 2929.91    | 9.4658         | 2.1679 | 0.0108     |
| Exp. Values                | 2412.84    | 23.19          | 2.083  | 0.0195     |
| Cade et al.                | 3191.0     | 19.38          | 2.285  | 0.0280     |

TABLE VII  
 $N_2^+$  ( $\Lambda$   $^2 \Pi_u$ ) USING OPTIMIZED  $N_2^+$  ( $^2 \Sigma^+$ ) MOLECULAR CONSTANTS

| Re    | Derived       | Cade et al. | Experimental |
|-------|---------------|-------------|--------------|
| $R_e$ | 2.23103 a.u.  | 2.1345      | 2.2286       |
| $D_e$ | -108.13686840 |             |              |

| v  | $G(v)$   | $F_v$  |
|----|----------|--------|
| 0  | 1091.57  | 1.7198 |
| 1  | 3175.81  | 1.7096 |
| 2  | 5310.62  | 1.6996 |
| 3  | 7402.65  | 1.6862 |
| 4  | 9475.32  | 1.6769 |
| 5  | 11521.65 | 1.6558 |
| 6  | 13543.01 | 1.6542 |
| 7  | 15551.18 | 1.6431 |
| 8  | 17547.39 | 1.6319 |
| 9  | 19526.65 | 1.6201 |
| 10 | 21489.95 | 1.6098 |
| 11 | 23439.86 | 1.5988 |



TABLE VIII

Derived Values of  $N_2^+ (A^2 \Sigma_u^-)$  Using Optimized  $N_2^+ ({}^2 \Sigma_g^-)$  Screening Constants

| # of Vibrational Levels Used | $\omega_e$ | $\omega_e x_e$ | $B_e$  | $\alpha_e$ |
|------------------------------|------------|----------------|--------|------------|
| 3                            | 2099.03    | -10.5557       | 1.7243 | 0.0101     |
| 4                            | 2106.35    | -4.2768        | 1.7260 | 0.0111     |
| 5                            | 2112.34    | -0.2826        | 1.7257 | 0.0109     |
| 6                            | 2117.36    | 2.4549         | 1.7257 | 0.0109     |
| 7                            | 2121.51    | 4.3691         | 1.7258 | 0.0110     |
| 8                            | 2124.69    | 5.6400         | 1.7259 | 0.0110     |
| 9                            | 2127.02    | 6.4632         | 1.7260 | 0.0110     |
| 10                           | 2128.78    | 7.0187         | 1.7262 | 0.0111     |
| 11                           | 2130.12    | 7.4014         | 1.7262 | 0.0111     |
| 12                           | 2131.11    | 7.6612         | 1.7261 | 0.0111     |
| Exp. Values                  | 1902.84    | 14.9100        | 1.7261 | 0.0180     |
| Code et al.                  | 2312.5     | 6.089          | 1.807  | 0.0155     |

Table IX

 $N_2^+ (B^2 \Sigma_u^-)$  Using Ionized Ground State Optimized Screening Constants

|    | Derived       | Code  | Experimental |
|----|---------------|-------|--------------|
| Re | 1.9903 a.u.   | 1.965 | 2.0314       |
|    | -107.95539761 |       |              |

| v  | G(v)     | $B_v$  |
|----|----------|--------|
| 0  | 1452.14  | 2.1625 |
| 1  | 4340.28  | 2.1519 |
| 2  | 7217.96  | 2.1402 |
| 3  | 10085.14 | 2.1298 |
| 4  | 12944.33 | 2.1179 |
| 5  | 15780.05 | 2.1069 |
| 6  | 18597.27 | 2.0965 |
| 7  | 21395.73 | 2.0855 |
| 8  | 24173.65 | 2.0725 |
| 9  | 26935.30 | 2.0619 |
| 10 | 29687.32 | 2.0527 |
| 11 | 32434.37 | 2.0432 |

TABLE X

Derived Values  $\bar{M}_2^+$  ( $B \frac{Z}{u}$ ) Using Ionized Ground State Optimized Screening Constants

| # of Vibrational Levels | $\omega_e$ | $\omega_e x_e$ | $\omega_e$ | $\alpha_e$ |
|-------------------------|------------|----------------|------------|------------|
| 3                       | 2907.81    | 8.9461         | 2.1672     | 0.0107     |
| 4                       | 2906.56    | 7.4755         | 2.1672     | 0.0107     |
| 5                       | 2905.48    | 6.7565         | 2.1676     | 0.0109     |
| 6                       | 2905.28    | 6.6457         | 2.1677     | 0.0110     |
| 7                       | 2905.51    | 6.7492         | 2.1676     | 0.0110     |
| 8                       | 2905.95    | 6.9261         | 2.1676     | 0.0110     |
| 9                       | 2906.54    | 7.1339         | 2.1680     | 0.0111     |
| 10                      | 2907.17    | 7.3347         | 2.1681     | 0.0111     |
| 11                      | 2907.62    | 7.4617         | 2.1679     | 0.0111     |
| 12                      | 2907.83    | 7.5166         | 2.1675     | 0.0110     |
| Exp. Values             | 2419.84    | 23.1900        | 2.0830     | 0.0195     |
| Gade et.al              | 3101.8     | 19.83          | 2.296      | 0.01280    |

constants were calculated in the same manner as described above for the ionized states.

- (3) Development of the Computer Program to Calculate Best LCAO MO's of Homopolar Molecules Using 3s and 3p Functions in Addition to 1s, 2s and 2p Functions  
 by C. D. La Bude, Birbal Singh, O. P. Anand and G. K. Verma

It was stated in the previous report that an 'Auto vary' program has been built which varies the screening constants of 1s, 2s and 2p basic functions to obtain the best LCAO MO's. In the previous report it was also stated that the inclusion of 3s and 3p functions involved many more integrals and the solution of the eigenvalue problem was more complicated. Since for every variation of the screening constants, the whole calculation has to be repeated, the machine time becomes very important. After overcoming many hurdles, an 'Auto vary' program has been built up for homopolar molecules. This program is now being used to calculate the different states of  $N_2$  molecule with a view to calculate their P. E. curves and molecular constants.

- (4) Calculation of the P.E. Curves and Molecular Constants of the Different States of Heteropolar Molecules Using Best LCAO MO's Involving 1s, 2s and 2p Functions  
 by R. C. Sahni, C. D. La Bude and E. C. Sawhney

The wave functions and total energies of a number of states of CO have been calculated at a number of internuclear distances. Due to limitation of machine time some of these calculations are not yet complete. In addition to CO, work has been done on CN, NF and NO molecules. We hope to report these results in the next report.

#### PUBLICATIONS AND GROUP ACTIVITIES

##### Publications

- (1) Electronic States of Molecules. I. Self-Consistent Field Calculations of the Ground, Ionized, and Excited States of  $N_2$  and  $O_2$ , by R. C. Sahni and S. J. De Lorenzo, J. Chem. Phys, 42, 3612, (1965)
- (2) Quantum Theory of the Defect Solid State, by R. C. Sahni  
 This paper has been accepted for publication in ASTM Symposium Journal

##### Group Activities

- (1) Dr. R. C. Sahni presented the following paper at the Molecular Spectroscopy Symposium, The Ohio State University, Columbus, Ohio, "Theoretical Calculation of the Electronic States, Total Energies, Ionization Potential and Excitation Energies of  $O_2$ ,  $N_2$ , CO, NO, CN and the Hydrides of the First Group," June 1965
- (2) Dr. R. C. Sahni presented the following paper at ASTM meeting, Seattle, Washington, "Quantum Theory of the Defect Solid State," November 1965
- (3) Dr. J. C. Browne of the University of Texas gave a number of lectures on Multicenter Integrals and Special Functions during the summer
- (4) Dr. G. R. Verma of the University of Rhode Island worked with our group during the summer on various mathematical projects.