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QUANTUM MECHANICAL STUDY OF MOLECULES:

PREDICTION OF THE GROUND, IONIZED AND EXCITED STATES OF THE UNKNOWN NF MOLECULE

by Roop C. Sahni

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NEW YORK UNIVERSITY
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QUANTUM MECHANICAL STUDY OF MOLECULES:
PREDICTION OF THE GROUND, IONIZED AND EXCITED STATES OF THE UNKNOWN NF MOLECULE*

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* The stability of the ground, ionized and excited states of NF molecule was reported in NASA Progress Report N65-85771, April 1965, and at the Symposium on Molecular Structure and Spectroscopy Conference at the Ohio State University, Columbus, Ohio, U. S. A. on June 1965. The configuration and stability of the ground and excited states of this molecule have been confirmed experimentally and reported at the Symposium on Molecular Structure and Spectroscopy Conference at the Ohio State University, Columbus, Ohio, U. S. A. on September 1966 by A. E. Douglas and W. E. Jones.

QUANTUM MECHANICAL STUDY OF MOLECULES

Prediction of the Ground, Ionized and Excited States of the Unknown NF Molecule

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SUMMARY

The ground, ionized and excited states of the unknown NF molecule have been computed at a number of internuclear distances (R) to determine their stability, equilibrium distances (R_e), ionization and excitation energies. In these calculations all the atomic and molecular integrals have been computed correctly to six decimal places. The configurations of the different states of NF have been derived from the configurations of the corresponding states of the isoelectronic O_2 molecule. The percentage accuracy of the computations of the states of NF has been estimated by carrying out similar types of calculations on the different states of the known N_2, CO and O_2 molecules.

INTRODUCTION

A large number of end products in the reactions of the gases of the upper atmosphere are obtained in the form of radicals, ions and excited states of diatomic molecules. The conditions of the low pressure and high vacuum of the upper atmosphere are difficult to produce in the laboratory. Moreover the experiments, which involve costly apparatuses, are very difficult and tedious to perform on each and every radical, ionized or excited state of a molecule.

For the last ten years at New York University, attempts have been made to develop a theoretical system for the study of these unknown molecules for the calculation of the transport properties of the gases of the upper atmosphere.

To standardize these techniques, the electronic states of a number of known molecules have been computed (refs. 1 to 4) and their data compared with the experimental results. As the system of these calculations became complete, an attempt was made in 1964 to find an unknown molecule for performing the theoretical calculations and to inform the experimentalists so as to confirm the predicted results. NF has been specially considered for this study. A number of laboratories, all over the world prior to these calculations, have been trying to detect this molecule. Since it is one of the missing diatomic molecules in the first group of the periodic table, it was considered to be of immense interest to the experimentalists to follow the theoretical results. For this reason a complete calculation of the ground, ionized and excited states of NF was carried out and reported in the NASA Progress Report N65-85771 (ref. 5) April 1965. Later, these results were presented at the Symposium on Molecular Structure and Spectroscopy at the Ohio State University, Columbus, Ohio, U.S.A. (ref. 6) on June 1965.

The experimental results carried out after the above prediction have confirmed (ref. 7) the predicted configuration (arrangement of electrons in the molecule) and also the internuclear distances of the ground and excited states of NF within the estimated accuracy of the calculations. The spectroscopists are still carrying out work on the ionized states of NF. It should be noted that it is for the first time that a Theoretical Chemist has predicted the stability and configuration of a molecule which spectroscopists could not detect for a long time. These calculations on an unknown molecule have opened many new fields of researches and have made it possible to study many fundamental problems which were not soluble without such a theoretical study.

Calculations of the Different States of NF and Related Molecules

Calculations were carried out on four molecules. Two of them are homopolar molecules and the other two are heteropolar molecules. A set of homopolar and heteropolar molecules such as N_2 and CO consist of 14 electrons and the second set such as O_2 and NF consist of 16 electrons. A cross relation between the results was established as follows:

Relations between the results of the isoelectronic N_2 and CO molecules were considered to be of the same order as those of the isoelectronic O_2 and NF molecules. The second set of relations between the homopolar N_2 and O_2 molecules were considered of the same order as those between the heteropolar CO and NF molecules. A brief sketch of these relations is given in Table I.

Equations for Self-consistent Field (SCF)* Molecular Orbitals

The molecular orbitals, ϕ's, are expressed as linear combination of atomic orbitals, χ's,

$$\phi_i = \sum_p a_{ip} \chi_p \tag{1}$$

where a_{ip} are undetermined coefficients. Equation (1) in matrix notation is expressed as

$$\phi_i = a_i \chi \tag{2}$$

The equations for the undetermined a_i, are then given as

$$(\underline{H} + \underline{J} - \underline{K}^{\alpha})\, a_i^{\alpha} = \epsilon_i^{\alpha}\, \underline{S}\, a_i^{\alpha} \tag{3a}$$

$$(\underline{H} + \underline{J} - \underline{K}^{\beta})\, a_i^{\beta} = \epsilon_i^{\beta}\, \underline{S}\, a_i^{\beta} \tag{3b}$$

where $\underline{S}$, $\underline{H}$, $\underline{J}$ and $\underline{K}^{\alpha}$ or $\underline{K}^{\beta}$ are overlap, bare-nuclear field Hamiltonian, coulomb and exchange matrices respectively; α and β refer to α and β spins respectively.

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* Symbols are explained in Appendix B

Table I

SKETCH OF RELATIONS BETWEEN N_2, O_2, CO AND NF MOLECULES

Table I(a).— SPECIES, NUMBER OF ELECTRONS AND KNOWN STATUS OF THE ABOVE MOLECULES

Molecule	No. of Electrons	Nature of Molecule		Detection
N_2	14	Homopolar	(N —— N)	Known
O_2	16	Homopolar	(O —— O)	Known
CO	14	Heteropolar	(C —— O)	Known
NF	16	Heteropolar	(N —— F)	Unknown

Table I(b).— CROSS RELATIONS OF THE ABOVE MOLECULES

$N_2 \longrightarrow O_2$	Homopolar
$CO \longrightarrow NF$	Heteropolar
$N_2 \longrightarrow CO$	Isoelectronic
$O_2 \longrightarrow NF$	Isoelectronic

Table I(c).— MAP OF CROSS RELATIONS OF THE ABOVE MOLECULES

	Isoelectronic (14 Electrons)	Isoelectronic (16 Electrons)	
Homopolar	N_2	O_2	
Heteropolar	CO	NF	unknown

Table I(d).— CONFIGURATION OF THE DIFFERENT STATES OF NF

Nomenclature*	Electronic Configuration									State
NF X $^3\Sigma$:	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$	$4\sigma^2$	$5\sigma^2$	Π_x^2	Π_y^2	Π_x^*	Π_y^*	(ground state)
NF $^1\Delta$:	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$	$4\sigma^2$	$5\sigma^2$	Π_x^2	Π_y^2	Π_x^{*2}		(excited state)
NF^+ $^2\Pi$:	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$	$4\sigma^2$	$5\sigma^2$	Π_x^2	Π_y^2	Π_x^*		(ionized state)
NF^+ $^4\Pi$:	$1\sigma^2$	$2\sigma^2$	$3\sigma^2$	$4\sigma^2$	$5\sigma^2$	Π_x^2	Π_x	Π_x^*	Π_y^*	(ionized state)

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* The nomenclature and configurations of the different states of NF were derived from the corresponding states of the isoelectronic O_2 molecule.

The secular equations corresponding to the self-consistent field equations (3a) and (3b) can be written as

$$| \underline{F}^{\alpha} - \epsilon^{\alpha} \underline{S} | = 0 \quad \text{and} \quad |\underline{F}^{\beta} - \epsilon^{\beta} \underline{S} | = 0 \qquad (4)$$

where

$$\underline{F}^{\alpha(\beta)} = \underline{H} + \underline{J} - \underline{K}^{\alpha(\beta)} \qquad (5)$$

Equations (4) and (5) are solved iteratively until self-consistency is achieved for both the α and β spin sets.

For closed shell states, the symmetry adapted Hartree-Fock solutions of equations (3a) and (3b) become identical and only one of them need be solved iteratively. If the number of electrons n_{α}, with α spin, is not equal to the number of electrons n_{β}, with β spin, or in the general open-shell state with unpaired electrons one needs to solve both the equations (3a) and (3b) for the undetermined coefficients a_i^{α} and a_i^{β}. Though these equations represent separate pseudo-eigenvalue problems, they are related through the dependence of $\underline{J}$ upon both a_i^{α} and a_i^{β} and are best solved simultaneously in an iterative manner.

For computing the wave function of the open shell state of a molecule a number of treatments (refs. 8 and 9) have been suggested. However it has been shown by Sahni and De Lorenzo (refs. 10 and 11) that for molecules like N_2, CO and O_2, the spin polarized and restricted treatments give energy values which are not appreciably different. Therefore, the simpler restricted treatment has been adopted for these calculations to avoid tedious computations. In this treatment the a_i^{α} and a_i^{β} for the paired occupied orbitals are restricted to be identical at each step of the SCF molecular orbital calculation and the resulting state is a pure spin state as it is a function of both $\underline{S}^2$ and $\underline{S}_z$ operators.

Computational Details

A. Units

All the integrals and orbital energies have been calculated in atomic units (a.u.). The ionization and excitation energies of the states of NF are expressed in electron volts. The latest adopted conversion factors (ref. 12) given below are used whenever needed for comparison:

$$1 \text{ a.u. (distance)} = 0.52917 \text{ Å},$$
$$1 \text{ a.u. (energy)} = 27.211 \text{ eV},$$
$$1 \text{ eV} = 8065.73 \text{ Cm}^{-}.$$

B. Atomic Orbitals (AO's)

The choice of AO's from which MO's are constructed is an important factor in these calculations. It has been shown by Sahni and his co-worker (refs. 3 to 5) that optimized AO's should be used wherever such calculations are possible. The optimized AO's have been used by Sahni et al (refs. 3 to 5) for a number of states of CO and N_2 molecules. However, a preliminary examination shows that the restricted optimized set; that is, 1s, 2s, $2p_z$, $2p_x$ and $2p_y$ AO's which gave good computed values for R_e and other molecular constants for the states of CO and N_2, was not adequate (ref. 13) for the computation of the states of O_2 and NF. This is due to the fact that for a 16 electron system the variation of the eigenvectors becomes restricted as more MO's are occupied. Therefore, it becomes essential to extend the basis set of functions to include 3s and 3p AO's. As it is difficult to optimize such a large set on the IBM 7094 computer owing to the restriction of the computer memory, the only possibility was to compute the wave functions of all the four molecules with the following set of Slater (ref. 14) AO's,

$$
\begin{aligned}
1s &= (\alpha^3/\Pi)^{1/2} \exp(-\alpha r) , \\
2s &= (\beta^5/3\Pi)^{1/2} \exp(-\beta r) , \\
2p_z &= (\gamma^5/\Pi)^{1/2} \exp(-\gamma r) , \\
\left.\begin{matrix} 2p_x \\ 2p_y \end{matrix}\right\} &= \left(\gamma^5/\Pi\right)^{1/2} \exp(-\gamma r) \quad X \begin{cases} \sin\theta \cos\phi \\ \sin\theta \sin\phi \end{cases}
\end{aligned}
\tag{6}
$$

where α, β, γ are the usual Slater screening constants. For states of NF molecule the orbital exponent values for the 1s functions of Flourine and Nitrogen were taken as 8.6501 and 6.6652 respectively. The Z-axes centered on each atom lie along the internuclear axis, with positive Z-directions toward each other.

C. Symmetry Orbitals and Molecular Orbitals

The LCAO MO's of the homopolar N_2 and O_2 molecules belong in sets to the irreducible representations of the point group $D_{\infty h}$. To obtain proper symmetry for these MO's, symmetry orbitals (ref. 15) are introduced. The MO's of a given symmetry are then constructed from the basic symmetry orbitals of the same symmetry. The 10 MO's which can be constructed from the chosen basis fall into the six symmetry classes or species labelled as σ_g, σ_u, Π_u, Π_g, $\bar{\Pi}_u$ and $\bar{\Pi}_g$. Three MO's each belong to σ_g and σ_u and one each to the others.

The LCAO MO of the heteropolar CO and NF molecules belong in sets to the irreducible representation of the point group $C_{\infty v}$. The MO's are constructed from the AO's of the same symmetry. The 10 MO's that can be constructed from the 10 AO's fall into two symmetry groups labelled as σ and Π. Six MO's belong to the σ symmetry and two MO's each are of the Π_x or Π_y symmetry.

D. Electron Configurations

The electron configurations of the different states of N_2 and O_2 molecules considered in this paper, are given in Table II, and those of CO and the unknown NF molecules are given in Table III. The symbols + and - denote electrons with α spin and β spin, respectively. In these calculations a single antisymmetrical product (AP) function or electronic configuration is used for each state.

E. Eigenvalues (ϵ_i) and Eigenvectors (a_i)

All the integrals required in the evaluation of the matrix elements were calculated with the programs written for the IBM 7094 computer and were checked with the values calculated from the tables of integrals (refs. 16 to 19) computed by Sahni and Cooley. On inserting the necessary integrals the matrices $\underline{S}$ and $\underline{H}$ were determined. The elements of the matrices $\underline{J}$ and $\underline{K}$ involved undetermined coefficients a_i in addition to the integrals. The SCF procedure for calculating the a_i was performed in the usual manner (refs. 20 to 23). After the self-consistency was obtained, the ϵ_i^α and ϵ_i^β gave the energy values for the orbitals with α spin and β spin respectively and a_i gave the LCAO coefficients.

F. Total Energies

The total energies for the various states of the above four molecules were calculated by the expressions (refs. 3 and 4) given in Appendix A. The computed total energies of the states of N_2, CO and O_2 at various R are given in Tables IV to VI respectively. The total energies of the four states of the unknown molecule NF, considered in this paper, are given in Table VII for various R values. The calculated equilibrium distances for the states of three known molecules are given in Tables VIII to X along with the observed data and percentage error. The predicted equilibrium distances of the states of NF along with excitation and ionization energies are given in Table XI.

Table II

ELECTRON CONFIGURATION OF DIFFERENT STATES OF THE HOMOPOLAR N_2 AND O_2 MOLECULES

STATE	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\Pi_u$	$1\bar{\Pi}_u$	$1\Pi_g$	$1\bar{\Pi}_g$	$3\sigma_u$
N_2 (X $^1\Sigma_g^+$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -			
N_2 (A $^3\Sigma_u^+$)	+ -	+ -	+ -	+ -	+ -	+ -	+		+	
N_2 (B $^3\Pi_g$)	+ -	+ -	+ -	+ -	+	+ -	+ -	+		
N_2 (C $^3\Pi_u$)	+ -	+ -	+ -	+	+ -	+ -	+ -	+		
N_2^+ (X $^2\Sigma_g^+$)	+ -	+ -	+ -	+ -	+	+ -	+ -			
N_2^+ (B $^2\Sigma_u^+$)	+ -	+ -	+ -	+	+ -	+ -	+ -			
O_2 (X $^3\Sigma_g^-$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+	+	
O_2 (a $^1\Delta_g$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+ -		
O_2^+ (X $^2\Pi_g$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+		
O_2^+ (a $^4\Pi_u$)	+ -	+ -	+ -	+ -	+ -	+ -	+	+	+	

Table III

ELECTRON CONFIGURATION OF DIFFERENT STATES OF THE HETEROPOLAR CO AND OF THE UNKNOWN NF MOLECULE

STATE	1σ	2σ	3σ	4σ	5σ	1Π	$1\bar{\Pi}$	2Π	$2\bar{\Pi}$	6σ
CO (X $^1\Sigma$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -			
CO (a $^3\Pi$)	+ -	+ -	+ -	+ -	+	+ -	+ -	+		
CO (d $^3\Delta$)	+ -	+ -	+ -	+ -	+ -	+ -	+	+		
CO^+ (X $^2\Sigma^+$)	+ -	+ -	+ -	+ -	+	+ -	+ -			
CO^+ (A $^2\Pi^+$)	+ -	+ -	+ -	+ -	+ -	+ -	+			
CO^+ (B $^2\Sigma^+$)	+ -	+ -	+ -	+	+ -	+ -	+ -			
CO^+ (C $^2\Sigma^+$)	+ -	+ -	+	+ -	+ -	+ -	+ -			
NF (X $^3\Sigma$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+	+	
NF (a $^1\Delta$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+ -		
NF^+ (X $^2\Pi$)	+ -	+ -	+ -	+ -	+ -	+ -	+ -	+		
NF^+ (a $^4\Pi_u$)	+ -	+ -	+ -	+ -	+ -	+ -	+	+	+	

TABLE IV

TOTAL ENERGIES OF DIFFERENT STATES OF N_2 MOLECULE AT VARIOUS INTERNUCLEAR DISTANCES* WITH EXPONENT VALUES, $\alpha = 6.6675 \quad \beta = \gamma = 1.95$ FOR N ATOM

R	$N_2\ (X\ ^1\Sigma_g^+)$	$N_2\ (A\ ^3\Sigma_u^+)$	$N_2\ (B\ ^3\Pi_g)$	$N_2\ (C\ ^3\Pi_u)$	$N_2^+\ (X\ ^2\Sigma_g^+)$	$N_2^+\ (B\ ^2\Sigma_u^+)$
1.90	-108.50664330	-108.14582634	-108.17588425	-108.01993752	-107.93795967	-107.78673363
1.95	-108.53651524	-108.20601940	-108.22309208	-108.05690098	-107.97514248	-107.81339931
2.00	-108.55782509	-108.25635147	-108.26107407	-108.08470917	-108.00359535	-107.83136559
2.05	-108.57176781	-108.29803848	-108.29107285	-108.10457802	-108.02455139	-107.84182167
2.10	-108.57941532	-108.33224010	-108.31420422	-108.11762142	-108.03909779	-107.84589291
2.15	-108.58167553	-108.35986996	-108.33141232	-108.12478161	-108.04816914	-107.84448910
2.20	-108.57934761	-108.38181686	-108.34355545	-108.12689400	-108.05259895	-107.83843040
2.25	-108.57315159	-108.39881802	-108.35136890	-108.12469196	-108.05310917	-107.82843494
2.30	-108.56365585	-108.41148567	-108.35544968	-108.11878967	-108.05029297	-107.81511116
2.35	-108.55139446	-108.42039585	-108.35637760	-108.10974216	-108.04468250	-107.79898167
2.40	-108.53680134	-108.42603970	-108.35460949	-108.09802151	-108.03675747	-107.78052998
2.45	-108.52032661	-108.42888641	-108.35062021	-108.08408356	-108.02693748	-107.76018524
2.50	-108.50224304	-108.42924881	-108.34469891	-108.06823254	-108.01551723	-107.73824596
2.55	-108.48290920	-108.42751884	-108.33721066	-108.05084324	-108.00286388	-107.71506596
2.60	-108.46249199	-108.42391586	-108.32836246	-108.03211498	-107.98914433	-107.69085979
2.0675	-108.57510948	-108.31080437	-108.29988861	-108.10986519	-108.03031731	-107.84392548
2.4435	-108.52298260	-108.42868519	-108.35072613	-108.08627224	-108.02801609	-107.76351261
2.1699	-108.58127213	-108.36924934	-108.33681107	-108.12618828	-108.05045509	-107.84259796
2.2910	-108.56557846	-108.40950012	-108.35496712	-108.12010384	-108.05101776	-107.81772614
2.1094	-108.58020973	-108.33788681	-108.31785011	-108.11937714	-108.04117966	-107.84600639
2.0315	-108.56740284	-108.28355122	-108.28082180	-108.09807873	-108.01760006	-107.83875751

* The last six columns of this table give the computed total energies of the above states of N_2 at their observed equilibrium internuclear distances given in Table IX.

TABLE V

TOTAL ENERGIES OF DIFFERENT STATES OF CO MOLECULE AT VARIOUS INTERNUCLEAR DISTANCES WITH EXPONENT VALUES, $\alpha = 7.6528$, $\beta = \gamma = 2.275$ FOR O ATOM AND $\alpha = 5.6726$, $\beta = \gamma = 1.625$ FOR C ATOM

R	CO (X $^1\Sigma^+$)	CO (a $^3\Pi$)	CO (d $^3\Delta$)	CO$^+$ (X $^2\Sigma^+$)	CO$^+$ (A $^2\Pi^+$)	CO$^+$ (B $^2\Sigma^+$)	CO$^+$ (C $^2\Sigma^+$)
1.90		-111.97424603		-111.78087902		-111.42243862	
1.95	-112.29486847	-112.01778221	-111.89608574	-111.81227303		-111.45487213	
2.00	-112.31681442	-112.05291748	-111.94694138	-111.83583450		-111.47964859	-110.78995514
2.05	-112.33207321	-112.08070755	-111.99008560	-111.85273170		-111.49787331	-110.83036613
2.10	-112.34168434	-112.10238266	-112.02656937	-111.86396408	-111.78398895	-111.51057243	-110.86468315
2.15	-112.34640408	-112.11864948	-112.05714130	-111.87039852	-111.80711269	-111.51859188	-110.89357662
2.20	-112.34704590	-112.13039207	-112.08272362	-111.87287712	-111.82560539	-111.52266884	-110.91785812
2.25	-112.34418869	-112.13831711	-112.10388184	-111.87201118	-111.84011650	-111.52353287	-110.93803787
2.30	-112.33818436	-112.14287376	-112.12103271	-111.86835098	-111.85105324	-111.52169418	-110.95444298
2.35	-112.32978153	-112.14478207	-112.13495731	-111.86255360	-111.85912228	-111.51773167	-110.96789074
2.40	-112.31918526	-112.14426422	-112.14583397	-111.85496330	-111.86448479	-111.51213264	-110.97831154
2.45	-112.30690193	-112.14194870	-112.15419960	-111.84608841	-111.86773300	-111.50533485	-110.98631859
2.50	-112.29314895	-112.13806438	-112.16026592	-111.83613110	-111.86907482	-111.49762440	-110.99185658
2.55	-112.27814102	-112.13303375	-112.16435432	-111.82550240	-111.86875916	-111.48933601	-110.99520874
2.60	-112.26219940	-112.12682152	-112.16669083	-111.81435966	-111.86703491	-111.48070717	-110.99636650
2.65	-112.24554920	-112.11972904	-112.16752929	-111.80296421	-111.86421871	-111.47183132	-110.99544621
2.70	-112.22819042	-112.11221027	-112.16697788	-111.79129505	-111.86032772	-111.46261311	-110.99233150
2.75	-112.21033096		-112.16510201	-111.77958488	-111.85550777	-111.45306969	-110.98709869
2.80	-112.19238758		-112.16249371	-111.76816273	-111.85039997	-111.44330311	-110.98032475
2.85	-112.17424583		-112.15889549	-111.75688362	-111.84469986	-111.43299675	-110.97213364

TABLE VI

TOTAL ENERGIES OF DIFFERENT STATES OF O_2 MOLECULE AT VARIOUS R^* WITH EXPONENT VALUES, $\alpha = 7.6528$, $\beta = \gamma \doteq 2.275$ FOR O ATOM

R	O_2 $(X\ ^3\Sigma_g^-)$	O_2 $(a\ ^1\Delta_g)$	O_2 $(X\ ^2\Pi_g)$	O_2 $(a\ ^4\Pi_u)$
2.00	-149.02007866	-148.93554115	-148.66397476	-148.48109627
2.05	-149.04732704	-148.96336937	-148.68243599	-148.53122520
2.10	-149.06742668	-148.98403314	-148.69430542	-148.57303238
2.15	-149.08137894	-148.99849701	-148.70056343	-148.60758781
2.20	-149.09014702	-149.00779533	-148.70213509	-148.63587379
2.25	-149.09440804	-149.01255989	-148.69966125	-148.65863800
2.30	-149.09491158	-149.01353455	-148.69385719	-148.67663765
2.35	-149.09214592	-149.01122856	-148.68519783	-148.69046211
2.40	-149.08661842	-149.00615120	-148.67414665	-148.70061684
2.45	-149.07877731	-148.99873161	-148.66114235	-148.70763397
2.50	-149.06890488	-148.98927879	-148.64645576	-148.71180344
2.55	-149.05746460	-148.97822571	-148.63051987	-148.71364784
2.60	-149.04456902	-148.96571732	-148.61343002	-148.71332932
2.65	-149.03048897	-148.95200157	-148.59544945	-148.71114159
2.70	-149.01558113	-148.93743706	-148.57689476	-148.70748901
2.28170	-149.09510422	-149.01355362	-148.69631004	-148.67054176
2.29705	-149.09498596	-149.01357651	-148.69429779	-148.67571831
2.12163	-149.07416344	-148.99098587	-148.69765663	-148.58880615
2.61025	-149.04183960	-148.96305084	-148.60987091	-148.71307755

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* The last four columns give the total energies of the states of O_2 at their equilibrium internuclear distance given in Table X.

TABLE VII

TOTAL ENERGIES OF DIFFERENT STATES OF NF AT VARIOUS R WITH EXPONENT VALUES' $\alpha = 8.6501$, $\beta = \gamma = 2.6$ FOR F ATOM AND $\alpha = 6.6652$, $\beta = \gamma = 1.95$ FOR N ATOM

INTERNUCLEAR DISTANCE (R) (ATOMIC UNITS)	TOTAL ENERGIES (ATOMIC UNITS)			
	NF $X^3\Sigma$	NF $^1\Delta$	NF^+ $^2\Pi$	NF^+ $^4\Pi$
2.00	-153.0760	-152.9849	-152.7468	-152.4587
2.20	-153.1754	-153.0842	-152.8141	-152.6454
2.25	-153.1877	-153.0965	-152.8194	-152.6773
2.30	-153.1963	-153.1051	-152.8214	-152.7048
2.35	-153.2011	-153.1101	-152.8197	-152.7282
2.40	-153.2044	-153.1135	-152.8175	-152.7484
2.45	-153.2046	-153.1138	-152.8121	-152.7653
2.50	-153.2026	-153.1120	-152.8049	-152.7793
2.55	-153.1991	-153.1087	-152.7965	-152.7911
2.60	-153.1939	-153.1039	-152.7866	-152.8007
2.80	-153.1619	-153.0740		-152.8224
2.85	-153.1508	-153.0638		-152.8235
2.90	-153.1398	-153.0538		-152.8248
2.95		-153.0432		-152.8242
3.00		-153.0329		-152.8235

TABLE VIII

EQUILIBRIUM DISTANCES (Re) OF THE VARIOUS ELECTRONIC STATES OF N_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	PERCENTAGE ERROR
N_2 X $^1\Sigma_g^+$	2.15	2.0675	3.99°/o
A $^3\Sigma_u^+$	2.48	2.4435	1.49°/o
C $^3\Pi_u$	2.20	2.1699	1.39°/o
B $^3\Pi_g$	2.34	2.2910	2.14°/o
N_2^+ X $^2\Sigma_g^+$	2.23	2.1094	5.72°/o
B $^2\Sigma_u^+$	2.11	2.0315	3.86°/o

TABLE IX

EQUILIBRIUM DISTANCES OF THE VARIOUS ELECTRONIC STATES OF CO MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	PERCENTAGE ERROR
CO X $^1\Sigma^+$	2.18	2.132	2.25°/o
a $^3\Pi$	2.365	2.2853	3.49°/o
d $^3\Delta$	2.65	2.5888	2.36°/o
CO^+ X $^2\Sigma^+$	2.21	2.1072	4.87°/o
A $^2\Pi_i^+$	2.51	2.3502	6.79°/o
B $^2\Sigma^+$	2.24	2.2085	1.42°/o
C $^2\Sigma^+$	2.60	—	—

TABLE X

EQUILIBRIUM DISTANCES OF THE VARIOUS STATES OF O_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	PERCENTAGE ERROR
O_2 X $^3\Sigma_g^-$	2.28	2.28170	—
a $^1\Delta_g$	2.29	2.29705	—
O_2^+ X $^2\Pi_g$	2.19	2.1216	3.22°/o
a $^4\Pi_u$	2.57	2.6103	1.54°/o

TABLE XI

PREDICTED EQUILIBRIUM DISTANCES OF THE VARIOUS STATES OF NF MOLECULE ALONG WITH PREDICTED IONIZATION AND EXCITATION ENERGIES

STATE*	CALCULATED EQUILIBRIUM DISTANCES (a.u.)	VERTICAL IONIZATION AND EXCITATION ENERGIES (eV)
NF $^3\Sigma$	2.44	—
$^1\Delta$	2.43	2.47
NF^+ $^2\Pi$	2.30	10.65
$^4\Pi$	2.89	12.04

* The electronic configuration, equilibrium distances of NF (X $^3\Sigma$) (ground state of NF) NF($^1\Delta$)(excited states of NF) have been confirmed later on by experimental results within the predicted accuracy of above theoretical calculations.

DISCUSSION

The results of this study of the different states of the NF molecule show beyond doubt the value of the SCF LCAO MO method in dealing with both the closed and open shells states of molecules. It has been shown by Sahni and his workers (refs. 2 to 4) that wherever possible optimized AO's should be used in these calculations. However, as the number of calculations were extended to HF and NF molecules it was found (ref. 13) that the restricted set of orbitals; that is, 1s, 2s and 2p functions, was not sufficient to deal with these molecules. This is due to the fact that the Flourine atom of NF having nine electrons nearly completes the second shell and, therefore, restricts the variation of the a_i coefficients. For any exact treatment of molecules such as NF one needs to introduce the 3s and 3p orbitals. Such an effort is being made on N_2, FH and NF molecules but the computation is very tedious and slow on the IBM 7094 computer due to the limited memory and speed of the machine. At present the IBM 7094 programs are being converted to the IBM 360-70 system of the Institute for Space Studies, 2880 Broadway, New York, New York and it is hoped that it will be possible to compute the states of the above molecules with the enlarged optimized set of orbitals including 3s and 3p AO's. It was the computer limitation due to which the author has thought it best to use Slater AO's for the states of N_2, CO, O_2 and NF molecules to compare the computed results with the available experimental data. These calculations have shown that SCF LCAO MO method can accurately predict the stability of a state of a molecule and R_e value within 96-98°/o accuracy and the ionization and excitation energies within 90°/o accuracy if the values are higher than 10 eV. Usually the error in ionization and excitation energies is one eV if the experimental value of ionization or excitation energy is less than 5 eV.

COMMENTS

For the above calculations we have used a limited set of non-optimized basis functions. For more exact computation one needs to use an extended set of optimized basis functions. Moreover we have only used a single determinant wave function. It has been shown by Coulson and Fischer (ref. 24) that for large separation of the nuclei the MO wave function does not describe the separate atoms in their ground, ionized or excited state. Therefore, one needs to use more than one determinant (configuration interaction) for calculating molecular wave functions of NF beyond 3R. The author is at present extending the above calculation to include 3s and 3p functions, in addition to 1s, 2s and 2p functions, and configuration interaction treatment. All the AO's are also being optimized at each R value to obtain the potential energy curves of the different states.

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APPENDIX (A)

The total energy of an electronic state of a diatomic molecule is given as

$$E_{el} = \sum_{i}^{\alpha+\beta} \underline{H}_i + \frac{1}{2} \sum_{i}^{\alpha+\beta} \sum_{j}^{\alpha+\beta} \underline{J}_{ij} - \frac{1}{2} \left(\sum_{i,j}^{\alpha} + \sum_{i,j}^{\beta} \right) \underline{K}_{ij} \qquad (7)$$

where α and β denote the number of electrons with α and β spins.

The eigenvalues ϵ_i are given by the expression

$$\epsilon_i^{\alpha(\beta)} = \underline{H}_i^{\alpha(\beta)} + \sum_{j}^{\alpha+\beta} \underline{J}_{ij} - \sum_{j}^{\alpha(\beta)} \underline{K}_{ij} \; . \qquad (8)$$

Using equation (8) we can reduce equation (7) to equation (9)

$$E_{el} = \frac{1}{2} \sum_{i}^{\alpha} (\epsilon_i^{\alpha} + \underline{H}_i^{\alpha}) + \frac{1}{2} \sum_{i}^{\beta} (\epsilon_i^{\beta} + \underline{H}_i^{\beta}) \qquad (9)$$

where

$$\underline{H}_i^{\alpha} = a_i^{\alpha *} \, \underline{Ha}_i^{\alpha} \; ; \quad \underline{H}_i^{\beta} = a_i^{\beta *} \, \underline{Ha}_i^{\beta} \; . \qquad (10)$$

For a closed shell equation (7) reduces to

$$E_{el} = \sum_{i}^{\alpha} (\epsilon_i^{\alpha} + \underline{H}_i^{\alpha}) = \sum_{i}^{\beta} (\epsilon_i^{\beta} + \underline{H}_i^{\beta}) \; . \qquad (11)$$

The total potential energy of the electronic state of the molecule is obtained by adding the nuclear repulsion term $\frac{Z_a Z_b}{r_{ab}}$ to the expressions (7) or (11). Here Z_a and Z_b represent the charges of the nuclei a and b respectively and r_{ab} is the internuclear distance

APPENDIX (B)

SYMBOLS

R	internuclear distance
R_e	equilibrium internuclear distance
SCF	self-consistent field
ϕ_i	molecular orbitals
χ_i	atomic orbitals
a_i	undetermined coefficients
$\underline{S}$, $\underline{H}$, $\underline{J}$ and $\underline{K}$	overlap, bare-nuclear Hamiltonian, Coulomb and Exchange matrices
ϵ_i	energy of ith electron
$X\ {}^3\Sigma$	ground state of NF
${}^1\Delta$	excited state of NF
${}^2\Pi$, ${}^4\Pi$	ionized states of NF
1σ, 2σ, 3σ, 4σ, 5σ	molecular orbitals of σ symmetry
Π_x, Π_y, Π_x^*, Π_y^*	molecular orbitals of Π symmetry
$F^{\alpha(\beta)}$	matrices defined by equation (4)
n_α	n electrons with α spin
n_β	n electrons with β spin
a_i^α	undetermined coefficients for orbitals with α spin
a_i^β	undetermined coefficients for orbitals with β spin
S^2	square of spin operator
S_z	component of spin operator along the Z direction

a.u.	atomic units
eV	electron volt
Å	armstrong unit
AO	abbreviation for atomic orbitals
1s, 2s, 2p, 3s, 3p	atomic orbitals
α, β, γ	Slater screening constants
LCAO-MO	linear combination of atomic orbitals-molecular orbitals
$D_{\infty h}$	point group
σ_g, σ_u, Π_u, Π_g, $\bar{\Pi}_u$, $\bar{\Pi}_g$	symmetry orbitals
$C_{\infty v}$	point group
σ and Π	molecular orbitals of σ and Π symmetries
$X\ {}^1\Sigma_g$	ground state of N_2
$a\ {}^3\Sigma_u^+$, $B\ {}^3\Pi_g^+$, $C\ {}^3\Pi_u^+$	excited state of N_2
$X\ {}^1\Sigma^+$	ground state of CO
$X\ {}^1\Sigma^+$, $a\ {}^3\Pi$, $d\,{}^3\Delta$	excited states of CO
$X\ {}^2\Sigma^+$, $A\ {}^2\Pi^+$, $B\ {}^2\Sigma^+$, $C\ {}^2\Sigma^+$	ionized states of CO
$X\ {}^3\Sigma_g^-$	ground state of O_2
$a\ {}^1\Delta_g$	excited state of O_2
$X\ {}^2\Pi_g$, $a\ {}^4\Pi_u$	ionized states of O_2
a_i^*	Hermitian conjugate of the vector a_i

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