

## Electronic Structure of Nitric Oxide and Nitric Oxide Ion

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The wave functions of the ground state and several low excited states of NO and NO<sup>+</sup> (<sup>2</sup>*Π*, <sup>4</sup>*Π*, <sup>4</sup>*Σ*<sup>-</sup>, <sup>2</sup>*A*, <sup>2</sup>*Σ*<sup>+</sup>, <sup>2</sup>*Σ*<sup>-</sup>, <sup>4</sup>*A*, and <sup>4</sup>*Σ*<sup>+</sup> states for NO, and <sup>1</sup>*Σ*<sup>+</sup>, <sup>1</sup>*Σ*<sup>-</sup>, <sup>3</sup>*Σ*<sup>+</sup>, <sup>3</sup>*A*, <sup>3</sup>*Σ*<sup>-</sup>, <sup>1</sup>*A*, <sup>3</sup>*Π*, and <sup>1</sup>*Π* states for NO<sup>+</sup>) are calculated non-empirically at nuclear distance 1.15 Å by LCAO SCF MO CI method, where all fifteen and fourteen electrons are considered and Slater type 1s, 2s, and 2p atomic orbitals are used. By using the wave functions obtained, dissociation energies, excitation energies, dipole moments, gradients of the electric field at nitrogen nucleus, oscillator strengths, and spin-orbit coupling constants are calculated.

### 1. Introduction

The free radical nitric oxide is a particularly interesting diatomic molecule to study in detail, since this molecule is a heteropolar one with a non-closed shell configuration.

In the previous paper,<sup>1)</sup> we calculated the self-consistent-field molecular orbitals for nitric oxide in the linear-combination-of-atomic-orbitals molecular orbital approximation using 1s, 2s, and 2p Slater atomic orbitals. Three different calculations were made. (1) An incomplete treatment in which mixing of the inner 1s orbitals to the outer orthogonalized 2s and 2p orbitals was neglected. (2) A similar calculation, but here the outer orbitals were forced to be orthogonal to the inner orbitals. (3) The complete treatment in which all the orbitals were the linear combinations of 1s, 2s, and 2p orbitals. The single Slater determinant wave function built from the orbitals calculated from the complete treatment gave a negative dissociation energy, and a limited configuration interaction calculation accounted for 26% of the observed dissociation energy. The agreement between the calculated and observed first ionization potential was very good. Certain aspects of the uv spectra were reasonably well explained from this calculation. The dipole moment

was calculated to be 0.27D (N-O<sup>+</sup>) as compared to an observed value of 0.16 D with undetermined sign.

In order to obtain more accurate wave functions, full configuration interaction calculations are carried out in this paper not only for the ground state but also for the several lower excited states of the nitric oxide molecule and the nitric oxide ion.

By using the wave functions here obtained, dissociation energies, excitation energies, dipole moments, spin-orbit coupling constants, oscillator strengths, and gradients of the electric field at nitrogen nucleus are calculated and reported in this paper.

## 2. Construction of Wave Functions

All the integral values over atomic orbitals, upon which the results of the present configuration interaction studies are based, are collected in reference 1. Conversions from integral values over atomic orbitals to over molecular orbitals was performed by Hijikata's program and IBM 650.

The present calculations are carried out by making use of SCF molecular orbitals consisting of 1s, 2s, and 2p type atomic orbitals, which were reported in the previous paper<sup>1</sup>). They are :

1σ	-0.0008	1s <sub>N</sub>	+1.0004	1s <sub>0</sub>	-0.0054	2s <sub>N</sub>	+0.0178	2s <sub>0</sub>	-0.0048	2pσ <sub>N</sub>	+0.0046	2pσ <sub>0</sub>
2σ	1.0002	1s <sub>N</sub>	-0.0010	1s <sub>0</sub>	+0.0164	2s <sub>N</sub>	-0.0050	2s <sub>0</sub>	+0.0048	2pσ <sub>N</sub>	-0.0028	2pσ <sub>0</sub>
3σ	-0.0432	1s <sub>N</sub>	-0.0352	1s <sub>0</sub>	+0.3583	2s <sub>N</sub>	+0.6836	2s <sub>0</sub>	+0.1665	2pσ <sub>N</sub>	+0.1944	2pσ <sub>0</sub>
4σ	-0.0020	1s <sub>N</sub>	-0.0215	1s <sub>0</sub>	+0.7978	2s <sub>N</sub>	-0.7259	2s <sub>0</sub>	-0.0147	2pσ <sub>N</sub>	+0.2995	2pσ <sub>0</sub>
5σ	0.0217	1s <sub>N</sub>	+0.0192	1s <sub>0</sub>	+0.4727	2s <sub>N</sub>	+0.2368	2s <sub>0</sub>	-0.6149	2pσ <sub>N</sub>	-0.5794	2pσ <sub>0</sub>
6σ	0.0799	1s <sub>N</sub>	-0.0906	1s <sub>0</sub>	+0.7382	2s <sub>N</sub>	-0.7703	2s <sub>0</sub>	+1.0899	2pσ <sub>N</sub>	-1.0092	2pσ <sub>0</sub>
1π	0.5232	2pπ <sub>N</sub>	+0.7508	2pπ <sub>0</sub>								
2π	0.8781	2pπ <sub>N</sub>	-0.6936	2pπ <sub>0</sub>								

where

$$1s = (Z_1^3 / \pi)^{1/2} \exp(-Z_1 r),$$

$$2s^* = (Z_2^5 / 3\pi)^{1/2} r \exp(-Z_2 r), \quad 2s = N(2s^* - C 1s),$$

$$\left. \begin{array}{l} 2p\sigma \\ 2p\pi^+ \\ 2p\pi^- \end{array} \right\} = (Z_2^5 / \pi)^{1/2} r \exp(-Z_2 r) \left\{ \begin{array}{l} \cos \theta \\ (1/\sqrt{2}) \sin \theta \exp(+i\varphi) \\ (1/\sqrt{2}) \sin \theta \exp(-i\varphi) \end{array} \right.$$

The parameters  $Z$ 's are given by Slater's rule and

$$Z_{1N} = 6.7, \quad Z_{2N} = 1.95, \quad Z_{10} = 7.7, \quad \text{and} \quad Z_{20} = 2.275.$$

The parameters  $N$  and  $C$  are chosen such that the orbital 2s is normalized and orthogonal to the corresponding inner 1s orbital.

Since the Hamiltonian of our problem has  $C_{\infty v}$  symmetry, its wave functions are the bases of an irreducible representation of  $C_{\infty v}$  group and are classified by the quantum numbers  $\Lambda$  and  $v$ .  $\Lambda$  is the component of the orbital angular momen-

tum of the electron along the internuclear axis.  $v$  is the character of the reflection at any plane passing through both nuclei (for the case of  $A=0$ ). Moreover, since the Hamiltonian is free from spin operators, the total spin quantum number  $S$  and its component along a fixed axis  $M$  are good quantum numbers. Therefore the wave functions of our problem have the symmetry character specified by  $A$ ,  $v$ ,  $S$ , and  $M$ .

In the case of NO molecule we must assign fifteen electrons to the ten SCF MO's each of which can accommodate at most two electrons. Therefore the number of orbitals which accommodate only one electron is at most five. These orbitals we call the *unpaired orbitals*. In the case of NO<sup>+</sup> ion the number of unpaired orbitals is at most six. Therefore our present problem is the so-called five-electrons and six-electrons problems.

We define the spin functions  $\theta_{S, M, k}^N$  with the following form :

I  $\theta_{S, M, k}^N$  for NO doublet ( $S = \frac{1}{2}$ ,  $M = \frac{1}{2}$ )

1. One unpaired orbital ( $N=1$ ,  $S=M=\frac{1}{2}$ )

$$\theta_{\frac{1}{2}, \frac{1}{2}}^1 = \alpha(1)$$

2. Three unpaired orbitals ( $N=3$ ,  $S=M=\frac{1}{2}$ )

$$\theta_{\frac{1}{2}, \frac{1}{2}, 1}^3 = \frac{1}{\sqrt{2}}[\alpha(1)\alpha(2)\beta(3) - \alpha\beta\alpha]$$

$$\theta_{\frac{1}{2}, \frac{1}{2}, 2}^3 = \frac{1}{\sqrt{6}}[2\beta(1)\alpha(2)\alpha(3) - \alpha\alpha\beta - \alpha\beta\alpha]$$

3. Five unpaired orbitals ( $N=5$ ,  $S=M=\frac{1}{2}$ )

$$\theta_{\frac{1}{2}, \frac{1}{2}, 1}^5 = \frac{1}{2}[\alpha(1)\alpha(2)\beta(3)\alpha(4)\beta(5) - \alpha\alpha\beta\beta\alpha - \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha]$$

$$\theta_{\frac{1}{2}, \frac{1}{2}, 2}^5 = \frac{1}{\sqrt{12}}[-\alpha(1)\alpha(2)\beta(3)\alpha(4)\beta(5) - \alpha\beta\alpha\alpha\beta + \alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\beta\alpha + 2\beta\alpha\alpha\alpha\beta - 2\beta\alpha\alpha\beta\alpha]$$

$$\theta_{\frac{1}{2}, \frac{1}{2}, 3}^5 = \frac{1}{\sqrt{12}}[-2\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5) + \alpha\alpha\beta\alpha\beta + \alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha - 2\alpha\beta\beta\alpha\alpha]$$

$$\theta_{\frac{1}{2}, \frac{1}{2}, 4}^5 = \frac{1}{6}[-2\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5) - \alpha\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha + \alpha\alpha\beta\alpha\beta + \alpha\alpha\beta\beta\alpha + 2\alpha\beta\beta\alpha\alpha + 2\beta\alpha\alpha\alpha\beta + 2\beta\alpha\alpha\beta\alpha - 4\beta\alpha\beta\alpha\alpha]$$

$$\theta_{\frac{1}{2}, \frac{1}{2}, 5}^5 = \frac{1}{\sqrt{18}}[-\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5) - \alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha + \beta\alpha\alpha\alpha\beta + \beta\alpha\alpha\beta\alpha + \beta\alpha\beta\alpha\alpha - 3\beta\beta\alpha\alpha\alpha]$$

II  $\theta_{S, M, k}^N$  for NO quartet ( $S=3/2$ ,  $M=3/2$ )

1. Three unpaired orbitals ( $N=3$ ,  $S=M=\frac{3}{2}$ )  $\theta_{\frac{3}{2}, \frac{3}{2}}^3 = \alpha(1)\alpha(2)\alpha(3)$

2. Five unpaired orbitals ( $N=5$ ,  $S=M=\frac{3}{2}$ )

$$\Theta_{\frac{3}{2}, \frac{3}{2}, 1}^5 = \frac{1}{\sqrt{2}} [\alpha(1)\alpha(2)\alpha(3)\alpha(4)\beta(5) - \alpha\alpha\alpha\beta\alpha]$$

$$\Theta_{\frac{3}{2}, \frac{3}{2}, 2}^5 = \frac{1}{\sqrt{6}} [\alpha(1)\alpha(2)\alpha(3)\alpha(4)\beta(5) + \alpha\alpha\alpha\beta\alpha - 2\alpha\alpha\beta\alpha\alpha]$$

$$\Theta_{\frac{3}{2}, \frac{3}{2}, 3}^5 = \frac{1}{\sqrt{12}} [\alpha(1)\alpha(2)\alpha(3)\alpha(4)\beta(5) + \alpha\alpha\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha - 3\alpha\beta\alpha\alpha\alpha]$$

$$\Theta_{\frac{3}{2}, \frac{3}{2}, 4}^5 = \frac{1}{\sqrt{20}} [\alpha(1)\alpha(2)\alpha(3)\alpha(4)\beta(5) + \alpha\alpha\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha + \alpha\beta\alpha\alpha\alpha - 4\beta\alpha\alpha\alpha\alpha]$$

### III $\Theta_{S, M, k}^N$ for $\text{NO}^+$ singlet ( $S=0, M=0$ )

1. Two unpaired orbitals ( $N=2, S=M=0$ )  $\Theta_{0,0}^2 = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta\alpha]$

2. Four unpaired orbitals ( $N=4, S=M=0$ )

$$\Theta_{0,0,1}^4 = \frac{1}{2} [\alpha(1)\beta(2)\alpha(3)\beta(4) + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha]$$

$$\Theta_{0,0,2}^4 = \frac{1}{\sqrt{12}} [2\alpha(1)\alpha(2)\beta(3)\beta(4) + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\alpha\beta - \beta\alpha\beta\alpha - \alpha\beta\beta\alpha]$$

3. Six unpaired orbitals ( $N=6, S=M=0$ )

$$\Theta_{0,0,1}^6 = \frac{1}{\sqrt{8}} [\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) + \beta\alpha\beta\alpha\alpha\beta + \beta\alpha\alpha\beta\beta\alpha + \alpha\beta\beta\alpha\beta\alpha - \beta\alpha\beta\alpha\beta\alpha - \alpha\beta\alpha\beta\beta\alpha - \alpha\beta\beta\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha\beta]$$

$$\Theta_{0,0,2}^6 = \frac{1}{\sqrt{24}} [2\alpha(1)\alpha(2)\beta(3)\beta(4)\alpha(5)\beta(6) + 2\beta\beta\alpha\alpha\alpha\beta - \beta\alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\beta\alpha\beta - \beta\alpha\beta\alpha\alpha\beta - \alpha\beta\beta\alpha\alpha\beta + \alpha\beta\beta\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha + \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\alpha\beta\beta\alpha - 2\beta\beta\alpha\alpha\beta\alpha - 2\alpha\alpha\beta\beta\beta\alpha]$$

$$\Theta_{0,0,3}^6 = \frac{1}{6} [3\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5)\beta(6) - \beta\alpha\alpha\alpha\beta\beta - \alpha\beta\alpha\alpha\beta\beta - \alpha\alpha\beta\alpha\beta\beta - \beta\alpha\alpha\beta\alpha\beta - \alpha\beta\alpha\beta\beta\beta - \alpha\alpha\beta\beta\beta\alpha + \alpha\beta\beta\beta\alpha\alpha + \beta\alpha\beta\beta\alpha\alpha + \alpha\beta\beta\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha + \beta\beta\alpha\alpha\beta\alpha + \alpha\beta\beta\alpha\alpha\beta + \beta\alpha\beta\alpha\alpha\beta - 3\beta\beta\beta\alpha\alpha\alpha]$$

$$\Theta_{0,0,4}^6 = \frac{1}{\sqrt{72}} [4\alpha(1)\alpha(2)\beta(3)\alpha(4)\beta(5)\beta(6) - 2\beta\alpha\alpha\alpha\beta\beta - 2\alpha\beta\alpha\alpha\beta\beta - 2\alpha\alpha\beta\beta\alpha\beta - 2\alpha\alpha\beta\beta\beta\alpha - \beta\alpha\beta\alpha\alpha\beta - \alpha\beta\beta\alpha\alpha\beta - \beta\alpha\beta\alpha\beta\alpha - \alpha\beta\beta\alpha\beta\alpha + \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\beta\alpha\beta + 2\alpha\beta\beta\beta\alpha\alpha + 2\beta\alpha\beta\beta\alpha\alpha + 2\beta\beta\alpha\alpha\beta\alpha + 2\beta\beta\alpha\alpha\alpha\beta - 4\beta\beta\alpha\beta\alpha\alpha]$$

$$\Theta_{0,0,5}^6 = \frac{1}{\sqrt{24}} [2\alpha(1)\beta(2)\alpha(3)\alpha(4)\beta(5)\beta(6) + 2\alpha\beta\beta\beta\alpha\alpha - \alpha\beta\beta\alpha\alpha\beta - \alpha\beta\alpha\beta\alpha\beta - \alpha\beta\beta\alpha\beta\alpha - \alpha\beta\alpha\beta\beta\alpha + \beta\alpha\alpha\beta\beta\alpha + \beta\alpha\beta\alpha\beta\alpha + \beta\alpha\beta\alpha\beta\alpha - 2\beta\alpha\beta\beta\alpha\alpha - 2\beta\alpha\alpha\alpha\beta\beta]$$

### IV $\Theta_{S, M, k}^N$ for $\text{NO}^+$ triplet ( $S=1, M=1$ )

1. Two unpaired orbitals ( $N=2, S=M=1$ )  $\Theta_{1,1}^2 = \alpha(1)\alpha(2)$

2. Four unpaired orbitals ( $N=4, S=M=1$ )

$$\Theta_{1,1,1}^4 = \frac{1}{\sqrt{2}} [\alpha(1)\alpha(2)\alpha(3)\beta(4) - \alpha\alpha\beta\alpha]$$

$$\Theta_{1,1,2}^4 = \frac{1}{\sqrt{6}} [-2\alpha(1)\beta(2)\alpha(3)\alpha(4) + \alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha]$$

$$\Theta_{1,1,3}^4 = \frac{1}{\sqrt{12}} [-3\beta(1)\alpha(2)\alpha(3)\alpha(4) + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta + \alpha\beta\alpha\alpha]$$

3. Six unpaired orbitals ( $N=6$ ,  $S=M=1$ )

$$\Theta_{1,1,1}^6 = \frac{1}{2} [\alpha(1)\alpha(2)\beta(3)\alpha(4)\beta(5)\alpha(6) + \alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\alpha\beta - \alpha\alpha\beta\beta\alpha]$$

$$\Theta_{1,1,2}^6 = \frac{1}{\sqrt{12}} [2\alpha(1)\beta(2)\alpha(3)\alpha(4)\beta(5)\alpha(6) - 2\alpha\beta\alpha\alpha\beta - \alpha\alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha\beta + \alpha\alpha\alpha\beta\alpha\beta]$$

$$\Theta_{1,1,3}^6 = \frac{1}{\sqrt{24}} [3\beta(1)\alpha(2)\alpha(3)\alpha(4)\beta(5)\alpha(6) - 3\beta\alpha\alpha\alpha\beta - \alpha\alpha\alpha\beta\beta\alpha - \alpha\alpha\beta\alpha\beta\alpha - \alpha\beta\alpha\alpha\beta\alpha + \alpha\alpha\beta\alpha\alpha\beta + \alpha\alpha\alpha\beta\alpha\beta + \alpha\beta\alpha\alpha\alpha\beta]$$

$$\Theta_{1,1,4}^6 = \frac{1}{\sqrt{240}} [12\beta(1)\beta(2)\alpha(3)\alpha(4)\alpha(5)\alpha(6) - 3\beta\alpha\alpha\alpha\beta - 3\beta\alpha\alpha\alpha\beta\alpha - 3\beta\alpha\alpha\beta\alpha\alpha - 3\beta\alpha\beta\alpha\alpha\alpha - 3\alpha\beta\alpha\alpha\alpha\beta - 3\alpha\beta\alpha\alpha\beta\alpha - 3\alpha\beta\alpha\beta\alpha\alpha - 3\alpha\beta\beta\alpha\alpha\alpha + 2\alpha\alpha\beta\beta\alpha\alpha + 2\alpha\alpha\beta\alpha\beta\alpha + 2\alpha\alpha\alpha\beta\beta\alpha + 2\alpha\alpha\alpha\alpha\beta\beta + 2\alpha\alpha\alpha\beta\alpha\beta + 2\alpha\alpha\beta\alpha\alpha\beta]$$

$$\Theta_{1,1,5}^6 = \frac{1}{12} [9\beta(1)\alpha(2)\beta(3)\alpha(4)\alpha(5)\alpha(6) - 3\beta\alpha\alpha\alpha\beta - 3\beta\alpha\alpha\alpha\beta\alpha - 3\beta\alpha\alpha\beta\alpha\alpha - 3\alpha\beta\beta\alpha\alpha\alpha - 2\alpha\alpha\beta\alpha\alpha\beta - 2\alpha\alpha\beta\alpha\beta\alpha - 2\alpha\alpha\beta\beta\alpha\alpha + 2\alpha\alpha\alpha\alpha\beta\beta + 2\alpha\alpha\alpha\beta\alpha\beta + 2\alpha\alpha\alpha\beta\beta\alpha + \alpha\beta\alpha\alpha\alpha\beta + \alpha\beta\alpha\alpha\beta\alpha + \alpha\beta\alpha\beta\alpha\alpha]$$

$$\Theta_{1,1,6}^6 = \frac{1}{\sqrt{72}} [6\beta(1)\alpha(2)\alpha(3)\beta(4)\alpha(5)\alpha(6) - 3\beta\alpha\alpha\alpha\beta - 3\beta\alpha\alpha\alpha\beta\alpha - 2\alpha\alpha\beta\beta\alpha\alpha - 2\alpha\beta\alpha\beta\alpha\alpha - \alpha\alpha\alpha\beta\alpha\beta - \alpha\alpha\alpha\beta\beta\alpha + 2\alpha\alpha\alpha\alpha\beta\beta + \alpha\alpha\beta\alpha\alpha\beta + \alpha\beta\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha\beta\alpha + \alpha\beta\alpha\alpha\beta\alpha]$$

$$\Theta_{1,1,7}^6 = \frac{1}{\sqrt{18}} [3\alpha(1)\beta(2)\beta(3)\alpha(4)\alpha(5)\alpha(6) - \alpha\beta\alpha\alpha\alpha\beta - \alpha\beta\alpha\alpha\beta\alpha - \alpha\beta\alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha - \alpha\alpha\beta\beta\alpha\alpha + \alpha\alpha\alpha\beta\beta\alpha + \alpha\alpha\alpha\alpha\beta\beta + \alpha\alpha\alpha\beta\alpha\beta]$$

$$\Theta_{1,1,8}^6 = \frac{1}{6} [4\alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\alpha(6) - 2\alpha\beta\alpha\alpha\alpha\beta - 2\alpha\beta\alpha\alpha\beta\alpha - 2\alpha\alpha\beta\beta\alpha\alpha - \alpha\alpha\alpha\beta\alpha\beta - \alpha\alpha\alpha\beta\beta\alpha + \alpha\alpha\beta\alpha\alpha\beta + \alpha\alpha\beta\alpha\beta\alpha + 2\alpha\alpha\alpha\alpha\beta\beta]$$

$$\Theta_{1,1,9}^6 = \frac{1}{\sqrt{12}} [2\alpha(1)\alpha(2)\beta(3)\beta(4)\alpha(5)\alpha(6) - \alpha\alpha\beta\alpha\alpha\beta - \alpha\alpha\beta\alpha\beta\alpha - \alpha\alpha\alpha\beta\alpha\beta - \alpha\alpha\alpha\beta\beta\alpha + 2\alpha\alpha\alpha\alpha\beta\beta]$$

In these formulas the  $i$ -th spin orbital, if numbered from left to right, accommodates the  $i$ -th electron.

Configurations used in the present CI calculations for various symmetry states of the nitric oxide molecule and the nitric oxide ion are collected in Tables I~VI.

TABLE I  
Configurations Used in CI Calculation for  ${}^2\Pi$  and  ${}^4\Pi$  States of NO

Doublet	Quartet	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma$	$3\sigma$	$2\sigma$	$1\sigma$
0			1	2	2		2	2	2	2	2
1			2	2	1		2	2	2	2	2
$2_{1,2}$	2	1	1	1	2		2	2	2	2	2
3		2	1		2		2	2	2	2	2
$4_{1,2}$	4	1	2	1	1		2	2	2	2	2
5		2	2		1		2	2	2	2	2
$6_{1,2}$	6		1	2	2	1	1	2	2	2	2
$7_{1,2}$	7		2	2	1	1	1	2	2	2	2
$8_{1,2,3,4,5}$	$8_{1,2,3,4}$	1	1	1	2	1	1	2	2	2	2
$9_{1,2}$	9	2	1		2	1	1	2	2	2	2
$10_{1,2,3,4,5}$	$10_{1,2,3,4}$	1	2	1	1	1	1	2	2	2	2
$11_{1,2}$	11	2	2		1	1	1	2	2	2	2
12		1	2	2	2			2	2	2	2
13		2	2	1	2			2	2	2	2
14				1	2	2	2	2	2	2	2
15		1			2	2	2	2	2	2	2
$16_{1,2}$	16		1	1	1	2	2	2	2	2	2
17			2	1		2	2	2	2	2	2
$18_{1,2}$	18	1	1		1	2	2	2	2	2	2
19		1	2			2	2	2	2	2	2
20			1	2	2	2		2	2	2	2
21			2	2	1	2		2	2	2	2
$22_{1,2}$	22	1	1	1	2	2		2	2	2	2
23		2	1		2	2		2	2	2	2
$24_{1,2}$	24	1	2	1	1	2		2	2	2	2
25		2	2		1	2		2	2	2	2
$26_{1,2}$	26		1	2	2	1	2	1	2	2	2
$27_{1,2}$	27		2	2	1	1	2	1	2	2	2
$28_{1,2,3,4,5}$	$28_{1,2,3,4}$	1	1	1	2	1	2	1	2	2	2
$30_{1,2,3,4,5}$	$30_{1,2,3,4}$	1	2	1	1	1	2	1	2	2	2
$32_{1,2}$	32		1	2	2	2	1	1	2	2	2
$34_{1,2,3,4,5}$	$34_{1,2,3,4}$	1	1	1	2	2	1	1	2	2	2
$38_{1,2}$	38	1	2	2	2		1	1	2	2	2
42			1	2	2	2	2		2	2	2
$44_{1,2}$	44	1	1	1	2	2	2		2	2	2
48		1	2	2	2		2		2	2	2
$54_{1,2}$	54		1	2	2	1	2	2	1	2	2
$55_{1,2}$	55		2	2	1	1	2	2	1	2	2
$56_{1,2,3,4,5}$	$56_{1,2,3,4}$	1	1	1	2	1	2	2	1	2	2
$57_{1,2}$	57	2	1		2	1	2	2	1	2	2
$58_{1,2,3,4,5}$	$58_{1,2,3,4}$	1	2	1	1	1	2	2	1	2	2
$60_{1,2}$	60		1	2	2	2	1	2	1	2	2
$62_{1,2,3,4,5}$	$62_{1,2,3,4}$	1	1	1	2	2	1	2	1	2	2
$66_{1,2}$	66	1	2	2	2		1	2	1	2	2
$70_{1,2}$	70		1	2	2	2	2	1	1	2	2
$76_{1,2}$	76	1	2	2	2		2	1	1	2	2
86			1	2	2	2	2	2		2	2
$88_{1,2}$	88	1	1	1	2	2	2	2	2	2	2
92		1	2	2	2		2	2		2	2

TABLE II

Configurations Used in CI Calculation for  $2\Sigma^+$ ,  $2\Sigma^-$ ,  $4\Sigma^+$ , and  $4\Sigma^-$  States of NO

Doublet	Quartet	$2\Sigma^+$	$2\Sigma^-$	$4\Sigma^+$	$4\Sigma^-$	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma^a$
$1_{1,2}^{c)}$	1	$1_1$	$1_2$		1	1	1	2	2		1	2
$2_{1,2}$	2	$2_{1,2}$	$2_{1,2}$	2	2	2	1	1	2		1	$2^b)$
$3_{1,2}$	3	$3_1$	$3_2$		3	2	2	1	1		1	2
4		4						2	2	1	2	2
$5_{1,2}$	5	$5_{1,2}$	$5_{1,2}$	5	5	1		1	2	1	2	2
6		6	6			2			2	1	2	2
$7_{1,2,3,4,5}^{d)}$	$7_{1,2,3,4}^{e)}, f)$	$7_{1,3,5'}$	$7_{2,4'}$	$7_{2,4'}$	$7_{1,3'}$	1	1	1	1	1	2	2
$8_{1,2}$	8	$8_{1,2}$	$8_{1,2}$	8	8	2	1		1	1	2	2
9		9				2	2			1	2	2
$10_{1,2}$	10	$10_1$	$10_2$		10	1	1	2	2	1		2
$11_{1,2}$	11	$11_{1,2}$	$11_{1,2}$	11	11	2	1	1	2	1		2
$12_{1,2}$	12	$12_1$	$12_2$		12	2	2	1	1	1		2
13		13						2	2	2	1	2
$14_{1,2}$	14	$14_{1,2}$	$14_{1,2}$	14	14	1		1	2	2	1	2
15		15	15			2			2	2	1	2
$16_{1,2,3,4,5}$	$16_{1,2,3,4}$	$16_{1,3,5'}$	$16_{2,4'}$	$16_{2,4'}$	$16_{1,3'}$	1	1	1	1	2	1	2
$17_{1,2}$	17	$17_{1,2}$	$17_{1,2}$	17	17	2	1		1	2	1	2
18		18				2	2			2	1	2

Table II Foot Notes

- a)  $1\sigma$ ,  $2\sigma$ , and  $3\sigma$  are doubly occupied for all configurations.
- b) The set of orbitals contained with the positive coefficient in the orbital product function of each configurational wave function ( $\Sigma^-$  state) is shown by specifying numbers of electrons occupying each orbital.
- c) It is assumed for  $2\Sigma^\pm$  states that, in making the orbital product functions, the unpaired  $\sigma$ -orbital must be put first and then the unpaired  $\pi$ -orbitals both with the order we read from left to right in the table.
- d) For  $2\Sigma^\pm$  states,  $7_4$  and  $7_5$  do not give the functions with the correct space symmetry, while  $7_{4'}$  and  $7_{5'}$  made from these two yield the ones with the correct space symmetry.

$$\begin{aligned} (7_{4'}) &= -\sqrt{(1/3)} (7_4) + \sqrt{(2/3)} (7_5) & 2\Sigma^- \\ (7_{5'}) &= \sqrt{(2/3)} (7_4) + \sqrt{(1/3)} (7_5) & 2\Sigma^+ \end{aligned}$$

- e) It is assumed for  $4\Sigma^\pm$  states that the orbital product function of configuration 7 is  $2\pi^-(1)2\pi^+(2)6\sigma(3)1\pi^-(4)1\pi^+(5) (5\sigma)^2(4\sigma)^2(3\sigma)^2(2\sigma)^2(1\sigma)^2$ .

- f) For  $4\Sigma^\pm$  states,  $7_3$  and  $7_4$  do not give the functions with the correct space symmetry, while  $7_{3'}$  and  $7_{4'}$  made from these two yield the ones with the correct space symmetry.

$$\begin{aligned} (7_{3'}) &= -\sqrt{(3/8)} (7_3) + \sqrt{(5/8)} (7_4) & 4\Sigma^- \\ (7_{4'}) &= -\sqrt{(5/8)} (7_3) - \sqrt{(3/8)} (7_4) & 4\Sigma^+ \end{aligned}$$

TABLE III  
Configurations Used in CI Calculation for  $2A$  and  $4A$  States of NO

Doublet	Quartet	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma^{(a)}$
1 <sub>1,2</sub>	1	1	2	1	2		1	2
2			2	2	2		1	2
3		2	2		2		1	2
4 <sub>1,2</sub>	4		1	1	2	1	2	2
5 <sub>1,2</sub>	5	1	1		2	1	2	2
6 <sub>1,2</sub>	6		2	1	1	1	2	2
7 <sub>1,2</sub>	7	1	2		1	1	2	2
8 <sub>1,2</sub>	8	1	2	1	2	1		2
9			2	2	2	1		2
10		2	2		2	1		2
11 <sub>1,2</sub>	11		1	1	2	2	1	2
12 <sub>1,2</sub>	12	1	1		2	2	1	2
13 <sub>1,2</sub>	13		2	1	1	2	1	2
14 <sub>1,2</sub>	14	1	2		1	2	1	2

a)  $1\sigma$ ,  $2\sigma$ , and  $3\sigma$  are doubly occupied for all configurations.

TABLE IV  
Configurations Used in CI Calculation for  $1\Sigma^+$ ,  $1\Sigma^-$ ,  $3\Sigma^+$  and  $3\Sigma^-$  States of NO<sup>+</sup>

Singlet	Triplet	$1\Sigma^+$	$1\Sigma^-$	$3\Sigma^+$	$3\Sigma^-$	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma^{(a)}$
1		1						2	2		2	2
2		2	2				2	2			2	2
3		3					2	2			2	2
4 <sub>1,2</sub>	4 <sub>1,2,3</sub> <sup>(d)</sup>	4 <sub>1,2</sub>		4 <sub>3'</sub>	4 <sub>1,2'</sub>	1	1	1	1		2	2
5	5	5	5	5	5	1		1	2		2	2 <sup>(b)</sup>
6	6	6	6	6	6	1	2	1			2	2
7	7	7		7				2	2	1	1	2
8	8	8	8	8	8		2	2		1	1	2
9	9	9		9		2	2			1	1	2
10 <sup>(c)</sup> <sub>1,2,3,4,5</sub>	10 <sup>(e),f)</sup> <sub>1,2,3,4,5,6,7,8,9</sub>	10 <sub>1,3,4</sub>	10 <sub>2,5</sub>	10 <sub>1,4,5',7',9</sub>	10 <sub>2,3,6',8'</sub>	1	1	1	1	1	1	2
11 <sub>1,2</sub>	11 <sub>1,2,3</sub>	11 <sub>1,2</sub>	11 <sub>1,2</sub>	11 <sub>1,2,3</sub>	11 <sub>1,2,3</sub>	1		1	2	1	1	2
12 <sub>1,2</sub>	12 <sub>1,2,3</sub>	12 <sub>1,2</sub>	12 <sub>1,2</sub>	12 <sub>1,2,3</sub>	12 <sub>1,2,3</sub>	1	2	1		1	1	2
13		13						2	2	2		2
14		14	14					2	2	2		2
15		15				2	2			2		2
16 <sub>1,2</sub>	16 <sub>1,2,3</sub>	16 <sub>1,2</sub>		16 <sub>3'</sub>	16 <sub>1,2'</sub>	1	1	1	1	2		2
17	17	17	17	17	17	1		1	2	2		2
18	18	18	18	18	18	1	2	1		2		2
19	19	19			19	1	1	2	2			2
20	20	20	20	20	20	1	2	2	1			2
21	21	21			21	2	2	1	1			2



Table IV Foot Notes

- a)  $1\sigma$ ,  $2\sigma$ , and  $3\sigma$  are doubly occupied for all configurations.
- b) The set of orbitals contained with the positive coefficient in the orbital product function of each configurational wave function ( $\Sigma^-$  state) is shown by specifying the numbers of electrons occupying each orbital.
- c) It is assumed for  $1\Sigma^\pm$  states that the orbital product function of configuration 10 is

$$2\pi^-(1)2\pi^+(2)6\sigma(3)5\sigma(4)1\pi^-(5)1\pi^+(6) \quad (4\sigma)^2(3\sigma)^2(2\sigma)^2(1\sigma)^2.$$

- d) For  $3\Sigma^\pm$  states,  $4_{2,3}$  and  $16_{2,3}$  do not give the functions with the correct space symmetry, while  $4_{2',3'}$  and  $16_{2',3'}$  made from these unprimed ones yield the ones with the correct space symmetry (the transformation for configurations  $16_{2',3'}$  is the same as that for  $4_{2',3'}$ ).

$$(4_{2'}) = -\sqrt{(1/3)}(4_2) + \sqrt{(2/3)}(4_3) \quad 3\Sigma^-$$

$$(4_{3'}) = \sqrt{(2/3)}(4_2) + \sqrt{(1/3)}(4_3) \quad 3\Sigma^+$$

- e) It is assumed for  $3\Sigma^\pm$  states that the orbital product function of configuration 10 is

$$6\sigma(1)5\sigma(2)2\pi^-(3)2\pi^+(4)1\pi^-(5)1\pi^+(6) \quad (4\sigma)^2(3\sigma)^2(2\sigma)^2(1\sigma)^2.$$

- f) For  $3\Sigma^\pm$  states,  $10_{5,6,7,8}$  do not give the functions with the correct space symmetry, while  $10_{5',6',7',8'}$  made from these unprimed yield the ones with the correct space symmetry.

$$(10_{5'}) = \sqrt{(1/3)}(10_5) + \sqrt{(2/3)}(10_6) \quad 3\Sigma^+$$

$$(10_{6'}) = \sqrt{(2/3)}(10_5) - \sqrt{(1/3)}(10_6) \quad 3\Sigma^-$$

$$(10_{7'}) = \sqrt{(1/3)}(10_7) + \sqrt{(2/3)}(10_8) \quad 3\Sigma^+$$

$$(10_{8'}) = \sqrt{(2/3)}(10_7) - \sqrt{(1/3)}(10_8) \quad 3\Sigma^-$$

TABLE V

Configurations Used in CI Calculation for  $1\Pi$  and  $3\Pi$  States of  $\text{NO}^+$ 

Singlet	Triplet	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma^a$
1	1		1	2	2		1	2
2	2		2	2	1		1	2
$3_{1,2}$	$3_{1,2,3}$	1	1	1	2		1	2
4	4	2	1		2		1	2
$5_{1,2}$	$5_{1,2,3}$	1	2	1	1		1	2
6	6	2	2		1		1	2
7	7		1	2	2	1		2
8	8		2	2	1	1		2
$9_{1,2}$	$9_{1,2,3}$	1	1	1	2	1		2
10	10	2	1		2	1		2
$11_{1,2}$	$11_{1,2,3}$	1	2	1	1	1		2
12	12	2	2		1	1		2
13	13			1	2	1	2	2
14	14	1			2	1	2	2
15	15		2	1		1	2	2
16	16	1	2			1	2	2

- a)  $1\sigma$ ,  $2\sigma$ , and  $3\sigma$  are doubly occupied for all configurations.

TABLE VI  
Configurations Used in CI Calculation for  $^1A$  and  $^3A$  States of  $\text{NO}^+$

Singlet	Triplet	$2\pi^-$	$2\pi^+$	$1\pi^-$	$1\pi^+$	$6\sigma$	$5\sigma$	$4\sigma^a$
1	1		1	1	2		2	2
2	2	1	1		2		2	2
3	3		2	1	1		2	2
4	4	1	2		1		2	2
5			2	2	2			2
6		2	2		2			2
7	7	1	2	1	2			2
$8_{1,2}$	$8_{1,2,3}$		1	1	2	1	1	2
$9_{1,2}$	$9_{1,2,3}$	1	1		2	1	1	2
$10_{1,2}$	$10_{1,2,3}$		2	1	1	1	1	2
$11_{1,2}$	$11_{1,2,3}$	1	2		1	1	1	2
12	12		1	1	2	2		2
13	13	1	1		2	2		2
14	14		2	1	1	2		2
15	15	1	2		1	2		2

a)  $1\sigma$ ,  $2\sigma$ , and  $3\sigma$  are doubly occupied for all configurations.

we can define unambiguously our wave functions by determining the forms of spin functions and orbital functions. The recipe used how to define orbital product functions is, except otherwise noted, that in each of sets of fifteen (and fourteen) one-electron orbitals, which are collected in Tables I~VI, the  $i$ -th unpaired orbital, if numbered from left to right in those tables, accommodates the  $i$ -th electron, and that the  $j$ -th paired orbital accommodates the  $(2j-1+u)$ -th and the  $(2j+u)$ -th electron ( $u$  is the number of unpaired electrons). The recipe how to define some orbital product functions for  $\Sigma^\pm$  states is different from that stated in the above and it is explained in detail in the foot notes of Tables II and IV. The subscript  $k$  added to some labels for configuration collected in Tables I~VI expresses that, in order to obtain the desired wave function, we must associate the  $k$ -th spin function of the proper set of spin functions  $\Theta_{S,M,k}^N$  with the orbital product function.

### 3. Ground State $^2\Pi$ of NO

We can construct two hundred eighteen configurations with  $^2\Pi$  symmetry from our ten MO's on the assumption that  $1\sigma$  and  $2\sigma$  orbitals are always doubly occupied. Among two hundred eighteen configurations forty four configurations have the non-zero elements of energy matrix against the ground configuration 0. Twenty five configurations are selected from these forty four ones by the energy criterion  $(H_{oi})^2/(H_{ii}-H_{oo})$ . The result of CI calculation is listed in Table VII,

TABLE VI  
Wave Functions for Ground and Two Lower Excited  ${}^2\Pi$  States of NO

	Ground ${}^2\Pi$					First Excited ${}^2\Pi$		Second Excited ${}^2\Pi$	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>d</i>	<i>e</i>	<i>d</i>	<i>e</i>
0	0.9692	0.9670	0.9587	0.9562	0.9562	0.0509	0.0503	0.0226	0.0199
1			-0.0302	-0.0206	-0.0206	-0.6743	-0.6703	0.4326	0.4351
2 <sub>1</sub>			-0.0765	-0.0780	-0.0776	0.6916	0.6956	0.4738	0.4587
2 <sub>2</sub>			0.0493	0.0371	0.0375	-0.0745	-0.0640	0.7267	0.7311
3	-0.1338	-0.1289	-0.1358	-0.1495	-0.1495	0.0802	0.0790	-0.0681	-0.0706
4 <sub>1</sub>	-0.1267	-0.1108	-0.1224	-0.1388	-0.1389	0.0318	0.0327	0.1148	0.1121
4 <sub>2</sub>	-0.0921	-0.0843	-0.0869	-0.0996	-0.0997	-0.0611	-0.0606	0.0358	0.0351
5				-0.0329	-0.0327	0.0496	0.0501	0.0538	0.0519
6 <sub>1</sub>			0.0513	0.0610	0.0613	0.0270	0.0285	0.0503	0.0529
6 <sub>2</sub>				0.0013	0.0010	-0.1388	-0.1401	-0.1072	-0.1023
7 <sub>1</sub>	-0.0751	-0.0737	-0.0747	-0.0753	-0.0753	-0.0851	-0.0844	0.0313	0.0323
7 <sub>2</sub>	0.0039				0.0043		0.0129		-0.0011
8 <sub>1</sub>	-0.0396	-0.0386	-0.0453	-0.0467	-0.0466	0.0695	0.0701	0.0471	0.0459
8 <sub>2</sub>	0.0899	0.0867	0.0891	0.0907	0.0906	0.0035	0.0047	0.0912	0.0903
8 <sub>4</sub>					0.0068		0.0043		0.0110
8 <sub>5</sub>					-0.0013		-0.0016		0.0039
9 <sub>1</sub>				-0.0170	-0.0172	-0.0635	-0.0630	0.0439	0.0452
10 <sub>1</sub>				-0.0167	-0.0161	-0.0262	-0.0270	-0.0802	-0.0796
10 <sub>2</sub>				-0.0107	-0.0106	0.0639	0.0645	0.0182	0.0187
12		0.0310	0.0324	0.0441	0.0440	0.0117	0.0115	0.0383	0.0332
13					-0.0012		-0.0176		-0.0693
14					-0.0003		0.0169		0.0506
16 <sub>1</sub>		0.0233	0.0218						
17					0.0001		-0.0175		0.0020
20	-0.0536	-0.0504	-0.0501	-0.0521	-0.0523	-0.0012	-0.0011	0.0049	0.0049
21				-0.0023	-0.0026	0.0433	0.0424	-0.0313	-0.0322
22 <sub>1</sub>				0.0042	0.0038	-0.0482	-0.0481	-0.0322	-0.0297
26 <sub>1</sub>		-0.0011	-0.0046						
26 <sub>2</sub>		-0.0312	-0.0329						
27 <sub>1</sub>		0.0178	0.0141						
28 <sub>1</sub>		0.0104							
28 <sub>2</sub>		-0.0209	-0.0164						
38 <sub>1</sub>		-0.0265							
42		-0.0233	-0.0224						
48		0.0495	0.0471						
54 <sub>1</sub>			0.0073						
55 <sub>1</sub>		0.0319	0.0320						
56 <sub>1</sub>		0.0200	0.0200						
56 <sub>2</sub>		-0.0364	-0.0376						
56 <sub>4</sub>		-0.0238							
60 <sub>1</sub>		-0.0285	-0.0292						
66 <sub>1</sub>		-0.0100							
86		-0.0242	-0.0231						
92		0.0099							
energy in au	-128.861	-128.884	-128.889	-128.873	-128.873	-128.626	-128.626	-128.501	-128.507
binding energy in ev	1.71	2.34	2.48	2.04	2.04				

“ground state b” The energy depression due to CI calculation is 0.131 au, and the wave function obtained gives the dissociation energy 2.34ev, which is 36% of the experimental one. Next, by the wave function criterion  $H_{oi}/(H_{ii}-H_{oo})$  twenty five configurations are selected from forty four configurations mentioned before. Configurations 1, 2<sub>1</sub>, 2<sub>2</sub>, 6<sub>1</sub>, and 26<sub>1</sub> are preserved because they have non-zero matrix elements of one-electron operator against the ground configuration 0 and therefore they play important roles for some molecular quantities. The result of CI calculation is listed in Table VII, “ground state c”. This wave function gives the dissociation energy 2.48ev (38% of the experimental one). The value for “case c” is better than that for „case” b”. A CI calculation corresponding to the wave function (equation 18) in reference 1 is shown in Table VII, „ground state a”.

Magnetic hyperfine structure constants for the ground  $^2\Pi$  state of the NO molecule have been calculated and reported elsewhere<sup>3)</sup>.

#### 4. Excited States of NO

By several pilot CI calculations, configurations are selected which are important for the first excited  $^2\Pi$  state. Two CI calculations are carried out using configurations chosen by pilot calculations. The wave functions and energies obtained are shown in Table VII. “excited state d and c”. The wave functions and energies for the ground  $^2\Pi$  state obtained from these calculations are listed in Table VII. “ground state d and e”.

Two CI calculations for  $^4\Pi$  state are carried out using configurations which are chosen in the calculations “d and e” for  $^2\Pi$  state. The results are shown in Table VIII. “lowest a and b”. In that table the wave functions for the second lowest  $^4\Pi$  state are also shown (“second lowest a and b”). It turned out that the configuration 2 makes very large contribution to the wave function for the lowest  $^4\Pi$  state. In order to obtain more accurate wave function for the lowest  $^4\Pi$  state, a CI calculation is carried out using configurations, which are selected by the wave function criterion  $H_i^2/(H_i-H_2^2)$  from all the configurations within our framework, the number of which is one hundred fourteen. The result is shown in Table VIII. „lowest c”.

For  $^2\Sigma^\pm$ ,  $^4\Sigma^\pm$ ,  $^2A$ , and  $^4A$  states, CI calculations are carried out using configurations in which 1 $\sigma$ , 2 $\sigma$ , 3 $\sigma$ , and 4 $\sigma$  MO's are doubly occupied. Some configurations are dropped out which have small matrix elements against the important configurations for the sake of simplification. The results are listed in Tables IX~XIV.

The vertical excitation energies from the ground state  $^2\Pi$  to each of the excited states are obtained by taking the differences of the respective total energies. The results are given in Table XV.

TABLE VIII  
Wave Functions for  ${}^4\Pi$  States of NO

	Lowest ${}^4\Pi$			Second Lowest ${}^4\Pi$	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>
2	0.9822	0.9807	0.9769	-0.0230	-0.0281
4	-0.1107	-0.1144	-0.0934	0.0809	0.0280
6	0.0259	0.0278	0.0341	0.9654	0.9582
7	0.0022	0.0007		-0.0403	-0.0397
8 <sub>1</sub>	0.0953	0.0983	0.1076	0.0237	0.0106
8 <sub>2</sub>	0.0157	0.0159	0.0140	0.0797	0.0711
8 <sub>3</sub>		0.0065			-0.0373
8 <sub>4</sub>		0.0056			-0.0344
9	-0.0080	-0.0079		-0.2282	-0.1830
10 <sub>1</sub>	0.0958	0.0977	0.0922	0.0154	0.0004
10 <sub>2</sub>		0.0038			0.0441
10 <sub>3</sub>		-0.0042			-0.1515
10 <sub>4</sub>		0.0011			0.1063
11		-0.0004			-0.0366
16		-0.0014			0.0017
18		0.0180	0.0167		-0.0004
22	-0.0621	-0.0618	-0.0584	0.0023	-0.0004
24		0.0230			-0.0002
26			-0.0099		
28 <sub>1</sub>			-0.0024		
28 <sub>2</sub>			0.0417		
28 <sub>3</sub>			0.0346		
28 <sub>4</sub>			0.0251		
30 <sub>1</sub>			-0.0090		
34 <sub>1</sub>			-0.0353		
38			-0.0040		
44			-0.0247		
54			-0.0461		
56 <sub>1</sub>			-0.0147		
56 <sub>2</sub>			-0.0060		
57			0.0181		
58 <sub>1</sub>			-0.0347		
58 <sub>2</sub>			-0.0127		
62 <sub>1</sub>			-0.0357		
76			-0.0166		
88			-0.0245		
energy in au	-128.659	-128.661	-128.681	-128.300	-128.334

TABLE IX  
Wave Functions for  ${}^2\Sigma^+$  States of NO

	Lowest ${}^2\Sigma^+$	Second Lowest ${}^2\Sigma^+$
1	0.9580	-0.0605
2 <sub>1</sub>	-0.0842	0.0193
2 <sub>2</sub>	0.0416	-0.0552
3 <sub>1</sub>	-0.2366	0.0159
4	0.0634	0.9393
5 <sub>1</sub>	0.0289	0.1286
5 <sub>2</sub>	0.0148	-0.0060
6	-0.0065	-0.1971
7 <sub>1</sub>	0.0055	0.1820
7 <sub>3</sub>	-0.0075	-0.0959
7 <sub>5'</sub>	-0.0002	-0.0006
8 <sub>1</sub>	-0.0066	0.0145
8 <sub>2</sub>	-0.0043	0.0012
10 <sub>1</sub>	0.0226	-0.0583
11 <sub>1</sub>	-0.0910	0.0146
11 <sub>2</sub>	-0.0020	-0.0034
13	-0.0554	-0.0215
14 <sub>1</sub>	-0.0129	-0.0904
14 <sub>2</sub>	0.0010	-0.0020
16 <sub>1</sub>	0.0110	-0.0096
16 <sub>5'</sub>	0.0014	-0.0006
energy in au	-128.522	-128.458

TABLE X  
Wave Function for  
 ${}^2\Sigma^-$  State of NO

	Lowest ${}^2\Sigma^-$
1 <sub>2</sub>	0.9790
2 <sub>1</sub>	-0.0592
2 <sub>2</sub>	0.0371
3 <sub>2</sub>	-0.1549
5 <sub>1</sub>	0.0175
5 <sub>2</sub>	0.0133
6	0.0000
7 <sub>2</sub>	-0.0108
7 <sub>4'</sub>	0.0007
8 <sub>1</sub>	-0.0022
8 <sub>2</sub>	0.0001
11 <sub>1</sub>	-0.0002
11 <sub>2</sub>	0.1062
14 <sub>1</sub>	-0.0029
14 <sub>2</sub>	0.0004
16 <sub>2</sub>	0.0278
16 <sub>4'</sub>	-0.0034
energy ni au	-128.516

TABLE XI  
Wave Function for  
 ${}^4\Sigma^+$  State of NO

	Lowest ${}^4\Sigma^+$
2	0.9926
5	-0.0113
7 <sub>2</sub>	-0.0114
7 <sub>4'</sub>	-0.0325
8	0.0024
11	0.1065
14	0.0434
16 <sub>2</sub>	0.0029
16 <sub>4'</sub>	0.0011
17	0.0155
energy in au	-128.352

TABLE XII  
Wave Function for  
 ${}^4\Sigma^-$  State of NO

	Lowest ${}^4\Sigma^-$
1	0.9813
2	0.0112
3	-0.1457
5	0.0394
7 <sub>1</sub>	-0.0099
7 <sub>3'</sub>	-0.0020
8	0.0041
10	0.0221
11	0.1106
12	-0.0216
14	-0.0014
16 <sub>1</sub>	0.0296
16 <sub>3'</sub>	-0.0031
17	-0.0016
energy in au	-128.636

TABLE XIII.  
Wave Function for  
 $^2\Delta$  State of NO

	Lowest $^2\Delta$
1 <sub>1</sub>	-0.0533
1 <sub>2</sub>	-0.0445
2	0.9667
3	-0.1891
4 <sub>1</sub>	-0.0028
4 <sub>2</sub>	-0.0366
5 <sub>1</sub>	-0.0006
5 <sub>2</sub>	0.0012
6 <sub>1</sub>	0.0038
6 <sub>2</sub>	0.0066
7 <sub>1</sub>	-0.0016
7 <sub>2</sub>	-0.0002
8 <sub>1</sub>	-0.0461
8 <sub>2</sub>	-0.1373
9	0.0296
10	-0.0262
11 <sub>1</sub>	-0.0018
11 <sub>2</sub>	-0.0001
12 <sub>1</sub>	0.0046
12 <sub>2</sub>	0.0048
13 <sub>1</sub>	-0.0160
13 <sub>2</sub>	-0.0242
energy in au	-128.571

TABLE XIV.  
Wave Function for  
 $^4\Delta$  State of NO

	Lowest $^4\Delta$
1	0.9930
4	-0.0022
5	0.0103
6	-0.0234
7	-0.0005
8	0.1067
11	0.0412
12	0.0019
13	0.0003
14	0.0155
energy in au	-128.358

TABLE XV.  
Vertical Excitation Energies  
Relative to the Ground  
 $^2\Pi$  State of NO in eV

	calc.	obs.
$^4\Sigma^+$	14.17	
$^4\Delta$	14.01	
$^2\Sigma^+$	11.29	
$^2\Pi$	10.12	
$^2\Sigma^-$	9.71	
$^2\Sigma^+$	9.55	8.5(?) <sup>4)</sup>
$^2\Delta$	8.22	7.75 <sup>5)</sup>
$^2\Pi$	6.72	6.54 <sup>4)</sup>
$^4\Sigma^-$	6.45	
$^4\Pi$	5.82	4.76 <sup>6)</sup>

## 5. Ground and Low Excited states of NO<sup>+</sup>

NO<sup>+</sup> ion is known to play important roles for some reactions occurring in the upper atmosphere. Therefore it is interesting to study this ion in detail. In the calculations of the wave functions of the NO<sup>+</sup> ion we used the same MO's as used in the calculations of the wave functions of the NO molecule. The MO's used are orthogonal MO's. Therefore they still can be used as the basis orbitals for CI calculations of NO<sup>+</sup>. Configurations used for various symmetry states are collected in Tables IV~VI. For the sake of simplification we consider only the configuration in which 1 $\sigma$ , 2 $\sigma$ , 3 $\sigma$ , and 4 $\sigma$  MO's are doubly occupied. The results

are listed in Tables XVI~XXIII. The vertical excitation energies from the ground state  $1\Sigma^+$  to each of the excited states are given in Table XXIV. The calculated dissociation energy is 4.00ev (37% of the experimental one 10.95ev). The ionization energy of the NO molecule is obtained by taking the difference of the respective ground state energies of NO and  $\text{NO}^+$ . The calculated ionization energy is 7.48ev (81% of the experimental one 9.25ev<sup>7)</sup>).

TABLE XVI.  
Wave Functions for Ground and  
First Excited  $1\Sigma^+$  States of  $\text{NO}^+$

	Ground $1\Sigma^+$	First Excited $1\Sigma^+$
1	0.9273	-0.2051
2	-0.0952	-0.0993
3	0.0454	0.0988
4 <sub>1</sub>	0.1937	0.0698
4 <sub>2</sub>	0.1236	-0.1854
5	0.1640	0.6963
6	-0.0209	-0.3427
7	0.0998	0.5262
8	-0.0152	-0.0520
9	0.0177	-0.0204
10 <sub>1</sub>	0.0281	0.0460
10 <sub>3</sub>	-0.0013	-0.0384
10 <sub>4</sub>	0.0304	0.0070
11 <sub>1</sub>	0.1550	0.0763
11 <sub>2</sub>	0.0132	0.0194
12 <sub>1</sub>	-0.0594	-0.0345
12 <sub>2</sub>	-0.0067	-0.0038
13	-0.0512	0.0155
14	0.0132	0.0054
16 <sub>1</sub>	-0.0199	-0.0021
16 <sub>2</sub>	-0.0201	0.0064
17	0.0038	0.0462
18	-0.0063	-0.0007
19	-0.0692	0.0537
20	0.0094	0.0181
21	0.0170	-0.0105
energy in au	-128.598	-128.323

TABLE XVII.  
Wave Function for  
 $1\Sigma^-$  State of  $\text{NO}^+$

Lowest $1\Sigma^-$	
2	-0.0756
5	0.9581
6	0.1937
8	0.1641
10 <sub>2</sub>	0.0018
10 <sub>5</sub>	-0.0016
11 <sub>1</sub>	0.0690
11 <sub>2</sub>	0.0016
12 <sub>1</sub>	0.0162
12 <sub>2</sub>	0.0012
14	0.0253
17	-0.0632
18	0.0012
20	-0.0477
energy in au	-128.487

TABLE XVIII.  
Wave Function for  
 $3\Sigma^+$  State of  $\text{NO}^+$

Lowest $3\Sigma^+$	
4 <sub>3'</sub>	-0.0142
5	0.9537
6	-0.2056
7	-0.0469
8	0.0216
9	-0.0024
10 <sub>1</sub>	-0.0143
10 <sub>4</sub>	-0.0124
10 <sub>5'</sub>	-0.1055
10 <sub>7'</sub>	0.0759
10 <sub>9</sub>	0.0199
11 <sub>1</sub>	0.1276
11 <sub>2</sub>	0.0173
11 <sub>3</sub>	0.0061
12 <sub>1</sub>	-0.0627
12 <sub>2</sub>	-0.0051
12 <sub>3</sub>	-0.0057
16 <sub>3'</sub>	-0.0135
17	-0.0624
18	0.0249
20	0.0488
energy in au	-128.404



TABLE XIX.  
Wave Function for  
 ${}^3\Sigma^-$  State of  $\text{NO}^+$

Lowest ${}^3\Sigma^-$	
4 <sub>1</sub>	0.2016
4 <sub>2'</sub>	-0.0164
5	0.9537
6	-0.0815
8	0.0023
10 <sub>2</sub>	0.0715
10 <sub>3</sub>	-0.1142
10 <sub>6'</sub>	0.0743
10 <sub>8'</sub>	-0.0567
11 <sub>1</sub>	0.0734
11 <sub>2</sub>	0.0160
11 <sub>3</sub>	0.0089
12 <sub>1</sub>	-0.0554
12 <sub>2</sub>	-0.0023
12 <sub>3</sub>	-0.0019
16 <sub>1</sub>	-0.0245
16 <sub>2'</sub>	0.0076
17	-0.0572
18	0.0123
19	0.0425
20	0.0370
21	-0.0005
energy in au	-128.303

TABLE XX.  
Wave Function for  
 ${}^1\Pi$  State of  $\text{NO}^+$

Lowest ${}^1\Pi$	
1	0.9495
2	-0.0558
3 <sub>1</sub>	-0.0131
3 <sub>2</sub>	-0.0828
4	-0.1607
5 <sub>1</sub>	0.2024
5 <sub>2</sub>	-0.0813
6	-0.0329
7	0.0177
8	-0.0567
9 <sub>1</sub>	-0.0522
9 <sub>2</sub>	-0.0767
10	-0.0062
11 <sub>1</sub>	0.0029
11 <sub>2</sub>	-0.0094
12	0.0386
13	-0.0001
14	0.0018
15	0.0008
16	-0.0007
energy in au	-128.176

TABLE XXI.  
Wave Function for  
 ${}^3\Pi$  State of  $\text{NO}^+$

Lowest ${}^3\Pi$	
1	0.9302
2	0.0168
3 <sub>1</sub>	0.1587
3 <sub>2</sub>	-0.1118
3 <sub>3</sub>	-0.0249
4	-0.1693
5 <sub>1</sub>	0.0475
5 <sub>2</sub>	-0.1915
5 <sub>3</sub>	0.1083
6	-0.0390
7	0.0281
8	-0.0615
9 <sub>1</sub>	0.0402
9 <sub>2</sub>	-0.0197
9 <sub>3</sub>	-0.0808
10	0.0019
11 <sub>1</sub>	0.0062
11 <sub>2</sub>	-0.0055
11 <sub>3</sub>	0.0090
12	0.0389
13	0.0244
14	0.0024
15	-0.0047
16	-0.0004
energy in au	-128.224

TABLE XXII.  
Wave Functions for  
 ${}^1\Delta$  States of  $\text{NO}^+$

Lowest ${}^1\Delta$	
1	0.9694
2	-0.0940
3	0.1223
4	0.0548
5	0.0410
6	-0.0159
7	0.0559
8 <sub>1</sub>	0.0731
8 <sub>2</sub>	0.0040
9 <sub>1</sub>	0.0929
9 <sub>2</sub>	0.0027
10 <sub>1</sub>	-0.0883
10 <sub>2</sub>	-0.0032
11 <sub>1</sub>	0.0441
11 <sub>2</sub>	0.0007
12	-0.0626
13	0.0151
14	-0.0165
15	-0.0123
energy in au	-128.295

TABLE XXIII.  
Wave Function for  
 $^3A$  State of  $\text{NO}^+$

Lowest $^3A$	
1	0.9650
2	0.0424
3	-0.0065
4	-0.1574
7	0.0575
8 <sub>1</sub>	0.1164
8 <sub>2</sub>	0.0153
8 <sub>3</sub>	0.0090
9 <sub>1</sub>	-0.0872
9 <sub>2</sub>	0.0049
9 <sub>3</sub>	0.0056
10 <sub>1</sub>	0.0957
10 <sub>2</sub>	0.0068
10 <sub>3</sub>	0.0032
11 <sub>1</sub>	-0.0576
11 <sub>2</sub>	-0.0027
11 <sub>3</sub>	-0.0025
12	-0.0630
13	-0.0128
14	0.0098
15	0.0218
energy in au	-128.345

TABLE XXIV.  
Vertical Excitation Energies  
Relative to the Ground  
 $^1\Sigma^+$  State of  $\text{NO}^+$  in eV

calc.	
$^1\Pi$	11.48
$^3\Pi$	10.17
$^1\Sigma^+$	9.96
$^1A$	8.24
$^3\Sigma^-$	8.03
$^3A$	6.88
$^3\Sigma^+$	5.28
$^1\Sigma^-$	3.02

## 6. Dipole Moment

The dipole moments for the ground  $^2\Pi$ , first excited  $^2\Pi$ , and lowest  $^4\Pi$  states of the  $\text{NO}$  molecule as well as for the ground  $^1\Sigma^+$  state of the  $\text{NO}^+$  ion are calculated by using various wave functions. The molecular orbital integrals ( $\text{MO}|z|\text{MO}$ ) used are shown in Table XXV. All the values shown in this table are the

TABLE XXV.  
Molecular Integrals Used in Calculating Dipole Moment, Gradient of the  
Electric Field, and Oscillator Strength in Atomic Units

		$z_N^a)$	$(3\cos^2\theta_N-1)/r_N^3)^b)$			$x\pm iy$
1 $\sigma$	1 $\sigma$	2.17271	0.19531	5 $\sigma$	1 $\pi^\mp$	0.36707
2 $\sigma$	2 $\sigma$	0.00055	-0.00109	5 $\sigma$	2 $\pi^\mp$	0.21132
3 $\sigma$	3 $\sigma$	1.43840	0.29961	6 $\sigma$	1 $\pi^\mp$	0.00277
4 $\sigma$	4 $\sigma$	1.20300	0.01504	6 $\sigma$	2 $\pi^\mp$	0.37033
5 $\sigma$	5 $\sigma$	0.61362	0.91263			
6 $\sigma$	6 $\sigma$	1.00141	1.56198			
1 $\pi^\pm$	1 $\pi^\pm$	1.42023	-0.20209			
2 $\pi^\pm$	2 $\pi^\pm$	0.74267	-0.69767			
3 $\sigma$	4 $\sigma$	-0.77313	-0.03377			
3 $\sigma$	5 $\sigma$	0.05389	-0.37445			
3 $\sigma$	6 $\sigma$	-0.19335	0.26130			
4 $\sigma$	5 $\sigma$	-1.34825	0.01145			
4 $\sigma$	6 $\sigma$	-0.17272	-0.14126			
5 $\sigma$	6 $\sigma$	0.96834	-1.21997			
1 $\pi^\pm$	2 $\pi^\pm$	-1.31204	-0.51920			

Table XXV

### Foot Notes

- Brion, Moser, and Yamazaki, reference 1.
- Lefèbvre-Brion and Moser, reference 3.

TABLE XXVI. Dipole Moment

State	Case	calc.	obs.
Ground ${}^2\Pi$	SCF	0.27D(N-O <sup>+</sup> )	0.16D
	<i>d</i>	0.49	
	<i>c</i>	0.80	
	<i>e</i>	0.50	
First Excited ${}^2\Pi$	<i>d</i>	0.75D(N-O <sup>+</sup> )	
	<i>e</i>	0.80	
Lowest ${}^4\Pi$	<i>c</i>	0.85D(N-O <sup>+</sup> )	
Ground ${}^1\Sigma^+$ (NO <sup>+</sup> )	Single config.	2.15D(N-O <sup>+</sup> )	
	CI	2.70	

computed ones. These are taken from reference 1 and 3. The results are collected in Table XXVI. The observed dipole moment for the ground  ${}^2\Pi$  state of the NO molecule is 0.16D (sign unknown)<sup>8)</sup>.

## 7. Oscillator Strength

The oscillator strength  $f_{kl}$  with respect to the transition from a state  $k$  to an energetically higher state  $l$  is expressed, in atomic units, as

$$f_{kl} = -\frac{2}{3} |\langle \Psi_k | \sum_i \mathbf{r}_i | \Psi_l \rangle|^2 (\Delta E)_{kl},$$

where  $(\Delta E)_{kl} = E_l - E_k$ .

This method of calculation is called the dipole length method. The oscillator strengths from the ground  ${}^2\Pi$  state to the first excited  ${}^2\Pi$ , lowest  ${}^2\Sigma^+$ , lowest  ${}^2\Sigma^-$ , and lowest  ${}^2\Delta$  states are calculated. The molecular integrals used are shown in Table XXV. The wave functions "d" in Table VII are used in this section as the wave functions for the ground and first excited  ${}^2\Pi$  states. The results are listed in Table XXVII.

TABLE XXVII. Oscillator Strength

$k$	$l$	$\langle k   \sum_i \mathbf{r}_i   l \rangle$	$(\Delta E)_{kl}$	$f_{kl}$
Ground ${}^2\Pi$	First Excited ${}^2\Pi$	-0.1261	0.247	0.0026
Ground ${}^2\Pi$	Lowest ${}^2\Sigma^+$	-0.1419	0.351	0.0057
Ground ${}^2\Pi$	Lowest ${}^2\Sigma^-$	-0.2339	0.357	0.0130
Ground ${}^2\Pi$	Lowest ${}^2\Delta$	-0.2153	0.302	0.0093

## 8. Gradient of Electric Field at Nitrogen Nucleus

The gradient of the electric field at nitrogen nucleus is given by the relation

$$q = q(\text{nuclear}) - q(\text{electronic}) = (2Z/R^3) - \langle \Psi | \sum_i (3\cos^2\theta_{Ni} - 1)/r_{Ni}^3 | \Psi \rangle.$$

$Z$  is the nuclear charge of oxygen, and  $R$  is the internuclear distance. The gradients  $q$ 's for the ground  ${}^2\Pi$ , first excited  ${}^2\Pi$ , lowest  ${}^4\Pi$  states of the NO molecule as well as for the ground  ${}^1\Sigma^+$  state of the NO<sup>+</sup> ion are calculated. The molecular integrals used are shown in Table XXV. The results are listed in Table XXVIII. The experimental value<sup>9)</sup> of  $eqQ$  for the ground  ${}^2\Pi$  state of NO is  $-1.75$  Mc/sec. The calculated gradient  $q=0.60$ au leads to  $Q(N^{14}) = -0.001 \times 10^{-24} \text{cm}^2$ . A

negative value of  $Q$  is in contradiction with the hypothesis proposed by Moskowski and Towns<sup>10)</sup> that positive  $Q$  should be associated with an odd-odd nucleus.

### 9. Spin-Orbit Coupling Constant

The spin-orbit coupling operator is expressed as

$$E = \sum_i \xi_i \mathbf{l}_i \cdot \mathbf{s}_i = A \mathcal{M},$$

where  $i$  denotes the coordinates of the  $i$ -th electron, and

$$\xi_i = \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{dU}{dr_i}$$

with  $U$  being the potential energy of the  $i$ -th electron at a point  $r_i$ . In the Russell-Saunders case the effective spin-orbit coupling term is  $A \mathcal{M}$  and this coupling constant  $A$  can be expressed by means of  $(MO | \xi | MO)$ . We calculated the spin-orbit coupling constants for the ground  ${}^2\Pi$ , first excited  ${}^2\Pi$ , and lowest  ${}^4\Pi$  states. The matrix elements of the spin-orbit coupling operator  $\sum_i \xi_i \mathbf{l}_i \cdot \mathbf{s}_i$  for the  ${}^2\Pi$  state of NO are shown in Table XXIX. As  $\frac{dU}{dr_i}$  falls off very rapidly with  $r_i$

TABLE XXVIII.  
Gradient of the Electric Field at  
Nitrogen Nucleus

State	case	calc.
Ground ${}^2\Pi$	SCF	0.226au
	$d$	0.602
	$c$	0.581
First Excited ${}^2\Pi$	$e$	0.598
	$d$	0.722
	$e$	0.910
Lowest ${}^4\Pi$	$c$	0.929
Ground ${}^1\Sigma^+$ (NO <sup>+</sup> )	Single Config.	-0.476
	CI	0.199

TABLE XXIX. Matrix Elements of the Spin-Orbit Coupling Operator  
for  ${}^2\Pi$  State of NO

$\langle 0   E   0 \rangle$		$\langle 13   E   13 \rangle$	
	$(1/2)(2\pi   \xi   2\pi)$		$(-1/2)(1\pi   \xi   1\pi)$
1 1	$(1/2)(1\pi   \xi   1\pi)$	14 14	$(-1/2)(1\pi   \xi   1\pi)$
2 <sub>1</sub> 2 <sub>1</sub>	$(-1/2)(2\pi   \xi   2\pi)$	17 17	$(-1/2)(1\pi   \xi   1\pi)$
2 <sub>2</sub> 2 <sub>2</sub>	$(1/2)(2\pi   \xi   2\pi) - (1/3)(1\pi   \xi   1\pi)$	20 20	$(1/2)(2\pi   \xi   2\pi)$
3 3	$(1/2)(2\pi   \xi   2\pi)$	21 21	$(1/2)(1\pi   \xi   1\pi)$
4 <sub>1</sub> 4 <sub>1</sub>	$(-1/2)(2\pi   \xi   2\pi)$	22 <sub>1</sub> 22 <sub>1</sub>	$(-1/2)(2\pi   \xi   2\pi)$
4 <sub>2</sub> 4 <sub>2</sub>	$(1/6)(2\pi   \xi   2\pi)$	0 1	$(1/2)(1\pi   \xi   2\pi)$
5 5	$(1/2)(1\pi   \xi   1\pi)$	3 5	$(1/2)(1\pi   \xi   2\pi)$
6 <sub>1</sub> 6 <sub>1</sub>	$(1/2)(2\pi   \xi   2\pi)$	20 21	$(1/2)(1\pi   \xi   2\pi)$
6 <sub>2</sub> 6 <sub>2</sub>	$(-1/6)(2\pi   \xi   2\pi)$	3 2 <sub>1</sub>	$(-1/2\sqrt{2})(1\pi   \xi   2\pi)$
7 <sub>1</sub> 7 <sub>1</sub>	$(1/2)(1\pi   \xi   1\pi)$	3 2 <sub>2</sub>	$(-1/2\sqrt{6})(1\pi   \xi   2\pi)$
7 <sub>2</sub> 7 <sub>2</sub>	$(-1/6)(1\pi   \xi   1\pi)$	5 4 <sub>1</sub>	$(-1/2\sqrt{2})(1\pi   \xi   2\pi)$
8 <sub>1</sub> 8 <sub>1</sub>	$(-1/2)(2\pi   \xi   2\pi)$	5 4 <sub>2</sub>	$(1/2\sqrt{6})(1\pi   \xi   2\pi)$
8 <sub>2</sub> 8 <sub>2</sub>	$(1/2)(2\pi   \xi   2\pi) - (1/3)(1\pi   \xi   1\pi)$	0 2 <sub>1</sub>	$(1/2\sqrt{2})(1\pi   \xi   2\pi)$
8 <sub>4</sub> 8 <sub>4</sub>	$(1/2)(2\pi   \xi   2\pi) - (1/9)(1\pi   \xi   1\pi)$	0 2 <sub>2</sub>	$(1/2\sqrt{6})(1\pi   \xi   2\pi)$
8 <sub>5</sub> 8 <sub>5</sub>	$(-5/8)(1\pi   \xi   1\pi)$	1 4 <sub>1</sub>	$(1/2\sqrt{2})(1\pi   \xi   2\pi)$
9 <sub>1</sub> 9 <sub>1</sub>	$(1/2)(2\pi   \xi   2\pi)$	1 4 <sub>2</sub>	$(-1/2\sqrt{6})(1\pi   \xi   2\pi)$
10 <sub>1</sub> 10 <sub>1</sub>	$(-1/2)(2\pi   \xi   2\pi)$	2 <sub>2</sub> 4 <sub>2</sub>	$(-1/3)(1\pi   \xi   2\pi)$
10 <sub>2</sub> 10 <sub>2</sub>	$(1/6)(2\pi   \xi   2\pi)$	6 <sub>1</sub> 7 <sub>1</sub>	$(1/2)(1\pi   \xi   2\pi)$
12 12	$(-1/2)(2\pi   \xi   2\pi)$	6 <sub>2</sub> 7 <sub>2</sub>	$(-1/6)(1\pi   \xi   2\pi)$

$\langle 9_1   \mathcal{E}   8_1 \rangle$	$(-1/2\sqrt{2})(1\pi   \xi   2\pi)$	$\langle 12   \mathcal{E}   13 \rangle$	$(-1/2)(1\pi   \xi   2\pi)$
9 <sub>1</sub> 8 <sub>2</sub>	$(-1/2\sqrt{6})(1\pi   \xi   2\pi)$	2 <sub>1</sub> 2 <sub>2</sub>	$(-1/\sqrt{12})[(2\pi   \xi   2\pi) + (1\pi   \xi   1\pi)]$
6 <sub>1</sub> 8 <sub>1</sub>	$(1/2\sqrt{2})(1\pi   \xi   2\pi)$	4 <sub>1</sub> 4 <sub>2</sub>	$(1/\sqrt{3})(1\pi   \xi   1\pi)$
6 <sub>1</sub> 8 <sub>2</sub>	$(1/2\sqrt{6})(1\pi   \xi   2\pi)$	10 <sub>1</sub> 10 <sub>2</sub>	$(1/\sqrt{3})(1\pi   \xi   1\pi)$
7 <sub>1</sub> 10 <sub>1</sub>	$(1/2\sqrt{2})(1\pi   \xi   2\pi)$	8 <sub>1</sub> 8 <sub>2</sub>	$(-1/\sqrt{12})[(2\pi   \xi   2\pi) + (1\pi   \xi   1\pi)]$
7 <sub>1</sub> 10 <sub>2</sub>	$(-1/2\sqrt{6})(1\pi   \xi   2\pi)$	8 <sub>4</sub> 8 <sub>5</sub>	$(-\sqrt{2}/9)(1\pi   \xi   1\pi)$
8 <sub>2</sub> 10 <sub>2</sub>	$(-1/3)(1\pi   \xi   2\pi)$	2 <sub>1</sub> 4 <sub>2</sub>	$(1/\sqrt{12})(1\pi   \xi   2\pi)$
20 22 <sub>1</sub>	$(1/2\sqrt{2})(1\pi   \xi   2\pi)$	2 <sub>2</sub> 4 <sub>1</sub>	$(-1/\sqrt{12})(1\pi   \xi   2\pi)$
6 <sub>2</sub> 8 <sub>3</sub>	$(-1/2\sqrt{2})(1\pi   \xi   2\pi)$	8 <sub>1</sub> 10 <sub>2</sub>	$(1/\sqrt{12})(1\pi   \xi   2\pi)$
6 <sub>2</sub> 8 <sub>4</sub>	$(-1/6\sqrt{6})(1\pi   \xi   2\pi)$	8 <sub>2</sub> 10 <sub>1</sub>	$(-1/\sqrt{12})(1\pi   \xi   2\pi)$
6 <sub>2</sub> 8 <sub>5</sub>	$(-1/3\sqrt{3})(1\pi   \xi   2\pi)$		

we can neglect the two center atomic integrals. For the one center atomic integrals we used the values which was estimated by Ishiguro<sup>11)</sup> from the atomic spectral data. Those are :

$$(2p\pi_N | \xi | 2p\pi_N) = 73.3\text{cm}^{-1}, (2p\pi_o | \xi | 2p\pi_o) = 151\text{cm}^{-1}.$$

The results are collected in Table XXX.

TABLE XXX.  
Spin-Orbit Coupling Constant

State	case	calc.	obs.
Ground <sup>2</sup> I <sub>1</sub>	d	130.0cm <sup>-1</sup>	123.8cm <sup>-1</sup> 9)
	e	130.0	
First Excited <sup>2</sup> I <sub>1</sub>	d	1.2	
	e	- 2.0	
Lowest <sup>4</sup> I <sub>1</sub>	a	- 38.4	
	b	- 38.5	
	c	- 37.1	

## 10. Discussion and Summary

In the present calculations on the energies and wave functions for various symmetry states of the NO molecule and the NO<sup>+</sup> ion, the effective nuclear charges are chosen as  $Z_{1N}=6.7$ ,  $Z_{2N}=1.95$ ,  $Z_{1O}=7.7$ , and  $Z_{2O}=2.275$ , as Slater's rule<sup>2)</sup> indicates. The values of the effective nuclear charge  $Z$  should be determined, in principle, to make the total energies of the electron

system (molecule and separated atoms) in the various states minima. Values given by Slater's rule are used in the present calculations because of the situation of the computational facilities. Values used for the effective nuclear charges are nearly the best values for the case of NO molecule, while a little deviated from the best values for the case of the NO<sup>+</sup> ion, as we can see in Table XXXI<sup>12)</sup>.

The calculated dissociation energies accounted for 38% of the experimental one for the case of the NO molecule, and 37% of the experimental one for the case of the NO<sup>+</sup> ion. The dissociation energy  $D_e$  is obtained by subtracting the energy  $E$  of the molecule from the energy  $E_\infty$  of the separated atoms in their ground states  $D_e = E_\infty - E$ , where the quantities  $E$  and  $E_\infty$  should be minimized with respect to variation of the effective nuclear charges  $Z$ 's respectively. The effective nuclear charges used are nearly the best ones for the state of the separa-

TABLE XXXI. Calculated and Empirical Energies of Atomic States in au

	calc.		obs. <sup>13)</sup>
	present $Z'$ 's	best $Z'$ 's <sup>12)</sup>	
N ( $s^2 p^3 4S^0$ )	-54.265	-54.269	-54.611
N <sup>+</sup> ( $s^2 p^2 3P$ )	-53.782	-53.810	-54.076
O ( $s^2 p^4 3P$ )	-74.533	-74.540	-75.109
O <sup>+</sup> ( $s^2 p^3 4S^0$ )	-74.185	-74.226	-74.609
N ( $s^2 p^3 4S^0$ )+O ( $s^2 p^4 3P$ )	-128.798	-128.809	-129.720
N ( $s^2 p^3 4S^0$ )+O <sup>+</sup> ( $s^2 p^3 4S^0$ )	-128.451	-128.495	-129.220

ted atoms  $N(4S)+O(3P)$ , therefore the calculated dissociation energy for the NO molecule may be the lower limit to the true value. The discrepancy of the calculated ionization energy 7.48ev of the NO molecule and the dissociation energy 4.00 ev of the NO<sup>+</sup> ion from the experimental Values 9.25ev and 10.95ev, respectively, is mainly due to the fact that the empirical separation between the states  $N(4S)+O(3P)$  and  $N(4S)+O+(4S)$  is 13.602ev<sup>13)</sup>, whereas the calculated separation is 8.54ev (9.44ev if the best  $Z'$ 's<sup>12)</sup> are used for each of the states). We can see evidence of a very difficult situation arising in this type of non-empirical molecular calculation. The dissociation energy is the difference between two large figures, and the errors of our calculation may be of the same order as the dissociation energy.

In order to obtain more accurate wave functions than those shown in the present paper, first we should include  $M$  shell orbitals in the calculation, and secondly we should use different values for each of the effective nuclear charges of the  $1\pi$  molecular orbital and the  $2\pi$  molecular orbital. The first improvement is particularly effective on the wave functions for the  $\Sigma^\pm$  states and  $d$  state of the NO molecule, and the second improvement particularly on the wave functions for the  $\Pi$  state of the NO molecule. The energies of these states will be depressed somewhat, and will approach to the true values.

The dipole moment and the gradients of the electric field depend upon the structure of inner electrons as well as upon the structure of valence electrons. The spin-orbit coupling constant is determined by the structure of  $\pi$ -electrons (valence electrons), because the spin-orbit coupling operator contains  $L_z$ . Compared with dipole moment and the gradient of the electric field, some oscillator strengths ( $2\Pi \rightarrow 2\Sigma^+, 2\Sigma^-, 2d$ ) do not to a large extent depend upon the structure of inner electrons. The wave functions obtained in the present calculations take account of the correlation of valence electrons to larger extents than the correlation of inner electrons.

As shown in Tables XXVIII and XXVI, the values calculated from the wave functions obtained in the present calculations are much different from the experimental values for the gradient of the electric field at nitrogen nucleus, and also

different, though not so much as compared with the ones for  $q$ 's, for the dipole moment. These facts may give us the feeling that the wave function which gives the better value for the energy is not always the one which is satisfactory for the description of some other molecular quantities. The calculated value of the spin-orbit coupling constant for the  ${}^2\Pi$  ground state of the NO molecule is in good agreement with experiment, as shown in Table XXX. The work in progress shows that, as well known by the experiment, the equilibrium internuclear distance of the first excited  ${}^2\Pi$  state of the NO molecule is much different from that of the ground  ${}^2\Pi$  state. So the calculated value  $1.2\sim 2.0\text{cm}^{-1}$ , which is shown in Table XXX, for the spin-orbit coupling constant of the first excited  ${}^2\Pi$  state may not be directly compared with the experiment. This will be reported in the future paper. The agreement of the calculated values with the experimental ones is rather satisfactory for the case of the vertical excitation energies of the NO molecule, as we see in Table XV. So we may have the same order of reliance upon the calculated values, shown in Table XXIV, for the vertical excitation energies of the  $\text{NO}^+$  ion, of which the experimental data seem to be lacking. Recently Broida and Peyson<sup>6)</sup> gave the experimental value 4.7ev for the vertical  ${}^2\Pi$  (ground)- ${}^4\Pi$  transition of the NO molecule. The present calculated value is 5.82ev. The agreement is rather satisfactory. Concerning the  ${}^4\Sigma^-$  state of the NO molecule, Ogawa<sup>14)</sup> has given the experimental value 1.47ev for the  ${}^4\Pi$ - ${}^4\Sigma^-$  transition. This value 1.47ev may be compared with the present calculated value 0.63ev for the  ${}^4\Pi$ - ${}^4\Sigma^-$  interval. The calculated lowest vertical excitation energy relative to the ground state  ${}^1\Sigma^+$  of the  $\text{NO}^+$  ion is 3.02 ev and the calculated dissociation energy of the  $\text{NO}^+$  ion is 4.00ev. So we can say that there exists at least one bound excited state, which has  ${}^1\Sigma^-$  symmetry, for the  $\text{NO}^+$  ion. Experimentally the excited state of the  $\text{NO}^+$  ion has not definitely been studied.

The wave functions for some of various symmetry states can be written to a certain extent by a single configurational wave function, as shown in the tables of the wave functions. So we can say the present calculations show that the SCF orbitals for the ground state are satisfactory for simple description of excited states. Quantities concerning the first excited  ${}^2\Pi$  state and the lowest  ${}^4\Pi$  state of the NO molecule, as well as those concerning the ground  ${}^2\Pi$  state the NO molecule and the ground  ${}^1\Sigma^+$  state of the  $\text{NO}^+$  ion, are calculated particularly in detail. The energy level of the lowest  ${}^4\Pi$  state of the NO molecule is 0.90ev lower than the level of the first excited  ${}^2\Pi$  state. There is a state of the NO molecule with  ${}^4\Sigma^-$  symmetry, the level of which is 0.27ev lower than that of the first excited  ${}^2\Pi$  state.

According to Mulliken's definition<sup>15)</sup>, atomic populations are calculated in order to obtain a useful insight for the wave functions for various states. They are shown in Table XXXII.

TABLE XXXII. Atomic Population<sup>a),15)</sup>

	$2s_N$	$2p\sigma_N$	$2p\pi_N$	$2s_O$	$2p\sigma_O$	$2p\pi_O$	$1\pi$	$2\pi$
Ground $2\Pi$	1.83	1.05	2.10	1.92	1.20	2.90	3.87	1.13
first excited $2\Pi$	1.83	1.05	1.77	1.92	1.20	3.23	3.00	2.00
$4\Pi$	1.83	1.05	2.36	1.92	1.20	2.64	2.98	2.02
$2\Sigma^+$	1.67	0.62	2.75	1.87	0.84	3.25	3.88	2.12
$2\Sigma^-$	1.67	0.61	2.73	1.88	0.84	3.27	3.94	2.06
$4\Sigma^+$	1.67	0.61	3.00	1.88	0.84	3.00	3.00	3.00
$4\Sigma^-$	1.67	0.61	2.73	1.88	0.84	3.27	3.94	2.06
$2\Delta$	1.68	0.60	2.74	1.88	0.84	3.26	3.90	2.10
$4\Delta$	1.67	0.62	3.00	1.88	0.83	3.00	3.00	3.00
$1\Sigma^+$	1.83	1.05	1.48	1.92	1.20	2.52	3.80	0.20
$1\Sigma^-$	1.83	1.05	1.75	1.92	1.20	2.25	2.87	1.13
$3\Sigma^+$	1.83	1.05	1.74	1.92	1.20	2.26	2.89	1.11
$3\Sigma^-$	1.83	1.05	1.74	1.92	1.20	2.26	2.91	1.09
$1\Pi$	1.67	0.61	2.12	1.88	0.84	2.88	3.82	1.18
$3\Pi$	1.67	0.61	2.13	1.88	0.84	2.87	3.78	1.22
$1\Delta$	1.83	1.05	1.73	1.92	1.20	2.27	2.95	1.05
$3\Delta$	1.83	1.05	1.74	1.92	1.20	2.26	2.91	1.09

a) There are slight immigrations of electron between  $\sigma$  and  $\pi$  orbital due to Cl. The amount of immigrated electron is at most  $\sim 0.01$ . These immigrations of electron are neglected in making this table.

We started the present full configuration interaction calculation to see how the results are improved by this type of calculation. It turned out that the improvement is rather not much compared with human labours involved in finding the matrix elements of 10th-20th-degree matrices. The single determinantal wave functions for various states, which are made by the SCF orbitals for the ground state, seem to be satisfactory for simple description of these states, though one should not state definitely conclusions from the results of a single calculation on one molecule. We are now working to obtain the potential curves, including the M shell orbitals in the calculation, for various states of the NO molecule and the  $\text{NO}^+$  ion.

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