

Calculation of the Magnetic Hyperfine Structure Coupling Constants of NO

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A calculation of the magnetic hyperfine structure (hfs) coupling constants of NO has been made using an *ab initio* configuration interaction wave function built from LCAO-MO-SCF orbitals. The constants predicted by this wave function are in good agreement with experiment for the two constants related to the quantities $\langle L_z/r^3 \rangle_{av}$ (constant a) and $\langle (\sin^2\theta)S^-/r^3 \rangle_{av}$ (constant d). The direct calculation of $\langle (3\cos^2\theta-1)S_z/r^3 \rangle_{av}$ (constant c) gives a value which is about 25% less than that predicted by an approximation which implies that unpaired l and s are associated with the same electron. From this calculated value of c the quantity $\langle \psi^2(0) \rangle_{av} - \frac{1}{3}c$ (constant b) now is found to be about 40 Mc/sec instead of 68.91 Mc/sec which has been previously used by experimentalists.

The same wave function has been used to calculate the fine structure constant (spin-orbit coupling) for the $^2\Pi$ ground state of NO. The agreement with experiment is quite satisfactory.

The calculation of the nuclear quadrupole coupling constant q gives about 73% of the observed electronic part assuming that $Q(N^{14}) = 0.02 \times 10^{-24}$ cm².

I. INTRODUCTION

RECENTLY Dousmanis¹ and Mizushima² have calculated the coupling constants of the magnetic hfs spectrum of NO. These authors have constructed simple wave functions which consider only the π electrons of the system in such a way as to obtain agreement with the experimentally observed magnetic hfs constants.^{3,4}

We have felt it would be interesting to calculate these magnetic constants using an *ab initio* wave function which was in no way built to obtain agreement with any of these quantities. For this purpose a configuration interaction function built from LCAO-MO-SCF orbitals seemed quite suitable.

There are, in effect, two parts to a completely *ab initio* calculation: (1) the wave function which describes the molecule; (2) the matrix elements of a particular operator which, as we are using an LCAO type of function, comes down to the calculation of certain kinds of atomic integrals. In the calculation of the magnetic constants the values of these atomic integrals are those used in the previous works.^{1,2}

The procedure of building a wave function to specifically account for some particular observed property seems open to a number of objections: (a) this is by no means an unequivocal procedure. Mizushima developed a perfect pairing VB function while Dousmanis found that a function containing more than one-third ionic character also gave satisfactory results. It is certainly possible that by adjusting molecular parameters to fit the experimental magnetic spectrum a number of other kinds of wave functions would give equally good results. (b) A number of other physical properties of NO have been (or could be in principle) measured—viz., binding

energy, dipole moment, electronic spectra, nuclear quadrupole coupling constants, etc.—and it is not at all sure that a special wave function suitable to explain the magnetic constants would be at all suitable for an understanding of the other properties. (c) Such a procedure cannot go beyond experimental results already known. However, even very approximate theoretical predictions for unstable radicals would be useful as experimental results for these substances are often very difficult to obtain.

In addition, we have felt it would be interesting to use the same wave function to calculate the fine structure constant (spin-orbit coupling) of the ground state of NO as well as the nuclear quadrupole coupling constant. In the former calculation the atomic integrals have been approximated from atomic spectral data. The latter calculation, on the contrary, is completely *ab initio*.

II. MAGNETIC HFS COUPLING CONSTANTS

The explicit form of the energy of magnetic interaction has been given by Gallagher⁴ who has followed the theories developed by Frosch and Foley⁵ and by Dousmanis, Sanders, and Townes.⁶ For example, for the $^2\Pi_{\frac{1}{2}}^+$ state of NO this energy has the following expression:

$$E^{\text{mhf}}(^2\Pi_{\frac{1}{2}}^+) = \left\{ \frac{X-2+\lambda}{2X} \left[\left(a - \frac{b+c}{2} \right) - d(J+\frac{1}{2}) \right] + 2b'X^{-1}(J-\frac{1}{2}) \right. \\ \left. \times (J+\frac{3}{2}) + \frac{X+2-\lambda}{2X} 3 \left(a + \frac{b+c}{2} \right) \right\} \\ \times \frac{F(F+1) - I(I+1) - J(J+1)}{4J(J+1)},$$

¹ G. C. Dousmanis, Phys. Rev. **97**, 967 (1955).

² M. Mizushima, Phys. Rev. **105**, 1262 (1957).

³ C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953); J. J. Gallagher, E. D. Bedard, and C. M. Johnson, Phys. Rev. **93**, 729 (1954).

⁴ J. J. Gallagher and C. M. Johnson, Phys. Rev. **103**, 1727 (1956).

⁵ R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

⁶ G. C. Dousmanis, T. M. Sanders, and C. H. Townes, Phys. Rev. **100**, 1735 (1955).

where I is the angular momentum of the nucleus N , J the total angular momentum of the molecule (except for nuclear spin), F is the vectorial sum of the momenta I and J , and, X which has a large numerical value, is a function of J and the molecular parameter λ with the form:

$$X = [\lambda(\lambda - 4) + 4(J + \frac{1}{2})^2]^{\frac{1}{2}}.$$

The parameter $\lambda = A/B_v$, where A is the fine structure constant and B_v the rotation constant.

The coupling constants are the matrix elements of sums of mono-electronic operators taken between wave functions which are functions of the space and spin coordinates of the electrons of the molecule. These constants are given by the expressions:

$$a = 2g_I\mu_0\mu_n[\Psi(^2\Pi_3^+) | \sum_i (l_{iz}/r_{in}^3) | \Psi(^2\Pi_3^+)]/L_z,$$

$$b = g_I\mu_0\mu_n\{\Psi(^2\Pi_3^+) | 16\pi/3 \sum_i [\delta(r_{in})s_i] - \sum_i [(3\cos^2\theta_{in} - 1)s_{iz}/r_{in}^3] | \Psi(^2\Pi_3^+)\}/S.$$

b' is the nondiagonal matrix element of the same operator taken between the functions $\Psi(^2\Pi_3^+)$ and $\Psi(^2\Pi_1^+)$

$$c = 3g_I\mu_0\mu_n\{\Psi(^2\Pi_3^+) \times [\sum_i [(3\cos^2\theta_{in} - 1)s_{iz}/r_{in}^3] | \Psi(^2\Pi_1^+)\}/S_z,$$

$$d = g_I\mu_0\mu_n\{\Psi(^2\Pi_3^+) \times [\sum_i [3\sin^2\theta_{in}s_i^- \exp(+2i\varphi_i)] | \Psi(^2\Pi_1^-)]/S^-.$$

l_i and s_i are the orbitals angular and spin momenta of

the i th electron; r_{in} , θ_{in} and φ_i are the coordinates of the i th electron measured along the molecular axis Oz starting from the nitrogen nucleus. L and S are the total electronic orbital and spin angular momenta. g_I is the g factor of the N nucleus, μ_n the nuclear magneton and μ_0 the Bohr magneton. s_i^- is the step down spin operator.

Experimentally one can precisely determine only the values of $a - (b+c)/2$ and of d . From the spectrum of the $^2\Pi_3$ state the value of $a + (b+c)/2$ can be also found.⁷ From these two values then by addition and subtraction a and $b+c$ are determined.

In order to give a value to b , the experimental interpretation has used the relation $c = 3(a-d)$. This relation implies that the electron with unpaired angular momentum is the one with unpaired spin. This relation does hold for the particular case of a single determinantal wave function. But it does not usually hold in other kinds of wave functions; for in general the matrix elements of the operator S_z are not identical with the elements of the operator L_z . In addition, as Mizushima² has observed, such a relation cannot hold rigorously since a and c are diagonal matrix elements while d is a nondiagonal element.

III. ELECTRONIC WAVE FUNCTION

A LCAO-MO SCF wave function for NO was previously determined⁸ considering all 15 electrons of the molecule using the $1s$, $2s$, and $2p$ atomic functions with Slater exponents. The one determinant function has the form:

$$\psi_0 = \det[1\sigma 1\bar{\sigma} 2\sigma 2\bar{\sigma} 3\sigma 3\bar{\sigma} 4\sigma 4\bar{\sigma} 5\sigma 5\bar{\sigma} 1\pi^+ 1\bar{\pi}^+ 1\pi^- 1\bar{\pi}^- 2\pi^+],$$

where σ indicates a molecular orbital with projection of orbital angular momentum along the molecular axis

TABLE I. Molecular orbital functions.

Function	Coefficient	1σ	2σ	3σ	4σ	5σ	6σ	$1\pi^+$	$1\pi^-$	$2\pi^+$	$2\pi^-$
ψ_0	1	+-	+-	+-	+-	+-		+-	+-	+	
ψ_1	-1	+-	+-	+-	+-	+-		+	+-	+-	
ψ_2	$-1/\sqrt{2}$	+-	+-	+-	+-	+-		+-	+	+	-
	$+1/\sqrt{2}$	+-	+-	+-	+-	+-		+-	-	+	+
$\psi_{2'}$	$-2/\sqrt{6}$	+-	+-	+-	+-	+-		+-	+	-	+
	$+1/\sqrt{6}$	+-	+-	+-	+-	+-		+-	+	+	-
	$+1/\sqrt{6}$	+-	+-	+-	+-	+-		+-	-	+	+
ψ_3	1	+-	+-	+-	+-	+-		+-		+	+-
ψ_4	$1/\sqrt{2}$	+-	+-	+-	+-	+-		+	-	+-	+
	$-1/\sqrt{2}$	+-	+-	+-	+-	+-		-	+	+-	+
$\psi_{4'}$	$2/\sqrt{6}$	+-	+-	+-	+-	+-		+	+	+-	-
	$-1/\sqrt{6}$	+-	+-	+-	+-	+-		+	-	+-	+
	$-1/\sqrt{6}$	+-	+-	+-	+-	+-		-	+	+-	+
ψ_7	1	+-	+-	+-	+-		+-	+-	+-	+	
ψ_8	$2/\sqrt{6}$	+-	+-	+-	+-	+	+	+-	+-	-	
	$-1/\sqrt{6}$	+-	+-	+-	+-	+	-	+-	+-	+	
	$-1/\sqrt{6}$	+-	+-	+-	+-	-	+	+-	+-	+	
ψ_9	$2/\sqrt{6}$	+-	+-	+-	+	+-	+	+-	+-	-	
	$-1/\sqrt{6}$	+-	+-	+-	+	+-	-	+-	+-	+	
	$-1/\sqrt{6}$	+-	+-	+-	-	+-	+	+-	+-	+	

⁷ R. Beringer, E. B. Rawson, and A. F. Henry, Phys. Rev. **94**, 343 (1954); W. Gordy, Bull. Am. Phys. Soc. **4**, 290 (1959).

⁸ H. Brion, C. M. Moser, and M. Yamazaki, J. Chem. Phys. **30**, 673 (1959).

equal to zero and π indicates a molecular orbital with projection equal to ± 1 . The absence of a bar above σ or π indicates the electron is associated with α spin, the presence of the bar indicates β spin.

One can pass from this function for the ${}^2\Pi_3^+$ state ($\Lambda = +1, \Sigma = +\frac{1}{2}$) to the function ${}^2\Pi_3^+(\Lambda = 1, \Sigma = -\frac{1}{2})$ by changing α spins to β spins and β spins to α spins. One can go from the function for the ${}^2\Pi_3^+$ to the function for the ${}^2\Pi_3^-(\Lambda = -1, \Sigma = +\frac{1}{2})$ state by changing π^+ to π^- and π^- to π^+ . With these conventions the coefficients calculated for the configuration interaction function for the ${}^2\Pi_3^+$ state are the same as those of the configuration interaction function for the ${}^2\Pi_3^+$ and ${}^2\Pi_3^-$ states.

The matrix elements between the ground state and monoexcited π functions for the operators which give rise to the constants a and d are, in general, nonzero.

For the constants b and b' it will be necessary to consider elements between the ground state and monoexcited σ functions for these are the only nonzero terms for the operator $\sum_i \delta(r_{in})s_{iz}$. For c (and also part of b and b') both monoexcited π and σ function will give, in principle, nonzero terms. Di-excited functions with respect to the ground-state function will have only a second order effect; (a) to lower the weight of the ground state configuration; (b) to give a small effect due to interaction between the monoexcited and di-excited configurations. However these two effects are likely to be small.

Thus we have calculated a CI function which includes some of the possible monoexcited π and σ configurations. We have eliminated from the calculation the monoexcited σ functions which have zero interaction with the ground state (two doublets) because we have used the virtual SCF orbitals to construct the excited states.⁹ In this configuration interaction calculation all orbitals are as we have indicated linear combinations of the $1s$, $2s$, and $2p$ atomic functions. Thus with this function we cannot see how important the $3s$ and $3p$ functions would be.

The configuration interaction wave function which we have obtained is:

$$\Psi = 0.93194\psi_0 + 0.00838\psi_1 + 0.06242\psi_2 + 0.05360\psi_{2'} \\ - 0.15546\psi_3 - 0.14363\psi_4 + 0.11157\psi_{4'} - 0.25771\psi_7 \\ + 0.00691\psi_8 + 0.03078\psi_9.$$

The explicit expressions for the ψ_i 's are given in Table I.

IV. THE CALCULATION OF THE MAGNETIC COUPLING CONSTANTS

Using this function, the coupling constants can be evaluated if the values of the matrix elements for the various operators are known. The nonzero matrix elements are listed in Table II. For b we have only given the part $\sum_i \delta(r_{in})s_{iz}$ as the second term is the same as for c . For our functions $b \equiv b'$.

⁹ H. C. Longuet-Higgins and J. A. Pople, Proc. Phys. Soc. (London) A68, 591 (1955).

TABLE II. Matrix elements of operator which gives rise to magnetic constants.^a

	a	c	d	$\sum_i \delta(r_{in})s_{iz}$
H_{00}	a_2	c_2	d_2	0
H_{11}	$2a_2 - a_1$	c_1	0	0
H_{22}	a_1	c_2	$\frac{1}{2}d_1$	0
$H_{2'2'}$	a_1	$\frac{1}{2}(2c_1 + c_2)$	$\frac{1}{2}d_1$	0
H_{33}	$2a_1 - a_2$	c_2	0	0
H_{44}	a_2	c_2	d_2	0
$H_{4'4'}$	a_2	$\frac{1}{2}(4c_1 - c_2)$	$\frac{1}{2}d_2$	0
H_{77}	a_2	c_2	d_2	0
H_{01}	a_{12}	$-c_{12}$	0	0
H_{02}	$-\sqrt{2}a_{12}$	0	$-(1/\sqrt{2})d_{12}$	0
$H_{02'}$	0	$(\sqrt{2}/\sqrt{3})c_{12}$	$(1/\sqrt{6})d_{12}$	0
H_{12}	0	0	$(1/\sqrt{2})d_2$	0
$H_{12'}$	0	0	$(1/\sqrt{6})d_2$	0
H_{13}	0	0	$-d_{12}$	0
H_{14}	$-(1/\sqrt{2})a_{12}$	$(1/\sqrt{2})c_{12}$	0	0
$H_{14'}$	$-(1/\sqrt{6})a_{12}$	$(1/\sqrt{6})c_{12}$	0	0
$H_{22'}$	0	$(1/\sqrt{3})(c_2 - c_1)$	$-(1/2\sqrt{3})d_1$	0
H_{23}	$-\sqrt{2}a_{12}$	0	0	0
H_{24}	$\frac{1}{2}a_{12}$	$-\frac{1}{2}c_{12}$	0	0
$H_{24'}$	$-\frac{1}{2}\sqrt{3}a_{12}$	$\frac{1}{2}\sqrt{3}c_{12}$	$(1/\sqrt{3})d_{12}$	0
$H_{2'3}$	0	$-(\sqrt{2}/\sqrt{3})c_{12}$	0	0
$H_{2'4}$	$(1/\sqrt{3})a_{12}$	$(1/2\sqrt{3})c_{12}$	$(1/\sqrt{3})d_{12}$	0
$H_{2'4'}$	$\frac{1}{2}a_{12}$	$\frac{1}{6}c_{12}$	$\frac{2}{3}d_{12}$	0
H_{34}	0	0	0	0
$H_{34'}$	0	0	$-(\sqrt{2}/\sqrt{3})d_1$	0
$H_{44'}$	0	0	0	0
H_{08}	0	$(\sqrt{2}/\sqrt{3})c_{56}$	0	$(\sqrt{2}/\sqrt{3})\delta_{56}$
H_{09}	0	$(\sqrt{2}/\sqrt{3})c_{46}$	0	$(\sqrt{2}/\sqrt{3})\delta_{46}$
H_{89}	0	$\frac{2}{3}c_{45}$	0	$\frac{2}{3}\delta_{45}$
H_{88}	a_2	$\frac{1}{2}(2c_5 + 2c_6 - c_2)$	$-\frac{1}{2}d_2$	$\frac{1}{2}(2\delta_5 + 2\delta_6 - \delta_2)$
H_{99}	a_2	$\frac{1}{2}(2c_4 + 2c_6 - c_2)$	$-\frac{1}{2}d_2$	$\frac{1}{2}(2\delta_4 + 2\delta_6 - \delta_2)$
H_{78}	0	$-(\sqrt{2}/\sqrt{3})c_{56}$	0	$-(\sqrt{2}/\sqrt{3})\delta_{56}$

^a $n_{ij} = n_{ii}(n = a, c, d, \delta)$. Here n_{ij} indicates a matrix element taken over molecular orbitals i and j , where

$$4 = -0.0020(1s_n) - 0.0215(1s_0) + 0.7978(2s_n) - 0.7259(2s_0) \\ - 0.0147(2p\sigma_n) + 0.2995(2p\sigma_0), \\ 5 = 0.0217(1s_n) + 0.0192(1s_0) + 0.4727(2s_n) + 0.2368(2s_0) \\ - 0.6149(2p\sigma_n) - 0.5794(2p\sigma_0), \\ 6 = 0.0799(1s_n) - 0.0906(1s_0) + 0.7382(2s_n) - 0.7703(2s_0) \\ + 1.0899(2p\sigma_n) - 1.0092(2p\sigma_0), \\ 1 = 0.5232(2p\pi_n) + 0.7508(2p\pi_0), \\ 2 = 0.8781(2p\pi_n) - 0.6936(2p\pi_0).$$

The numerical value of these matrix elements might be obtained by using Slater orbitals to represent the atomic functions. But it seems well established by now that the Slater orbitals would give too small values for the atomic integrals over $1/r^3$. Agreement with experimental results for the constants a and d are only possible if the values given by Mizushima¹⁰ are used. These are listed in Table III. The same for the one-center integrals values could be obtained using Slater orbitals if the exponent Z for the $2p\pi$ orbital is larger than would be deduced from Slater's rules. This is in agreement with the conclusion of Kotani et al.¹¹ on the O_2 molecule who found that the $2p$ orbitals had to be contracted in order to account for the magnetic structure of this molecule.

It might seem inconsistent to use Hartree orbitals for

¹⁰ That is to say the values found from Hartree orbitals for the two-center integrals and those proposed by Dousmanis¹ for the one-center integrals which were determined using the Hartree function and modifying the result.

¹¹ M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, J. Phys. Soc. (Japan) 12, 707 (1957).

TABLE III. Values of atomic integrals (in units of 10^{24} cm^{-3}) used to calculate the magnetic coupling constants.

$2p\pi_N(1/r_N^3)2p\pi_N = 22.5$	$2p\pi_N[(3 \cos^2\theta_N - 1)/r_N^3]2p\pi_N = -9$	$2p\pi_N(\sin^2\theta_N/r_N^3)2p\pi_N = 18.0$
$2p\pi_N(1/r_N^3)2p\pi_O = 0.9$	$2p\pi_N[(3 \cos^2\theta_N - 1)/r_N^3]2p\pi_O = -0.15$	$2p\pi_N(\sin^2\theta_N/r_N^3)2p\pi_O = 0.65$
$2p\pi_O(1/r_N^3)2p\pi_O = 0.6$	$2p\pi_O[(3 \cos^2\theta_N - 1)/r_N^3]2p\pi_O = 0.69$	$2p\pi_O(\sin^2\theta_N/r_N^3)2p\pi_O = 0.17$

the atomic functions to calculate the magnetic constants and Slater orbitals to determine the molecular functions. But from previous work¹² it can be inferred that the coefficients of the molecular orbitals would not be significantly changed if Hartree-Fock atomic orbitals has been used in the computation.

For the calculation of constant c , the atomic integrals over σ and s orbitals are also necessary. The values of the monocentric integrals can be derived from those given by Dousmanis; the two-center integrals were taken from the values over Slater orbitals calculated by Dr. Richardson. (Table VIII). As the contribution to c from these integrals over s and σ orbitals is only about $0.2 \times 10^{24} \text{ cm}^{-3}$ it would seem that the error involved in using this approximation is not important.

The results for both the single determinant and configuration interaction function are assembled in Table IV. The agreement for the two constants a and d between the values predicted by the configuration interaction function and found from experiment is satisfactory. The experimental value of these two constants can be obtained from the spectrum unambiguously. There is a small difference for d about 6% which might be explained, following Dousmanis,¹ by assuming that the π molecular orbitals are not linear combinations of pure $2p\pi$ atomic orbitals but the atomic orbitals are, in fact, somewhat "flattened out." The same effect might be found from a configuration interaction function which included d basis functions. In any event even if we assume these flattened atomic functions make up the molecular orbital it would only lower the value of c which we have calculated by about 3%.

TABLE IV. Values of magnetic hfs constants a , c , and d (in units of 10^{24} cm^{-3}).

Function	$\frac{1}{2}a = \left\langle \frac{L_z}{r^3} \right\rangle_{av}$	$\frac{1}{2}d = \left\langle \frac{\sin^2\theta S_z}{r^3} \right\rangle_{av}$	$\frac{1}{2}c = \left\langle \frac{(3 \cos^2\theta - 1)S_z}{r^3} \right\rangle_{av}$
One determinant ^a (this paper)	16.54	13.17	-6.4 ^b
Configuration interaction (this paper)	14.54	12.55	-7 (-8.6) ^b
Dousmanis ^c	14.8	11.7	-5.6 ^b
Mizushima ^d	14.9	13.4	-11.8
Observed ^e			(-10.4) ^b

^a Dr. M. Karplus has independently made the same calculation for the one determinant function [communication given before the Quantum Mechanical Conference, Boulder, Colorado, June, 1959, to be published in *Revs. Modern Phys.*].

^b Deduced using the relation $c = 3(a - d)$.

^c See reference 1.

^d See reference 2.

^e See reference 4.

¹² See A. Freeman, *J. Chem. Phys.* **28**, 230 (1958) and M. Krauss, *J. Chem. Phys.* **28**, 102 (1958) for a comparison of wave functions for OH.

It seems thus reasonable to believe that the experimental value of c should not be greatly different from the value predicted by our configuration interaction function. It will be seen that this value differs by 23% from that which would be found from the approximation $c = 3(a - d)$.

From the readily obtained experimental value of $b + c = -6.57 \times 10^{24} \text{ cm}^{-3}$ and from this calculated value of c , a value of $b = 14.4 \times 10^{24} \text{ cm}^{-3}$ is obtained instead of the value $24.6 \times 10^{24} \text{ cm}^{-3}$ which has been proposed experimentally using for c the formula $c = 3(a - d)$.

The calculation of $b + c$ is straight forward since it is equal to¹³:

$$\frac{16\pi}{3}\psi^2(0) + \frac{2c}{3},$$

where

$$\psi^2(0) = g_I \mu_0 \mu_N \{ \Psi(^2\Pi_1^+) | \sum_i [\delta(r_{in}) s_{iz}] | \Psi(^2\Pi_1^+) \} / S_z.$$

Using the single determinant wave function, $\psi^2(0)$ would be zero. A nonzero value is found from the configuration interaction function which includes, as we have indicated, some monoexcited σ configurations. The importance of these has been stressed in earlier work on O_2 .¹¹

Using Hartree-Fock atomic orbitals¹⁴ the value of wave function at the nitrogen nucleus is:

$$\psi^2(0) = 0.092 \text{ a.u.},$$

from which it is readily found:

$$(16\pi/3)\psi^2(0) = 10 \times 10^{24} \text{ cm}^{-3}.$$

Adding to this the value previously calculated for c , then: $b + c = -4.01 \times 10^{24} \text{ cm}^{-3}$ instead of the experimental value of $-6.57 \times 10^{24} \text{ cm}^{-3}$.

It may be that the disagreement with the experimental result is due principally to the error in the calculation of $\psi^2(0)$ which is rather sensitive to small changes in the wave function.¹⁵ If, nonetheless, b is deduced from this calculated above value for $\psi^2(0)$ and the experimental value of $b + c$, there is found for b :

$$b = 18.3 \times 10^{24} \text{ cm}^{-3}.$$

In fact, the experimental constant $(b + c)$ is the differ-

¹³ We use here the notation $\psi^2(0)$ that usage has consecrated even though evidently incorrect.

¹⁴ For N: D. R. Hartree and W. Hartree, *Proc. Phys. Soc. (London)* **A193**, 302 (1948); for O: D. R. Hartree, W. Hartree, and B. Swirls, *Phil. Trans. Roy. Soc. (London)* **A238**, 229 (1939).

¹⁵ Using Slater orbitals, which exaggerates the value of the wave function at the nucleus,¹¹ there is found for $\psi^2(0)$ 0.103 a.u. and $b + c = -2.8 \times 10^{24} \text{ cm}^{-3}$.

ence between two large numbers and both constants can be increased or decreased and still more or less the same value found for the sum.

However, it seems reasonable to set the limits of b as:

$$14.4 \leq b \leq 18.3 \times 10^{24} \text{ cm}^{-3},$$

with a rather marked preference for the lower figure. Table V lists the different possibilities.

Gallagher⁴ has commented on the small difference between the hfs spectra which he measured and calculated. The difference may be due to an incorrect value of b chosen by Gallagher. Also this might be due to the l uncoupling effect on the magnetic interaction energy due to mixing with the $^2\Sigma_3$ state. We are unfortunately not able to calculate this effect theoretically with our wave function for the lowest observed $^2\Sigma_3$ state probably corresponds to an excitation to a $3s$ orbital, which was not included in the set of basis functions. We hope to investigate this possibility in the near future.

As the term in b in the expression for the energy of the magnetic interaction is very small in comparison with the terms which include the constants a , d and $b+c$, it is difficult, in view of the experimental error present in the determination of the hyperfine spectra, to try to find a better fit in order to verify the theoretical value proposed for b .

V. CALCULATION OF FINE STRUCTURE CONSTANT AND NUCLEAR QUADRUPOLE COUPLING CONSTANT

(a) Spin-Orbit Coupling Constant A

The energy splitting due to spin-orbit interaction in NO is AL_zS_z , where A is the spin-orbit coupling constant:

$$A = \frac{1}{2m^2c^2} \left[\Psi(^2\Pi_{3/2}) \left| \sum_i \frac{1}{r_i} \frac{dU}{dr_i} l_{zi} s_{zi} \right| \Psi(^2\Pi_{3/2}) \right] / L_z S_z$$

U is the potential energy of the i th electron at a point r_i . The matrix elements of the spin-orbit coupling operator

TABLE V. Values of $\langle \psi^2(0) \rangle_{av}$ and $b = (16\pi/3)\psi^2(0) - \frac{1}{3}c$ (in units of 10^{24} cm^{-3}).

	$\langle \psi^2(0) \rangle_{av}$
From $b+c$ experimental and $c=3(a-d)$	0.85
Mizushima ^a	0.5
This paper, from c calculated and $b+c$ experimental	0.44
This paper, direct calculation	0.6
$b = (16\pi/3)\psi^2(0) - \frac{1}{3}c$	
Used by experimentalists	24.6
This paper, from calculated c and $b+c$ experimental	14.4
This paper, from calculated $\psi^2(0)$ and $b+c$ experimental	18.3
This paper, direct calculation	17

^a See reference 2.

TABLE VI. Matrix elements of spin-orbit coupling operator.^a

H_{00}	A_2	$H_{02'}$	$-(\sqrt{2}/\sqrt{3})A_{12}$
H_{11}	A_1	H_{14}	$-(1/\sqrt{2})A_{12}$
H_{22}	A_2	$H_{14'}$	$-(1/\sqrt{6})A_{12}$
$H_{2'2'}$	$-\frac{1}{3}(2A_1+3A_2)$	$H_{22'}$	$(1/\sqrt{3})(A_1-A_2)$
H_{33}	A_2	H_{34}	$-\frac{1}{2}A_{12}$
H_{44}	$-A_2$	$H_{34'}$	$\frac{1}{2}\sqrt{3}A_{12}$
$H_{4'4'}$	$\frac{1}{3}A_2$	$H_{2'3}$	$\sqrt{2}A_{12}$
H_{77}	A_2	$H_{2'4}$	$(1/2\sqrt{3})A_{12}$
H_{01}	$-A_{12}$	$H_{2'4'}$	$\frac{1}{6}A_{12}$

^a The subscripts of A are defined in Table II.

are given in Table VI. As dU/dr_i falls off very rapidly with r_i it seems reasonable to neglect the two center atomic integrals (as is usually done in this kind of calculation). For the one center atomic integrals we have taken the values given by Ishiguro¹⁶ which he estimated from atomic spectral data. These are:

$$2p\pi_N \frac{1}{r_N} \frac{dU}{dr_N} = 2p\pi_N = 73.3 \text{ cm}^{-1},$$

$$2p\pi_O \frac{1}{r_O} \frac{dU}{dr_O} = 2p\pi_O = 151 \text{ cm}^{-1}.$$

In Table VII the results of our calculations using both the single determinant and configuration interaction functions (eliminating ψ_8 and ψ_9) are given as well as the results obtained by Mizushima. The agreement with experiment is very good for both of our functions. It is of interest to note that the values of the atomic integrals suggested by Ishiguro are somewhat different from those given by Mizushima.

(b) The Coupling Constant of the Electric Quadrupole hfs

The electric quadrupole coupling constant q is given by the relation:

$$q = q(\text{nuclear}) - q(\text{electronic})$$

$$= \frac{2Z}{R^3} \left[\Psi(^2\Pi_{3/2}) \left| \sum_i \frac{3 \cos^2\theta_{in} - 1}{r_{in}^3} \right| \Psi(^2\Pi_{3/2}) \right],$$

where Z = nuclear charge of oxygen, and R = equilibrium distance (1.15 Å).

TABLE VII. Fine structure constant A (in cm^{-1}).

One determinant function ^a (this paper)	129.2
Interaction configuration function (8 terms) (this paper)	124.1
Mizushima ^b	112
Observed ^b	123.8

^a Also calculated by Ishiguro.¹⁶
^b See reference 4.

¹⁶ E. Ishiguro, Quarterly Progress Report, SSMPG, Massachusetts Institute of Technology, October 15, 1958, p. 61.

TABLE VIII. Values of atomic integrals $\chi_1[(3 \cos^2\theta_N - 1)/r_N^3]\chi_2$ (in a.u.) (over orthogonalized Slater orbitals).

1s _N	1s _N	0
1s _N	1s _O	0.000033
1s _N	2s _N	0
1s _N	2s _O	0.055177
1s _N	2p _{σN}	0
1s _N	2p _{σO}	0.097083
1s _O	1s _O	0.195217
1s _O	2s _N	0.008539
1s _O	2s _O	0.000001
1s _O	2p _{σN}	0.014164
1s _O	2p _{σO}	0.014573
2s _N	2s _N	0
2s _N	2s _O	0.077091
2s _N	2p _{σN}	0
2s _N	2p _{σO}	0.105250
2s _O	2s _O	0.174843
2s _O	2p _{σN}	0.214281
2s _O	2p _{σO}	0.136493
2p _{σN}	2p _{σN}	1.977300
2p _{σN}	2p _{σO}	0.316346
2p _{σN}	2p _{σO}	0.215596
2p _{πN}	2p _{πN}	-0.988650
2p _{πN}	2p _{πO}	-0.003257
2p _{πO}	2p _{πO}	0.126131

In the calculation reported earlier in this paper nearly always we were concerned only with the π electrons of the molecules. For these electrons it was often possible to use more or less the "best" atomic integrals. By "best" we mean not only Hartree-Fock integrals, but either these adjusted to give the best results or the integrals taken from experimental data. But in the calculation of q , the operator contains neither L_z nor S_z so we must know the values of atomic integrals for all the electrons. Thus it has only seemed feasible to carry out a completely *ab initio* calculation using Slater orbitals to calculate the atomic integrals as were used to calculate the molecular functions. The values of the atomic integrals are those collected in Table VIII.

For the one determinant function there is found:

$$q = 1.559 - 1.333 = 0.226 \text{ a.u.},$$

and for the complete configuration interaction function:

$$q = 1.559 - 1.405 = 0.154 \text{ a.u.}$$

This positive value of q taken with the experimental value⁴ of eqQ for NO = -1.75 Mc/sec would lead to:

$$Q(\text{N}^{14}) = -0.05 \times 10^{-24} \text{ cm}^2.$$

A negative value of Q would be in contradiction with the

hypothesis proposed by Moszkowski and Townes¹⁷ that positive Q should be associated with an odd-odd nucleus. Some more or less empirical calculations have given positive values of Q between the limits^{1,18}:

$$0.007 \leq Q \leq 0.03 \times 10^{-24} \text{ cm}^2.$$

It is interesting to compare our results with a very similar calculation of q in CO¹⁷ recently reported by Richardson.¹⁹ Using a single determinant function built on LCAO-MO-SCF orbitals (with Slater exponents for the atomic functions) he found about 74% of the electronic part of q (if one assumes) the value $Q(\text{O}^{17}) = -0.03 \times 10^{-24} \text{ cm}^2$ proposed by Rosenblum and Nethercot.²⁰ In a similar way if we assume that $Q(\text{N}^{14}) = +0.02 \times 10^{-24} \text{ cm}^2$ then we find that our configuration interaction calculation accounts for about 73% of the true value of q electronic.

Thus it seems that Slater orbitals underestimate the values of atomic integrals in $(3 \cos^2\theta - 1)/r^3$.²¹

Recently Kato and Nakahara²² have calculated $Q(\text{N}^{14})$ using an LCAO-MO-SCF function for NH₃ calculated by Duncan²³ and Slater orbitals for the atomic functions. They have found that $Q(\text{N}^{14}) \sim 0.01 \times 10^{-24} \text{ cm}^2$. But it should be remembered that the Slater 1s hydrogen functions which surround the nitrogen nucleus are also the Hartree-Fock functions. Thus if we could repeat the calculation for NO using better atomic functions it seems entirely plausible that the agreement with experiment should be much better.

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¹⁷ S. A. Moszkowski and C. H. Townes, Phys. Rev. **93**, 306 (1954).

¹⁸ A. Bassompierre, Discussions Faraday Soc. **19**, 260 (1955).

¹⁹ J. Richardson, Revs. Modern Phys. (to be published).

²⁰ B. Rosenblum and H. Nethercot, J. Chem. Phys. **27**, 828 (1957).

²¹ T. P. Das, Bull. Am. Phys. Soc. **1**, 215 (1956).

²² Y. Kato and O. Nakahara, J. Phys. Soc. (Japan) **14**, 690 (1959).

²³ A. B. F. Duncan, J. Chem. Phys. **27**, 423 (1957).