basis of the comparison of the first-approximation potential function used here with the previous exact calculations,[7,8] we conclude that the correct eigenvalues are systematically lower by 4 to 5×10^{-3} electron volt than the values calculated here. Note that this absolute error is of the same order of magnitude as the g_{00} term. We believe the differences in the eigenvalues are more accurate than this error in the absolute values, however.

To test the convergence of the numerical integration for the rapidly varying higher state wave functions, the integration was done for an interval $\Delta r_n = 0.025$, and by using a linear interpolation for the potential at the intermediate points; this test shifted the eigenvalues downward approximately three parts in 10^5, which is small compared with the effect of the uncertainties in the potential.

[7] E. A. Hylleraas, Z. Physik 71, 739 (1931).
[8] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) A246, 215 (1953–1954).

III. D_2^+ ION

As a final calculation we have determined the number of bound states of the D_2^+ ion. The number of bound states is one less than the number of nodes of the lowest free-state solution. For this calculation the g_{00} term appropriate to D_2^+ was neglected; the integration proceeded in steps of $\Delta r_n = 0.025$, using a linear interpolation of the potential. In this approximation and for $J=0$ we find 27 bound states for the D_2^+ ion.

Note that for D_2^+ there are $\sqrt{2}$ times as many levels as for H_2^+. This result would follow rigorously for a parabolic potential or in the limit of applicability of the WKB solution.

ACKNOWLEDGMENT

Hyperfine Structure of the Microwave Spectra of the NO Molecule and the Nuclear Quadrupole Moment of Nitrogen

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(Received March 23, 1960)

The frequencies of the magnetic resonance spectrum of the NO molecule has been recalculated by using the new value of spin-orbit coupling constants and by taking the effect of l uncoupling into consideration. The agreement between the theoretical and experimental results is improved over the previous calculation. By combining the magnetic hyperfine and nuclear quadrupole coupling constants the ratio of the quadrupole moment to the magnetic moment of the nitrogen nucleus is obtained. The nuclear quadrupole moment of nitrogen is found to be $(0.016\pm0.007)\times10^{-24}$ cm^2. The uncertainty of this value is chiefly due to that of the coupling constants rather than to the nature of the method itself.

THE theory of the hyperfine structure of the microwave spectra of NO and the interactions between the various spin angular momenta have been discussed in several papers in the literature.[1-9] Recently Favero, Mirri, and Gordy[10] have measured the rotational transitions of the NO molecule in the $^2\pi_{\frac{3}{2}}$ state and by combining the frequencies of this set of lines with those associated with the $^2\pi_{\frac{1}{2}}$ levels they made an accurate determination of the hyperfine coupling constants. They also obtained the spin-orbit coupling constant as 122.094 cm^{-1} instead of 124.2 cm^{-1}, the value determined by optical spectroscopy.[11] The theory of magnetic resonance spectrum of NO has been given by Lin and Mizushima.[8] These authors used the old value of spin-orbit interaction constant in their calculation and were able to fit the experimental data only within 5 Mc/sec. They suggested that this discrepancy might be due to the uncertainty in the spin-orbit term. With the new value of the various coupling constants given by Favero, Mirri, and Gordy[10] we have recalculated the frequencies of the resonance spectrum. The calculation has also been slightly modified to include the effect of l uncoupling[9] which was neglected in reference 8. The results are given in Table I. It may be noted that with the exception of H_7 the theoretical frequencies agree with experiment within 1 Mc/sec.

[1] R. Beringer and J. G. Castle, Jr., Phys. Rev. 78, 581 (1950).
[2] H. Margenau and A. Henry, Phys. Rev. 78, 587 (1950).
[3] A. Henry, Phys. Rev. 80, 549 (1950).
[4] C. A. Burrus and W. Gordy, Phys. Rev. 92, 1437 (1953).
[5] R. Beringer, E. B. Rawson, and A. F. Henry, Phys. Rev. 94, 343 (1954).
[6] M. Mizushima, Phys. Rev. 94, 569 (1954).
[7] G. C. Dousmanis, Phys. Rev. 97, 967 (1955).
[8] C. C. Lin and M. Mizushima, Phys. Rev. 100, 1726 (1955).
[9] J. J. Gallagher and C. M. Johnson, Phys. Rev. 103, 1727 (1956).
[10] P. G. Favero, A. M. Mirri, and W. Gordy, Phys. Rev. 114, 1534 (1959).
[11] M. Guillery, Z. Physik 42, 121 (1927); F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. 30, 150 (1927).

Line	Transitions $M_J, M_I \to M_{J-1}, M_I$		Resonance field (in gauss)	Observed frequency (in Mc/sec)	Calculated frequency (in Mc/sec)
H_1	$\frac{3}{2}, 1 \to$	$\frac{1}{2}, 1$	8398.61	9269.94	9269.9
H_2	$\frac{3}{2}, 0 \to$	$\frac{1}{2}, 0$	8425.71	9270.65	9270.7
H_3	$\frac{3}{2}, -1 \to$	$\frac{1}{2}, -1$	8453.44	9270.65	9271.0
H_4	$\frac{1}{2}, 1 \to$	$-\frac{1}{2}, 1$	8501.49	9270.65	9269.8
H_5	$\frac{1}{2}, 0 \to$	$-\frac{1}{2}, 0$	8528.28	9270.65	9269.7
H_6	$\frac{1}{2}, -1 \to$	$-\frac{1}{2}, -1$	8555.84	9270.65	9270.6
H_7	$-\frac{1}{2}, 1 \to$	$-\frac{3}{2}, 1$	8600.97	9269.81	9268.2
H_8	$-\frac{1}{2}, 0 \to$	$-\frac{3}{2}, 0$	8629.71	9270.65	9269.6
H_9	$-\frac{1}{2}, -1 \to$	$-\frac{3}{2}, -1$	8656.46	9270.65	9270.3

Two nuclear quadrupole coupling constants of the NO molecule have been determined.[8–10] The first one, eQq_1, is the usual coupling term[12] which is proportional to $(\partial^2 V/\partial z^2)$, while the second,

$$eQq_2 = e^2 Q (3 \sin^2\chi / r^3)_{av}, \qquad (1)$$

is observable only in molecules with $|\Lambda| = 1$, and, in fact, NO is the only molecule for which this constant has been evaluated from experiment. In this equation r is the length of the line joining the electron to the nitrogen nucleus and χ is the angle between this line and the internuclear axis. The quantity eQq_2 here is identical to eQq' in reference 8, but is three times the corresponding constant defined by Gallagher and Johnson.[9,13] With the self-consistent field approximation for the electronic structure of the molecule (i.e., the electronic wave function is expressed in the form of a Slater determinant), it can be shown that the average process in Eq. (1) applies only to the unpaired electron rather than all electrons. In other words the "effective number" n in Eq. (19) of reference 8 is equal to one provided that the configuration interaction is neglected.

From the study of the magnetic hyperfine structure in the rotational spectrum it has been found that[7]

$$3\mu\mu_0 (\sin^2\chi / r^3)_{av} = 112.6 \text{ Mc/sec}, \qquad (2)$$

where μ is the magnetic moment of the nitrogen nucleus and μ_0, the Bohr magneton. Again the average symbol

here pertains only to the odd electron. By combining Eqs. (1) and (2) we obtain the ratio of the electric quadrupole moment to the magnetic moment which leads to a direct determination of the former quantity. Using 22 Mc/sec for eQq_2 as given in reference 10 one finds $Q = 0.016 \times 10^{-24}$ cm². In this procedure we have avoided the difficult task of ascertaining the magnitude of $(\partial^2 V/\partial z^2)$ at the nucleus and thus eliminated the main source of error in the determination of nuclear quadrupole moment. The accuracy of this method is only limited by the use of Hartree-type approximate electronic wave functions and the neglect of the Stern-heimer correction.[14] The latter effect arises from the polarization of the inner core electrons by the valence electrons. The distorted inner core cloud interacts with the nucleus in a way similar to the interaction between the valence electrons and the nuclear quadrupole moment. This causes the "observed" quadrupole coupling parameter to be somewhat different from the expression in Eq. (1). The magnitude of this effect has not been obtained accurately, but is estimated to be about ten percent of the value of the nuclear quadrupole coupling term. The nuclear quadrupole moment of nitrogen has been determined previously by Sheridan and Gordy[15] and by Bassompierre[16] as 0.01×10^{-24} cm² and 0.0071×10^{-24} cm², respectively, from the coupling constant $eQ(\partial^2 V/\partial z^2)$ in molecules.

The uncertainty of Q of nitrogen in this particular case is mainly due to that of eQq_2. Since the term containing eQq_2 in the Hamiltonian for the rotation of the NO molecule contributes a very small amount to the energy,[8] one may vary this coupling parameter over a certain range while still keeping good agreement between the calculated and experimental frequencies of the rotational transitions. When the possibility of such a variation of the coupling constant is considered, the uncertainty of eQq_2 is estimated to be ± 9 Mc/sec.[17] Thus the nuclear quadrupole moment of nitrogen is $(0.016 \pm 0.007) \times 10^{-24}$ cm².

[12] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949); C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 9.
[13] P. G. Favero, A. M. Mirri, and W. Gordy (reference 10) indicated that their value of 22 Mc/sec for eQq_2 is more than double that in reference 9, 9.3 Mc/sec. This discrepancy actually does not exist since the definitions of eQq_2 in these two papers differ by a factor of three.

[14] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **86**, 316 (1952); **95**, 736 (1954).
[15] J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).
[16] A. Bassompierre, Discussions Faraday Soc. **19**, 260 (1955); Compt. rend. **240**, 285 (1955).
[17] W. Gordy and J. G. Baker (private communication).