Bei zukünftigen präparativen Arbeiten kann dieses „Ausbleiben" der ^{195}Pt-Resonanz von polykristallinen Proben zusammen mit der metallischen Reflexion als sicherer Nachweis des eindimensionalen Metallcharakters gewertet werden [3]. Bei günstigen Relaxationsverhältnissen läßt sich dieser Zustand zusätzlich an einem charakteristischen ESR-Signal erkennen [15].

Die KMR-Messungen erfolgten mit einem Varian VF 16-Breitliniengerät, das mit einem PAR „lock in"-Verstärker HR 8 und einem Spektrenakkumulator Varian C 1024 ausgestattet ist, bei einer Senderfrequenz von 7,3 MHz. Das Magnetfeld wurde mit 21 Hz moduliert.

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[15] W. Gitzel, H. J. Keller, H. H. Rupp u. K. Seibold, noch unveröffentlichte Ergebnisse.

Calculation of the Quadrupole Coupling Constant of ^{17}O in the Oxygen Molecule

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The purpose of this note is to examine the quality of the molecular wavefunction of the oxygen molecule, constructed by the Nesbet-open-shell-approximation [1] and to study the electronic charge distribution around the oxygen atom by evaluating the field gradient at the site of an oxygen nucleus from the molecular wavefunctions. This quantity may be compared with the nuclear quadrupole coupling constant recently deduced by Gerber [2] from the hyperfine structure of the ESR spectrum of $^{16}O^{17}O$.

Very accurate molecular wavefunctions which are beyond the Hartree-Fock limit are reported by Schaeffer and Harris [3]. However, no field gradients have been evaluated by these authors. We consider it worthwhile to check the degree of accuracy in the field gradient which can be reached with simpler ab initio methods suitable for the application to larger molecules.

We started with the approximate Hartree-Fock SCF atomic orbitals obtained by Whitten [4] which we designate as the frozen basis set (I). It consists of three contractions of 4, 3, and 3 primitive Gaussians respectively for s-orbitals and 5 pairs of primitive Gaussians for each of the three p-orbitals of each oxygen atom. In order to study the influence of the basis on the result we first extended the frozen basis set by including a further s-type contraction of 3 Gaussians which is orthogonal to the previous ones on each oxygen atom (II: frozen + 3s). Secondly we have split the p-functions [5] into two contractions of 3 and 2 pairs (III: split p). Finally both modifications were applied at once (IV: split p + 3s).

Table 1 summarizes the contribution to the electric field gradient from each occupied molecular orbital to the total electric field gradient in the principal axis system (q_{mol}) for ^{17}O in the oxygen molecule. For the sake of comparison we include the total molecular electronic energy (E_T). The quadrupole coupling constant ($e^2 Q q_{mol}$) of ^{17}O is evaluated with the use of

$$Q(^{17}O) = -0.0263 \cdot 10^{-24}\ \mathrm{cm}^2,$$

reported by Kelly [6]. All calculations are carried out at the experimental geometry with $R(O-O) = 2.2815$

Table 1. q_{mol} values for ^{17}O in the oxygen molecule [a].

MO	(I)	(II)	(III)	(IV)
$1\sigma_g$	−0.0845	−0.0845	−0.0846	−0.0846
$1\sigma_u$	−0.0838	−0.0838	−0.0841	−0.0840
$2\sigma_g$	−0.3308	−0.3301	−0.3551	−0.3570
$2\sigma_u$	−0.1502	−0.1493	−0.1030	−0.1024
$3\sigma_g$	−1.7334	−1.7040	−2.5671	−2.5565
π_u	0.7734	0.7733	1.0004	1.0002
π_g	1.1665	1.1664	1.4936	1.4921
Electronic contribution	0.6611	0.7227	0.6010	0.6161
Nuclear contribution	1.3473	1.3473	1.3473	1.3473
Net contribution	2.0084	2.0700	1.9483	1.9634
E_T	−149.4888	−149.4955	−149.5234	−149.5287
$e^2 Q q_{mol}$ (MHz)	−12.429	−12.810	−12.057	−12.150

[a] Atomic units. For basis set (I) to (IV) see text for explanation.

[1] R. K. Nesbet, Proc. Roy. Soc. London A **230**, 312, 322 [1955]. — W. H. Fink, J. Chem. Phys. **49**, 5054 [1968]. — J. A. Horseley and W. H. Fink, J. Chem. Phys. **50**, 750 [1969].

[2] P. Gerber, to be published.

[3] H. F. Schaeffer III and F. E. Harris, J. Chem. Phys. **48**, 4946 [1968]. — H. F. Schaeffer III, J. Chem. Phys. **54**, 2207 [1971].

[4] J. Whitten, J. Chem. Phys. **44**, 359 [1966].

[5] C. T. O'Konski and T.-K. Ha, J. Chem. Phys. **49**, 5354 [1968]. — T.-K. Ha and C. T. O'Konski, J. Chem. Phys. **51**, 460 [1969].

[6] H. P. Kelly, Phys. Rev. **180**, 55 [1969].

a. u. From Table 1 we notice several interesting features. First of all we notice that the total electronic contributions as well as the nuclear contribution are both positive, meaning that the electronic charge distribution as a whole is somewhat compressed along the O – O-axis. Inspecting in detail the contributions to the field gradient from each orbital we notice that the most important contributions come from the $3\sigma_g$-orbital, the two degenerate π_u-orbitals, and the π_g-orbital. All of them consisting to a large amount or entirely of atomic p-orbitals it is to be expected that some additional flexibility of these orbitals may improve the result. Indeed the value of the quadrupole coupling constant calculated with the "split p" basis set

$$e^2 Q\, q_{\mathrm{mol}} = -12.06 \text{ MHz}$$

is the nearest to the experimental value $-8.42 \pm .18$ MHz measured by GERBER [2]. We also notice that including the 3s-orbital to the basis set – still lowering the total energy – does not improve the field gradient value. Thus the main problem in evaluating the field gradient is to find an appropriate description of the atomic p-orbitals. A similar problem arises in calculating ^{14}N-quadrupole coupling constants where the field gradient is very sensitive to the shape of the lone pair orbital [5].

Using the same frozen basis set for a closed shell calculation on formaldehyde yields the q_{mol} value of -3.5142 a.u. (for ^{17}O $e^2 Q\, q_{\mathrm{mol}} = 21.6$ MHz) [7] which is 1.75 times the experimental value of 12.37 MHz [8]. This provides some evidence that Nesbet's open-shell approximation employed in this note introduces no additional errors and may be applicable to the study of the electron distribution in open shell systems in general.

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[7] T.-K. HA, unpublished result.

[8] W. H. FLYGARE and J. T. LOWE, J. Chem. Phys. **43**, 3654 [1965].

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