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Semi-Empirical All Valence Electrons SCF-MO-CNDO Theory

V. Quadrupole Coupling Constants

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The semi-empirical SCF-MO-CNDO theory is used to calculate nuclear quadrupole coupling constants, considering only contributions to the electric field gradient from valence-shell *p* orbitals of the same atom as the nucleus of interest, as suggested originally by Townes and Dailey. For halogen nuclei, fairly accurate results are obtained, but for nitrogen nuclei the results are much poorer.

Unsere SCF-MO-CNDO-Methode wird zur Berechnung von Kernquadrupolkopplungskonstanten nach der Townes-Dailey-Theorie herangezogen. Für Halogene werden recht gute Resultate erhalten, nicht aber für Stickstoff.

On a calculé à l'aide de la théorie SCF-MO-CNDO des constants de couplage nucleaire quadrupolaire en ne considerant que des contributions au gradient de champ électrique des orbitales *p* du même atome, selon la proposition de Townes et Dailey. Pour des noyaux d'halogène les résultats obtenus sont assez bon, mais pour des noyaux d'azot les résultats sont moins bien.

A. Introduction

In the preceding papers of this series [1, 2, 3, 4] it was shown that semi-empirical parameters in the SCF-MO-CNDO calculations, lead to more accurate bonding energies [2] and ionization potentials [3] than do theoretical parameters, and to dipole moments of comparable accuracy for the first row molecules [4]. In this paper the calculation of nuclear quadrupole coupling constants from SCF-MO-CNDO theory is treated.

The quadrupole coupling constant (*QCC*) of a nucleus, A, in a molecule is a measure of the interaction of the nuclear quadrupole moment Q [6, 7, 8] with the molecular charge distribution external to the nucleus.

The energy levels are conventionally expressed in terms of the quadrupole coupling constant (*QCC*),

$$C = \frac{e^2 Q q}{h} \tag{1}$$

which has units of frequency.

B. Calculation of Nuclear Quadrupole Coupling Constants

For a closed-shell single-determinant wave function, with molecular orbitals composed of linear combinations of atomic orbitals, the effective field gradient

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(efg) is given by

$$e\,q = -e\,\mathrm{tr}(P q_A) + e \sum_{B \neq A} Z_B\, q_{AB} \tag{2}$$

where P is the expansion of the one-electron density matrix in terms of the basis orbitals defined by $P_{kl} = 2 \sum_{i}^{occ} C_{ki}^* C_{li}$. The matrix q_A describes the electric field gradient of the electrons at the nucleus A, and has elements which are, in the most general case, three-centre integrals,

$$(q_A)_{kl} = \int \phi_k^* \frac{(3\cos^2\theta - 1)}{r^3} \phi_l \, dV \tag{3}$$

while q_{AB} is the electric field gradient per unit charge, of nucleus B, at nucleus A,

$$q_{AB} = \frac{3\cos^2\theta_B - 1}{R_{AB}^3}. \tag{4}$$

The direct computation of electric field gradients, using Eq. (3), involves the evaluation [9] of the three-centre integrals, $(q_A)_{kl}$. A simple semi-empirical approach, originally due to Townes and Dailey [10], and first explicitly formulated for molecular orbital theory by Gordy *et al.* [11], is often used for the interpretation of nuclear quadrupole coupling constants. The electric field gradient is assumed to arise entirely from the electron population of atom A, since the effect of the electrons on each other atom approximately cancels the effect of the nuclei. The equation used for the semi-empirical evaluation of nuclear quadrupole coupling constants [11, 12], is

$$C = C_0 \left(n_z - \frac{n_x + n_y}{2} \right) \tag{5}$$

where the quadrupole coupling constant per p electron, C_0, is evaluated from atomic spectra.

A similar equation, applicable to the SCF-MO-CNDO theory for all valence electrons, can be formally derived from the exact formula, Eq. (2), by making certain simplifying approximations.

(i) The off-diagonal matrix elements of the electric field gradient, $(q_A)_{kl}$, which contain the differential overlap of two orbitals as a factor in the integrand, are neglected in accordance with the CNDO approximation. The matrix elements between two different orbitals on atom A vanish by symmetry in any case (for the $s-p$ basis set considered), while the others refer to overlap regions not on atom A, and are relatively small compared to the diagonal matrix elements for orbitals of atom A, since the electric field gradient operator decreases as r^{-3}. Eq. (2) therefore, reduces to

$$e\,q = -e \sum_k P_{kk} (q_A)_{kk} + e \sum_{B \neq A} Z_B\, q_{AB}. \tag{6}$$

(ii) The electric field gradient due to the electron population of each other atom in the molecule is assumed to cancel that due to the atomic core.

$$\sum_k^{B} P_{kk} (q_A)_{kk} = Z_B\, q_{AB}. \tag{7}$$

In accurate calculations of electric field gradients, this cancellation has been found to be approximately true. Therefore,

$$e\,q = -e\left(\sum_{k}^{\mathrm{A}} P_{kk}(q_{\mathrm{A}})_{kk}\right) \tag{8}$$

in the SCF-MO-CNDO theory; P_{kk} represents the electron population of the k^{th} orbital, so that the QCC is given by

$$C = C_0\left(P_{zz} - \frac{P_{xx}+P_{yy}}{2}\right). \tag{9}$$

In the Extended Hückel Theory [13], which includes overlap, the population of an orbital is given by [14]

$$Q_{rr} = P_{rr} + \sum_{s \neq r} P_{rs}\, S_{rs} \tag{10}$$

where the S_{rs} are overlap integrals. By analogy with Eq. (5),

$$C = C_0\left(Q_{zz} - \frac{Q_{xx}+Q_{yy}}{2}\right). \tag{11}$$

Cotton and Harris [15] derived an analogous equation by assuming that the electric field gradient matrix element between the k^{th} orbital on atom A, and the l^{th} orbital on atom B, is approximated by

$$(q_{\mathrm{A}})_{kl} = S_{kl}(q_{\mathrm{A}})_{kk}\,. \tag{12}$$

The off-diagonal matrix elements between pairs of orbitals, both of which are on other atoms, are still neglected.

Gordy *et al.* [16] have suggested, however, that the effect of the overlap populations be neglected, since the overlap regions are far from the nucleus, so that Eq. (9) should be used even with the EHT. In order to verify this claim, quadrupole coupling constants have been calculated from the EHT using both Eq. (9) and (11).

Quadrupole coupling constants have been calculated for Cl^{35}, Br^{79}, I^{127}, and N^{14} in various molecules. The values of the quadrupole coupling constant per p electron, C_0, are 109.746, -769.756, and 2292.712 Mc/s, for Cl^{35}, Br^{79} and I^{127} respectively [5, 17, 18, 19]. The ground state of the nitrogen atom is an S state, so that there is no electric field gradient at the nucleus, and C_0 cannot be determined. Jeffrey and Sakurai [8] have proposed the value $C_0 = -7.4$ Mc/s for N^{14}, based on a value for $\langle r^{-3}\rangle_{2p}$ interpolated [20] from values derived from the hyperfine structure of other atoms in the first row of the periodic table, and an estimate [21] of Q based on the magnetic hyperfine structure of NO. This value of -7.4 Mc/s has been used here, since it was derived independently of the QCC in any molecule.

A possible source of error in Eq. (6) is the Sternheimer effect [22, 23, 24], which has been neglected, since in semi-empirical calculations of quadrupole coupling constants, it is assumed that the Sternheimer polarization effects in the molecule are similar to those in the free atom, so that Eq. (5) is valid if C_0 is determined from atomic hyperfine spectra [5].

C. Comparisons of Calculated Quadrupole Coupling Constants for Halogens with Experiment

Quadrupole coupling constants calculated from the semi-empirical SCF-MO-CNDO theory, using Eq. (9) are listed in Tables 1 to 3 and compared to experimental values measured in the gas phase, except for homonuclear diatomics. The *QCC*'s, unlike the dipole moments for the same molecules [4], are in fair

Table 1. *Nuclear quadrupole coupling constants for* Cl^{35}

	From semi-empirical SCF-MO-CNDO theory		From Extended Hückel Theory		Exptl.	Ref.
	Mataga γ_{AB}[a] $M2$	Ohno γ_{AB}[a] $O2$	From gross orbital populations[a]	From net orbital populations[a]	Mc/s	
HCl	− 88.25	− 82.02	− 49.33	− 75.49	−67.3	[27]
CH_3Cl	− 78.63	− 79.01	− 51.59	− 75.16	− 74.77	[28]
ClF	−126.81	−132.87	−162.79	−182.40	−146.00	[29]
Cl_2	−106.16	−106.88	− 88.21	−117.40	−108.95	[30]
BrCl	− 98.27	− 97.04	− 68.44	− 95.11	−103.6	[31]
ICl	− 94.47	− 92.64	− 58.68	− 83.28	− 82.5	[32]
ClCN	− 73.96	− 69.48	− 44.80	− 65.38	− 83.2	[33]

[a] $Z'_{H}=1.2$.

Table 2. *Nuclear quadrupole coupling constants for* Br^{79}

	From semi-empirical SCF-MO-CNDO theory		From Extended Hückel Theory		Exptl.	Ref.
	Mataga γ_{AB}[a] $M2$	Ohno γ_{AB}[a] $O2$	From gross orbital populations[a]	From net orbital populations[a]	Mc/s	
HBr	657.9	642.7	441.2	653.7	530.5	[27]
CH_3Br	607.6	616.7	481.5	669.9	577.15	[28]
BrF	952.4	1007.3	1252.2	1366.9	1089.0	[34]
BrCl	806.9	824.5	777.4	991.2	876.8	[31]
Br_2	750.8	754.7	626.8	842.5	765	[35]
IBr	721.2	718.4	556.4	761.9	722	[36]
BrCN		588.9	379.0	534.8	686.5	[33]

[a] $Z'_{H}=1.2$.

Table 3. *Nuclear quadrupole coupling constants for* I^{127}

	From semi-empirical SCF-MO-CNDO Theory		From Extended Hückel Theory		Exptl.	Ref.
	Mataga γ_{AB}[a] $M2$	Ohno γ_{AB}[a] $O2$	From gross orbital populations[a]	From net orbital populations[a]	Mc/s	
HI	−2020	−2009	−1521	−2169	−1823.3	[27]
CH_3I	−1907	−1949	−1640	−2180	−1934	[37]
IF	−2920	−3078	−4056	−4584		
ICl	−2463	−2529	−2529	−3130	−2930.0	[32]
IBr	−2305	−2338	−2086	−2713	−2731	[36]
I_2	−2214	−2227	−1866	−2483	−2153	[38]
ICN	−1995	−1962	−1399	−1876	−2420	[33]

[a] $Z'_{H}=1.2$.

agreement with experiment, despite the absence of d orbitals in the MO calculations [4]. They do not vary greatly with the value of the interatomic electron-repulsion integrals, or of the Slater exponent for hydrogen, hence only the $Z'_{\mathrm{H}} = 1.2$ results are shown explicitly [1–4]. The results for bromine are as accurate as for chlorine and iodine, so that the approximate form of the orbital used to calculate overlap integrals

$$R_4(r) = N_4\, r^{2.7}\, e^{-Z' r/3.7\, a_0}$$

does not affect the accuracy of the theory [2].

Quadrupole coupling constants calculated from the EHT, using both Eq. (9) and (11) are also listed. The *QCC*'s for polar molecules calculated from gross orbital populations, Eq. (11), correspond to exaggerated polarities, since the calculated values are too low, except when the halogen nucleus of interest is bonded to fluorine, so that it carries a partial positive charge, and exaggeration of the polarity leads to a high *QCC*. The results are, therefore, consistent with the high dipole moments computed from the EHT [4].

The effect of calculating the *QCC* from net, instead of gross, orbital populations is invariably to increase the *QCC*. The halogen atoms are predominantly σ-bonded so that there is a greater overlap population, and a smaller total population, in the p σ-orbital than in the p π-orbital. The calculated *QCC* depends on the difference between the p σ- and p π-populations, so that it is increased if the overlap population is not counted. While those results which are too low are improved by using net orbital populations, other which are too high are made worse. On the whole, more accurate results are obtained using the SCF-MO theory.

D. Comparison of Calculated Quadrupole Coupling Constants with Experiment for Nitrogen

The calculated quadrupole coupling constants for nitrogen are generally in poor agreement with experiment, Table 4. Many of the calculated values have the wrong sign, corresponding to smaller electron populations along the symmetry axis than normal to it. Most of the *QCC*'s calculated using the Pople-Segal bonding parameters, on the other hand, have the correct sign, but the values are still in poor agreement with experiment, except for NH_3.

The *QCC*'s calculated from the Extended Hückel Theory, are also quite different from the experimental values. The values calculated from gross and from net orbital populations are not too different for most molecules, since the overlap populations along the symmetry axis and normal to it are about the same.

The reasons for the failure of the approximate MO theories to predict accurate *QCC*'s for nitrogen may be obtained from the results of an ab initio calculation [25] of electric field gradients for N_2, using Eq. (2). The field gradient is found to be very sensitive to the basis set, since the eq_0 per p electron is proportional to the cube of the orbital exponent, Z'. The other electronic terms in Eq. (2) are insensitive to changes in the basis set, and there is a cancellation between them and the nuclear terms, as assumed in the semi-empirical formula, Eq. (5).

In semi-empirical calculations of quadrupole coupling constants, it is hoped that the errors inherent in ab initio calculations of electric field gradients, as well

Table 4. *Nuclear quadrupole coupling constants for* N^{14} [a]

	From SCF-MO-CNDO theory with empirical bonding parameters			With Pople-Segal bonding parameters			From Extended Hückel Theory		Exptl.	Ref.
	Mataga γ_{AB} *M2*	Ohno γ_{AB} *O2*	*R2*	*MP*	*OP*	*RP*	From gross orbital populations	From net orbital populations	Mc/s	
NH_3	+1.098	+0.674	−0.502	−4.111	−3.930	−4.256	−4.840	−6.935	−4.0842	[39]
N_2	−0.663	−0.482	−0.911	−2.290	−2.290	−2.317	−3.600	−3.476	−4.65	[40]
$\underline{N}NO$		+6.104	+5.817	+0.612	+0.840	+0.437	−1.418	−1.111	−0.792	[41]
$N\underline{N}O$		−3.007	−4.792	+0.152	−0.015	−0.528	+1.786	+2.818	−0.238	[41]
HCN	+6.664	+6.280	+6.108	−1.923	−1.903		−1.592	−1.791	−4.58	[42]
CH_3CN		+6.676		−1.527	−1.482	−1.908	−1.114	−1.206	−4.214	[43]
FCN	+8.823	+9.208	+8.150	−0.597	−0.468	−0.995	−0.594	−0.509	−2.67	[44]
ClCN	+7.956	+7.897					−0.649	−0.564	−3.63	[33]
BrCN		+7.220					−0.667	−0.560	−3.83	[33]
ICN	+7.048	+6.680					−0.785	−0.718	−3.80	[45]

[a] $Z'_H = 1.2$.

as any error in the uncertain nuclear quadrupole moment of N^{14}, will be eliminated by evaluating C_0 from the hyperfine structure of the atomic spectra [5]. The results in this paper show that this approach works fairly well for halogens, but not for nitrogen.

The above analysis suggests that the errors in the calculated *QCC*'s are primarily due to the failure of Eq. (5), but comparison of the orbital populations with those obtained from complete minimum-basis set SCF-MO calculations shows that part of the error lies in the wave functions calculated using the CNDO approximation [26]. Although the total atomic charges predicted by the semi-empirical SCF-MO-CNDO theory are more accurate than those in the EHT [4], the distribution of the valency-shell electronic populations of each atom among the valence orbitals is often quite inaccurate. The calculated orbital populations are sensitive to the bonding parameters, and the Pople-Segal parameters lead to *QCC*'s which are somewhat better than those obtained using the empirical bonding parameters.

In summary, then, the quadrupole coupling constants calculated for halogens using the semi-empirical SCF-MO-CNDO theory are in fairly good agreement with experiment, while those calculated for nitrogen are unsatisfactory. The Extended Hückel Theory leads to somewhat poorer results for halogens, and also fails for nitrogen.

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