Theoret. Chim. Acta (Berl.) 32, 321—330 (1974)

Unrestricted Hartree-Fock Spin Density Calculations with Orthogonalized Atomic Orbitals on Aza and Nitroaromatic Radical Anions

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Received March 13, 1973

The spin density distributions in some aza and nitroaromatic radical anions have been calculated using Löwdin's orthogonalized basis set of atomic orbitals in the Unrestricted Hartree-Fock method of Amos and Snyder. The present calculations lead to a satisfactory account of proton splittings in these radicals. Least squares analyses correlating the observed ^{14}N splittings and the spin density results over completely localized nonorthogonal basis have been separately carried out for aza and nitroaromatic radical anions and the sigma-pi parameters thus obtained are discussed and compared with earlier estimates for these quantities. Unlike the earlier results, the present estimate of Q_{NN}^{N} for aza and nitroaromatic radicals are not very much different from each other.

Key words: Spin density – Aza and nitroaromatic radical anions – Proton and nitrogen hyperfine splittings

1. Introduction

The study of spin density distributions in heteroaromatic radical ions provides useful information regarding the relation between the spin density and hyperfine splitting of the heteroatom present. On the basis of the Karplus-Fraenkel theory [1] nitrogen splittings in azaaromatic radical ions can be expressed as:

$$a_N = Q_{NN}^{N} + Q_{CC}^{N} \sum_{C} \varrho_{CC} \,. \tag{1}$$

Here ϱ_{NN} and ϱ_{CC} are spin densities on nitrogen and the adjacent carbon atoms respectively. Similarly, the Karplus-Fraenkel relation for the nitrogroup nitrogen can be written as:

$$a_N = Q_{NN}^{N} \varrho_{NN} + Q_{CC}^{N} \varrho_{CC} + Q_{OO}^{N} (\varrho_{OO} + \varrho_{O'O'}) \tag{2}$$

where $(\varrho_{OO} + \varrho_{O'O'})$ is the sum of spin densities on the oxygen atoms O and O′ of the nitro group. Although several attempts have been made earlier to estimate the sigma-pi parameters for ^{14}N splittings in azaaromatic radical ions [2–13], only a few calculations are available on nitroaromatic radical ions. Rieger and Fraenkel [14] estimated the sigma-pi parameters for the nitro group nitrogen splittings from McLachlan type of spin density calculations on a series of nitrosubstituted aromatic radicals. Hinchliffe [15] studied the spin density distributions in nitrosubstituted radicals by the configuration interaction (SCFCI) method as well as the unrestricted Hartree-Fock (UHF) method of Amos and Snyder [16]. He assumed a linear relationship between ^{14}N splitting and the spin density on nitrogen and thus obtained the parameter $Q^{\mathrm{N}}_{\mathrm{NN}}$. A study of ^{14}N sigma-pi parameters based on the Karplus-Fraenkel relation [Eq. (2)] and UHF spin density results has also been carried out [17]. However, these estimates of sigma-pi parameters for the nitrogroup nitrogen are unusually high compared to the values [18, 19] deduced from ^{14}N splittings in various small radicals.

The UHF method of Amos and Snyder has been used in the present investigation on spin density distributions in the aza and nitroaromatic radical ions. All the earlier calculations on these radicals were done with the usual Pariser-Parr-Pople type of integral approximations [20, 21] and assuming the basis set to be orthogonal. In the present UHF calculations with "zero differential overlap" (ZDO) approximation, various integrals entering the theory have been interpreted as involving Löwdin's orthogonalized basis set [22] of atomic orbitals (OAO) rather than the usual overlapping atomic orbitals (AO) of Slater's type. This ensures complete transferability of various integrals and the validity of ZDO approximation to a high degree of accuracy [23–25]. Because of the many-centre character of OAO's, the use of the spin density matrix over the OAO basis, $\bar{\varrho}$, in the Eqs. (1) and (2) for obtaining ^{14}N splittings is objectionable. If the results of the earlier spin density calculations with ZDO approximation are interpreted as being over the OAO basis, the same remark holds for these calculations also. In the present work, the spin density results over the completely localized non-orthogonal basis obtained by transformation of the corresponding results over the OAO basis [26] were, therefore, used in the calculation of ^{14}N splittings.

2. Method of Calculation

2.1. Hartree-Fock Matrix Elements and Integral Approximations

A detailed description of the OAO adaptation of the UHF method of Amos and Snyder and the integral approximations has been presented elsewhere [27] and only a brief account shall be given here. With the simplification due to ZDO approximation, the Hartree-Fock (HF) matrix elements for the α-spin electrons over OAO basis, $\bar{\chi}$ assume the form:

$$\bar{F}^{\alpha}_{ii} = \bar{H}^{\mathrm{core}}_{ii} - \bar{P}^{\alpha}_{ii}(\overline{ii/ii}) + \sum_{j} \bar{P}_{jj}(\overline{ii/jj}) \tag{3}$$

and

$$\bar{F}^{\alpha}_{ij} = \bar{H}^{\mathrm{core}}_{ij} - \bar{P}^{\alpha}_{ij}(\overline{ii/jj}), \tag{4}$$

where $\overline{ii/jj}$ is the electron repulsion integral between $\bar{\chi}_i$ and $\bar{\chi}_j$. Other symbols have their usual meaning [28]. The integrals in Eqs. (3) and (4) over OAO's (quantities indicated by bars) were obtained by suitable transformation of the corresponding integrals over the overlapping basis (quantities without bars).

The one-centre electron repulsion integrals, (ii/ii) were estimated by the usual "I–A" approximation. The two-centre repulsion integrals were obtained using Ohno's relation [29]. Mulliken approximation [30] was used to estimate three-centre and four-centre two-electron integrals. Burns' rules [31] were used to determine the exponents of various $2p_z$ AO's employed in the present calculations.

The calculations of core matrix elements over the overlapping basis were done using the expressions

$$H_{ii}^{\text{core}} = \omega_i - \sum_{j \neq i} Z_j (ii/jj) \tag{5}$$

and

$$H_{ij}^{\text{core}} = \tfrac{1}{2}(H_{ii}^{\text{core}} + H_{jj}^{\text{core}})\, S_{ij} - \tfrac{1}{2}(T_{ii} + T_{jj})\, S_{ij}(1 - S_{ij})\,. \tag{6}$$

Here ω_i and T_{ii} are respectively the valence state ionisation potential and kinetic energy integral for the orbital i and Z_i is the appropriate core charge. S_{ij} is the overlap integral between orbitals i and j. The core matrix elements $\bar{H}_{ij}^{\text{core}}$'s over the OAO basis are easily obtained by a transformation of H^{core} elements given by Eqs. (5) and (6). As usual, $\bar{H}^{\text{core}}$ elements between non-bonded atoms were neglected. The integrals T_{ii} were estimated in the following way. T_{CC} (for carbon $2p_z$ AO) was adjusted so that $\bar{H}_{ij}^{\text{core}}$ corresponding to the C–C distance in benzene reproduced the value of -2.475 eV obtained by spectral matching procedure [32]. The integrals T_{ii} for all other orbitals were estimated by scaling the corresponding theoretically calculated integrals, T_{ii}^{th} obtained using Slater-type orbitals by a factor $(T_{\text{CC}}/T_{\text{CC}}^{\text{th}})$. Interestingly, although the $\bar{H}^{\text{core}}$ elements involving the heteroatoms have been directly calculated using the T_{ii} values thus estimated, the values for these core elements generally agree well with the empirical estimates for these integrals. Thus, the present estimate of $\bar{H}_{\text{CN}}^{\text{core}}$ of -2.719 eV in pyridine is close to the spectroscopic value of -2.72 eV [33]. Also, $\bar{H}_{\text{CN}}^{\text{core}}$ in nitrobenzene of -2.375 eV agrees reasonably well with the value -2.576 eV suggested by Peacock [34]. The orbital exponents, ζ and the values of various integrals for the $2p_z$ orbitals on the heteroatoms of interest are listed in Table 1. In the calculations on the methyl substituted radicals the methyl group was represented by a pseudo $2p_z$ orbital, X with core charge $Z_{\text{X}} = 2$. The repulsion integral (XX/XX) was taken from the literature [35]. ω_{X} was estimated as

$$\omega_{\text{X}} = -I(\text{CH}_4) - (\text{XX/XX}) \tag{7}$$

where $I(\text{CH}_4)$ is the observed ionisation potential of methane [36]. For evaluating the overlap integrals involving X and T_{XX} the orbital exponent ζ_{X} is necessary. This was obtained as

$$\zeta_{\text{X}} = \zeta_{\text{C}} \frac{(\text{XX/XX})}{(\text{CC/CC})}\,. \tag{8}$$

Here ζ_{C} and (CC/CC) are respectively the orbital exponent and one-centre electron repulsion integral for $2p_z$ AO on carbon.

Table 1. Orbital exponents, ζ and values of integrals (in eV) for $2p_z$ orbitals on different atoms

Core	ζ_i [a]	ω_i [b]	(ii/ii) [b]	T_{ii}
C^+	1.4	-11.16	11.13	9.00
N^+	1.7	-14.12	12.34	13.26
N^{++}	1.9	-28.775	16.47	16.57
O^+	2.0	-17.7	15.24	18.36

[a] Ref. [31].

[b] Hinze, H., Jaffe, H. J.: J. Am. Chem. Soc. **84**, 540 (1962).

2.2. *Geometry of Radicals*

The geometry of nitrobenzene and substituted nitrobenzenes was taken to be same as that in our earlier calculation [17]. Calculations on the azaaromatic radical ions were carried out with a standard geometry of all C–C bond lengths equal to 1.397 Å and all C–N bond lengths equal to 1.34 Å. For nitrobenzene a regular hexagon geometry (1.397 Å) was assumed for the six-membered ring and C–N and N–O bond lengths were taken as 1.4 Å and 1.21 Å, respectively.

2.3. *Proton Hyperfine Splittings*

Employing the spin density results after annihilation of the quartet function [16] the proton splittings were obtained using the procedure already discussed elsewhere [26]. Both McConnell [37] and Colpa-Bolton [38] type of relations have been used for this purpose.

$$a_{\mathrm{H}} = -27\,\varrho^{g}_{ii} \tag{9}$$

and

$$a_{\mathrm{H}} = -27\,\varrho^{g}_{ii} - 12.8\,(1 - P^{g}_{ii})\,\varrho_{ii} \tag{10}$$

Here ϱ^{g}_{ii} and P^{g}_{ii} are respectively the "gross atomic spin density" and "gross atomic charge density" [26] for the carbon atom *i*, to which the proton is bonded. In all further discussions on proton as well as ^{14}N splittings the spin densities after annihilation shall be employed.

3. Results and Discussion

3.1. *Proton Splittings*

The present results on proton splittings in the aza and nitroaromatic radical anions are presented in Table 2. The expectation values of S^2 operator before annihilation, $\langle S^2 \rangle_{ba}$ and those after annihilation, $\langle S^2 \rangle_{aa}$ are also listed there. In the nitroaromatic radical anions the Colpa-Bolton type of relation [Eq. (10)] yields proton splittings which are not very much different from those obtained using the McConnell type of relation [Eq. (9)]. The predictions based on both the relations are in reasonably good agreement with experiment. In the azaaromatic radical anions the Colpa-Bolton type of relation leads to a better estimate of proton splittings. The spin densities on some of the carbon atoms in the azaaromatic radical anions are considerably higher than those on the ring carbon atoms in the nitroaromatic radical anions. Therefore, the excess charge theory of Colpa and Bolton is more reliably tested in the former radicals. In the sulphur-containing radicals also the Colpa-Bolton relation leads to an improved estimate of proton splitting [27].

3.2. ^{14}N *Splittings*

We shall first discuss the ^{14}N splittings in azaaromatic radical anions. In the present work the sigma-pi parameters for ^{14}N splittings in Eq. (1) have been obtained by a least squares analysis correlating the experimental ^{14}N splittings

Table 2. Proton hyperfine splittings, a_H (in Gauss) in the aza and nitroaromatic radical anions

Radical[a]	Position	$\langle D^2\rangle_{ba}$	$\langle S^2\rangle_{aa}$	a_H (calcd.)		$\lvert a_H\rvert$ (obsd.)
				Eq. (9)	Eq. (10)	
I	2	0.7832	0.7505	−3.17	−3.23	3.55[b]
	3			−0.54	−0.43	0.82
	4			−12.48	−10.34	9.70
II	2	0.7668	0.7500	−2.42	−2.39	2.63[c]
III	1	0.8113	0.7503	0.36	0.40	0.72[b]
	3			−11.06	−10.48	9.78
	4			2.25	2.13	1.31
IV	2	0.8042	0.7512	−2.62	−2.64	3.14[d]
V	2	0.8093	0.7521	−2.46	−2.52	2.95[c]
	3			−1.10	−0.99	1.69
	4			−7.05	−6.30	5.77
VI	2	0.8262	0.7537	−3.31	−3.46	4.38[e]
	3			−0.20	−0.13	0.50
	4			−8.22	−7.53	6.69
VII	1	0.8081	0.7522	−9.14	−8.77	7.43
	3			−0.82	−0.89	2.06
	4			−3.52	−2.90	3.68
VIII	2	0.7910	0.7511	0.50	0.54	0.54[f]
	3			−3.20	−3.01	−3.00
IX	2	0.8324	0.7545	−3.79	−3.69	3.39[g]
	3			1.32	1.30	1.09
	4			−4.15	−3.88	3.97
X	2	0.7865	0.7501	−1.53	−1.53	1.12
XI	2	0.8368	0.7550	−3.88	−3.83	3.39
	3			1.45	1.39	1.11
	4			4.56[c]	—	3.98
XII	2	0.8377	0.7551	−3.87	−3.85	3.36
	3			1.49	1.39	1.12
XIII	2	0.8282	0.7540	−3.57	−3.52	3.12
	3			0.97	0.95	0.76
XIV	2	0.8239	0.7534	−3.72	−3.63	3.10
	3			0.78	0.79	0.44
	5			0.71	0.69	0.44
	6			−3.03	−2.99	2.37
	7			−0.83	−0.95	1.23
XV	2	0.7942	0.7511	−2.14	−2.03	3.02[h]
	3			0.69	0.68	1.03
	4			−2.82	−2.54	3.91
	5			0.94	0.93	1.03
	6			−2.50	−2.26	4.11

[a] See Fig. 1.

[b] Ref. [9].

[c] Ref. [7].

[d] Gerson, F., Armarego, W. L. F.: Helv. Chim. Acta **48**, 112 (1965).

[e] D'Oro, P. C., Danieli, R., Maccagnani, G., Pedulli, G. F., Palmieri, P.: Molecular Physics **20**, 365 (1971).

[f] Itoh, M., Okamoto, T., Nagakura, S.: Bull. Chem. Soc. Japan **36**, 1665 (1963).

[g] Ref. [14].

[h] Ayscough, P. B., Sargent, F. P., Wilson, R.: J. Chem. Soc. (B), 903 (1966).

Table 3. Spin density results and ^{14}N splittings, a_N (in Gauss) in the radical anions of azaaromatic compounds

Radical[a] anion	ϱ_N	$\sum_C \varrho_C$[b]	a_N (calcd.) Bilinear relation [Eq. (11)]	a_N (calcd.) Linear relation [Eq. (12)]	a_N(obsd.)[c]
I	0.4178	0.3054	6.27	6.27	6.28
II	0.4866	0.2350	7.45	7.30	7.18
III	0.2395	0.5228	3.16	3.59	3.26
IV	0.2295	0.0800	3.55	3.44	3.37
V	0.1967	0.0777	3.02	2.94	3.37
VI	0.1443	0.1340	2.13	2.16	2.39
VII	0.0636	0.4710	0.43	0.95	0.36
VIII	0.1400	−0.0406	2.28	2.10	2.55

[a] See Fig. 1.
[b] See Eq. (1) of text.
[c] The sources of experimental ^{14}N splittings are same as those for the experimental proton splittings which are already referred in Table 2.

and the spin density results over the completely localized nonorthogonal basis set. The expression for ^{14}N splitting thus obtained is:

$$a_N = 15.90\varrho_{NN} - 1.24 \sum_C \varrho_{CC} . \tag{11}$$

The spin density values and the ^{14}N splittings in azaaromatic radical anions calculated using Eq. (11) together with the experimental values are listed in Table 3. Also presented there are the results of a linear correlation between the ^{14}N splitting and ϱ_{NN} obtained by least squares method:

$$a_N = 15.00\varrho_{NN} . \tag{12}$$

The standard deviations of the fit using Eqs. (11) and (12) are respectively ±0.36 and ±0.25. Small and negative value for Q^N_{CC} obtained here [see Eq. (11)] is in agreement with the result of *a priori* calculation [12] and also with most of the earlier semiempirical estimates for this quantity. The present estimate of Q^N_{NN} is somewhat lower than the earlier semiempirical estimates for this parameter which varies from around 18 Gauss to around 30 Gauss [2–13]. This is to be attributed primarily to the fact that while in the present calculations the spin density results over the nonorthogonal basis have been employed in Eq. (1), in all the earlier calculations the results over a basis set assumed to be orthogonal were used. In these anion radicals transformation to the nonorthogonal basis has the effect of increasing the spin density assigned to nitrogen (ϱ_{NN} is higher than $\bar{\varrho}_{NN}$). Thus, Q^N_{NN} obtained by fitting the spin density results over nonorthogonal basis with experimental splittings is expected to be smaller than that obtained with spin density results over orthogonal basis.

In the present calculation the contribution of the spin densities in the overlapping regions to ^{14}N splittings has been neglected. However a least squares analysis further including the terms of the type ϱ_{NC}, where the carbon atom C is near-

Table 4. Spin density results and ^{14}N splittings, a_N (in Gauss) in the radical anions of nitroaromatic compounds

Radical[a] anion	ϱ_N	ϱ_C	$\sum_O \varrho_O$ [b]	a_N (calcd.) Trilinear relation [Eq. (13)]	a_N (calcd.) Linear relation [Eq. (14)]	a_N (obsd.)
VIII	0.4694	0.1200	0.3916	9.13	9.19	8.72[c]
IX	0.4895	0.0729	0.3826	10.04	9.59	10.32
X	0.1492	0.2049	0.1878	1.29	2.92	1.75
XI	0.5177	0.0534	0.3898	10.85	10.14	10.79[d]
XII	0.5520	0.0323	0.3980	11.82	10.81	12.18[c]
XIII	0.3811	0.1205	0.3340	7.18	7.46	7.15
XIV	0.3506	0.1326	0.3176	6.39	6.87	5.83
XV	0.4141	0.0609	0.5324	8.27	8.11	8.34

[a] See Fig. 1.
[b] See Eq. (2) of text.
[c] Ref. [14].
[d] Bowers, K. W.: In: Urberg, M. M., Kevan, L. (Eds.): Radical ions, p. 224. New York: Interscience 1968.

neighbour to N, shows that the calculated couplings, the sigma-pi parameters and the standard deviation of the fit change only to a small extent from the respective values obtained with Eq. (1):

We shall next consider the ^{14}N splittings in nitroaromatic radical anions. A least square analysis of the spin density results over nonorthogonal basis with respect to Eq. (2) yielded the following relation for nitrogroup nitrogen splitting:

$$a_N = 22.73\,\varrho_{NN} - 9.29\,\varrho_{CC} - 1.08\,(\varrho_{OO} + \varrho_{O'O'})\,. \tag{13}$$

A linear correlation, similar to Eq. (12), for nitrogroup nitrogen was obtained as:

$$a_N = 19.58\,\varrho_{NN}\,. \tag{14}$$

The spin density results and the ^{14}N splittings in nitroaromatic radicals calculated using Eqs. (13) and (14) are listed in Table 4. The standard deviations of the fit using Eqs. (13) and (14) are respectively ±0.43 and ±0.90. These standard deviations are smaller than the values obtained in earlier works [14, 15, 17]. The values for Q^N_{CC} and Q^N_{OO} are seen to be negative and compared to Q^N_{NN} they are small. This is in agreement with the earlier estimates of Q's [17, 18, 39]. However, the present estimate of Q^N_{NN} [see Eqs. (13) and (14)] is considerably smaller than the earlier semiempirical estimates for this quantity which vary from around 50 Gauss to around 100 Gauss [14, 15, 17]. Also, unlike the earlier results, our present estimates of Q^N_{NN} for aza and nitroaromatic radicals are not largely different from each other.

Gross and Symons [18] obtained the spin population on nitrogen in the nitrobenzene radical anion from the nitrogen anisotropic hyperfine coupling deduced from solid state spectra. Assuming that only the spin density on nitrogen contributes to its splitting and using the integral $\langle r^{-3}\rangle$ for $2p_z$ AO calculated from free atomic SCF wavefunction, they estimated the spin density of 0.411 on

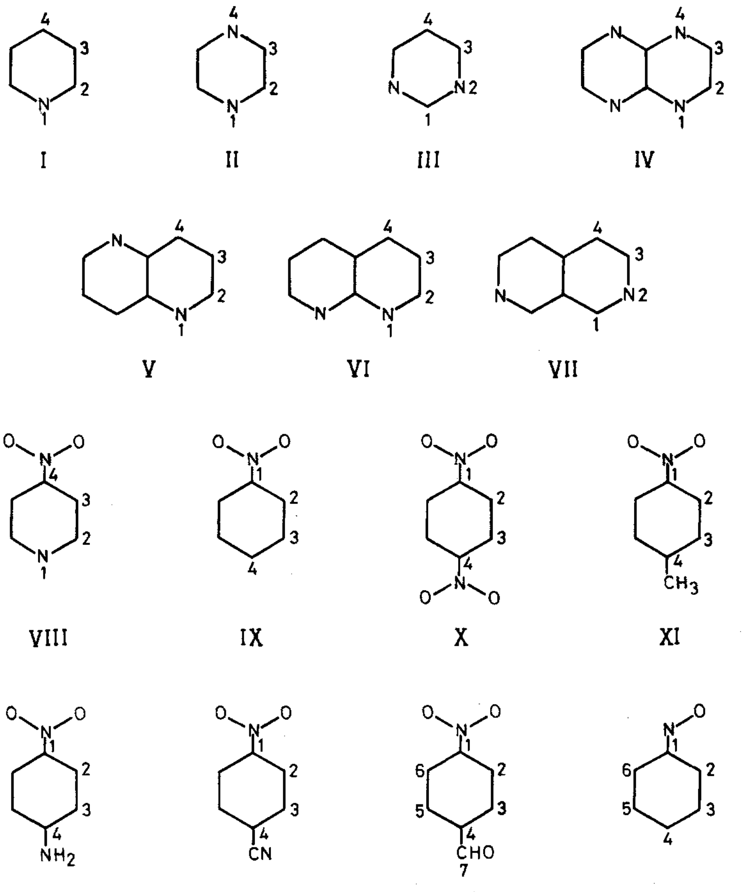

Fig. 1. Topology and numbering of atoms

$2p_z$ AO on nitrogen. This seems to be the only estimate of spin density on nitrogen in nitrobenzene radical anion without recourse to any spin density calculation. This is to be compared with the value of ϱ_{NN} of 0.469 obtained in the present MO calculation. The spin density on nitrogen predicted by earlier MO calculations, where the basis set is assumed to be orthogonal, varies from 0.050 to 0.238 [14, 15, 17, 39]. Clearly, the present result over the non-orthogonal basis compares most closely with the result of Gross and Symons. The low values of spin densities obtained in earlier MO calculations are reflected in the very high values for Q^{N}_{NN} derived using these spin densities.

The amino nitrogen splitting in *p*-nitroaniline radical anion (XII, see Fig. 1) and the nitrile group nitrogen splitting in *p*-nitrobenzonitrile radical anion (XIII, see Fig. 1) calculated using the spin density results over nonorthogonal basis and the relations already described earlier [17] are 1.14 Gauss and 1.66 Gauss respectively. These may be compared with the experimental values [17] of 1.21 Gauss and 0.76 Gauss respectively.

4. Conclusion

The present UHF spin density calculations using orthogonalized basis set of atomic orbitals are shown to give an adequate account of proton and ^{14}N splittings in aza and nitroaromatic radical anions. This procedure has also been successfully extended [27] to the study of spin density distribution in sulphur-containing conjugated radicals. This is encouraging in view of the fact that the present approach of integral evaluation is free from the choice of parameters for the heteroatoms based on comparison with certain molecular properties of some reference molecules. Our spin density results over the completely localized nonorthogonal basis lead to a better description of ^{14}N splittings in the nitro-aromatic radical anions compared to the earlier molecular orbital results over a basis set assumed to be orthogonal.

Acknowledgements. We wish to thank the staff of Computer Centre at I.I.T. Kanpur for their valuable cooperation and the Council of Scientific and Industrial Research, New Delhi for a grant. D.N.N. acknowledges with gratefulness the award of a CSIR Senior Research Fellowship.

References

1. Karplus, M., Fraenkel, G. K.: J. Chem. Phys. **35**, 1312 (1961)
2. Ward, R. L.: J. Am. Chem. Soc. **84**, 332 (1962)
3. Carrington, A., dos Santos-Veiga, J.: Mol. Phys. **5**, 21 (1962)
4. Atherton, N. M., Gerson, F., Murrell, J. N.: Mol. Phys. **5**, 509 (1962)
5. Stone, E. W., Maki, A. H.: J. Chem. Phys. **39**, 1635 (1963)
6. Geske, D. H., Padmanabhan, G. R.: J. Am. Chem. Soc. **87**, 1651 (1965)
7. Henning, J. C. M.: J. Chem. Phys. **44**, 2139 (1966)
8. Adams, J. Q., Nicksic, S. W., Thomas, J. R.: J. Chem. Phys. **45**, 654 (1966)
9. Talcott, C. L., Myers, R. J.: Mol. Phys. **12**, 549 (1967) and references therein
10. Cottrell, P. T., Rieger, P. H.: Mol. Phys. **12**, 149 (1967)
11. Black, P. J., McDowell, C. A.: Mol. Phys. **12**, 233 (1967)
12. Yonezawa, T., Kawamura, T., Kato, H.: J. Chem. Phys. **50**, 3482 (1969)
13. Chiu, M. F., Sutcliffe, B. T.: Theoret. Chim. Acta (Berl.) **16**, 331 (1970)
14. Rieger, P. H., Fraenkel, G. K.: J. Chem. Phys. **39**, 609 (1963)
15. Hinchliffe, A.: Theoret. Chim. Acta (Berl.) **5**, 451 (1965)
16. Amos, A. T., Snyder, L. C.: J. Chem. Phys. **41**, 1773 (1971); see also Snyder, L. C., Amos, A. T.: J. Chem. Phys. **42**, 3670 (1962)
17. Nanda, D. N., Subramanian, J., Narasimhan, P. T.: Theoret. Chim. Acta (Berl.) **22**, 369 (1971)
18. Gross, J. M., Symons, M. C. R.: J. Chem. Soc. (A), 451 (1966)
19. Abronin, I. A., Sysoeva, N. A., Zhidomirov, G. M., Buchachenko, A. L., Chuvylkin, N. D.: J. Struct. Chem. **12**, 907 (1971)
20. Pariser, R., Parr, R. G.: J. Chem. Phys. **21**, 466, 767 (1953)
21. Pople, J. A.: Trans. Faraday Soc. **48**, 1375 (1953)
22. Löwdin, P. O.: J. Chem. Phys. **18**, 365 (1950)
23. Löwdin, P. O.: Proc. Intern. Conf. Theoret. Phys., Kyoto Tokyo, Japan, 1953, 599 (1954)
24. McWeeny, R.: Proc. Roy. Soc. (London), Ser. A **227**, 288 (1955)
25. Fischer-Hjalmars, I.: J. Chem. Phys. **42**, 1962 (1965)
26. Nanda, D. N., Narasimhan, P. T.: Int. J. Quant. Chem. **6**, 819 (1972)
27. Nanda, D. N., Narasimhan, P. T.: Mol. Phys. **24**, 1341 (1972)
28. Pople, J. A., Nesbet, R. K.: J. Chem. Phys. **22**, 571 (1954)
29. Ohno, K.: Theoret. Chim. Acta (Berl.) **2**, 219 (1964)
30. Mulliken, R. S.: J. Chim. Phys. **46**, 497 (1949)
31. Burns, G.: J. Chem. Phys. **41**, 1521 (1964)
32. Lykos, P. G.: J. Chem. Phys. **35**, 1253 (1961)

33. Fischer-Hjalmars, I., Sundbom, M.: Acta Chem. Scand. **22**, 607 (1968)
34. Peacock, T. E.: Proc. Phys. Soc. (London) A**78**, 460 (1961)
35. Roos, B.: Acta Chem. Scand. **21**, 2318 (1967)
36. Turner, D. W.: Advan. Phys. Org. Chem. **4**, 31 (1966)
37. McConnell, H. M.: J. Chem. Phys. **28**, 1188 (1958)
38. Colpa, J. P., Bolton, J. R.: Mol. Phys. **6**, 273 (1963); Bolton, J. R.: J. Chem. Phys. **43**, 309 (1965)
39. Geske, D. H., Ragle, J. L., Bambenek, M. A., Balch, A. L.: J. Am. Chem. Soc. **86**, 987 (1964)

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