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Annotatio

RHF CI INDO Spin Density Calculation

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In their recent article [1] Bellagamba and his co-workers compared their results of RHF CI calculation of spin densities with those obtained by the UHF method at the INDO level of approximation in [2]. After least squares analysis, they came to the conclusion that the RHF CI method leads to hfs coupling constants in better agreement with the experimental values than the UHF technique and thus the RHF CI should be preferred in the calculation of spin densities of organic radicals. Since the UHF and RHF CI calculations have not been carried out under the same conditions, the conclusion drawn by the authors may be misleading. The RHF CI calculation was done for a set of radicals different from that calculated with UHF; moreover, the geometry of most of the calculated radicals was optimized and the number of points used for the least-square analysis of the results is not the same in the two methods as it is seen from Table 9 in Ref. [1]. In our opinion, in the statistical comparison of methods identical conditions should be retained and the set of radicals should be the same. Elimination (or addition) of several radicals may distort the results completely. To illustrate this statement, we present the results of the UHF INDO calculation [3] of a set of radicals different from that

Table 1. Results of the least-square fitting between a_N and spin densities for the ^1H nucleus

Method	No. of data points			Correlation coefficient			Standard deviation (gauss)		
	[1]	[2]	[3]	[1]	[2]	[3]	[1]	[2]	[3]
RHF CI	101	—	17	0.95	—	0.990	9.2	—	7.34
UHF	—	141	17	—	0.88	0.994	—	6.3	4.46

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employed by the authors [1] (Table 1). The results indicate strong dependence of the correlation coefficients and standard deviations on the set of radicals selected.

In comparing the methods, one has to consider that the UHF calculations are much simpler for practical application and less time-consuming (also in the projected version [4]) than the RHF CI calculations.

References

1. Bellagamba, V., Ercoli, R., Gamba, A., Morosi, G.: Theoret. Chim. Acta (Berl.) **47**, 329 (1978)
2. Beveridge, D. L., Dobosh, P. A.: J. Chem. Phys. **48**, 5532 (1968)
3. Klimo, V., Tiňo, J.: Chem. Phys. Letters **37**, 311 (1976)
4. Mestechkin, M. M., Whyman, G. E.: Intern. J. Quantum Chem. **8**, 45 (1974)

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