Theoret. chim. Acta (Berl.) 18, 385—388 (1970)

Relationes

Convergence of the Perturbation Theory Expansion for Spin-Spin Coupling Constants

WALDEMAR ADAM, ALEC GRIMISON, and PHILLIP A. SPRANGLE
Department of Chemistry and Puerto Rico Nuclear Center*
University of Puerto Rico, Río Piedras, Puerto Rico

Received March 2, 1970/May 25, 1970

The convergence of the full perturbation theory expansion for the Fermi contact term in the spin-spin coupling constant of hydrogen fluoride has been studied. By examining the contribution of higher virtual states as the basis set is expanded to 18 atomic orbitals, it is shown that at this level of approximation the expansion does not converge. The need to also establish convergence before accepting values calculated from configuration interaction wavefunctions is discussed.

Introduction

The perturbation theory for the calculation of nuclear-spin spin coupling constants was first formulated by Ramsey [1a, 1b], and has been applied to molecular orbital wavefunctions in a number of calculations at various levels of sophistication [1b, 2–10].

While the earlier calculations simplified the calculation by the use of a "mean excitation energy" approximation [2], this has proved unsatisfactory, and more recent calculations explicitly include the excited state contributions [6–10]. It has been demonstrated that there can be a significant contribution from inner-shell atomic orbitals [10, 11] so that neglect of these contributions requires corrective parametrization, usually made in the atomic orbital densities at the nuclei [9–12]. We have found that for best accord with experimental coupling constants (*i*) the expression for the triplet state excitation energies must retain the Coulomb integral J_{ij} between molecular orbitals φ_i and φ_j

$$\Delta E = \varepsilon_j - \varepsilon_i - J_{ij}$$

(ii) that inner shell orbitals contributions are very significant with a Slater A.O. basis set, as a result of the large density of the 1*s* orbital at the nucleus for the second-row elements (iii) retaining two center integrals permits the use of purely theoretical atomic orbital densities at the nuclei, and greatly improves the calculated values. Exactly similar conclusions were reached by Barbier and Berthier [10].

---

* The Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the United States Atomic Energy Commission under Contract No. AT(40-1)-1833.

Armour and Stone [8], and Ditchfield and Murrell [9] further demonstrated the improvement in the calculated coupling constants by the inclusion of correlation effects, through a limited configuration interaction treatment. We shall have reason to refer back to this conclusion later.

By far the most penetrating analysis of the fundamental usefulness of the perturbational treatment was that of Kato and Saika [7]. These authors appear to have been the first to question the convergence of the truncated perturbational theory expansion as higher virtual states are included. Hydrogen fluoride was used as the model system, in view of the range of basis sets available [13–16]. In addition to the Fermi contact term, Kato and Saïka evaluated the spin-dipolar contribution to the H–F coupling constant. All two-center integrals were retained, all the basis sets explicity involved inner-shell orbitals, and one-electron excitation energies were corrected for the Coulomb repulsion. Their theoretical value for HF, using Ransil's molecular orbitals [13] was −1483 hz, compared to the experimental magnitude (sign not established) of 614 hz [17]. The use of Nesbet's molecular orbitals [16], which correspond to a larger basis set (9 Slater atomic orbitals) was +612 hz. While this latter value is in excellent agreement with the magnitude of the experimental coupling constant, Kato and Saika point out that their results do not permit them to conclude whether the ordinary perturbation treatment of spin coupling converges or not. They showed that the coupling constant contributions from progressively higher excitation varied erratically in sign and in magnitude. Similar results were obtained for ammonia [18].

Present Calculation and Discussion of the Results

We are at present engaged in a very critical examination of the convergence of the spin coupling perturbation expression. We have repeated the type of calculation carried out by Kato and Saika, since the present concern is with the convergence, rather than a close (and possibly fortuitious) fit with the experimental data. We have attempted to resolve the questions raised by Kato and Saika's work by extending this analysis to larger basis-set calculations on HF by McLean and Yoshimine [19] (16 Slater orbitals) and by Cade [20] (18 Slater orbitals).

The contributions of the individual excitations to the coupling constant are summarized in theTable for the basis sets of Nesbet [16], McLean and Yoshimine [19] and Cade [20]. The results for Nesbet's wavefunctions are in very close correspondence with the values quoted by Kato and Saika, as is to be expected, although there is a difference of around 2% in the actual numerical values. The most revealing feature of this table are the horizontal summations, at the right hand side of each block in the table, of all coupling constant contributions arising from excitations from a particular occupied level to the various empty levels. The contributions of the excitations from the lowest occupied level are all positive, but relatively small. Irrespective of the basis set used, the sum of contributions from the second occupied level is always large and positive, while that from the highest occupied level is always large and

Table. *Hydrogen fluoride coupling constants contributions from the individual excitations as a function of the choice of basis set*

Nesbet MO's [16]

occ. MO's \ unocc. MO's	4	5	6	7	8	9	Sum
1	0	0	0	0	3	−2	1
2	489	−352	172	−443	−3900	−2309	1519
3	−458	209	−91	217	−1824	1028	−920
Sum	31	−142	81	−226	2138	−1282	598

McLean and Yoshimine [19]

occ. MO's \ unocc. MO's	4	5	6	7	8	9	10	11	12	13	14	15	16	Sum
1	5	1	2	9	1	7	3	1	20	29	40	0	82	69
2	590	−114	−203	509	63	269	−99	−99	414	468	−482	3	581	1146
3	−520	78	122	−250	−29	−115	41	11	165	−181	182	1	−213	−709
Sum	75	−48	−84	267	35	161	−59	−16	259	315	−340	−2	455	501

Cade MO's [20]

occ. MO's \ unocc. MO's	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Sum
1	0	0	0	0	0	0	0	0	0	0	0	−1	0	0	2	2
2	582	−80	−23	379	56	−545	29	168	33	−230	4	337	18	−35	−576	116
3	−587	70	16	−222	−31	278	−14	−80	−16	105	−2	−148	−8	15	240	−384
Sum	−5	−10	−7	158	25	−268	15	88	17	−125	2	188	10	−20	−334	−270

negative. The vertical summations show no sign of convergence as higher virtual levels are included. Consequently, as more and more virtual states are included, the individual contributions become larger and larger and fluctuate in sign.

Conclusion

We can therefore conclude that with the single-determinant wavefunctions at present available, there is no sign of convergence of the perturbation theory expansion as the size of the basis sets is increased. This defect can obviously be related to the poor description provided of the virtual orbitals. It has been pointed out [8, 9], that it is necessary to include electron correlation effects by the use of configurationally-interacted wavefunctions to improve the agreement with experimental values. However, it is imperative to point out that even this process cannot be considered rigorously justified at present. It is still necessary to establish the convergence of the perturbation theory expansion as a function of the number of excited configurations included. We are currently carrying out a full examination of this further question, using hydrogen fluoride as a model system.

Acknowledgements. This work was supported by a grant from the University of Puerto Rico. We wish to thank Dr. McLean and Dr. Cade for communicating their results prior to publication.

References

1a. Ramsey, N. F., Purcell, E. M.: Physic. Rev. **85**, 143 (1952).
1b. — Physic. Rev. **91**, 303 (1953).
2. McConnell, H. M.: J. chem. Physics **24**, 460 (1956).
3. Saika, A.: Physica **25**, 51 (1959).
4. Barton, D. S., Richardson, J. W.: J. chem. Physics **42**, 4019 (1965).
5. Loève, P., Salem, L.: J. chem. Physics **43**, 3402 (1965).
6. Pople, J. A., Santry, D. P.: Molecular Physics **9**, 311 (1964).
7. Kato, Y., Saika, A.: J. chem. Physics **46**, 1975 (1967).
8. Armour, E. A. G., Stone, A. J.: Proc. Roy. Soc. (London) A **302**, 25 (1967).
9. Ditchfield, R., Murrell, J. N.: Molecular Physics **14**, 481 (1968).
10. Barbier, C., Berthier, G.: Theoret. chim. Acta (Berl.) **14**, 71 (1969).
11. Adam, W., Grimison, A., Sprangle, P. A.: M.S. Thesis (P. A. Sprangle), Univ. of Puerto Rico, January 1969.
12. Pople, J. A., McIver, J. N., Jr., Ostlund, N. S.: J. chem. Physics **49**, 2965 (1968).
13. Ransil, B. J.: Rev. Mod. Physics **32**, 245 (1960).
14. Karo, A. M., Allen, L. C.: J. chem. Physics **31**, 968 (1959).
15. Mukherji, A., Karplus, M.: J. chem. Physics **38**, 44 (1963).
16. Nesbet, R. K.: J. chem. Physics **36**, 1518 (1962).
17. Solomon, I., Bloembergen, N.: J. chem. Physics **25**, 261 (1956).
18. Kato, Y., Minra, M., Saika, A.: Molecular Physics **13**, 491 (1967).
19. McLean, A. D., Yoshimine, M.: Private communication.
20. Cade, P. E.: Private communication.

Dr. Alec Grimison
Puerto Rico Nuclear Center
Caparra Heights Station
San Juan, Puerto Rico, 00935