eliminated by a simple iterative process prescribed by McWeeny[9].

Applicability of the method — Although a steepest descent procedure guarantees convergence, very often the convergence is rather poor. It is thus necessary to test whether a particular method involving a steepest descent procedure leads to reasonable convergence to be of any practical value. For this we have done two test calculations the results of which seem quite encouraging.

In Table 1 we present the electron densities on the terminal atoms of allyl cation after successive iterations using the present method. The results obtained by the conventional ω-technique[3] and those improved by Hakala's method[8] are also included in Table 1. A comparison among the three sets shows a great improvement in the convergence by the present method.

Conventional ω-technique is known to lead to a divergence for benzyl cation[6]. Convergence can only be achieved by the application of rather elaborate methods involving averaging after successive iterations[7] or including ω'- and ω''-techniques[10]. In Table 2 we present the electron densities on the first atom (outside the ring) of benzyl cation after successive iterations using the present method. A comparison with the values given in literature[7] again shows a great improvement in the convergence by the present method.

In order to see whether the charge densities calculated by the present method give a better picture of the actual π-electron charge densities the authors have started calculations of dipole moments of a series of non-alternants using the charge densities obtained by the present method. The results of these calculations, which will be presented in a later paper, are expected to be very hopeful indeed. The values of dipole moments of fulvene and azulene so far calculated appear even better than those[10] obtained by ω'- and ω''-techniques. In conclusion we may say that as the convergence here is quite good, the charge distributions and hence the dipole moments are better than those obtained by the conventional ω-technique and as the method avoids repeated diagonalization of the Hamiltonian matrix, generally a time-consuming step in a self-consistent field calculation, the present method seems to have a significant promise and hence should be extensively applied.

TABLE 1 — ELECTRON DENSITIES ON THE TERMINAL CENTRES OF ALLYL CATION AFTER SUCCESSIVE ITERATIONS

No. of iterations	Present method	As in ref. 3	As in ref. 8
0	0·500	0·500	0·500
1	0·601	0·621	0·621
2	0·598	0·534	0·579
3	0·598	0·597	0·569
⋮	⋮		⋮
10			0·571

TABLE 2 — CHARGE DENSITIES ON THE FIRST ATOM (i.e. THAT OUTSIDE THE RING) OF BENZYL CATION AFTER SUCCESSIVE ITERATIONS

No. of iterations	Present method	ω-Technique[7]	Arithmetic mean[7]
0	0·5714	0·5714	0·5714
1	0·3680	0·1697	0·3701
2	0·3510	0·5697	0·3938
3	0·3182	0·1532	0·3726
4	0·3158	0·5879	0·3948
5	0·3140	0·1212	0·3728

One of the authors (N.G.M.) is indebted to Prof. R. McWeeny of the University of Sheffield, UK, for making him acquainted with the principles of the steepest descent technique and to the UGC, New Delhi, for financial assistance. The authors are also grateful to the Centre of Computer Science, University of Calcutta, for computer facility.

References

1. Coulson, C. A. & Rushbrooke, G. S., *Proc. Cambridge Phil Soc.*, **36** (1940), 193.
2. McWeeny, R., *Molecular orbitals in chemistry, physics and biology, a tribute to R. S. Mulliken*, edited by P. O. Lowdin & B. Pullman (Academic Press, New York), 1964, 304.
3. Streitwieser, (Jr) A., *Molecular orbital theory for organic chemists* (John Wiley, New York), 1961.
4. Harris, F. E., *J. chem. Phys.*, **48** (1968), 4027.
5. Goodisman, J., *Theoret. Chim. Acta (Berl.)*, **36** (1974), 117.
6. Streitwieser (Jr), A. & Nair, P. M., *Tetrahedron*, **5** (1959), 149.
7. Coulson, C. A. & Wille, F., *Tetrahedron*, **22** (1966), 3549.
8. Hakala, R. W., *Intern. J. Quantum Chem.* (Symposium), **1** (1967), 227.
9. McWeeny, R., *Proc. roy. Soc.*, **A235** (1957), 496.
10. Streitwieser (Jr), A., Heller, A. & Feldman, M., *J. phys. Chem.*, **68** (1964), 1224.

Floating Spherical Gaussian Orbital (FSGO) Studies with a Model Potential: Methane, Silane & Germane

S. P. Mehandru & N. K. Ray*

Department of Chemistry, University of Delhi, Delhi 110007

Received 30 *December* 1976

A Gaussian-based model potential is used within FSGO formalism to study the equilibrium geometries of CH_4, SiH_4 and GeH_4. The predicted bond lengths are in excellent agreement with the experimental values.

VALENCE electron studies with model potentials have drawn considerable attention in recent years[1-18]. Most of these calculations have been made within the LCAO-SCF-MO formalism and only a few have been carried out in the framework of floating orbital basis[4,5,10,16-18].

In the present communication we have used the model potential suggested by Schwartz and Switalski[19] within FSGO formalism[20] to study the equilibrium geometries of CH_4, SiH_4 and GeH_4. This method has been used quite successfully earlier by Ray and Switalski to study the first row atom

---

*Author to whom all correspondence should be made.

hydrides[17] and a series of two-valence electron diatomic and triatomic ions[18]. The core model potential used here has the form

$$V_m = -\frac{Z_c}{r}+[A_s \text{ or } A_p]\,\frac{\exp\,(-\gamma r^2)}{r} \qquad \ldots(1)$$

where Z_c is the nuclear charge minus the number of core electrons. A_s and A_p are the model potential parameters for the s and p state of the atom under consideration. Core model potential parameters needed for the present study are obtained by a procedure similar to the one suggested earlier by Ray and Switalski[17,18]. These parameters are listed in Table 1.

Only valence electrons are taken into consideration and the effect of the core is simulated through the use of a model potential. The molecular wave function is constructed using the FSGO method[20]. The floating basis orbital does not possess a well-defined angular momentum[21]. Because of this arbitrariness in the components of the angular momenta of the FSGOs, V_m as defined in Eq. (1) cannot be directly used. An effective A (A_{av}) should be used which should be a function of A_s and A_p. The A_{av} values are listed in Table 1 and are obtained using Eq. (2).

$$A_{av} = k\left[\frac{A_sN_s+A_pN_p}{N_s+N_p}\right] \qquad \ldots(2)$$

where N and N_p are the number of s and p valence electrons respectively. k is a constant equal to 1 for first row atoms and is 0·75 for the second and third row atoms. Hence, the model potential used in the present study reduces to the form

$$V_m' = -\frac{Z_c}{r}+A_{av}\left[\frac{\exp\,(-\Upsilon r^2)}{r}\right] \qquad \ldots(3)$$

The best values for the positions of the Gaussians, orbital radii and the nuclear positions are obtained by minimizing the valence energy, E_{val}. The optimization is carried out using the subroutine STEPIT[22]. Tetrahedral geometry (T_d) was maintained for all the molecules studied here during the optimization.

The results of the present study are given in Table 2. The predicted bond lengths are in excellent agreement with the experimental values and the results of the other *ab initio* studies[25,26]. Recently Amos and Yoffe[23] have used symmetry adopted perturbation theory[24] to successfully calculate the average electric polarizabilities of molecules from FSGO wave functions. In view of this fact it was considered worth while to compare our calculated polarizabilities with those obtained from normal FSGO studies. Our calculated results are given in Table 3 along with those obtained from FSGO wave functions. Fairly good agreement between the two is observed. The model potential method used here appears to be quite promising. We are currently extending the method for the study of larger polyatomic molecules. These results will be reported elsewhere.

TABLE 1 — MODEL POTENTIAL PARAMETERS FOR C, Si AND Ge

Atom	A_s	A_p	Υ	A_{av}
C	2·6765	−0·1729	1·082	1·2518
Si	2·8978	1·6072	0·4710	1·6894
Ge	2·7510	1·5959	0·4156	1·6301

TABLE 2 — RESULTS FOR THE BOND LENGTH OF CH_4, SiH_4, GeH_4

Molecule	Bond length (a.u.)		
	Model potential	FSGO[a]	Exptl[b]
CH_4	2·14	2·11	2·10
SiH_4	2·76	2·80	2·76
GeH_4	2·82	—	2·89

(a) Obtained from references 25 and 26.
(b) Obtained from references 27 and 28.

TABLE 3 — CALCULATED AVERAGE POLARIZABILITIES (UNITS OF 10^{-25} CM^3)

Molecule	Average polarizability[a]	
	Model potential	FSGO
CH_4	29·6	24·4
SiH_4	58·5	44·0
GeH_4	58·7	—

(a) Average polarizabilities were calculated using the procedure given by Amos and Yoffe in reference 23.

A part of the work presented here was carried out at the University of North Carolina at Chapel Hill, USA. One of the authors (N.K.R.) thanks Prof. Robert G. Parr for his warm and generous hospitality at Chapel Hill. Thanks are also due to Dr J. D. Switalski for helpful discussions.

References

1. KUTZELNIGG, W., KOCH, R. J. & BINGEL, W. A., *Chem. Phys. Lett.*, **2** (1968), 197.
2. SIMONS, G., *Chem. Phys. Lett.*, **18** (1973), 315.
3. SIMONS, G., *J. chem. Phys.*, **55** (1971), 756.
4. BARTHELAT, J. C. & DURAND, PH., *Chem. Phys. Lett.*, **16** (1972), 63.
5. BARTHELAT, J. C. & DURAND, PH., *J. chim. Phys.*, **71** (1974), 505, 1105.
6. KLEINER, M. & MCWEENY, R., *Chem. Phys. Lett.*, **19** (1973), 479.
7. MELIUS, C. F., OLAFSON, B. D. & GODDARD, W. A. III, *Chem. Phys. Lett.*, **28** (1974), 457.
8. POHL, H. A. & FOWLER, D. R., *Intern. J. Quantum Chem.*, **8** (1974), 435.
9. MELIUS, C. F. & GODDARD, W. A. III, *Phys. Rev.*, **10** (1974), 1528.
10. GASPAR, R. & TOMASSY-LENTEI, I., *Acta Phys. Acad. Sci. Hung.*, **33** (1973), 387.
11. SWITALSKI, J. D., HUANG, J. T. H. & SCHWARTZ, M. E., *J. chem. Phys.*, **60** (1974), 2252.
12. SWITALSKI, J. D. & SCHWARTZ, M. E., *J. chem. Phys.*, **62** (1975), 1521.
13. ZERNER, M. C., *Mol. Phys.*, **23** (1972), 963.
14. HORN, M. & MURRELL, J. N., *J. chem. Soc., Faraday II*, (1974), 769.
15. MURRELL, J. N. & VINCENT, I. G., *J. chem. Soc., Faraday II*, (1975), 890.
16. SEMKOW, A. M., SUTHERS, R. A. & LINNETT, J. W., *Chem. Phys. Lett.*, **32** (1975), 116.
17. RAY, N. K. & SWITALSKI, J. D., *J. chem. Phys.*, **63** (1975), 5053.
18. RAY, N. K. & SWITALSKI, J. D., *Theoret. Chim. Acta*, **41** (1976), 329.

19. Schwartz, M. E. & Switalski, J. D., *J. chem. Phys.*, **57** (1972), 4125.
20. Frost, A. A., *J. chem. Phys.*, **47** (1967), 3707.
21. Christoffersen, R. E., Spangler, D., Hall, G. G. & Maggiora, G. M., *J. Am. chem. Soc.*, **95** (1973), 8526.
22. Obtained from QCPE, Chemistry Department, Indiana University, Bloomington, Indiana 47401, USA.
23. Amos, A. T. & Yoffe, J. A., *Chem. Phys. Lett.*, **31** (1975), 57.
24. Amos, A. T. & Yoffe, J. A., *Chem. Phys. Lett.*, **31** (1975), 53.
25. Chu, S. Y. & Frost, A. A., *J. chem. Phys.*, **54** (1971), 760.
26. Frost, A. A. & Rouse, R. A., *J. Am. chem. Soc.*, **90** (1968), 1965.
27. Pauling, L., *The nature of the chemical bond* (Cornell University Press), 1960.
28. Moccia, R., *J. chem. Phys.*, **40** (1964), 2164, 2176, 2186.

Strong Solvent Dependence of Phosphorus Chemical Shift in Lanthanide Complexes $[(CH_3)_2PS_2]_3Ln$

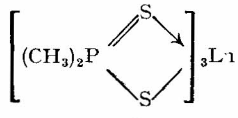
G. Hägele, W. Kuchen & P. N. Mohan Das

Institut für Anorganische und Strukturchemie
Universität Düsseldorf, Universitätsstrasse 1
4000 Düsseldorf, West Germany

Received 13 *December* 1976; *accepted* 27 *December* 1976

The ^1H and $^1H(^{31}P)$ NMR spectra of the paramagnetic complexes LnL_3 [Ln=Pr(III), Nd(III), Eu(III), L=$(CH_3)_2PS_2$] are found to be strongly solvent dependent. Solutions in acetone-d_6 exhibit greater half-widths in P-CH_3 doublet and larger δ_P values than the corresponding solutions in methanol-d_4.

Reactions between stoichiometric amounts of lanthanide ions and the sodium salt of dimethyldithiophosphinic acid $(CH_3)_2P(S)SNa.2H_2O$ in ethanol medium gave the octahedral complexes of the type (I)[1].



I

Ln=La(III), Pr(III), Nd(III), Eu(III), Sm(III)

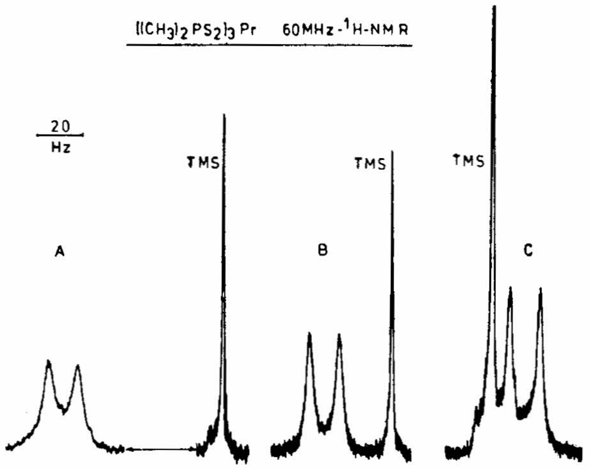


Fig. 1 — 60 MHz NMR spectrum for protons in $[(CH_3)_2PS_2)]_3Pr$ [40 mg complex dissolved in 0·4 ml of solvents: CD_3COCD_3 = A; CD_3COCD_3/CD_3OD (1:1) = B; and CD_3OD=C]

It is found that the 60 MHz ^1H and $^1H(^{31}P)$ NMR spectra of the paramagnetic Pr(III), Nd(III) and Eu(III) complexes are strongly solvent dependent. Solutions of I in acetone-d_6 exhibited greater half-widths in P-CH_3 doublet lines and larger δ_P values than in methanol-d_4 (see Fig. 1). An unusual strong sensitivity of δ_P in I towards change of the solvent is observed. δ_P values were observed in the wide range of about 100 ppm widths (see Table 1). As we were able to prepare well-defined diadducts, $LnL_3.2B$ of some complexes (I) (e.g. Ln=Pr(III); L=$(CH_3)_2PS_2$; B=CH_3OH, C_5H_5N) as stable solid compounds, we assume that the coordination number six in I is expanded to eight in the solutions of the above-mentioned solvents. We suggest that the magnitude of the extremely strong shift in δ_P and the change in the spectral half-widths may be in correlation with the solvent donor properties. Therefore, we intend to use the paramagnetic complexes (I) in particular $[(CH_3)_2PS_2]_3Pr$ for systematic studies of their interactions with a wide variety of donor solvents.

References

1. Mohan Das, P. N., Kuchen, W., Keck, H. & Hägele, G., *J. inorg. nucl. Chem.*, (in press).

Table 1—Solvent Dependent Chemical Shifts of Phosphorus, Proton and Spectral Half-widths of P-CH_3 Doublets

Compound	CD_3COCD_3			CD_3OD		
	δ_P	δ_H	$\Delta\nu_{1/2}$	δ_P	δ_H	$\Delta\nu_{1/2}$
LH	—	2·117	0·5	+50·9	2·083	0·5
LaL_3	—	—	—	+52·2	2·000	1
PrL_3	+19·2	1·167	10	−51·4	**−0·242**	3
NdL_3	−26·7	2·767	15	−58·4	1·558	1
SmL_3	+57·6	1·783	10	+53·7	1·792	6
EuL_3	+51·2	**−0·222**	3·5	−24·3	1·735	1·5

δ_P= phosphorus chemical shift calc. vs H_3PO_4 85% (ppm).
δ_H= proton chemical shift vs TMS (ppm).
$\Delta\nu_{1/2}$ = spectral half-width of P-CH_3 doublets (Hz).
LH=$(CH_3)_2PS_2H$.