the authors have started calculations of dipole moments of fulvene and azulene, so far calculated appear even better than those obtained by the conventional \( \omega \)-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.

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


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

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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. 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.

In the present communication we have used the model potential suggested by Schwartz and Switalski within FSGO formalism 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

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

\[ V_m = -\frac{Z_e}{r} + A_s A_p \exp \left( -\frac{\gamma r^2}{r} \right) \]  

(1)

where \( Z_e \) 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\textsuperscript{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\textsuperscript{20}. The floating basis orbital does not possess a well-defined angular momentum\textsuperscript{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).

\[ A_{av} = k \frac{A_s N_s + A_p N_p}{N_s + N_p} \]  

(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

\[ V' = -\frac{Z_e}{r} + A_s A_{av} \exp \left( -\frac{\gamma r^2}{r} \right) \]  

(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\textsuperscript{22}. Tetrahedral geometry (Td) 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 \textit{ab initio} studies\textsuperscript{25,26}. Recently Amos and Yoffe\textsuperscript{23} have used symmetry adapted perturbation theory\textsuperscript{24} to successfully calculate the average electric polarizabilities of molecules from FSGO wave functions. In view of this fact it was considered worthwhile 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.

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

22. Obtained from QCPE, Chemistry Department, Indiana University, Bloomington, Indiana 47401, USA.
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Strong Solvent Dependence of Phosphorus
Chemical Shift in Lanthanide Complexes
\[ [(\text{CH}_3)_2PS]_3\text{Ln} \]
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The \(^1\)H and \(^1\)H\(^{31}\)P) NMR spectra of the paramagnetic complexes \(\text{LnL}_3\) (\(\text{Ln} = \text{Pr(III)}, \text{Nd(III)}, \text{Eu(III)}, \text{L} = (\text{CH}_3)_2\text{PS}_2\)) are found to be strongly solvent dependent. Solutions in acetone-\(d_6\) exhibit greater half-widths in P-\(\text{CH}_3\) doublet lines and larger \(\delta_p\) values than the corresponding solutions in methanol-\(d_4\).

REACTIONS between stoichiometric amounts of lanthanide ions and the sodium salt of dimethyl dithiophosphinic acid \((\text{CH}_3)_2\text{P(S)SNa}\) in ethanol medium gave the octahedral complexes of the type (I):

\[
[(\text{CH}_3)_2PS]_3\text{Ln} \quad (\text{I})
\]

\(\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Eu(III)}, \text{Sm(III)}\)

It is found that the 60 MHz \(^1\)H and \(^1\)H\(^{31}\)P) NMR spectra of the paramagnetic \(\text{Pr(III)}, \text{Nd(III)}\) and \(\text{Eu(III)}\) complexes are strongly solvent dependent. Solutions of (I) in acetone-\(d_6\) exhibited greater half-widths in P-\(\text{CH}_3\) doublet lines and larger \(\delta_p\) values than in methanol-\(d_4\) (see Fig. 1). An unusual strong sensitivity of \(\delta_p\) in (I) towards change of the solvent is observed. \(\delta_p\) values were observed in the wide range of about 100 ppm widths (see Table 1). As we were able to prepare well-defined diadducts, \(\text{LnL}_2\cdot2\text{B}\) of some complexes (I) (e.g. \(\text{Ln} = \text{Pr(III)}\); \(\text{L} = (\text{CH}_3)_2\text{PS}_2\); \(\text{B} = \text{CH}_3\text{OH}, \text{C}_2\text{H}_5\text{N}\)) 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 \(\delta_p\) 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 \([(\text{CH}_3)_2\text{PS}_2]_3\text{Pr}\) for systematic studies of their interactions with a wide variety of donor solvents.

References

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<th>Compound</th>
<th>CD$_2$COCD$_3$</th>
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<tr>
<td></td>
<td>(\delta_p)</td>
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<tr>
<td>EuL$_3$</td>
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\(\delta_p\): phosphorus chemical shift calc. vs H$_3$PO$_4$ 85% (ppm).
\(\delta_H\): proton chemical shift vs TMS (ppm).
\(\Delta\nu/2\): spectral half-width of P-\(\text{CH}_3\) doublets (Hz).
LH = (\text{CH}_3)$_2$PS$_2$H.

Fig. 1 — 60 MHz NMR spectrum for protons in
\([(\text{CH}_3)_2\text{PS}_2]_3\text{Pr}\) [40 mg complex dissolved in 0.4 ml of solvents:
CD$_2$COCD$_3$ = A; CD$_2$COCD$_3$CD$_2$OD (1:1) = B; and
CD$_2$OD = C]