

# VALENCE-ELECTRON STUDIES WITH THE USE OF ATOMIC FUES POTENTIAL WITHIN FSGO FORMALISM : SOME HOMONUCLEAR DIATOMICS

S. P. MEHANDRU and N. K. RAY\*

*Quantum Chemistry Group, Department of Chemistry, University of Delhi,  
Delhi-110 007*

*(Received 10 May 1978; after revision 6 August 1979)*

Atomic Fues Potential (AFP) type model potential is used within the Floating Spherical Gaussian Orbital (FSGO) framework to calculate the equilibrium geometries and electronic structures of some homonuclear diatomics of the first-row and second-row atoms of the periodic table. The calculated results are compared with experiment and the results of other all-electron studies *ab initio*. The overall agreement is generally satisfactory. Calculations of the various integrals are facilitated by the use of spherical Gaussians and the use of model potential allows the extension of the method to larger systems.

## INTRODUCTION

The electrons of a molecule can be broadly divided into two parts : the 'core' electrons associated with the inner shells of atoms and the 'valence' electrons in the valence orbitals of the molecule. Such a partitioning allows valence orbitals to be treated by comparatively rigorous techniques *ab initio*, with a minimal amount of labour. Since there is considerable spectroscopic and other evidence that most of the molecular properties are associated with valence electrons, such methods should be able to predict these properties without significant loss of accuracy compared with the corresponding all-electron calculations. The methods of core-valence separation are based on the pseudopotential theory first proposed by Gombas (1935) and Hellmann (1935). The exact pseudopotentials can be replaced with little loss of accuracy by simple operators (see Weeks *et al.*, 1969). The valence-electron calculations using these operators are referred to as model potential calculations. There has been considerable interest over the last few years in applying the model potential method in molecular calculations. Simons (1971, 1973) proposed to apply the Fues (1926) potential to atoms and molecules. Most of the molecular calculations have been performed within the SCF-LCAO-MO formalism and only a few have been carried out in the framework of floating orbital basis. The first attempt to use FSGO's with model potentials was presented by Barthelat and Durand (1972, 1974). Some more studies using model potentials in FSGO formalism have been reported in recent years (Semkow *et al.*, 1975; Schwartz & Switalski, 1972; Switalski & Schwartz, 1975; Ray & Switalski, 1975, 1976; and Ray *et al.*, 1977, 1978; and Topiol *et al.*, 1976, 1977*a, b*). In this paper, we shall confine our attention to the use of AFP-type model potential within FSGO formalism of Frost (1967) in predicting

---

\*Author to whom all correspondence should be addressed.

the equilibrium geometries of the homonuclear diatomics of some first- and second-row atoms. The use of spherical Gaussians facilitates the calculations of all the integrals explicitly.

#### METHOD OF CALCULATION

Only valence electrons are taken into consideration and the effect of core is simulated through the use of a model potential. Each pair of electrons is assumed to occupy a normalized floating spherical gaussian, i.e.,

$$\varphi_i = \left[ \frac{2}{\pi \rho_i^2} \right]^{3/4} \exp \left[ - (r - R_i)^2 / \rho_i^2 \right], \quad \dots(1)$$

where  $\rho_i$  is the radius of the orbital and  $R_i$  its position. A single determinantal wave function ( $\Psi$ ) is constructed from the non-orthogonal gaussians ( $\varphi_i$ )

$$\Psi = [1/ |S| (N_v)!]^{1/2} | \varphi_1(1)\varphi_1(2) \dots \varphi_{N_v/2}(N_v-1)\varphi_{N_v/2}(N_v) |, \quad \dots(2)$$

where  $N_v$  is the number of valence electrons in the molecule and  $|S|$  is the determinant of the overlap matrix ( $S$ ) with the elements

$$S_{ij} = \int \varphi_i^* \varphi_j \, d\nu. \quad \dots(3)$$

The total valence energy ( $E_{\text{val}}$ ) of the molecule is given by

$$E_{\text{val}} = (\Psi | H_M | \Psi) / (\Psi | \Psi), \quad \dots(4)$$

where  $H_M$  is the model potential Hamiltonian given by

$$H_M = \sum_{i=1}^{N_v} h(i) + \frac{1}{2} \sum_i \sum_{j \neq i} r_{ij}^{-1} + \sum_{u < v}^M \frac{Z_u Z_v}{R_{uv}} \quad \dots(5)$$

and

$$h(i) = -\frac{1}{2} \nabla_i^2 + \sum_{a=1}^M V_a(i). \quad \dots(6)$$

$M$  is the number of nuclei in the molecule and  $Z_u$  is the effective nuclear charge of the nucleus  $u$ .  $V_a$  is the core model potential which, for the present work, is the generalized atomic Fues potential represented by

$$V'_a(i) = -\frac{Z_a}{r_{ai}} + \frac{\sum_l B_{al} P_l}{r_{ai}^2} \quad \dots(7)$$

$B_{al}$  are the atomic parameters for different  $l$ -states of the atom and  $P_l$  is the projection operator over the  $l^{\text{th}}$  subspace of spherical harmonics. This potential has the significant property that it has simple eigenvalues and eigenfunctions. The solution of the eigenvalue equation is

TABLE I  
Model potential parameters for the atoms

Atom	$Z_a$	$B_{av}^*$
Li	1	0.46768
Be	2	0.63018
B	3	0.45660
C	4	0.35751
N	5	0.29308
O	6	0.24812
F	7	0.21484
Na	1	0.51047
Si	4	1.04473
P	5	1.12638
Cl	7	1.25426

\*Calculated by using equations (8) and (9) of the text.

$$E_v = - \frac{2Z_a^2}{[2P + 1 + \{(2l + 1)^2 + 8B_{ai}\}^{1/2}]^2} \quad \dots(8)$$

This equation permits the calculation of the  $B_{ai}$  parameters from the ground valence-state ionization energy for a given  $l$ . For the sake of simplicity we have used an average value of  $B$ ,  $B_{av}$  in place of  $B_0$  and  $B_1$ , given by

$$B_{av} = \frac{\sum n_l B_{ai}}{\sum n_l} \quad \dots(9)$$

where  $n_l$  is the number of valence electrons, in the free atom, with the azimuthal quantum number  $l$ . Thus the model potential used here reduces to the form

$$V_a(i) = - \frac{Z_a}{r_{ai}} + \frac{B_{av}}{r_{ai}^2} \quad \dots(10)$$

The  $B_{av}$  values are given in Table I.

Complete optimization is carried out for all nuclear coordinates and gaussian orbital parameters by minimizing the valence energy. To prevent variational collapse of lone pairs, the  $\rho_i$  values are varied during optimization under the constraint that  $\rho_i$  for the lone pair on atom X is equal to the  $\rho_i$  for the X-X bond. In all other respects, the optimization is similar to that used by Frost (1967) in earlier all-electron standard FSGO scheme. All calculations are performed by using an IBM 360/44 computer.

#### RESULTS AND DISCUSSION

The calculated equilibrium bond-lengths for all the diatomics studied here are given in Table II alongwith the all-electron FSGO results and available experimental or Hartree-Fock data. The results are generally satisfactory, considering the simplicity

TABLE II  
Calculated equilibrium geometries for the diatomics

System	$R_e$ (a.u.)		
	Present work	FSGO*	Exptl.** or HF**
Li <sub>2</sub>	5.18	5.30	5.05
Be <sub>2</sub>	3.99	3.43	3.78
B <sub>2</sub>	3.97	3.61	(3.01) <sup>c</sup>
C <sub>2</sub>	2.58	2.61	2.68
N <sub>2</sub>	1.97	2.03	2.08
O <sub>2</sub>	1.89	2.03	2.32
F <sub>2</sub>	1.85	2.81	2.73
Na <sub>2</sub>	5.53	5.68	5.82
Si <sub>2</sub>	4.26	—	4.00
P <sub>2</sub>	3.57	3.24	3.58
Cl <sub>2</sub>	3.48	—	3.76

\*Obtained from the work of Chu and Frost (1971)

\*\*Obtained from literature (Wahl *et al.*, 1967; Fraga *et al.*, 1962; Herzberg, 1950; and Langhoff *et al.*, 1977).

<sup>c</sup>Value for triplet state.

of the model used. The predicted bond lengths are on the longer side on the left of the row and on the shorter side on the right. The agreement is fairly good in the centre. The error seems to be quite large for B<sub>2</sub> and F<sub>2</sub> molecules. For B<sub>2</sub>, of course, the available Hartree-Fock result is for the ground state triplet whereas our result corresponds to ground state singlet. The accuracy of our calculations improves for systems containing heavier atoms where our simple method would be most useful.

#### CONCLUSION

This work shows that the atomic Fues potential within simple floating spherical Gaussian orbital method can predict reasonably good values for the equilibrium geometries of the first- and second-row homonuclear diatomics. The authors are currently extending the method to study large polyatomic systems. Work is also in progress for the explicit introduction of angular momentum dependence in our model potential calculations.

#### ACKNOWLEDGEMENTS

One of the authors (SPM) thanks UGC, New Delhi for the grant of Teacher-Fellowship. Thanks are also due to the staff of Computer Centre, University of Delhi, for their valuable co-operation.

#### REFERENCES

- Barthelat, J. C., and Durand, Ph. (1972). Pseudopotentials and localized molecular orbitals : application to the methane molecule. *Chem. Phys. Lett.*, **16**, 63.  
 ——— (1974). Pseudopotential *et* orbitales moléculaires locales : Etude des propriétés de valence des molécules XH<sub>4</sub> (X = C, Si, Ge, Sn, Pb). *J. chem. Phys.*, **71**, 505.

- Chu, S. Y., and Frost, A. A. (1971). Floating spherical Gaussian orbital model of molecular structure. IX. Diatomic molecules of first-row and second-row atoms. *J. chem. Phys.*, **54**, 764.
- Fraga, S., and Ransil, B. J. (1962). Studies in molecular structure. VII. Limited configuration interaction for selected first-row diatomics. *J. chem. Phys.*, **36**, 1127.
- Frost, A. A. (1967). Floating spherical Gaussian Orbital model of molecular structure. I. Computational procedure. LiH as an example. *J. chem. Phys.*, **47**, 3707.
- Fues, E. (1926). *Ann. Phys.*, **80**, 367.
- Gombas, P. (1935). Über die metallische bindung. *Z. Phys.*, **94**, 473.
- Hellmann, H. (1935). A new approximate method in the problem of many electrons. *J. chem. Phys.*, **3**, 61.
- Herzberg, G. (1950). *Spectra of Diatomic Molecules*. Van Nostrand, N. York.
- Langhoff, S. R., Sink, M. L., Pritchard, R. H., Kern, C. W., Stickler, S., and Boyd, M. J. (1977). *J. chem. Phys.*, **67**, 1051.
- Mehandru, S. P., and Ray, N. K. (1977). Floating spherical Gaussian orbital (FSGO) studies with a model potential : some alkali halides. *Chem. Phys. Lett.*, **50**, 497.
- Ray, N. K., and Mehandru, S. P. (1978). Use of atomic Fues potential within the floating spherical Gaussian orbital method : study of some two-valence-electron diatomics and triatomic ions. *Pramāna*, **10**, 201.
- Ray, N. K., Mehandru, S. P., and Switalski, J. D. (1977). Floating spherical Gaussian orbital (FSGO) studies with a model potential : some second row hydrides. *Chem. Phys. Lett.*, **47**, 562.
- Ray, N. K., and Switalski, J. D. (1975). Floating spherical Gaussian orbital (FSGO) studies with a model potential : first row hydrides. *J. chem. Phys.*, **63**, 5053.
- (1976). Floating spherical Gaussian orbital (FSGO) studies with a model potential : application to two-valence-electron systems. *Theoret. Chim. Acta*, **41**, 329.
- Schwartz, M. E., and Switalski, J. D. (1972). Valence electron studies with Gaussian based model potentials and Gaussian basis functions. I. General discussion and application to the lowest *s* and *p* states of Li and Na. *J. chem. Phys.*, **57**, 4125.
- Semkow, A. M., Suthers, R. A., and Linnett, J. W. (1975). On the use of model potentials with floating type of wavefunctions. *Chem. Phys. Lett.*, **32**, 116.
- Simons, G. (1971). New model potential for pseudopotential calculations. *J. chem. Phys.*, **55**, 756.
- (1973). Pseudopotential studies of the water and hydrogen fluoride molecules. *Chem. Phys. Lett.*, **18**, 315.
- Switalski, J. D., and Schwartz, M. E. (1975). Valence electron studies with Gaussian based model potentials and Gaussian basis functions. IV. Application to molecular systems containing first row atoms. *J. chem. Phys.*, **62**, 1521.
- Topiol, S., Frost, A. A., Ratner, M. A., and Moskowitz, J. W. (1976). Use of pseudopotentials within the floating spherical Gaussian orbital method : calculations on methane. *J. chem. Phys.*, **65**, 4467.
- Topiol, S., Frost, A. A., Moskowitz, J. W., and Ratner, M. A. (1977a). A new, simple ab-initio pseudopotential for use in floating spherical Gaussian orbital calculations. 2. Some results for hydrocarbons. *J. Am. chem. Soc.*, **99**, 4276.
- Topiol, S., Frost, A. A., Ratner, M. A., Moskowitz, J. W., and Melius, C. F. (1977b). Pseudopotential calculations using the FSGO method : application to first-row hydrides. *Theoret. Chim. Acta*, **45**, 177.
- Wahl, A. C., Bertocini, P. J., Das, G., and Gilbert, T. J. (1967). *Int. J. Quantum. Chem.*, **1S**, 123.
- Weeks, J. D., Hazi, A., and Rice, S. A., (1969). On the use of pseudopotentials in the quantum theory of atoms and molecules. *Adv. chem. Phys.*, **16**, 283.