

## Use of atomic Fues potential within the floating spherical gaussian orbital method: Study of some two-valence-electron diatomic and triatomic ions

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**Abstract.** Atomic Fues potential type model potential is used within the floating spherical gaussian orbital formalism to study a series of two-valence-electron diatomic and triatomic ions. Calculated equilibrium geometries and force constants are in excellent agreement with available experimental data and results of all-electron *ab initio* studies. Electron populations are given for fourteen diatomic species and comparison has been made with the results of other theoretical studies. The predicted results are generally satisfactory.

**Keywords.** Atomic Fues potential; FSGO studies; two-valence-electron systems.

### 1. 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 *ab initio* techniques, with a minimal amount of labour. Since most 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. These methods are based on the pseudopotential theory. The first models of pseudopotentials were 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. An in-depth study of molecular problems was first started by Preuss (1955), Szasz and McGinn (1956, 1965, 1966, 1967, 1968) and McGinn (1969). The problem has recently been studied again by Simons (1971, 1973) who proposed to apply the Fues (1926) potential to atoms and molecules. The majority of these calculations have been performed within the SCF-LCAO-MO formalism and only a few have been carried out in the frame-work of floating orbital basis. In this paper, we shall confine our attention to the use of AFP in FSGO method. 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 recently reported

(Semkow *et al* 1975; Ray and Switalski 1975, 1976; Topiol *et al* 1976 and Ray *et al* 1977) for first- and second-row atom hydrides. Mehandru and Ray (1977) have recently used a Gaussian based model potential to study the valence electronic structures of a series of alkali halides. In this paper we plan to examine the suitability of the AFP-type model potential within FSGO formalism of Frost (1967) in predicting the equilibrium geometries, force constants and electron populations of some two-valence electron diatomics and tri-atomic ions.

## 2. Method of calculation

Only valence electrons are taken into consideration and the effect of the 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.

$$\varphi_i = (2/\pi \rho_i^3)^{1/2} \exp [-(r-R_i)^2/\rho_i^2] \quad (1)$$

where  $\rho_i$  is the radius of the orbital and  $R_i$  its position. A single determinantal wave function ( $\Psi$ ) is employed

$$\Psi = [1/|S| (2n)!]^{1/2} |\varphi_1(1) \bar{\varphi}_1(2) \dots \varphi_n(2n-1) \bar{\varphi}_n(2n)| \quad (2)$$

in which  $|S|$  is the determinant of the overlap matrix ( $S$ ) with the elements

$$S_{ij} = \int \varphi_i^* \varphi_j dv \quad (3)$$

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

$$E_{\text{val}} = \langle \Psi | H_{pp} | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (4)$$

and the model potential Hamiltonian,  $H_{pp}$ , by

$$H_{pp} = \sum_{i=1}^{N_v} \left[ -\frac{1}{2} \nabla_i^2 + \sum_{a=1}^M V_a(i) \right] + \frac{1}{2} \sum_{i \neq j} r_{ij}^{-1} + \sum_{\mu < \nu}^M \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \quad (5)$$

where  $N_v$  is the number of valence electrons,  $M$  the number of nuclei in the molecule and  $Z_\mu$  is the effective nuclear charge of the nucleus  $\mu$ .

The particular model potential employed for the present work is a generalized atomic Fues potential (AFP)

$$V'_a(i) = -\frac{Z_a}{r_{ai}} + \frac{\sum_i B_i P_i}{r_{ai}^2} \quad (6)$$

where the numerical values of the  $B_l$  parameters are obtained from the work of Simons (1971).  $P_l$  is the projection operator over the subspace of spherical harmonics of given  $l$ . In practice it is sufficient to keep all components of angular momentum up to  $l=l_{\text{core}}+1$  (see Kahn and Goddard 1972 and Topiol *et al* 1976). Following Barthelat and Durand (1974), we have introduced the angular momentum dependence by using  $B_{\text{av}}$  instead of  $B_0$  and  $B_1$ .  $B_{\text{av}}$  is given by

$$B_{\text{av}} = \frac{\sum_l n_l B_l}{\sum_l n_l} \quad (7)$$

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

$$V_a(i) = -\frac{Z_a}{r_{at}} + \frac{B_{\text{av}}}{r_{ai}^2} \quad (8)$$

$B_{\text{av}}$  values are given in table 1.

Complete optimization is carried out for all nuclear co-ordinates and gaussian orbital parameters by minimizing the valence energy. All calculations are made using an IBM 360/44 computer. Results of present calculations are given in tables 2-4.

### 3. Results and discussion

Table 2 summarizes the calculated equilibrium geometries and force constants for nineteen diatomic systems studied in the present work. Also shown in table 2 for comparison are *ab initio* FSGO results, some other model potential results and available experimental data. Our calculated results compare favourably with other theoretical estimates and available experimental geometries. Stretching force

Table 1. Model potential parameters for the atoms

Atom	Z	$B_{\text{av}}^*$
Li	1	0.46768
Na	1	0.51047
K	1	0.68234
Rb	1	0.72657
Cs	1	0.81277
Mg <sup>+</sup>	2	0.85894
Ca <sup>+</sup>	2	1.22213

\* $B_{\text{av}}$  values were obtained by using eq. (7) of the text.  $B_0$  and  $B_1$  values were taken from the work of Simons (1971).

Table 2. Calculated equilibrium geometries and force constants ( $k$ ) of some diatomics

Molecule	$R_e$ (a.u.)				Force constant ( $k$ ) (millidynes/Å)	
	Present work	other model potential <sup>a</sup>	FSGO <sup>b</sup>	Expt <sup>c</sup>	Present work <sup>d</sup>	Expt <sup>c</sup>
	1	2	3	4	5	6
LiH	3.32	3.63	3.22	3.06	0.92	1.03
NaH	3.49	3.81	3.76	3.57	0.79	0.79
KH	4.09	4.59	4.30	4.24	0.51	0.56
RbH	4.23	—	—	4.49	0.46	0.51
CsH	4.49	—	—	4.71	0.39	0.47
MgH <sup>+</sup>	3.24	3.32	3.18	3.12	1.83	1.64
CaH <sup>+</sup>	3.88	4.03	—	3.78	1.18	—
NaLi	5.37	5.49	5.51	—	0.23	—
KLi	6.05	6.18	—	6.22	0.16	0.15
KNa	6.23	6.33	—	6.56	0.14	0.13
RbLi	6.24	—	—	6.67	0.14	0.13
CsLi	6.58	—	—	7.24	0.12	0.11
RbNa	6.40	—	—	6.78	0.13	0.12
CsNa	6.76	—	—	7.09	0.11	0.11
Li <sub>2</sub>	5.18	5.34	5.30	5.05	0.25	0.26
Na <sub>2</sub>	5.53	5.65	5.68	5.82	0.21	0.17
K <sub>2</sub>	6.91	6.98	—	7.41	0.10	0.10
Rb <sub>2</sub>	7.27	—	—	7.90	0.09	0.08
Cs <sub>2</sub>	7.96	—	—	8.35	0.07	0.07

a. Results of gaussian based model potential (Ray and Swatalski 1976) calculations

b. Obtained from literature (Frost 1967, Chu and Frost 1971 and Talaty *et al* 1976)

c. Herzberg (1950)

d. Potential energy curves were fit by third degree polynomials in  $(R - R_e)$ , where  $R_e$  is the equilibrium distance and the values of  $(R - R_e)^2$  co-efficients were used to determine the force constants ( $k$ ).

Table 3. Calculated equilibrium geometries of some triatomic molecular ions

Molecule	Equilibrium geometry (a.u.)			
	This work		ab-initio <sup>a</sup>	
H <sub>2</sub> Li <sup>+</sup>	3.74,	1.61 <sup>b</sup>	3.91,	1.41 <sup>b</sup>
H <sub>2</sub> Na <sup>+</sup>	3.89,	1.67 <sup>b</sup>	4.71,	1.40 <sup>b</sup>
Li <sub>2</sub> Na <sup>+</sup>	5.86,	6.22 <sup>b</sup>	5.62,	5.73 <sup>b</sup>
Na <sub>2</sub> Li <sup>+</sup>	5.51,	6.89 <sup>b</sup>	5.24,	6.81 <sup>b</sup>
Li <sub>3</sub> <sup>+</sup>		6.35 <sup>c</sup>		5.75 <sup>c</sup>
Na <sub>3</sub> <sup>+</sup>		6.77 <sup>c</sup>		6.72 <sup>c</sup>
Li <sub>2</sub> H <sup>+</sup>		3.85 <sup>d</sup>		3.16 <sup>d</sup>
Na <sub>2</sub> H <sup>+</sup>		4.04 <sup>d</sup>		3.78 <sup>d</sup>

a. Results of *ab initio* SCF calculations using essentially "double-zeta" gaussian basis set (Raffetti and Rudenberg 1973).

b. Isosceles triangle; first number is height and second is base.

c. Length of side of an equilateral triangle.

d. Linear, symmetric; distance is metal-H distance.

Table 4. Electron populations of  $X-Y$  diatomics

System $X-Y$	Model potential		Standard FSGO <sup>a</sup>	
	$N(X)$	$N(Y)$	$N(X)$	$N(Y)$
LiH	2.26	1.74	2.21	1.79
NaH	10.23	1.77	10.16	1.84
KH	18.15	1.85	18.10	1.90
RbH	36.13	1.87	—	—
CsH	54.11	1.89	—	—
MgH <sup>+</sup>	10.59	1.41	10.52	1.48
CaH <sup>+</sup>	18.33	1.67	—	—
NaLi	10.95	3.05	10.94	3.06
KLi	18.73	3.27	—	—
RbLi	36.69	3.31	—	—
CsLi	54.60	3.40	—	—
KNa	18.79	11.21	—	—
RbNa	36.74	11.26	—	—
CsNa	54.65	11.35	—	—

<sup>a</sup>. FSGO wavefunctions (Frost 1967, Chu and Frost 1971 and Talaty *et al* 1976) were used.

constants ( $k$ ) have been calculated for all the diatomic systems studied here and they are also in good agreement with experimental data.

Table 3 summarizes the calculated equilibrium geometries for various triatomic ions composed of Li, Na and H. For comparison we have also included in table 3 the *ab initio* SCF results of Raffinetti and Rudenberg (1973). The overall agreement of our calculated geometries with the other calculations is fairly satisfactory. It is encouraging to note that the accuracy of our calculations improves in systems containing heavier atoms (e.g. Na<sub>3</sub><sup>+</sup>, Na<sub>2</sub>Li<sup>+</sup>) where our simple method would be most useful.

A procedure for analysing charge distributions by the use of FSGO wave functions has been described earlier by Simons and Talaty (1976). These authors have shown that electron populations obtained from FSGO wavefunctions are in excellent agreement with those obtained from virial partitioning (see Bader *et al* 1971) of Hartree-Fock wavefunctions. In view of this fact, it was considered desirable to compare the charge distributions obtained from the present model potential studies with those obtained from normal FSGO results. Excellent agreement between the two can be seen (table 4). Furthermore, it is quite gratifying to see that the predicted trend in electron distributions is consistent with the classical concept of ionic character and electronegativity difference between the two atoms of the diatom  $X-Y$ .

#### 4. Conclusion

This work shows that the generalized atomic Fues potential (AFP) can be used quite successfully in the framework of the FSGO method to study a number of two valence electron systems containing Li, Na, K, Rb, Cs, Mg, Ca and H. What is more important, the use of spherical gaussian function allows for a simple extension of the

present approach to large molecular systems since the various integrals encountered can be easily and rapidly evaluated. The FSGO model itself is attractive since the basis functions are deployed intuitively according to the valence concepts of Lewis (1916) and Langmuir (1919) and the use of AFP in FSGO further simplifies the model to study larger polyatomic molecules containing heavier atoms. We are extending the method for the study of larger polyatomic molecules and the initial results obtained for first- and second-row hydrides appear quite promising. These results will be reported elsewhere.

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