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Floating Spherical Gaussian Orbital (FSGO) Studies with a Model Potential: Application to Two-Valence-Electron Systems*

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A Gaussian based model potential is used within FSGO formalism to study a series of two-valence-electron diatomics (Li_2, Na_2, K_2, LiH, NaH, KH, MgH^+, CaH^+, LiNa, LiK and NaK) and triatomic ions (H_2Li^+, H_2Na^+, Li_2Na^+, Na_2Li^+, Li_3^+, Na_3^+, Li_2H^+ and Na_2H^+). Results for calculated equilibrium geometries, force constants, and energy changes for certain chemical reactions are compared to the corresponding quantities from available all-electron *ab initio* studies and experimental results. The predicted results are generally satisfactory.

Key words: Model potential – FSGO – Two-valence-electron systems

Valence electron studies with model potentials have drawn considerable attention in recent years [1–16]. Most of these calculations have been performed within the classical LCAO-SCF-MO formalism and only a few have been carried out in the framework of floating orbital basis [4, 5, 10, 16]. Barthelat and Durand [4, 5] and Semkow *et al.* [16] have used the model potential suggested by Simons [3] in their work to study some systems.

In the present paper we use the model potential suggested by Schwartz and Switalski [17] within FSGO formalism [18] to make a systematic study of a series of two-valence-electron diatomics and triatomic ions. For the present study we only use an s-type potential of the form:

$$V_m = -Z_c/r + A_s \exp[-\gamma r^2]/r, \tag{1}$$

where Z_c is the nuclear charge minus the number of core electrons and A_s and γ are model potential parameters. A_s and γ are obtained by doing a model potential calculation, with a completely uncontracted GTO basis set [19–21], on the one-valence-electron ion of the atom of interest A_s and γ are adjusted until the energy is exactly the experimental ionization energy for the s state with the additional constraint that the Gaussian exponential part ($\exp(-\gamma r^2)$) of V_m is 10% of $1/r$ at a

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distance equal to the covalent radius [22] of the atom under consideration. The model potential parameters thus obtained are listed in Table 1.

Table 1. Model potential parameters[a]

Atom	A_s	γ
Li	1.1113	0.361
Na	0.9915	0.272
K	0.9985	0.168
Mg	1.8104	0.393
Ca	2.8135	0.348

[a] Atomic wavefunctions from Refs. [19] (for Li), [20] (for Na and Mg) and [21] (for K and Ca).

The use of only an s-type potential for these systems is not strictly justified and for some systems, such as the lithium hydrides, it may be a poor approximation. The proper thing to do, of course, would be to decompose the valence orbital into its various angular components and construct an effective model potential. Such a procedure would be costly computationally and would destroy the most important feature of a FSGO model potential method, that is, the simplicity and ease with which calculations can be performed. The approximation is most severe for the small atoms but becomes less important as we go to larger systems where a model potential method would be most useful.

The FSGO method [18] is used for the molecular calculations. The cores are simulated by the model potentials described above and *only* valence electrons are considered in the FSGO calculations. Since the species studies are all two-valence-electron systems, only one floating spherical Gaussian orbital

$$\phi=(2/\pi\rho^2)^{3/4}\exp[-(\vec{r}-\vec{R})^2/\rho^2] \tag{2}$$

is used for each system. The valence electron energy (E_{val}) can be expressed as a function of ρ, $\vec{R}$ and the nuclear co-ordinates. The best values for these variable parameters are obtained by minimizing the valence energy. The optimization is done by the subroutine STEPIT [23].

Table 2 summarizes the calculated energies and equilibrium geometries for all the two-valence-electron diatomics which we have considered. Also shown in Table 2 for comparison are *ab initio* FSGO results, some model potential results using the same form of the model potential but a more extensive valence basis set and the experimental geometries. With the exception of LiH the model potential FSGO geometries are remarkably close to the *ab initio* FSGO results. The failure of LiH is no doubt due to the neglect of the p protein of the model potential. Our results also compare favorably with the experimental geometries, with the exception of LiH.

Table 3 summarizes the calculated valence energies and equilibrium geometries for various triatomic ions composed of Li, Na, and H. For comparison we have included in Table 3, where available, *ab initio* FSGO geometries, model potential

Table 2. Valence energies, equilibrium geometries and force constants (k) from model potential calculations on diatomics

Molecule	$-E_{\mathrm{val}}$ (a.u.)	*Re* (a.u.) FSGO Model Potential	FSGO	Model Potential[e]	Experimental[a]	Force Constant (k) This work (millidynes/Å)	Exptl.[a]
LiH	0.5906	3.63	3.22[b]	3.20	3.06	0.82	1.03
NaH	0.5755	3.81	3.76[c]	3.70	3.57	0.69	0.79
KH	0.5380	4.59	–	–	4.24	0.42	0.56
MgH^+	0.9219	3.32	3.18[c]	–	3.12	1.90	1.64
CaH^+	0.8127	4.03	–	–	–	1.50	–
LiNa	0.3717	5.49	5.51[d]	5.60	–	0.21	–
LiK	0.3409	6.18	–	–	6.22	0.15	0.15
NaK	0.3314	6.33	–	–	6.56	0.13	0.13
Li_2	0.3816	5.34	5.30[d]	5.35	5.05	0.23	0.26
Na_2	0.3619	5.65	5.68[d]	5.80	5.82	0.20	0.17
K_2	0.3020	6.98	–	–	7.41	0.11	0.11

[a] Experimental results from Ref. [24]. Potential energy curves were fit by fifth order polynomials in (*R*–*Re*), where *Re* is the equilibrium distance and the values of the $(R\text{–}Re)^2$ coefficients were used to determine the force constants (k).

[b] Ref. [18].

[c] Chu,S.Y., Frost,A.A.: J. Chem. Phys. **54**, 760 (1971).

[d] Chu,S.Y., Frost,A.A.: J. Chem. Phys. **54**, 764 (1971).

[e] Ref. [11].

Table 3. Valence energies and equilibrium geometries from model potential calculations on some triatomic molecular ions

Molecule	$-E_{\mathrm{val}}$ (a.u.)	Geometry FSGO Model Potential	FSGO[a]	Model Potential	*ab initio*[c]
H_2Li^+	0.9618	4.75, 1.49[d]	3.35, 1.57	4.25, 1.40[d]	3.91, 1.41[d]
H_2Na^+	0.9600	5.33, 1.49[d]	–	5.20, 1.40[d]	4.71, 1.40[d]
Li_2Na^+	0.4281	5.68, 6.12[d]	–	5.56, 5.80[d]	5.62, 5.73[d]
$NaLi^+$	0.4202	5.40, 6.72[d]	–	5.27, 6.66[d]	5.24, 6.81[d]
Li_3^+	0.4359	6.22[e]	5.89[e]	5.85[e]	5.75[e]
Na_3^+	0.4122	6.60[e]	–	6.60[e]	6.72[e]
Li_2H^+	0.6709	3.82[f]	3.08[f]	3.35[f]	3.16[f]
Na_2H^+	0.6512	4.09[f]	–	3.89[f]	3.78[f]

[a] Ray,N.K.: J. Chem. Phys. **52**, 463 (1970).

[b] Ref. [11].

[c] Ref. [25]. Basis set employed was essentially "double-zeta" Gaussian.

[d] Isosceles triangle, first number is height and second is base.

[e] Length of side of an equilateral triangle.

[f] Linear, symmetric; distance is metal–H distance.

geometries using the same form of the model potential and the *ab initio* SCF results of Raffenetti [25], who used a moderately flexible Gaussian basis set. The overall agreement of our calculated geometries with the other calculations is less satisfactory than for the diatomics, particularly for LiH_2^+, NaH_2^+ and Li_2H^+. The error is partially due to the neglect of the p portion of the model potential. Further difficulty in the metal-H_2^+ complexes is found because the metal is so weakly

Table 4. Some calculated reaction energies[a]

Reaction	ΔE (kcal/mole) Model potential	*ab initio*[b]
$LiH_2^+ \rightarrow Li^+ + H_2$	3.7 (3.8)	5.2
$Li_2H^+ \rightarrow Li^+ + LiH$	50.4 (53.7)	57.2
$Li_3^+ \rightarrow Li^+ + Li_2$	34.1 (41.9)	41.8
$NaH_2^+ \rightarrow Na^+ + H_2$	2.6 (1.8)	2.9
$Na_2H^+ \rightarrow Na^+ + NaH$	47.5 (48.1)	51.4
$Na_3^+ \rightarrow Na^+ + Na_2$	31.6 (33.7)	37.8
$NaLi_2^+ \rightarrow Na^+ + Li_2$	29.2 (33.1)	31.2
$\rightarrow Li^+ + NaLi$	35.4 (41.6)	44.0
$LiNa_2^+ \rightarrow Li^+ + Na_2$	36.6 (41.2)	48.3
$\rightarrow Na^+ + NaLi$	30.4 (33.4)	33.6

[a] Obtained using E_{val} values given in Table 2. E_{val} for H_2 is -0.9559 a.u. Numbers in parentheses are from Ref. [11].

[b] Obtained from Ref. [25].

bound it may not be possible to obtain an accurate potential energy surface with a single floating Gaussian orbital. This results in long metal–H distances, however the H–H distances are in good agreement with the other calculations. It is encouraging to note that the accuracy of our calculations improves in systems containing heavier atoms where our simple method would be most useful.

Stretching force constants (k) have been calculated for all the diatomic systems studied here and they are in good agreement with available experimental results (see Table 2).

We have computed the reaction energies of a number of simple reactions involving the triatomic ions studied. The calculated reaction energies are listed in Table 4 along with those obtained from standard all electron SCF MO studies [25] and other model potential results [11]. The agreement is quite satisfactory.

This work shows that the Gaussian-based model potential can be used quite successfully in the framework of the FSGO method to study a number of two-valence-electron systems containing Li, Na, H or their unipositive ions. Most importantly, the use of a 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. We are extending the method for the study of larger polyatomic molecules and the initial results obtained for first row hydrides appear quite promising. These results will be reported elsewhere [26].

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