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SCF Calculations for H_2^+, Li_2^+ and LiH^+ with Atomic Basis Sets Enlarged by Bond Functions*

San Y. Chu

Department of Chemistry, Rice University, Houston, Texas 77001, USA

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To simulate the charge distortion in the formation of a molecule from the separated atoms, a set of concentric *s*-type Gaussian functions is placed on the internuclear axis in addition to the *s*-type atomic basis functions to construct the molecular orbital for the one valence-electron systems H_2^+, Li_2^+ and LiH^+. This simple model gives 90.1%, 75.2% and 61.7%, respectively, of the improvement over minimal basis relative to Hartree-Fock energies.

1. Introduction

Based on the simple LCAO-MO approximation, the one-electron wavefunction for a diatomic molecule can be written as

$$\psi = N(\phi_a + \lambda\phi_b),$$

where ϕ_a and ϕ_b are the atomic basis functions. The charge density will have three contributions: two atomic contributions, ϕ_a^2 and $\lambda^2\phi_b^2$, and the interatomic interference term $2\lambda\phi_a\phi_b$. This interference term is often called the overlap charge [1]. For H_2^+, it has the spheroidal form $e^{-2(\gamma_a+\gamma_b)}$, with a maximum along the line joining the two nuclei, falling off as one goes away from the line. Since the total charge density is conserved, a buildup of the overlap charge in the bonding region implies a corresponding deletion of the atomic charges. In other words, the total charge has been distorted from the atomic region to the internuclear region. This charge distortion is an essential feature of the chemical bonding which can be shown even by a wavefunction approximated with the minimum basis functions. A calculation with a more extensive basis function set is better able to describe the charge distortion. For example, in the H_2^+ calculation [2], an *s* orbital and *p* orbital can mix to give direct atomic charge distortion in addition to the overlap charge. The purpose of the present study is to test a more economical way to represent the charge distortion. Instead of mixing the *s* atomic orbital with atomic orbitals of higher quantum number, the *p*, *d* and *f* orbitals, we adopt a set of concentric Gaussian *s*-type functions centered along the bond axis to simulate the charge distortion. In view of the reasonable validity of the united atom model [3], we expect the present "one-center" *s*-type orbitals to be effective basis functions complementary to the minimum atomic basis functions for the molecular wavefunction, especially those for the valence-electron part. In the present study, this model has been tested on systems containing one valence-electron, such as H_2^+, Li_2^+ and LiH^+, where there is a strong atomic charge distortion due to charge-

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induced dipole. However, this model can easily be generalized to include the electron-pair bond and polyatomic molecule. For these, a similar model has been proposed recently by Rothenberg and Schaefer [4]. A calculation on the closed shell system CH_4 was first performed using a small basis set containing only s, p orbitals on carbon and s orbital on hydrogen atoms. Then, by placing two s-type Gaussian functions with identical exponents along each C–H bond axis, they obtained about 60% of the energy improvement that was obtained by extending the basis set to include d orbitals on the carbon atom and p orbitals on the hydrogen atoms.

2. Calculation

The results reported in this paper were obtained using the MOLE Quantum Chemistry System [5]. This is a general purpose program for quantum-mechanical calculation of the electronic structure and electronic energy of molecules. The atomic basis sets used in this work are the grouped Gaussian orbitals suggested by Whitten [6]. For hydrogen the basis orbital is the five term $1s$. For lithium the s-type basis orbitals are the four term $1s$, three term $2s$, and three term $3s$ grouped orbitals. A set of three rather diffuse concentric s-type Gaussian functions are used as the bond functions. Thus, the molecular orbital is a linear combination of the atomic basis functions and the bond functions.

$$\psi_j = \sum_i C_{ai}\phi_{ai} + \sum_i C_{bi}\phi_{bi} + \sum_i C_i \exp(-\alpha_i(r-R)^2)\,. \tag{1}$$

The first two terms are summed over atomic functions and the third term is summed over the bond functions. The Roothaan's restricted open shell SCF method [7] is used. For convenience in choosing the value of the orbital exponent α_i, it is helpful to replace the orbital exponent α_i in Eq. (1) by

$$\alpha_i = 1/p_i^2\,.$$

The parameter p_i has dimension of length and may be called an "orbital radius" [8]. It has the simple interpretation that the sphere of this radium contains about 74% of the orbital electron density. Thus, a reasonable way to choose a set of bond functions is to select values of p_i such that they are of the same order of magnitude as the size of the molecule.

At the beginning, several trial sets of bond functions were combined with atomic basis sets for the calculation. Each set of bond functions consists of five concentric bond functions with smoothly increasing exponents. From these we choose a set such that the magnitudes of the SCF coefficients show a rough Gaussian distribution. For example, the set chosen for H_2^+ has exponents 2.0, 1.0, 0.5, 0.1 and 0.05. Their magnitudes of coefficients from SCF results are 0.014, 0.084, 0.099, 0.325 and 0.030, respectively. This procedure reduces the possibility that we may miss important basis functions in the function selection, since basis functions whose exponents lie outside the prescribed range will have negligible SCF coefficients following the Gaussian distribution, while basis functions whose exponents lie inside the prescribed range are redundant functions, i.e. they have too big an overlap with the chosen functions. Subsequently, these five functions

Table 1. Results of total energy and valence orbital for H_2^+, Li_2^+ and LiH^+. (Calculation (*A*) uses five bond functions, (*B*) uses three bond functions, and *R* is the bond function to proton distance. For H_2^+ and Li_2^+, bond functions are at middle of the two nuclei)

	H_2^+ ($R_e = 2.0$ a. u.)		Li_2^+ ($R_e = 5.051$)		LiH^+ ($R_e = 3.014$)		
	(*A*)	(*B*)	(*A*)	(*B*)	$R = 0.9$	$R = 1.1$	$R = 1.3$
$1s_H$	0.648	0.650			0.911	0.940	0.965
$1s_{Li}$			−0.198	−0.199	−0.114	−0.118	−0.121
$2s_{Li}$			0.157	0.150	0.066	0.081	0.102
$s(\alpha = 2.00)$	−0.014	–					
$s(\alpha = 1.00)$	0.084	0.051	−0.031	–			
$s(\alpha = 0.50)$	0.099	0.127	0.093	0.046	0.134	0.125	0.166
$s(\alpha = 0.10)$	−0.325	−0.362	0.591	0.635	0.060	0.048	0.040
$s(\alpha = 0.05)$	−0.030	–	0.178	0.151	−0.149	−0.166	−0.189
$s(\alpha = 0.01)$			−0.019	–			
$-E$	0.59792	0.59778	14.70006	14.69976	7.72408	7.72427	7.72414
$-E_{HF}$	0.60262[a]		14.70971[b]		7.72943[c]		

[a] See Ref. [9]. [b] See Ref. [10]. [c] See Ref. [11].

are truncated to three functions by deleting the two functions with smallest and largest exponents. The loss in energy that results from this procedure is essentially negligible, 0.14×10^{-3} a.u. for H_2^+ and 0.30×10^{-3} a.u. for Li_2^+. The remaining three functions have orbital radii comparable in size to the internuclear distance. For example, three functions for H_2^+ with exponents 1.0, 0.5 and 0.1 have corresponding values of orbital radii 1.0, 1.4 and 3.1 comparable with the internuclear distance 2.0 a.u. By the same procedure, a set of functions with more diffused exponents 0.5, 0.1 and 0.05 are obtained for the Li_2^+. Their orbital radii 1.4, 3.1 and 4.5 are to be compared with the internuclear distance 5 a.u. for Li_2^+. The same set of functions has been used for the LiH^+ system with three different positions along the H-Li axis: 0.9, 1.1 and 1.3 a.u. from the proton. The difference in their energies is less than 0.2×10^{-3} a.u.

3. Discussion

The final results are shown in Table 1 and 2. From the reported data and several other numerical experiments, the conclusions we shall draw are:

(1) The energy improvement is insensitive to the choice of the set of bond function exponents as long as the whole set of orbital radii are complete enough to be able to cover the molecule. For the heternuclear diatomic molecule LiH^+, the choice of the center for the bond function is not critical. The change in energies is less than 0.2×10^{-3} a.u. for the three values of bond function – proton distance: 0.9, 1.1 and 1.3 a.u. This is probably due to the fact that the variation of each linear coefficient of the bond functions can compensate for the improper choice of the function center to a large extent.

(2) As shown in Table 2, the improvement in the energy resulting from this type of bond function is more important than the splitting of the atomic grouped Gaussian function which provides the additional flexibility. Splitting the single

Table 2. Comparison of the calculation with Gaussian basis and slater basis for H_2^+ ($R_e = 2.0$ a.u.)

Gaussian basis	$-E$	Slater basis[a]	$-E$
1*s* (5)	0.55373	$s(\alpha = 1.0)$	0.55377[b]
1*s*(4,1)	0.59047	s	0.58651[c]
1*s* (3.1.1)	0.59049	$s+p$	0.59980[c]
1*s* (5) + bond function	0.59778	$s+p+d$	0.60183[c]

[a] See Ref. [2].
[b] Slater exponent is frozen at unity.
[c] Slater exponents are scaled to minimize the energies.

Table 3. Comparison of various types of bond function for H_2^+ and Li_2^+. (Cases *a*, *b* and *c* use a set of concentric bond function; cases *d*, *e* and *f* use two sets of bond functions placed at 1/3 and 2/3 along bond distance)

Case	Number of bond function[a]	% of the energy improvement over minimum basis relative to Hartree-Fock H_2^+	Li_2^+
a	3	90.1	75.2
b	2	88.5	73.1
c	1	69.3	73.1
d	(3,3)	90.6	70.0
e	(2,2)	87.8	67.8
f	(1,1)	70.2	67.7

[a] The set of bond functions used here are those in Table 1 with leading magnitudes of linear coefficients. The coefficients of bond functions are subjected to variation for each case here.

group of 1*s* orbitals with five Gaussian functions (denoted as 1*s* (5)) into two groups or three groups (denoted as 1*s* (4,1) or 1*s* (3,1,1)), gives an energy improvement of about 0.037 a.u. as compared with the value 0.044 a.u. by the present bond function method. The latter obtains 92% of the 0.048 a.u. improvement made by a rather accurate calculation with distorted atomic orbitals [2] where the *s* orbital is mixed with *p* and *d* orbitals with scaled Slater exponents. For the systems Li_2^+ and LiH^+, the present energies can reach 99.93% of the values calculated with extensive Slater-type atomic basis sets by Cade and Huo.

(3) For H_2^+, the number of bond-functions reduces from three to two, the energies improvement drops slightly, from 90.1–88.5% as shown in Table 3. However, one bond-function gives only 69.3% improvement. For Li_2^+, the energy improvement is rather insensitive to the number of bond functions. Furthermore, the concentric type of bond functions are compared with the new model where two sets of bond functions placed 1/3 and 2/3 along the internuclear distance. This model gives practically no improvement over former as shown in Table 3, case *d*, *e* and *f*. We shall conclude that the set of three concentric bond functions may be the optimal choice on account of the balance between effectiveness and economy.

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Dr. San Y. Chu
Chemistry Department
Rice University
Houston, Texas 77001, USA