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

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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 $\phi_a$ and $\phi_b$ are the atomic basis functions. The charge density will have three contributions: two atomic contributions, $\phi_a^2$ 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 $e^{-2(\sqrt{\alpha} + \sqrt{\beta})}$, 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 CH₄ 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.

\[ \psi_j = \sum_i C_{ai} \phi_{ai} + \sum_i C_{bi} \phi_{bi} + \sum_i C_i \exp\left(-\alpha_i(r - R)^2\right). \]  

(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 \( \alpha_i \), it is helpful to replace the orbital exponent \( \alpha_i \) 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 radius 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 H₂⁺ 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...