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Split Orbitals for the LiH Molecule*

PETER LINDNER

Quantum Chemistry Group, Uppsala University, Uppsala, Sweden

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The four-electron problem in LiH has been treated by use of Slater type orbitals for the 1*s* electrons on the Li atom and split molecular orbitals for the two valence electrons. Some properties of the two dimensional spin space present in the case of four different space-functions are discussed. Total electronic energies and electric dipole moments have been calculated.

LiH wird mit Slaterfunktionen für die 1*s*-Elektronen von Li und SMO's für die beiden Valenzelektronen behandelt. Einige Eigenschaften des zweidimensionalen Spinraums werden diskutiert. Elektronenenergien und Dipolmomente werden berechnet.

Nous avons traité le problème à quatre électrons de LiH en utilisant des orbitales de Slater pour les électrons 1*s* de Li et des orbitales moléculaires distinctes pour les deux électrons de valence. Certaines propriétés de l'espace de spin à 2 dimensions existant dans le cas de quatre fonctions d'espace différentes sont discutées. On a calculé les énergies électroniques totales et les moments dipolaires.

I. Introduction

The conventional Hartree-Fock method for treating molecular systems gives rise to an error in the calculated total energy [7]. This error, usually called correlation energy, is of the same order of magnitude as the binding energy in diatomic molecules [2]. It is thus of essential importance to improve this method. One kind of improvement is to remove the restriction of doubly occupied orbitals which is characteristic to the conventional approach. In order to retain the right spin-symmetry of the total wavefunction a spin-projection has to be performed after this splitting of the space orbitals. This extension of the original scheme is of importance mainly when the number of basis functions is small and a fairly limited configuration interaction treatment is made.

In the present work [5] four different orbitals for the electrons in the LiH molecule are used. The two dimensional spinspace in this case has been investigated to get the spin-eigenfunction corresponding to the lowest total energy. Further the polarization of the outer electron on the lithium atom has been investigated.

II. Details of the Calculations

1. Theoretical background

Splitting of the doubly filled orbitals in the conventional Hartree-Fock method gives rise to a spin problem, because the corresponding Slater determinant is no

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longer an eigenfunction of the spinoperator S^2. A proper spineigenfunction can be obtained by use of a spinprojection operator [6, 7].

The ground state of the LiH molecule is known to be a singlet state [3]. For this molecule we get two linearly independent projected Slater determinants if the four basic space orbitals all are different [6]. The spin-eigenfunction $(\alpha_1 \beta_2 - \beta_1 \alpha_2)(\alpha_3 \beta_4 - \beta_3 \alpha_4)$ used in the valence-bond method, is then a linear combination of these two spinprojected functions. We expect this valence-bond function to be rather near that function in the spin space which gives the lowest total energy, because a linear combination of the two basic spinfunctions adds the terms $\alpha_1 \alpha_2 \beta_3 \beta_4$ and $\beta_1 \beta_2 \alpha_3 \alpha_4$ to a total wavefunction of valence-bond type. These terms correspond to spin α or β for both $1s$ electrons on Li, and spin β or α for the two valence electrons. Such terms have a high energy and thus give a small contribution to the total wavefunction [5].

2. *Wavefunctions used*

The basic orbitals used are:

$$\begin{aligned} a &= (1s')_{\mathrm{Li}} = N_{1s'}\ e^{-3.3\,r} \\ b &= (1s'')_{\mathrm{Li}} = N_{1s''}\ e^{-2.065\,r} \\ c' &= (2s)_{\mathrm{Li}} = N_{2s}\ r\, e^{-0.65\,r} \\ c'' &= (2p\sigma)_{\mathrm{Li}} = N_{2p\sigma}\ r\cos\theta\, e^{-0.65\,r} \\ d &= (1s)_{\mathrm{H}} = N_{1s_{\mathrm{H}}}\, e^{-r} \end{aligned} \tag{1}$$

where the N_μ's are normalization constants. These orbitalfunctions were used by Robinson et al. in an earlier calculation on LiH [10]. They are fairly close to the optimum orbitals of the same form [4, 11].

The split molecular orbitals used for the two valence electrons are:

$$\begin{aligned} \varphi_1 &= \frac{1}{\sqrt{1+\lambda^2}}(c' + \lambda\, c'') + k_1 \cdot d \\ \varphi_2 &= k_2 \frac{1}{\sqrt{1+\lambda^2}}(c' + \lambda\, c'') + d \end{aligned} \tag{2}$$

where λ is a parameter governing the polarization of the $2s$-orbital and k_1 and k_2 are splitting parameters. These parameters are varied to give the energy minimum.

This type of split molecular orbitals are of the same type as used by McWeeny, Ohno and Tsuchida on H_2O and NH_3 [8, 12], and similar to the ones used by Coulson and Fischer on H_2 [1].

III. Results

The total electronic energy and the electric dipole moment were calculated at the fixed internuclear distance 3.015 a.u. (1.5954 Å) [3]. The results are given in Tab. 1—5.

The function Ψ_{MO} is constructed from orbitals a, b and φ_1, φ_1 for the core- and valence-electrons respectively. Ψ_{SMO} denotes the function built up from orbitals a, b, φ_1, and φ_2.

Table 1. *Total energies (E in* a.u.*) and dipole moment (μ in* Debye*) for Ψ_{MO} and Ψ_{SMO}* (SMO = split molecular orbital)

		$\lambda = 0$	λ_{min}	$\lambda = 1$
Ψ_{MO}	E	−7.971	−7.991	−7.989
	μ	−4.98	−6.45	−6.67
Ψ_{SMO}	E	−7.990	−8.006	−8.002
	μ	−3.62	−6.04	−6.48

Experimental values: $E = -8.0704$ a.u. [9]; $\mu = -5.882$ Debye [14].

Table 2. *Minimum parameter values for Ψ_{MO} and Ψ_{SMO}*

		$\lambda = 0$	λ_{min}[b]	$\lambda = 1$
Ψ_{SMO}	k_1	0.40	0.28	0.30
	k_2	0	0	0
Ψ_{MO}	k[a]	2.15	1.75	1.80

[a] $k = k_1 = 1/k_2$.
[b] $\lambda_{min} = 0.60$ for Ψ_{SMO}; $\lambda_{min} = 0.70$ for Ψ_{MO}.

The two linearly independent spineigenfunctions which we choose to span the two-dimensional spinspace are

$$\Theta_1 = \mathcal{O} \det \begin{Vmatrix} \alpha & \beta & \alpha & \beta \\ a & b & \varphi_1 & \varphi_2 \end{Vmatrix}$$
$$\Theta_2 = \mathcal{O} \det \begin{Vmatrix} \alpha & \beta & \beta & \alpha \\ a & b & \varphi_1 & \varphi_2 \end{Vmatrix} \tag{3}$$

where $\mathcal{O}$ is the spinprojection operator which annihilates all symmetry components except the singlet one. It was found that these two functions have their energy minimum for $k_1 = 1/k_2$ i.e. for the MO-case ($\varphi_1 \equiv \varphi_2$). For $\varphi_1 \equiv \varphi_2$ there is only a one-dimensional spinspace with $\Theta_1 \equiv \Theta_2 \equiv \Psi_{MO}$ (except for a constant factor).

In order to determine the spineigenfunction (Θ_{best}) which gives the lowest energy in the two dimensional space we use a wavefunction constructed from orbitals a, b, $(c' + \lambda c'')$ and d. The ordinary valence-bond function is:

$$\Psi_{VB} = \mathcal{A}_{op} \{a_1 b_2 (c' + \lambda c'')_3 d_4\} (\alpha_1 \beta_2 - \beta_1 \alpha_2) (\alpha_3 \beta_4 - \beta_3 \alpha_4) \tag{4}$$

where $\mathcal{A}_{op}$ is the antisymmetrization operator. The two basic spineigenfunctions Θ_1' and Θ_2' are as in Eq. (3) with $\varphi_1 = (c' + \lambda c'')$ and $\varphi_2 = d$.

Table 3. *Total energies for Ψ_{VB}, Θ_1', Θ_2' and Θ_{best}*

	$\lambda = 0$	λ_{min}	$\lambda = 1$
Ψ_{VB}	−7.969	−7.995	−7.992
Θ_1'	−7.894	−7.955	−7.954
Θ_2'	−7.895	−7.957	−7.956
Θ_{best} $= (c_1 \Theta_1' + c_2' \Theta_2')$	−7.969	−7.996	−7.992

Table 4. $\lambda_{\min}$-*values for* Ψ_{VB}, Θ_1', Θ_2' *and* Θ_{best}

	Ψ_{VB}	Θ_1'	Θ_2'	Θ_{best}
$\lambda_{\min}$	0.63	0.83	0.82	0.60

Table 5
Dipole moments for Ψ_{VB}, Θ_1' *and* Θ_2' (in Debye)

	$\lambda = 0$	$\lambda_{\min}$	$\lambda = 1$
Ψ_{VB}	−0.88	−5.49	−5.97
Θ_1'	−0.86	−5.86	−5.97
Θ_2'	−0.83	−5.84	−5.95

IV. Discussion

The improvement in the total energy when splitting the 1*s*-shell on Li in the way done by ROBINSON and others [*4, 10, 11*] is about 0.026 a.u. The further lowering of the energy by use of split molecular orbitals amounts to 0.015 a.u. This result is consistent with the work by MCWEENY and others [*12, 8*]. They however, get non-zero values for both k_1 and k_2 in Eq. (2). This probably depends on the different effective electronegativity values for the atoms involved.

The best wavefunction we get, Ψ_{SMO} in Tab. 1, is almost exactly equal to the one used by ROBINSON et al. [*10*]. They, however, started from

$$\varphi_1 = c_1 (2s)_{Li} + c_2 (2p\sigma)_{Li} + c_3 (1s)_H \qquad (5)$$
$$\varphi_2 = (1s)_H .$$

We notice further that the $\lambda_{\min}$values changes with the type of spineigenfunction used. This is expected as the projection in Eq. (3) changes the charge distribution of the determinantal wavefunction in different ways depending on the spincombination used.

The strong dependence of the dipole moment on the polarization of the 2*s*-orbital on the Lithium atom is also expected for physical reasons.

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Dr. PETER LINDNER
Quantum Chemistry Group
Uppsala University
Uppsala/Schweden