

AN IMPROVED AMO FUNCTION FOR THE  $\text{Li}_2$  MOLECULE

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Following Rai and Calais (D. K. Rai, J. L. Calais, *J. Chem. Phys.*, **47**, 906 (1967)) a  $2p_\sigma$  orbital was added in basis for calculation of energy of  $\text{Li}_2$  molecule in AMO method. With a trial function for  $2p_\sigma$  orbital energies were calculated for a specific internuclear distance ( $R = 6.0$ ) and compared. It is found that modification in energy is not much.

*1. Introduction*

The Lithium molecule has been subject of extensive research concerning its wave function, ground state energy and other properties. Generally such studies are carried out within the Hartree-Fock approximation. However, there have been several attempts to improve over the traditional Hartree-Fock method [1] to [5], especially by the AMO (Alternant Molecular Orbital) method proposed by Löwdin in 1954 [6].

The AMO method is a technique to calculate part of the correlation energy in systems which are too large for calculations by the method of superposition of configurations. It has indeed been successfully exploited by (see for survey [7]) Rai and Calais [8] to calculate energies of  $\text{Li}_2$  molecule and their results are very encouraging, although they have used a simple basis consisting of  $1s$ ,  $2s$  orbitals. In the present paper it is intended to extend the work of Rai and Calais to include contributions of higher orbitals.

*2. Energy expression*

Rai and Calais have worked out the energy expressions of  $\text{Li}_2$  molecule for projected and unprojected cases in the AMO method. They have treated  $\text{Li}_2$  as a six electron problem assuming that four electrons are lying in a closed shell  $1\sigma_g^2 1\sigma_u^2$  while the two valence electrons are represented by two AMOs (following the first of the three methods of constructing AMO for a diatomic molecule like  $\text{H}_2$  [9]).

The energy expressions of Rai and Calais have been extended in this paper to include the contribution of a  $2p_\sigma$  orbital utilizing a hybridization parameter  $Q$ . Then energy ex-

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pressions (projected and unprojected) become a function of  $Q$  and  $\lambda$  (correlation parameter). The projected energy takes the following form:

$$E_{\text{proj}} = E_1 + \frac{1}{2} (1 + \lambda^2)^{-1} [(1 + \lambda)^2 E_g(Q) + (1 - \lambda)^2 E_u(Q) - (1 - \lambda^2) E_{gu}(Q)], \quad (1)$$

$$E_1 = E_c + \frac{g}{R}, \quad (2)$$

where  $E_c$  is the same as in [8].

$$\begin{aligned} E_g(Q) = 2 \int h(1) \varrho_{g,Q}(1, 1) dv_1 + \int \frac{1}{r_{12}} [2 \varrho_c(1, 1) \varrho_{g,Q}(2, 2) + \\ + 2 \varrho_{g,Q}(1, 1) \varrho_c(2, 2) + \varrho_{g,Q}(1, 1) \varrho_{g,Q}(2, 2) - \\ - \varrho_c(1, 2) \varrho_{g,Q}(2, 1) - \varrho_{g,Q}(1, 2) \varrho_c(2, 1)] dv_1 dv_2, \end{aligned} \quad (3)$$

$E_u(Q)$  has the same expression as  $E_g(Q)$  with  $g$  replaced by  $u$ .

$$E_{gu}(Q) = \int \frac{1}{r_{12}} \varrho_{g,Q}(1, 2) \varrho_{u,Q}(1, 2) dv_1 dv_2, \quad (4)$$

where

$$\varrho_{x,Q} = \varrho_x^s + Q \cdot \varrho_x^{s,p} + Q^2 \varrho_x^p, \quad (5a)$$

$$\varrho_x^{s,p} = 2\sigma_x^s 2\sigma_x^p + 2\sigma_x^p 2\sigma_x^s, \quad (5b)$$

$$\varrho_x^y = 2\sigma_x^y 2\sigma_x^y, \quad (5c)$$

$$x = g, u; y = s, p.$$

It is clear from the above expressions that  $E_g(Q)$ ,  $E_u(Q)$  and  $E_{gu}(Q)$  for  $Q = 0$  reduce to  $E_g$ ,  $E_u$  and  $E_{gu}$  of reference [8]. This serves as a check for the present calculation. Similarly one can write down the energy expression for the unprojected case as a function of  $Q$  and  $\lambda$ .

### 3. Details of calculation

The calculation is a routine task, consisting in writing down the total Hamiltonian, basic functions, constructing the molecular orbitals, transforming the integrals and performing numerical computations. To save space we only point out the differences between [8] and our work. The first difference occurs in the basic function where we add a  $2p_\sigma$  orbital over the previous  $2s$  choice [8]

$$2p_\sigma = n_p \cdot z e^{-\alpha r} \quad (6)$$

with

$$\alpha = 1.00.$$

Let us now consider the construction of molecular orbitals. With the help of the above basic atomic orbitals, we form the following set of symmetry orbitals (M. OS):

$$\begin{aligned} 1\sigma_g &= N_1(1s_a + 1s_b), \\ 1\sigma_u &= N_2(1s_a - 1s_b), \\ 2\sigma'_g &= N_3[(2s_a + 2s_b) + Q(2p_{\sigma_a} + 2p_{\sigma_b})], \\ 2\sigma'_u &= N_4[(2s_a - 2s_b) + Q(2p_{\sigma_a} - 2p_{\sigma_b})]. \end{aligned} \quad (7)$$

However, the above set is unsuitable as  $2\sigma'_g$ ,  $2\sigma'_u$  are non-orthogonal to  $1\sigma_g$  and  $1\sigma_u$  respectively. Following Schmidt's procedure, the orthonormal orbitals are given by:

$$\begin{aligned} 2\sigma_g &= N_5[(2s_a + 2s_b) + Q(2p_{\sigma_a} + 2p_{\sigma_b}) + \mu(1s_a + 1s_b)], \\ 2\sigma_u &= N_6[(2s_a - 2s_b) + Q(2p_{\sigma_a} - 2p_{\sigma_b}) + \nu(1s_a - 1s_b)], \end{aligned} \quad (8)$$

where  $\mu$  and  $\nu$  are determined by  $(2\sigma_g, 1\sigma_g) = 0$ ,  $(2\sigma_u, 1\sigma_u) = 0$  respectively.

The next step is transforming M.O.S. to A.O.S. Let us assume,

$$\Psi = (1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u)$$

$$\Phi = (1s_a, 1s_b, 2s_a, 2s_b, 2p_{\sigma_a}, 2p_{\sigma_b})$$

Then  $T = \Phi^{-1}\Psi$  is the transformation matrix. With the help of these transformations, the energy expression can be written as:

$$E = \int \Psi^+ H \Psi d\tau = \int T^+ (\Phi^+ H \Phi) T d\tau. \quad (9)$$

Expression (9) is further simplified by letting  $H = H_1 + H_2$ , where  $H_1$  refers to one electron operator while  $H_2$  stands for the two electron operator. Further, the A.O. integrals (one and two centres) were calculated using the programme of Switendick and Corbató [11] for the above basic function. The results indicate that there are 39 non-vanishing one-electron integrals and 115 two-electron integrals respectively. These were arranged in matrices and a programme was elaborated to calculate  $E_{proj}$  and  $E_{unproj}$  which were expressed in terms

TABLE I

$Q$	$E_{MO}$	$E_{proj}$	$E_{unproj}$
0	-14.85892	-14.87700	-14.86792
0.05	-14.86179	-14.87796	-14.86864
0.1	-14.86287	-14.87825	-14.86883
0.15	-14.86312	-14.87888	-14.86844
0.2	-14.86254	-14.87688	-14.86789
0.25	-14.86118	-14.87525	-14.86579
0.3	-14.85907	-14.87303	-14.86392
0.35	-14.85624	-14.87026	-14.86138
0.4	-14.85274	-14.86698	-14.85841
0.45	-14.84862	-14.86324	-14.85506

TABLE II

Comparison of different energy calculations (atomic units)<sup>1</sup>.  $R$  — internuclear distance $R = 6.0$ 

Das and Wahl [12]			Rai and Calais [8]		
S.C.F.	O.D.C.	O.U.C.	H.F.	Proj.	Unproj.
-14.86865	-14.88104	-14.99367	-14.85961	14.87679	14.86772
Present work: $Q = 0$			-14.85982	14.87700	14.86792
			-14.86312	14.87888	14.86883
			( $Q = 0.15$ )	( $Q = 0.15$ )	( $Q = 0.1$ )

<sup>1</sup> When  $Q = 0$ : there is a slight difference between the energy values of [8] and those of the present calculation which should be identical. This difference is due to the refined mesh in the Switendick-Corbató programme [11] giving better values for two-electron integrals.

There are two misprints in [8], in table  $E_c$  and  $E_{gu}$  (pp909) should be replaced by  $E_1$  and  $2E_{gu}$ , respectively.

The transformation of M.Os to A.Os in [8], namely Eqs (24), (25) and (26), follows the Nesbet's method [10] while in the present case transformation is straightforward.

of matrix elements. For varying values of  $Q$  and  $R$  energies were minimized with respect to  $\lambda$  and  $E_{\min}$  were obtained. The values of  $E_{\min}$  are tabulated in Table I. A comparison of the present results with the values of other authors (for  $R = 6.0$ ) is made in Table II.

#### 4. Results and discussions

The aim of the present work consists in the modification of the energy values obtained by Rai and Calais by the inclusion of a higher orbital *i. e.*  $2p_\sigma$ . The numerical evaluation has resulted in an improvement of the energy value. It is interesting to observe that the hybridization parameter lies between 0.10 and 0.15. These conclusions have been drawn on a single set of energy values for  $R = 6.0$  and varying  $Q$  with a trial wavefunction. A more detailed calculation is required in this field using various sets of  $2p_\sigma$  orbitals with varying internuclear distance  $R$ .

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