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Natural Spin Orbital Analysis of Diatomic Molecular Wave Functions in Terms of Generalized Diatomic Orbitals

I. Outline of the Method. Results for the Ground State of H_2

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The method of linear combinations of generalized diatomic orbitals (LCGDO) is combined with the method of configuration interaction (CI). CI wave functions obtained in this way are finally submitted to a natural spin orbital analysis; the resulting natural spin orbitals are expansions in terms of generalized diatomic orbitals.

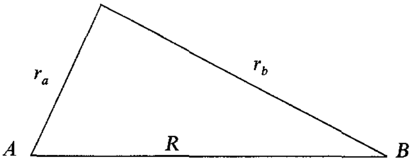
For the ground state of H_2, a one-determinantal-approach with a single completely optimized one-electron basis function nearly reproduces the Hartree-Fock-result. The two-determinantal approach with two optimized basis functions of type σ_g and σ_u nearly gives the optimized double configuration SCF result.

Key words: Natural spin orbitals – Generalized diatomic orbitals – LCDO- and LCGDO-methods.

A. Introduction

Generalized diatomic orbitals (GDOs) are the exact solutions of the one-particle Schrödinger equation

$$\left\{-\frac{\Delta}{2}-\frac{Z_a}{r_a}-\frac{Z_b}{r_b}-\frac{Q}{r_a\cdot r_b}\right\}\chi=\varepsilon\chi \qquad (1)$$



belonging to negative energy eigenvalues ε. The solutions of (1), which have been studied in three former papers [1–3], are chosen to be eigenfunctions of the z-component of angular momentum and will be denoted by

$$\chi=(nl\gamma_s;\, Z_a, Z_b, Q) \qquad (2)$$

where n and l are united-atom quantum numbers, γ is an irreducible representation of $C_{\infty v}$ (or $D_{\infty h}$ if $Z_a=Z_b$), and s is the sign of the eigenvalue $m\hbar$ of the z-component of angular momentum.

Attempts to construct approximate solutions of the Schrödinger equation for diatomic molecules with several electrons in terms of antisymmetrized spin orbital products using orbitals of class (2) are very old. Hylleraas [4] suggested, for the ground and excited states of H_2, the use of the following approximations:

$$\Psi=\frac{1}{\sqrt{2}}\left[|\chi_1\bar{\chi}_2|\pm|\bar{\chi}_1\chi_2|\right]$$

with

$$\chi_1 = |1s\sigma_g; 1,1,0). \quad \chi_2 = |nl\gamma(D_{\infty h}); \frac{1}{2}, \frac{1}{2}, 0). \tag{4}$$

As χ_1 is an H_2^+-ground state function and χ_2 a "demi"-H_2^+-function, this suggestion anticipates Mulliken's demi-H_2^+ model [5].

Hylleraas, however, used highly truncated expansions for the "diatomic orbitals" χ_1 and χ_2 in his numerical calculations. These calculations were later improved by Wallis [6]. Cooley [7] finally performed complete configuration interaction calculations on H_2, using up to 6 basis functions of the general type

$$\chi_k = |n_k l_k \gamma_k(D_{\infty h}); Z_k, Z_k, 0) \tag{5}$$

each depending on a variational parameter Z_k and being an exact solution of (1). Optimizing also these nonlinear parameters Z_k, he found: The use of a relatively few diatomic orbitals (5) whose symmetry $\gamma_k(D_{\infty h})$ permits the three major types of electron correlation gives approximately the same energy as the rank- and symmetry-equivalent truncated natural spin orbital expansion of very accurate H_2 wave functions.

We were able to reproduce Cooley's results and concentrated on some questions such as:

i) How can the results for the one- and two-determinantal treatment of H_2 be improved which are inferior to the ones given by the LCAO-method?

ii) Which basis is appropriate for the ground and excited states of HeH^+?

iii) Can diatomic molecules with more than two electrons be treated successfully?

This paper outlines the methods applied in all cases. Besides it gives the answer to question i), thus especially illustrating the use of symmetry-adapted linear combinations of generalized diatomic orbitals as one-electron basis functions.

B. Method of Linear Combinations of Generalized Diatomic Orbitals

In case of molecular symmetry $D_{\infty h}$, a symmetry-adapted linear combination of two generalized diatomic orbitals LCGDO is defined as the sum or difference

$$\begin{aligned} &|nl\gamma(D_{\infty h}); Z_a, Z_b, Q\rangle \\ &= N_\pm \{|nl\gamma(C_{\infty v}); Z_a, Z_b, Q) \pm |nl\gamma(C_{\infty v}); Z_b, Z_a, Q)\} \end{aligned} \tag{6}$$

where $N_\pm$ is a normalizing factor. Just as the generalized diatomic orbital (2), the linear combination (6) is a product of three functions depending on the spheroidal coordinates μ, v, φ respectively and behaves like a single basis function with regard to the computation of one- and two-electron-integrals.

The well-known most simple LCAO-approximation

$$\begin{aligned} &|10\sigma_g; Z, 0, 0\rangle \\ &= N\{|10\sigma; Z, 0, 0) + |10\sigma; 0, Z, 0)\} \end{aligned} \tag{7}$$

for a σ_g-type molecular orbital in H_2^+ or H_2 evidently is a special case of (6).

In case of molecular symmetry $C_{\infty v}$, we start from a set of generalized diatomic orbitals (2) as basis functions. Combining orthogonalized basis functions of type

(2) or (6) with spin factors α and β, a set of spin orbitals is generated. All linearly independent antisymmetrized products (Slater determinants) of these spin orbitals are then used within the frame of a full configuration interaction calculation. The final many-electron wave function obtained in this way is then submitted to a natural spin orbital analysis according to Löwdin's proposal. The resulting natural spin orbitals are expansions in terms of generalized diatomic spin orbitals (2) or symmetry-adapted linear combinations of generalized diatomic spin orbitals (6). Evidently natural spin orbitals appear as linear combinations of generalized diatomic spin orbitals. They are classified according to theorems proved by Bingel and Kutzelnigg [9] which are generalizations of the Delbrück-Roothaan-theorems [10] for Hartree-Fock-orbitals. All these operations are performed by means of two computer programs (CI 11($C_{\infty v}$) and CI 04 ($D_{\infty h}$)) which also optimize non-linear parameters Z_{a_k}, Z_{b_k}, Q_k.

Further details on the computational steps may be taken from [11]. Some details on the calculation of two-electron integrals between LCDOs are contained in the Appendix.

C. Ground State of H_2 in Single Configuration Approximation

Four types of single configuration calculations have been performed for various values of the internuclear distance R and will now be compared with the SCF results obtained by Kolos and Roothaan [12], especially for the internuclear distance $R = 1.4 a_0$ (Fig. 2 and Table 1).

I. In an MO-DO type of calculation, we used a single diatomic orbital $\psi_I = |1s\sigma_g; Z, Z, 0)$ [Eq. (5)] and optimized its effective charge Z, reproducing Cooley's result [7] for the special internuclear distance $R = 1.4\, a_0$.

II. In an MO-LCAO type of calculation, a σ_g-type linear combination ψ_{II} of two atomic 1s-functions centred at the two nuclei was used [Eq. (7)]; again the single parameter Z was optimized.

Table 1. H_2 1 configuration σ_g^2

I. MO-DO			II. MO-LCAO		III. MO-LCDO		
R	$Z = Z_a = Z_b (Q = 0)$	$-E_{tot}$	$Z(Q = 0)$	$-E_{tot}$	Z_a	$Z_b (Q = 0)$	$-E_{tot}$
0.6	0.808	0.72266	1.449	0.72455	1.364	0.132	0.72482
0.8	0.797	0.97417	1.370	0.97560	1.253	0.211	0.97670
1.0	0.789	1.07873	1.301	1.07993	1.187	0.243	1.08189
1.4	0.779	1.12647	1.189	1.12819	1.103	0.264	1.13132
1.5	0.777	1.12389	1.166	1.12591	1.088	0.265	1.12921
2.0	0.778	1.08223	1.072	1.08631	1.025	0.264	1.08988
2.6	0.795	1.01709	0.995	1.02355	0.971	0.262	1.02681
3.2	0.821	0.95950	0.942	0.96698	0.934	0.264	0.96978
IV. MO-LCGDO							
$R = 1.4$	$Z_a = 0.793$		$Z_b = -0.196$		$Q = 0.513$		$-E_{tot} = 1.133\,42\ e^2/a_0$
$R = 1.4\ a_0$			SCF [12]				$-E_{tot} = 1.133\,63\ e^2/a_0$

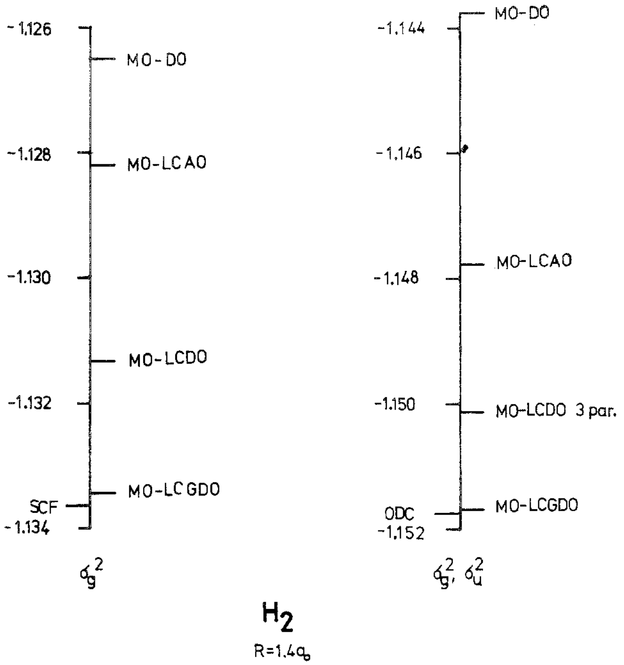


Fig. 1. Ground state of H_2 at equilibrium distance. A comparison of several single and double configuration model calculations

III. In an MO-LCDO type of calculation, the molecular orbital σ_g was approximated by a linear combination of two diatomic orbitals, the charges of which were exchanged according to Eq. (6):

$$\psi_{\text{III}} = |1s\sigma_g\,;Z_a, Z_b, 0\rangle \quad . \tag{8}$$

The two parameters Z_a and Z_b were optimized.

IV. In an MO-LCGDO type of calculation, a linear combination of two generalized diatomic orbitals was formed, the parameters Z_a and Z_b of which being exchanged according to Eq. (6):

$$\psi_{\text{IV}} = |1s\sigma_g\,;Z_a, Z_b, Q\rangle \quad . \tag{9}$$

The three parameters Z_a, Z_b, and Q were optimized. As the MO-LCDO method III (two variational parameters) contains methods I and II as special cases, it is superior to both of them (Fig. 1). The approximation ψ_{III} (Eq. (8)) is able to reflect the polarization of the electron charge clouds centred at the protons. In an MO-LCAO-SCF treatment, atomic $2p_0$-functions centred at the protons would have to be included in the basis to achieve this polarization effect.

The MO-LCGDO method IV is per definitionem (three parameters) superior to the MO-LCDO method. Nevertheless it is surprising how closely the SCF value obtained by Kolos and Roothaan [12] is approached (Fig. 1).

If the distance R is varied, the order of the results given by the four methods remains the same (Table 1). This may also be taken from Fig. 2, in which the differences H -E_{SCF} of the four types of calculations – as compared with the self-consistent values E_{SCF} – are shown for various values of R.

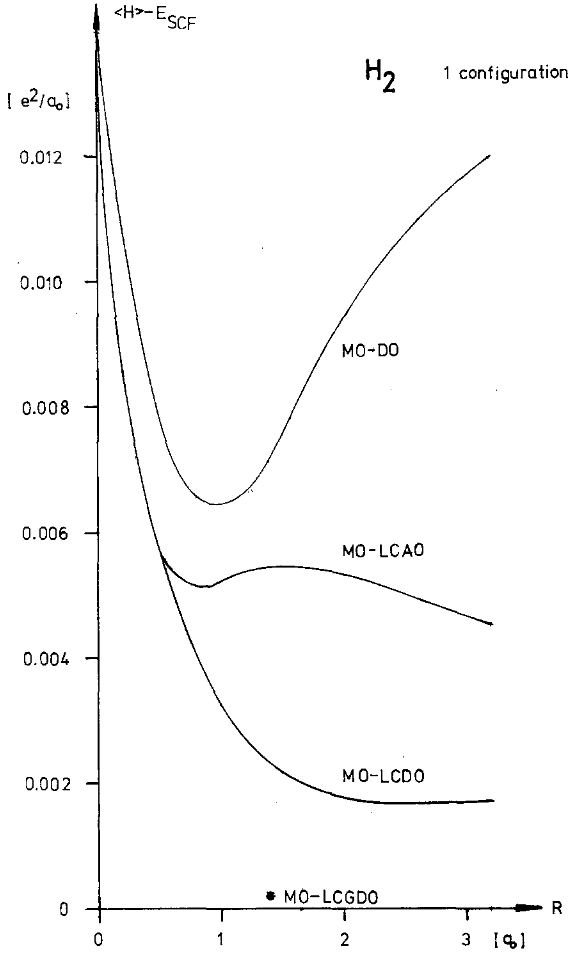


Fig. 2. Ground state of H_2. Deviations of single configuration model calculations from Hartree-Fock results

D. Ground State of H_2 in Double Configuration Approximation

A double configuration approximation based on two configurations σ_g^2 and σ_u^2 takes left-right correlation into account and ensures correct dissociation into two 1*s*-hydrogen atoms when the internuclear distance R is increased.

Four types of double configuration calculations have been performed for various values of the internuclear distance R and will now be compared with the optimized double configuration (ODC) result obtained by Das and Wahl [13], especially for $R = 1.4\ a_0$. (Fig. 1 and Table 2).

I. In an MO-DO type of calculation, σ_g and σ_u were approximated by $1s\sigma_g$ and $2p\sigma_u$ [Eq. (5)], and the two effective nuclear charges for σ_g and σ_u were optimized. Cooley's result was again reproduced.

II. In an MO-LCAO-double ζ type of calculation, σ_g and σ_u were approximated by two functions of kind (7), and Z_g (for σ_g) and Z_u (for σ_u) were optimized.

Table 2. H_2 2 configurations σ_g^2, σ_u^2

I. MO-DO				II. MO-LCAO-double ζ		
R	$Z(1s\sigma_g)$	$Z(2p\sigma_u)$	$-E_{tot}$	$Z(\sigma_g)$	$Z(\sigma_u)$	$-E_{tot}$
0.5	0.817	1.915	0.48770	1.495	1.314	0.48906
1.0	0.796	1.544	1.09167	1.308	1.249	1.09371
1.4	0.786	1.353	1.14376	1.201	1.189	1.14778
1.5	0.790	1.314	1.14244	1.179	1.179	1.14719
2.0	0.803	1.203	1.10865	1.095	1.120	1.11773
3.0	0.877	1.059	1.03106	1.012	1.045	1.04710

IIIa. MO-LCDO 2 par.				IIIb. MO-LCDO 3 par.			
				σ_g		$2p\sigma_u$	
R	Z_a	Z_b	$-E_{tot}$	Z_a	Z_b	Z	$-E_{tot}$
0.5	1.476	0.027	0.48884	1.469	0.039	1.923	0.49018
1.0	1.210	0.210	1.09515	1.208	0.217	1.532	1.09571
1.4	1.131	0.220	1.14997	1.130	0.227	1.354	1.15031
1.5	1.117	0.218	1.14943	1.116	0.224	1.319	1.14974
2.0	1.062	0.200	1.11970	1.062	0.204	1.183	1.11995
3.0	1.009	0.150	1.04774	1.007	0.148	1.048	1.04795

IV. MO-LCGDO $R = 1.4\ a_0$

$1s\sigma_g$: $Z_a = 0.793$ $Z_b = -0.196$ $Q = 0.513$ (*frozen*)

$2p\sigma_u$: $Z_a = 1.316$ $Z_b = 1.371$ $(Q = 0)$

$-E_{tot} = 1.151\,68\ e^2/a_0$

Das and Wahl [13]: $-E_{ODC} = 1.15175$

III. a) In a first MO-LCDO type of calculation, σ_g was approximated by the linear combination ψ_{III} [Eq. (8)]. σ_u was approximated by a linear combination $|10\sigma_u;\ Z_a, Z_b, 0\rangle$ of the same diatomic orbitals $|1s\sigma;\ Z_a, Z_b, 0)$ and $|1s\sigma;\ Z_b, Z_a, 0)$, the two effective charges of which were optimized.

This procedure is equivalent to using these two diatomic orbitals as a one-electron basis for a full configuration interaction.

b) In a second MO-LCDO type of calculation, σ_g was approximated by ψ_{III} [Eq. (8)]. σ_u was approximated by an H_2^+-type diatomic orbital $2p\sigma_u$ [Eq. (5)]. The three effective charges Z_a, $Z_b(\sigma_g)$ and $Z(\sigma_u)$ were optimized.

IV. Finally, in an MO-LCGDO type of calculation, σ_g was approximated by ψ_{IV} [Eq. (9)], determined in the one-configuration approximation and frozen. σ_u was approximated by $|21\sigma_u;\ Z_a, T_b, 0\rangle$ [Eq. (6)]. The two parameters Z_a and Z_b of σ_u were optimized. (Starting from a Coulson-type ground state one-configuration approximation [14], Callen [15] determined a σ_u-type orbital in quite a similar way.)

As can be seen from Fig. 1, each of the methods II, III, and IV is superior to any of the preceding ones. The MO-LCGDO result nearly equals the ODC-value obtained by Das and Wahl [13].

Again the internuclear distance was varied (Table 2). The differences between the four calculations and the optimized double configuration result E_{ODC} are presented in Fig. 3.

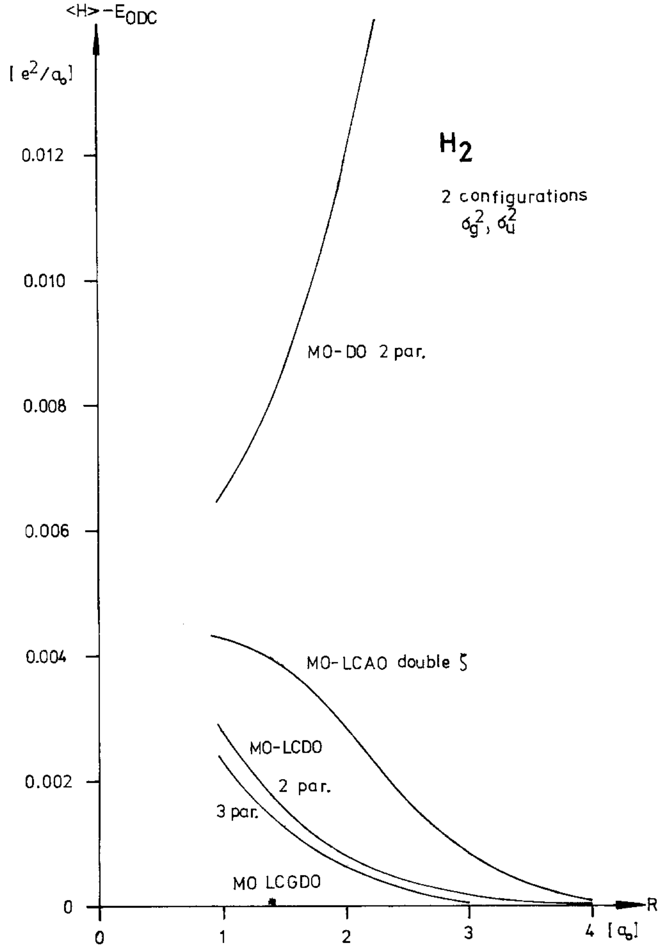


Fig. 3. Ground state of H_2. Deviations of double configuration model calculations from optimized double configuration SCF results

E. Appendix: Transformation Properties of Two-Electron Two-Center Integrals

Be

$$\chi_i'(r) = \sum_{p=1}^{N_{\text{base}}} C_{pi}\chi_p(r) \qquad (i = 1(1)N_{\text{orb}}) \tag{10}$$

a linear combination of K_{base} basis functions $\chi_p(r)$. For the CI calculation, all two-electron integrals $[\chi_i'\chi_j'|\chi_k'\chi_l']$ between these linear combinations are required.

Instead of transforming the set of two-electron integrals $[\chi_p\chi_q|\chi_r\chi_s]$ into the required set, we proceed as follows:

According to Ruedenberg's ideas [16], all integrals between linear combinations are decoupled:

$$[\chi_i'\chi_j'|\chi_k'\chi_l'] = \int_1^{\infty} \sum_L G_L'^{i,j}(\mu) G_L'^{k,l}(\mu) d\mu \,. \tag{11}$$

Here

$$G_L'^{i,j}(\mu) = \int \gamma_L^M(\mu, \boldsymbol{r}') \chi_i'^*(\boldsymbol{r}') \chi_j'(\boldsymbol{r}') dV' \tag{12}$$

may be considered as an integral transform of the mixed density $\chi_i'^* \chi_j'$ with the kernel $\gamma_L^M(\mu, \boldsymbol{r}')$ [11]. The integral transforms $G_L'^{i,j}(\mu)$ may be regarded as the elements of a second order tensor $G_L'(\mu)$ (L fixed). It transforms under a change of basis (10) described by the matrix $\boldsymbol{C}$ like

$$\boldsymbol{G}_L'(\mu) = \boldsymbol{C}^+ \boldsymbol{G}_L(\mu) \boldsymbol{C}\,, \tag{13}$$

as the component $G_L^{p,q}(\mu)$ of $\boldsymbol{G}_L(\mu)$ is defined by

$$G_L^{p,q}(\mu) = \int \gamma_L^M(\mu, \boldsymbol{r}') \chi_p^*(\boldsymbol{r}') \chi_q(\boldsymbol{r}') dV'. \tag{14}$$

So the transformation of a tensor of fourth order $[\chi_p \chi_q | \chi_r \chi_s]$ may be replaced by the transformation (13) of the tensors $\boldsymbol{G}_L(\mu)$ which are only of order two. Only the tensors $\boldsymbol{G}_L'(\mu)$ must be held in core to perform the integrations (11).

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