Calculation of the Electronic Energy of H_3

--Use of the Floating Atomic Orbitals--

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Abstract The ground state electronic energy of the H_3
molecule has been calculated taking the following steps of
approximations: SCF, SCF-Scale, SCF-CI and SCF-CI-Scale,
with and without the use of the floating atomic orbitals. The
results show that the scale and CI effects are significantly
important to lower the ground state energy, while the floating
effect is negligible against the authors' expectation.

§ 1. Introduction

The simplest triatomic system, H_3 attracts our theoretical interest, and several
non-empirical calculations have been already made. Our purpose in this paper is to
recalculate the H_3 energy and to discuss, to some extent, the correlation effects in
this molecule. The idea of the floating AOs (atomic orbitals), which we wish to use
here, has originated from Gurnee and Magee,[1] and using this Hurley[2] performed a
successful calculation on H_2.

According to Hurley, the floating parameter x, by which the origins of the AOs
are shifted from the positions of the corresponding nuclei, plays a significantly
important role to lower the ground state energy of the H_2 molecule. By the use of
the MO (molecular orbital) type wave function, the ground state energy has been
estimated to be -0.134 a.u. (atomic unit), for the optimum value of x, -0.07. This
value of energy is not so good compairing with the observed one, -0.174 a.u., but is
a little better than that obtained by the best MO treatment of Coulson[3]. Here the
negative sign of the floating parameter means that the origins of the AOs are
shifted inward along the molecular axis, so that the charge cloud is accumulated
around the center region of the molecule. The effect of the floating parameter is
related to the left-right correlation which can be taken into account alternatively by

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mixing the p-type orbital into s-orbital. Since, however, the latter treatment is considerably difficult for the polyatomic molecules from the v ew point of numerical calculations, we adopt the present treatment to discuss the correlation effect in H_3.

In §2, a theoretical approach is briefly given, and in the succeeding sections, numerical estimates and some discussions will be given.

§ 2. Theoretical

The MO is taken as a linear combination of $1s$ hydrogen AOs:

$$\phi_i = \sum_p C_{pi}\chi_p \qquad (1)$$

or in the vector form:

$$\phi = XC , \qquad (1a)$$

where C_{pi} is the LCAO coefficient of the p-th AO, and

$$\chi_p = (Z_p{}^3/\pi)^{1/2}\exp(-Z_p r_p). \qquad (2)$$

Here r_p is the distance from the origin of the AO to the electron. The origin coincides with the nuclear position in the usual treatment, while, in the floating AO, it is shifted by x from the corresponding nucleus. In our case of H_3, the floating AOs are used for the AOs of both molecular ends (see Fig. 1).
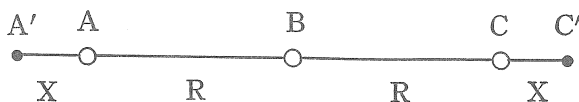

Fig. 1. The linear and symmetric structure of H_3.
A, B and C denote the nuclear positions.
A′ and C′ are the origins of the floating AOs
shifted by x, symmetrically and along the molecular axis.

Since the H_3 molecule has only one open shell electron, the Roothan's theory[4] can be applied. The eigenvalue equation for the closed shell is

$$[H + 2J_1 - K_1 + \frac{1}{2}(2J_2 - K_2) + \frac{1}{2}SC_2 C_2{}^*(2J_2 - K_2)]C_1 = SC_1\eta_1 \qquad (3a)$$

and that for the open shell is

$$[\boldsymbol{H} + 2\boldsymbol{J}_1 - \boldsymbol{K}_1 + S\boldsymbol{C}_1\boldsymbol{C}_1^*(2\boldsymbol{J}_2 - \boldsymbol{K}_2)]\boldsymbol{C}_2 = S\boldsymbol{C}_2\eta_2 \tag{3b}$$

Here $\boldsymbol{H}$ represents the sum of the kinetic energy and the nuclear attractions, $\boldsymbol{J}_i$ and $\boldsymbol{K}_i$ are the coulomb and exchange terms respectively, and S is the overlap matrix between the AOs. Further, $\boldsymbol{C}_i$ is the column vector of which elements are C_{pi} in (1), and η_i is the diagonal matrix representing orbital energies. The suffixes, *1* and *2*, refer to the closed and open shells respectively.

We should pick up the eigenvector with the lowest eigenvalue from $\boldsymbol{C}_1$'s, and the one with the second lowest eigenvalue from $\boldsymbol{C}_2$'s, and then construct the ground state configurations by use of the Pauli principle.

In this paper, however, a little bit modified formulas given by Roothaan* will be applied from the convenience of the computer calculation. Because of the existence of terms $S\boldsymbol{C}_2\boldsymbol{C}_2^*$ and $S\boldsymbol{C}_1\boldsymbol{C}_1^*$ in (3a) and (3b) respectively, the Hartree-Fock matrices are not symmetric. In order to symmetrize them, we define ρ_1 and ρ_2 by the following equations:

$$[-(2\boldsymbol{J}_2-\boldsymbol{K}_2)+\frac{1}{2}S\boldsymbol{C}_1\boldsymbol{C}_1^*(2\boldsymbol{J}_2-\boldsymbol{K}_2)+\frac{1}{2}(2\boldsymbol{J}_2-\boldsymbol{K}_2)(\boldsymbol{C}_1\boldsymbol{C}_1^*+\boldsymbol{C}_2\boldsymbol{C}_2^*)S]\boldsymbol{C}_1$$
$$=S\boldsymbol{C}_1\rho_1 \tag{4a}$$

$$[-\frac{1}{2}(2\boldsymbol{J}_2-\boldsymbol{K}_2)-\frac{1}{2}S\boldsymbol{C}_1\boldsymbol{C}_1^*(2\boldsymbol{J}_2-\boldsymbol{K}_2)+\frac{1}{2}S\boldsymbol{C}_2\boldsymbol{C}_2^*(2\boldsymbol{J}_2-\boldsymbol{K}_2)$$
$$+\frac{1}{2}(2\boldsymbol{J}_2-\boldsymbol{K}_2)(\boldsymbol{C}_1\boldsymbol{C}_1^*+\boldsymbol{C}_2\boldsymbol{C}_2^*)S]\boldsymbol{C}_2 = S\boldsymbol{C}_2\rho_2 \tag{4b}$$

Then adding (4a) and (4b) to (3a) and (3b) respectively, we obtain the equations having the same form for both the closed and open shells:

$$\boldsymbol{F}\boldsymbol{C}_i = \varepsilon_i S\boldsymbol{C}_i, \tag{5}$$

where

$$\boldsymbol{F} = \boldsymbol{H} + 2\boldsymbol{J}_1 - \boldsymbol{K}_1 - \frac{1}{2}(2\boldsymbol{J}_2-\boldsymbol{K}_2) + \frac{1}{2}S(\boldsymbol{C}_1\boldsymbol{C}_1^*+\boldsymbol{C}_2\boldsymbol{C}_2^*)(2\boldsymbol{J}_2-\boldsymbol{K}_2)$$
$$+\frac{1}{2}(2\boldsymbol{J}_2-\boldsymbol{K}_2)(\boldsymbol{C}_1\boldsymbol{C}_1^*+\boldsymbol{C}_2\boldsymbol{C}_2^*)S, \tag{6}$$

$$\varepsilon_i = \eta_i + \rho_i. \tag{7}$$

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*See Eq. (53) in ref. (4)

We should like to point out that the Hartree-Fock matrix shown in (6) is no longer asymmetric but symmetric. Here, ε_i is the fictitious orbital energy, but this does not matter for us to construct the ground state configuration, if we take care of the symmetry properties of the eigenvectors.

§ 3. Calculations

As to the geometrical structure of H_8, the linear and equidistant structure is adopted. Processes of our calculations are as follows:

(I). SCF. The value of the orbital exponent, Z is fixed to 1, and the SCF calculations are performed for various internuclear distances. The optimum ground state energy is obtained by the parabolic fit to the energy versus internuclear distance curve. The resulting energy is -1.562 a.u. and the equilibrium internuclear distance, R_e is 1.967 a.u.. Details are given in Table 1.

The SCF MOs for $R=R_e$ are

$$
\left.
\begin{aligned}
\phi_1 &= 0.3295\ (\chi_A + \chi_C) + 0.5531\ \chi_B \\
\phi_2 &= 0.7893\ (\chi_A - \chi_C) \\
\phi_3 &= 0.9566\ (\chi_A + \chi_C) - 1.4648\chi_B
\end{aligned}
\right\}
\tag{8}
$$

Table 1. Total energies for various internuclear
distances. Procedure I, SCF only.

R	Total Energy
1.50	$- 1.511$
1.78	$- 1.554$
1.86	$- 1.560$
2.00	$- 1.562$
2.20	$- 1.552$
2.50	$- 1.530$
3.00	$- 1.495$

(II). SCF+Scale. It is well known that the scaling procedure is nothing but to determine the orbital exponent to satisfy the virial theorem. As has been found by Löwdin[5], if we are interested in determining the energy and the internuclear distance for the equilibrium situation, the orbital exponent and total energy are given by

$$
Z = -V/2T,
\tag{9}
$$

$$
E = -V^2/4T,
\tag{10}
$$

where T and V are, respectively, the kinetic and potential energies at the equilibrium distance R_e for $Z=1$. After that, the equilibrium distance is replaced by R_e/Z.

The best value of energy obtained hereby, is *-1.574* a.u., with the scale factor, *1.092* and the equilibrium internuclear distance, *1.81* a.u.. The lowering of the gound state energy through the scaling procedure is counted by *0.012* a.u..

(III). SCF+CI. The configuration interaction is taken for the following doublet states:

$$\psi_1 = \frac{1}{\sqrt{6}} \sum_P (-1)^P P \phi_1 \alpha(1) \phi_1 \beta(2) \phi_2 \alpha(3),$$

$$\psi_2 = \frac{1}{\sqrt{12}} \sum_P (-1)^P P \{\phi_1 \alpha(1) \phi_2 \beta(2) \phi_3 \alpha(3) - \phi_1 \beta(1) \phi_2 \alpha(2) \phi_3 \alpha(3)\},$$

$$\psi_3 = \frac{1}{6} \sum_P (-1)^P P \{\phi_1 \alpha(1) \phi_2 \beta(2) \phi_3 \alpha(3) + \phi_1 \beta(1) \phi_2 \alpha(2) \phi_3 \alpha(3)$$
$$-2\phi_1 \alpha(1) \phi_2 \alpha(2) \phi_3 \beta(3)\},$$

$$\psi_4 = \frac{1}{\sqrt{6}} \sum_P (-1)^P P \phi_2 \alpha(1) \phi_3 \beta(2) \phi_3 \alpha(3).$$

The mixing coefficients given by

$$\psi = \sum_i c_i \psi_i, \qquad (i=1,2,3, \text{and } 4) \qquad (11)$$

are shown in Table 2 for various internuclear distances. The optimum energy through this procedure is *-1.591* a.u. at the internuclear distance, *2.00* a.u..

(IV). SCF+CI+Scale. Combining these procedures, we obtain the total energy of value, -1.603 a.u. with the scale factor *1.095* and the equilibrium internuclear distance, *1.82* a.u..

(V). SCF (float)+CI+Scale. One of the main purposes of this paper is to examine the effect of the floating parameter, x explained in §2. Varying the floating parameter, we repeated the above mentioned procedures, (I)~(IV). It was, however, unexpected for us that the floating effect was neglible for lowering the ground state energy. As an example, the ground state energies calculated by the SCF CI approximation based on the floating AOs with various values of the floating parameter are shown in Table 3. Conclusively, nothing is improved in our last step, compairing with the obtained results in the procedure (IV).

Table 2. The CI coefficents and total energies for various
internuclear distances. Procedure III, SCF+CI.

R	c_1	c_2	c_3	c_4	Energy
1.50	0.9925	−0.0662	−0.0916	−0.0458	−1.532
1.78	0.9894	−0.1160	−0.0691	−0.0542	−1.578
1.86	0.9882	−0.1289	−0.0606	−0.0567	−1.585
2.00	0.9855	−0.1499	−0.0473	−0.0642	−1.591
2.20	0.9793	−0.1864	−0.0296	−0.0736	−1.588
2.50	0.9673	−0.2353	−0.0004	−0.0946	−1.578

Table 3. The Total energies, at the internuclear distance
1.967 a. u., by the SCF CI procedure based on
floating AOs with various values of floating para-
meter x. The positive sign of x shows the orign of
the AO is shifted outward from the position of the
corresponding nucleus.

x	Energy
−0.15	−1.577
−0.05	−1.590
−0.03	−1.590
0.00	−1.589
0.05	−1.588
0.15	−1.557

§ 4. Discussions

The ground state electronic energy of H_3 has been calculated by several authors.
[6–10] Among them, Boys et al. have performed the elaborate calculation and obtained
the value of −1.628 a.u.. This value will be the standard reference for other
calculations, since we have no experimental value of this molecule.

Calculations based on the similar idea with ours have been carried out by Meador
[8] and Kimball et al..[9] The former is a little different from ours in treatment of the
floating parameter. We, first, fixed the internuclear distance, R and then varied the
floating parameter, x, while Meador fixed R-x, and varied x within the above
restriction in order that the tabulated values of integrals were available. Further,
the optimum condition for x is, in our case, that the total energy is minimum, while
in Meador's, that the sum of the orbital energies is minimum. Hence, the behavior
of the floating parameter is considerably different with each other. He obtained the
total energy of value, *−1.591* a.u..

The essential feature of the treatment of Kimball and Trulio lies in using five
1s AOs as basis functions instead of three. Roughly speaking. two more AOs are

inserted between the middle and outer AOs in our treatment. By this procedure, they expected that the charge cloud accumulates at the center region of the molecule as compaired to the usual treatment. However, they found that this effect was almost negligible. Their result is a little better than ours; value of the total enesgy is -1.615 a.u..

From these calculations including ours, we may give some remarks on the electronic correlation energy in H_3. As is commonly done, the correlation effects, in this molecule, will be discussed from two points, e.g., the left-right correlation and the in-out one. Considering that the floating parameter gives no appreciable effect in our calculation and from the above mentioned remark of Kimball and Trulio, the left-right correlation is nearly negligible. We may say that such situation will be generally expected in loosely combined molecules as H_3 and more extensively in molecular compounds. The optimum internuclear distance in our calculation, 1.82 a.u. is slightly shorter than the simple sum of the radii of the two $1s$ hydrogen AOs. This suggests that the overlap between AOs or the interference between atomic wave functions, which seems to cause the left-right correlation, is very small.

On the other hand, the scaling procedure, which improves the orbital exponent appreciably, produces a considerable lowering in the ground state energy. Therefore, the in-out correlation which is partly taken into account in this treatment is substantially important in H_3. In other words, the lowering in energy arises from the contruction of the electron clouds around the nuclei due to approach of other atoms. [11] This causes the decrease of the potential energy and the increase of the kinetic energy, but the latter diminishes to some extent due to the interference between atomic wave functions.

It is difficult to present a visual version for the configuration interaction. Though it involves the so-called many body effects in various way, we consider that its main part will be the interaction between the particle-hole pairs as shown in the inter-molecular interaction. Our calculation as well as others suggests that the extensive CI treatment is most important in this molecule.

Appendix. Three-center Integrals.

In our treatment of using the floating AOs, some of the two-center integrals representing the nuclear attraction in the usual treatment become three-center integrals. However, calculation of these integrals is not so combersome. The most difficult ones are still the electron-electron three-center integrals. For these, we used the entirely same method with Hirschfelder's, [12-14] and obtained slighty different values, which were shown in Table 4. The reason seems as follows: Hirschfelder used the differential analyser in his last step of calculation, while we performed the numerical integration by means of the Simpson rule.

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Table 4. Numerical values of the three center electron-electron integrals, where $(PQ:RS) = \int \chi_P(1)\chi_Q(1)1/r_{12}\chi_R(2)\chi_S(2)dv_1dv_2$. The values in paranthesis are obtained by Hirschfelder. The values of the first two integrals are exactly same with those of Hirschfelder.

R	1.00	1.50	2.00	2.50
(AA:BC)	0.41706	0.28605	0.18839	0.12196
(BB:AC)	0.33583	0.18631	0.09421	0.04487
(AB:AC)	0.27649	0.12596	0.05032	0.01836
	(0.27879)	(0.12776)	(0.05121)	(0.01872)
(AB:BC)	0.39536	0.24774	0.14175	0.07509
	(0.39946)	(0.24708)	(0.14120)	(0.07509)

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