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Some Calculations on the Ethylene Molecule

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A series of variational calculations are reported for the ethylene molecule, using ASMO LCAO method with CGTO's (combined Gaussian-type orbitals) as the basic atomic orbitals. The three electronic states, ${}^1A_g(N)$, ${}^3B_{1u}(T)$ and ${}^1B_{1u}(V)$, are investigated with a special emphasis on the ${}^1B_{1u}$ state.

Es werden die Ergebnisse einer Reihe von Variationsrechnungen am Äthylen-Molekül mitgeteilt, wobei den Rechnungen die ASMO LCAO-Methode mit CGTO's ("combined Gaussian-type orbitals") als Atombasisfunktionen zugrunde liegt. Untersucht werden die drei Elektronenzustände ${}^1A_g(N)$, ${}^3B_{1u}(T)$ und ${}^1B_{1u}(V)$, mit besonderem Nachdruck auf dem letzteren.

Série de calculs variationnels sur la molécule d'éthylène en utilisant la méthode ASMO LCAO avec des orbitales de type gaussien combiné (CGTO). Etude des trois états électroniques ${}^1A_g(N)$, ${}^3B_{1u}(T)$ et ${}^1B_{1u}(V)$ en insistant particulièrement sur ce dernier état.

Introduction

The present work describes some applications of the combined Gaussian-type orbitals (CGTO) to the theoretical study of the ethylene molecule. CGTO is a set of Gaussian-type orbitals combined linearly with certain fixed coefficients chosen in such a way that the set can be used, as a unit, profitably in molecular calculations. The more detailed description will be given in the next section.

The ethylene molecule is one of the simplest organic molecules possessing a double bond. Many theoretical attempts have been made to describe the electronic structures of the molecule in the ground and lower excited states. The work by Moskowitz and Harrison [1] represents the most extensive effort to date based on Gaussian-type orbitals (GTO), while the one by Kaldor and Shavitt [2] is the counterpart based on Slater-type orbitals.

In spite of these calculations, the theoretical study of the ethylene molecule is far from complete. Especially the knowledge about the wave function of the first ${}^1B_{1u}$ state still remains very unsatisfactory. A variational calculation by the present author [3] indicated that in the molecular orbital approximation the π_g orbital of the ${}^1B_{1u}$ state would have a very diffuse form. Recently a quite interesting calculation was conducted by Taketa *et al.* [4] on the oxygen molecule, which suggested that the outermost electron in the ${}^3\Sigma_u^-$ state would exhibit a very diffuse distribution. In view of an important similarity between the ${}^1B_{1u} - {}^3B_{1u}$ separation of C_2H_4 and the ${}^3\Sigma_u^- - {}^3\Sigma_u^+$ separation of O_2, we have initiated a series of investigations into the matter and the present work constitutes the first part.

CGTO and CSTO

The concept of the combined Gaussian-type orbital (CGTO) has been discussed elsewhere [5]. The same idea can also be applied to linear combinations of Slater-type orbitals, hence the CSTO (combined Slater-type orbital).

For example, Table 1 shows an approximate expansion of the Hartree-Fock (2*s*) orbital of the carbon atom in terms of primitive Gaussian-type orbitals;

$$\psi_{2s} = \sum_{i=1}^{10} C_i N(\alpha_i) \exp(-\alpha_i r^2), \tag{1}$$

where $N(\alpha_i)$ is a normalization factor. We generalize the above function by inserting a scaling parameter as follows,

$$g(\zeta) = \sum_{i=1}^{10} C_i N(\zeta^2 \alpha_i) \exp(-\zeta^2 \alpha_i r^2) \tag{2}$$

with the same $\{\alpha_i, C_i\}$ as in Eq. (1). It is easy to see that $\psi_{2s} = g(1.0)$ and if ψ_{2s} is normalized to unity, i.e., $\langle \psi_{2s} | \psi_{2s} \rangle = 1.0$, then

$$\langle g(\zeta) | g(\zeta) \rangle = 1.0$$

for any value of ζ. The idea is that we may use $g(\zeta)$ as a (2*s*) orbital in molecular calculations just like we do with a single STO, $r \exp(-\zeta r)$, and we call it a CGTO.

Table 1. CGTO *parameters for* (1*s*) *and* (2*s*) *of the carbon atom*[a]

i	α_i	C_i;(1*s*)	C_i;(2*s*)
1	9470.52	0.00045	−0.00010
2	1397.56	0.00358	−0.00076
3	307.539	0.01934	−0.00418
4	84.5419	0.07736	−0.01701
5	26.9117	0.22679	−0.05399
6	9.40900	0.42695	−0.12134
7	3.50002	0.35790	−0.17554
8	1.06803	0.04877	0.08502
9	0.40017	−0.00756	0.60689
10	0.13512	0.00213	0.43809

[a] See Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).

In the present work on C_2H_4, the idea is applied to all the atomic orbitals appearing in the calculations.

The idea of CGTO can be much more flexible. Necessary data are given in Table 3 to construct a set of CGTO basis functions for the carbon atom from which the approximate Hartree-Fock orbitals can be obtained in the form,

$$\psi_{\mathrm{HF}} = \sum_i C_i \chi_i, \tag{3}$$

and each χ_i is itself a linear combination of appropriately chosen GTO's. If we write

$$\chi_i(\zeta_i) = \sum_{j=1}^{n_i} c_{ij} N(\zeta_i^2 \alpha_{ij}) \exp(-\zeta_i^2 \alpha_{ij} r^2), \tag{4}$$

Table 2. CGTO *parameters for* (2*p*) *of the carbon atom*[a]

i	α_i	C_i
1	25.3655	0.00875
2	5.77636	0.05479
3	1.78730	0.18263
4	0.65771	0.35871
5	0.24805	0.43276
6	0.091064	0.20347

[a] See Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).

then these functions can be used as basis functions in the calculation of molecules containing the carbon atoms. The set given in Table 3 consists of four (1*s*)-type χ_i's ($n_1=3$, $n_2=3$, $n_3=2$, $n_4=3$) and two (2*p*)-type χ_i's ($n_1=3$, $n_2=3$). A convenient abbreviation to indicate the size of the set would be (3, 3, 2, 3; 3, 3) as introduced elsewhere [5]. With all ζ_i's equal to 1.0, this particular set yields -37.68727 a.u. as the ground state energy of the carbon atom. The corresponding value given by the well-known best double STO basis set is -37.68668 a.u. [6].

Actually, the concept of the combined orbitals can be extended to more general class of functions. The general form of the primitive GTO is given by

$$(n, l, m; \alpha)_g = R_{g,n}(r; \alpha)\, Y_{lm}(\theta, \phi)\,, \qquad (n + l = \text{even})\,, \tag{5}$$

where

$$R_{g,n}(r; \alpha) = (2/\pi)^{\frac{1}{4}}\, 2^{n+\frac{1}{2}}[(2n-1)!!]^{-\frac{1}{2}}\, \alpha^{\frac{n}{2}+\frac{1}{4}}\, r^{n-1} \exp(-\alpha r^2)\,. \tag{6}$$

Table 3. (3, 3, 2, 3; 3, 3) CGTO *set for the carbon atom*

χ_i	j	α_{ij}	c_{ij}
$\chi_{s,1}$	1	16371.074	0.02120912
	2	2439.1239	0.16414017
	3	545.16766	0.87510685
$\chi_{s,2}$	1	151.00382	0.08646063
	2	47.803990	0.28645409
	3	16.435665	0.69939809
$\chi_{s,3}$	1	5.9491182	0.72521862
	2	2.2158781	0.31046045
$\chi_{s,4}$	1	0.56937124	0.40210571
	2	0.21811018	0.51738733
	3	0.088432497	0.14631886
$\chi_{p,1}$	1	24.178811	0.04081133
	2	5.7634925	0.23370981
	3	1.7994821	0.81589670
$\chi_{p,2}$	1	0.62738153	0.44674694
	2	0.22321395	0.50433069
	3	0.079618113	0.18234560

The one-center overlap integral between the orbitals is

$$\langle (n, l, m; \alpha)_g | (n', l', m'; \beta)_g \rangle$$
$$= \delta_{ll'} \delta_{mm'} \frac{(n+n'-1)!!}{[(2n-1)!!(2n'-1)!!]} (1+\tau)^{\frac{n}{2}+\frac{1}{4}} (1-\tau)^{\frac{n}{2}+\frac{1}{4}}, \tag{7}$$

where $\tau = (\alpha - \beta)/(\alpha + \beta)$.

Thus,

$$\langle (n, l, m; \alpha)_g | (n', l', m'; \beta)_g \rangle = \langle n, l, m; \zeta^2 \alpha)_g | (n', l', m'; \zeta^2 \beta)_g \rangle . \tag{8}$$

A similar result can be derived also for Slater-type orbitals. The general form of the primitive STO is given by

$$(n, l, m; \alpha)_s = [(2n)!]^{-\frac{1}{2}} (2\alpha)^{n+\frac{1}{2}} r^{n-1} \exp(-\alpha r) \cdot Y_{lm}(\theta, \phi), \tag{9}$$

and

$$\langle (n, l, m; \alpha)_s | (n', l', m'; \beta)_s \rangle$$
$$= \delta_{ll'} \delta_{mm'} \frac{(n+n')!}{[(2n)!(2n')!]^{\frac{1}{2}}} (1+\tau)^{n+\frac{1}{2}} (1-\tau)^{n'-\frac{1}{2}}, \tag{10}$$

where $\tau = (\alpha - \beta)/(\alpha + \beta)$.

Here, again

$$\langle (n, l, m; \alpha)_s | (n', l', m'; \beta)_s \rangle = \langle (n, l, m; \zeta\alpha)_s | (n', l', m'; \zeta\beta)_s \rangle . \tag{11}$$

Because of the convenient properties shown above, we can construct CGTO's and CSTO's which may contain orbitals of mixed quantum numbers.

Hamiltonian and Wavefunctions

We treat the ethylene molecule in the planar form and derive the energy formulas in the framework of the ASMO LCAO method. The molecule is regarded as a system which consists of two π-electrons in a field of a σ-core skeleton. The construction of the energy formulas closely parallels the one described in the previous work [3] but as one can see below the charge distribution due to the ($1s$) electrons of the carbon atoms is considered explicitly in the Hamiltonian and the geometrical data are updated [7]; CC distance = 1.332 Å, CH distance = 1.084 Å, HCH angle = 115.5°.

The π-electron Hamiltonian may be written as (in atomic units)

$$\mathscr{H} = H(1) + H(2) + (1/r_{12}), \tag{12}$$

where

$$H(1) = -(1/2)\Delta + U_c(1) + U_h(1),$$
$$U_c(1) = U_a(1) + U_b(1),$$
$$U_h(1) = \sum_{n=1}^{4} U_n(1),$$
$$U_a(1) = -(6/r_{a1}) + \int (1/r_{1\mu}) \{2\bar{s}_a^2(\mu) + s_a^2(\mu) + x_a^2(\mu) + y_a^2(\mu)\} \, dV_\mu ,$$
$$U_n(1) = -(1/r_{n1}) + \int (1/r_{1\mu}) h_n^2(\mu) \, dV_\mu .$$

Similar expressions may be written for $H(2)$. The $\bar{s}_a$ and s_a functions are the $(1s)$ and $(2s)$ orbitals, respectively, on the carbon nucleus a; x_a and y_a are the $(2p)$ orbitals orthogonal to the π orbital, z_a. The $(1s)$ orbital of the hydrogen atom n is denoted by h_n.

We specify the π_u and π_g molecular orbitals as follows,

$$\begin{aligned}\phi_1 &= [2(1+S_1)]^{-\frac{1}{2}}(z_{1,a}+z_{1,b}),\\ \phi_2 &= [2(1-S_2)]^{-\frac{1}{2}}(z_{2,a}-z_{2,b}),\end{aligned} \tag{13}$$

where $S_i = \langle z_{i,a} | z_{i,b} \rangle$, $(i=1,2)$. As in the previous work [3], the π atomic orbitals z_1 and z_2 are supposed to be different in general. From the above two molecular orbitals we obtain the following four linearly independent antisymmetric wave functions of the molecule in the singlet and triplet states:

$$^1A_g\colon\ \psi_2 = \phi_2(1)\,\phi_2(2)\,X_s, \tag{14}$$

$$^1B_{1u}\colon \psi_V = (1/2)^{\frac{1}{2}}\,[\phi_1(1)\,\phi_2(2)+\phi_2(1)\,\phi_1(2)]\,X_s, \tag{15}$$

$$^3B_{1u}\colon\ \psi_T = (1/2)^{\frac{1}{2}}\,[\phi_1(1)\,\phi_2(2)-\phi_2(1)\,\phi_1(2)]\,X_t, \tag{16}$$

$$^1A_g\colon\ \psi_1 = \phi_1(1)\,\phi_1(2)\,X_s, \tag{17}$$

where X_s is the singlet and X_t the triplet spin function of the two electrons. The expressions for the expectation value of the Hamiltonian can be written down easily in terms of ϕ_1 and ϕ_2. The two states ψ_1 and ψ_2 interact with each other. We solve a two-dimensional secular equation to pick up the lower root, which we denote as E_N.

The characteristic feature of the present calculation is that the atomic orbitals are all expressed in the form of CGTO's with the scaling parameters. Accordingly we have computed all the necessary molecular integrals in good accuracy.

Variational Hartree-Fock Orbitals

First, we shall use the Hartree-Fock atomic orbitals of the carbon atom in the σ-core potential in the Hamiltonian (12). This is achieved, to a good approximation, by using appropriate GTO expansions of the Hartree-Fock orbitals. The general form of the radical parts of the s-type functions, h, $\bar{s}$ and s, may be written as

$$\sum_{i=1}^{10} C_i R_{g,1}(r;\zeta^2\alpha_i)\,. \tag{18}$$

For the orbitals $\bar{s}$ and s, $\{\alpha_i, C_i\}$ are taken from Table 1. Those for h are listed in Table 4. The parameter ζ is 1.0 for all of these s-type orbitals. The general form of the radial part of the p-type functions, x, y, z_1 and z_2, is given by

$$\sum_{i=1}^{6} C_i R_{g,2}(r;\zeta^2\alpha_i)\,, \tag{19}$$

where $\{\alpha_i, C_i\}$ are given in Table 2. We put $\zeta = 1.0$ for x and y, which implies that we use the unmodified Hartree-Fock $(2p)$ orbitals of the carbon atom for the σ-core potential. However, for the $2p\pi$ orbitals, z_1 and z_2, we retain the scaling parameters, ζ_1 and ζ_2 respectively, as the variational parameters in order to contract or expand the original form of the Hartree-Fock $(2p)$ orbital.

We have evaluated the necessary integrals for a number of combinations of ζ_1 and ζ_2.

$$\zeta_1 = 0.8\,(0.1)\,1.2\,, \qquad \zeta_2 = 0.1\,(0.1)\,1.2\,.$$

The energies of the first three states can be calculated individually by the variation principle. No attempt has been made to locate the optimum values of ζ_1 and ζ_2 more precisely than the employed grid of 0.1 mesh allows. The optimum values are ($\zeta_1 = 1.0$, $\zeta_2 = 1.0$) for E_N, ($\zeta_1 = 1.0$, $\zeta_2 = 0.9$) for E_T and ($\zeta_1 = 1.1$, $\zeta_2 = 0.2$) for E_V. The ionization potential is calculated by the formula,

$$I.P. = \langle \phi_1 | H | \phi_1 \rangle - E_N\,, \tag{20}$$

where

$$\langle \phi_1 | H | \phi_1 \rangle = \int \phi_1(\mu)\, H(\mu)\, \phi_1(\mu)\, \mathrm{d}V_\mu \tag{21}$$

is the energy of the ionized state. The lowest value of $\langle \phi_1 | H | \phi_1 \rangle$ is attained with $\zeta_1 = 1.1$. The relative positions of the states, N, T and V, are given in Table 6 together with the ionization potential.

Variational Slater-Type Orbitals

Taking advantage of the CGTO representation of atomic orbitals, we have conducted variational calculations based on the Slater-type orbitals. The GTO expansion of the STO's is discussed in detail by O-ohata *et al.* [9]. The most important point is that if an STO with unit exponent parameter is expressed as follows,

$$(n_s, l, m; 1.0)_s = \sum_i C_i (n_g, l, m; \alpha_i)_g\,, \tag{22}$$

then

$$(n_s, l, m; \zeta)_s = \sum_i C_i (n_g, l, m; \zeta^2 \alpha_i)_g\,. \tag{23}$$

Table 4 contains $\{\alpha_i, C_i\}$ for ($1s$) and ($2s$) STO's with unit exponent parameter, and Table 5 for ($2p$) STO with unit exponent parameter. The following choice of

Table 4. GTO *expansions of* ($1s$) *and* ($2s$) STO'*s with unit exponent parameter*[a]

i	$\alpha_i;(1s)$	$C_i;(1s)$	$\alpha_i;(2s)$	$C_i;(2s)$
1	1188.35	0.0000886225	432.099	−0.000163319
2	156.411	0.000622761	60.6176	−0.00120626
3	37.9276	0.00318156	14.1623	−0.00600006
4	10.5140	0.0139344	3.98351	−0.0223909
5	3.34954	0.0496090	1.30730	−0.0488578
6	1.18834	0.144647	0.263514	0.0457229
7	0.458596	0.313305	0.201066	0.265263
8	0.191073	0.401002	0.0991734	0.527807
9	0.0848076	0.203216	0.0497851	0.225661
10	0.0372356	0.0154199	0.0214081	0.00578359

[a] See O-ohata, Takata, and Huzinaga [9].

Table 5. GTO *expansion of* (2*p*) STO *with unit exponent parameter*[a]

i	α_i	C_i
1	39.9819	0.000264695
2	11.5715	0.00165711
3	3.94709	0.00998253
4	1.42281	0.0498749
5	0.548285	0.186151
6	0.227070	0.419549
7	0.100995	0.405415
8	0.0467295	0.0881035

[a] See O-ohata, Taketa, and Huzinaga [9].

ζ's, $\zeta = 1.0$ for h, $\zeta = 5.7$ for $\bar{s}$, $\zeta = 1.59$ for s, x and y, is equivalent, in good accuracy, to use the following set of STO's for the σ-core,

$$\begin{aligned} h &\sim \exp(-r)\,, \\ \bar{s} &\sim r\exp(-5.7r)\,, \\ s, x, y &\sim r\exp(-1.59r)\,, \end{aligned}$$

where the radial parts only are indicated. As for the z_1 and z_2 orbitals, we make use of the Eq. (23): We use $\{\alpha_i, C_i\}$ for (2*p*) shown in Table 5 but we insert parameters ζ_1 and ζ_2. This amounts to using

$$z_i \sim r\exp(-\zeta_i r)\,, \qquad (i = 1, 2)\,.$$

We have evaluated the necessary integrals for a number of combinations of ζ_1 and ζ_2,

$$\zeta_1 = 1.2\,(0.2)\,1.8\,, \qquad \zeta_2 = 0.2\,(0.2)\,1.6\,.$$

In order to confirm the energy minimum value of E_V at ($\zeta_1 = 1.6$, $\zeta_2 = 0.2$), we performed the calculation also for ($\zeta_1 = 1.6$, $\zeta_2 = 0.1$). The result of the calculations are summarized in Table 6.

Table 6. *Excitation energies and ionization energy for planar ethylene in electron volts*

State	Exptl.[a]	H–F[b]	STO[c]
$V(^1B_{1u})$	7.6	9.09	6.97
$T(^3B_{1u})$	4.6	4.07	4.22
$N(^1A_g)$	0.0	0.0	0.0
$V-T$	3.0	5.02	2.75
$I.P.$	10.52	10.72	8.50

[a] See Huzinaga [3].

[b] The variational Hartree-Fock treatment. ($\zeta_1 = 1.0$, $\zeta_2 = 1.0$) for N, ($\zeta_1 = 1.0$, $\zeta_2 = 0.9$), for T and ($\zeta_1 = 1.1$, $\zeta_2 = 0.2$) for V, ($\zeta_1 = 1.1$) for $\langle\phi_1|H|\phi_1\rangle$.

[c] The variational STO treatment ($\zeta_1 = 1.4$, $\zeta_2 = 1.4$) for N, ($\zeta_1 = 1.4$, $\zeta_2 = 1.2$) for T and ($\zeta_1 = 1.6$, $\zeta_2 = 0.2$) for V, ($\zeta_1 = 1.6$) for $\langle\phi_1|H|\phi_1\rangle$. This result roughly corresponds to the case (c) ($Z_\sigma = 3.18$) of Table 2 in the previous work [3].

Discussion

In the variational Hartree-Fock orbital treatment we obtained a bit too large *V-T* separation but the ionization potential is good. In the variational STO treatment the *V-T* separation is good but the ionization potentials is a little too small. However, the overall numerical results shown in Table 6 may be regarded as fairly satisfactory. An obviously disquieting but yet very interesting fact is that the shape of the π_g molecular orbital in the ${}^1B_{1u}$ state turns out to be extremely diffuse in both treatments. This was the finding made in the previous work [3]. As a matter of fact, the main purpose of the STO treatment in the present work has been to check the numerical accuracy of the previous calculation [3], and we conclude that the previous calculation has been confirmed essentially.

The *V-T* separation of the ethylene molecule has been playing an important role in the parameter adjustment of the semi-empirical molecular calculation. The result of the present work seems to call for a more close investigation of the nature of the ${}^1B_{1u}$ state of the ethylene molecule.

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