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Bond Orbital Calculations on the Methane and Silane Molecules

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The non-empirical calculations of CH_4 and SiH_4 are carried out by the bond orbital (BO) and McWeeny and Ohno (MBO) methods. The lowest total energies obtained in these calculations are -40.1621 and -290.1809 a.u. for CH_4 and SiH_4 respectively. The ordinary SC–LCAO–MO calculations are also made for the sake of comparison using the same parameters. The results are compared with the similar calculations of H_2O and NH_3, we can thus see that the BO and MBO calculations show almost the same features as in H_2O and NH_3.

With various approximations and different basis sets, many theoretical calculations have been done for a number of polyatomic molecules. The more complicated the molecular wave functions become, the less lucid the chemical intuition or pictorial image for the chemical bonds, lone pairs, and inner shells becomes. Hurley, Lennard-Jones, and Pople,[1] and Parr and Parks[2] gave satisfactory discussions of the separated-electron-pair method in which electrons in a molecule are classified into groups for the chemical bonds, lone pairs, and inner shells, and in which the total wave function is written as an anti-symmetrized product of the localized two-electron functions, one for each group. McWeeny and Ohno[3] have carried out the non-empirical calculations of the water molecule using such a concept. They proposed a method of constructing the electron-pair functions from orbitals with pair nonorthogonality which were not given by the former authors explicitly. They obtained a fairly good total energy as compared with the ordinary SC–LCAO–MO results. Tsuchida and Ohno[4] made a similar calculation of NH_3, and concluded that the general features were almost the same for H_2O and for NH_3.

In this investigation, we carried out the non-empirical calculations of CH_4 and SiH_4 using the SC–LCAO–MO, BO, and McWeeny and Ohno methods (They utilized

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[1] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc. Ser. A.*, **220**, 446 (1953).

[2] J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958).

[3] R. McWeeny and K. Ohno, *Proc. Roy. Soc. Ser. A*, **255**, 367 (1960).

[4] A. Tsuchida and K. Ohno, *J. Chem. Phys.*, **39**, 600 (1963).

the term "modified electron-pair method." Here we will call it the "modified bond orbital method," MBO). The MBO approximation is an extension of BO. We will describe these methods briefly in the following sections.

The CH_4 and SiH_4 molecules differ from H_2O and NH_3 in the point that the former molecules have no lone pair. In SiH_4, furthermore, the valence orbital quantum number is higher than in the others by one. Therefore, it seemed that it would be interesting to see, in the BO and MBO methods, whether or not the frozen-core approximation is as adequate in the CH_4 and SiH_4 molecules as in H_2O and NH_3.[3,4]

The basis sets used throughout this paper are the minimal Slater-type AO's. The orbital exponents have the following values, which were obtained from Slater's rules except for the hydrogen 1s AO's:

$$\delta_{1s}(C)=5.7,\ \delta_{2s}(C)=\delta_{2p}(C)=1.625 \text{ and } \delta_{1s}(H)=1.2$$

for CH_4, and:

$$\delta_{1s}(Si)=13.7,\ \delta_{2s}(Si)=\delta_{2p}(Si)=4.925,$$

$$\delta_{3s}(Si)=\delta_{3p}(Si)=1.383 \text{ and } \delta_{1s}(H)=1.2$$

for SiH_4. The molecular geometry is assumed to be tetrahedral for both molecules. The bond distances are fixed to be 2.05 a.u.[14] and 2.796 a.u.[5] for the C–H and Si–H bonds respectively.

SC-LCAO-MO Calculation

The CH_4 molecule has been studied by many authors using semi-empirical and non-empirical methods.[6–15] For the SiH_4 molecule, however, there have not been many studies.[16–18] Among others, Boers and Lipscomb[19] recently reported SC–LCAO–MO calculations with and without Si 3d AO's. The sets of orbital exponents and bond distances in our calculations are different from theirs. We made ordinary SC–LCAO–MO calculations[20] in order to compare them with the BO and MBO calculations.

TABLE 1. CH_4

1) Orbital energy and MO				
ε (a.u.)	H	1s	2s	2p
−11.2713 ($1a_1$)	−0.0058	0.9953	0.0279	0
−0.9366 ($2a_1$)	0.1587	−0.2016	0.6626	0
−0.5455 ($1t_2$)	0.2840	0	0	0.5957
−0.5455 ($1t_2$)	0.2840	0	0	0.5957
−0.5455 ($1t_2$)	0.2840	0	0	0.5957
2) Atomic population				
Orbital	H	1s	2s	2p
Population	0.865	1.996	1.271	1.091
3) Total energy			−40.1130 a.u.	

The results of the calculations on CH_4 and SiH_4 are shown in Tables 1 and 2, along with the atomic populations[21] and total energy, which are in reasonable agreement with the values of Palke and Lipscomb[13] and of Boers and Lipscomb.[19]

BO Calculation

Methane. Here we transformed the original nonorthogonal basis set:

$$a = (1s, 2s, 2p_x, 2p_y, 2p_z, H_1, H_2, H_3, H_4) \tag{3}$$

where H_i is the 1s AO of the ith hydrogen atom, into the orthonormalized basis:

TABLE 2. SiH_4

1) Orbital energy and MO						
ε (a.u.)	H	1s	2s	3s	2p	3p
−68.648 ($1a_1$)	0.001	0.995	0.016	−0.003	0	0
−6.001 ($2a_1$)	−0.009	−0.343	1.047	0.050	0	0
−4.110 ($1t_2$)	0.011	0	0	0	0.989	0.066
−4.110 ($1t_2$)	0.011	0	0	0	0.989	0.066
−4.110 ($1t_2$)	0.011	0	0	0	0.989	0.066
−0.738 ($3a_1$)	0.188	0.054	−0.192	0.648	0	0
−0.510 ($2t_2$)	0.296	0	0	0	−0.145	0.537
−0.510 ($2t_2$)	0.296	0	0	0	−0.145	0.537
−0.510 ($2t_2$)	0.296	0	0	0	−0.145	0.537
2) Atomic population						
Orbital	H	1s	2s	3s	2p	3p
Population	0.967	2.000	1.997	1.254	1.987	0.973
3) Total energy				−290.1690 a.u.		

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19) F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969).

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$$\boldsymbol{b} = (1s, b_1, h_1, b_2, h_2, b_3, h_3, b_4, h_4) \quad (4)$$

by the procedure of McWeeny and Ohno.[3] That is, all the valence orbitals were Schmidt-orthogonalized to the carbon inner shell (1s), the carbon 2s' and 2p orbitals were tetrahedrally hybridized, and finally all the obtained orbitals were orthonormalized according to Lowdin's method. The result is expressed by the matrix form as:

$$\boldsymbol{b} = \boldsymbol{aV} \quad (5)$$

where $\boldsymbol{V}$ is the (9×9) transformation matrix. The orthonormalized orbitals, b_i and h_i, were used to construct the bond orbitals (BO's). As the b_i points to the *i*th H atom, the *i*th BO is defined by:

$$B_i = \sqrt{1-\lambda^2}\, b_i + \lambda h_i \quad (6)$$

where λ is a variational parameter. We constructed the ground-state wave function from these BO's as follows:

$$\Psi = \det|1s\bar{1}\bar{s}B_1\bar{B}_1B_2\bar{B}_2B_3\bar{B}_3B_4\bar{B}_4|, \quad (7)$$

the orbitals without and with a bar in the Slater determinant accomodate electrons with α and β spins respectively.

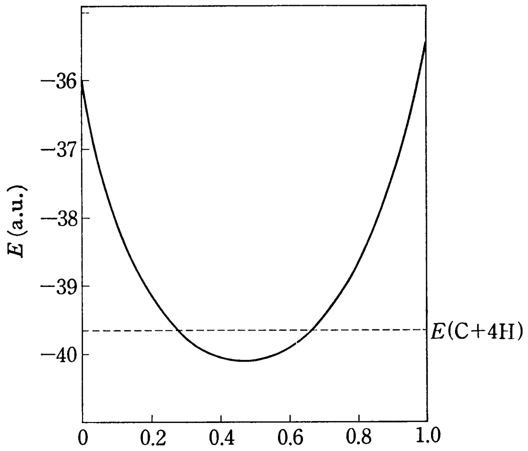

Fig. 1. The total energy of CH_4 as a function of λ^2. The dotted line is the energy of four atoms (E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

The total energy is expressed as a function of the parameter, λ^2, the calculated results are shown in Fig. 1. The variational parameter which makes the total energy minimum is found to be λ^2=0.46. This value is very close to those for H_2O (λ^2=0.43) and NH_3 (λ^2=0.42). The minimum value, −40.1074 a.u., of the total energy is only slightly higher than the SC–LCAO–MO result, −40.1130 a.u., presented in the previous section.

Silane. The valence orbitals of the Si atom are the 3s and 3p AO's, and we assume that the 2s and 2p AO's also form the inner shells. The basis set, $\boldsymbol{a}$, is transformed into the orthonormalized basis set, $\boldsymbol{b}$, in the same manner as in CH_4:

$$\boldsymbol{a} = (1s, 2s, 3s, 2p_x, 2p_y, 2p_z, 3p_x, 3p_y, 3p_z, H_1, H_2, H_3, H_4) \quad (8)$$

$$\boldsymbol{b} = (1s, 2s, 2p_x, 2p_y, 2p_z, b_1, h_1, b_2, h_2, b_3, h_3, b_4, h_4) \quad (9)$$

$$= \boldsymbol{aV} \quad (10)$$

where $\boldsymbol{V}$ is the (13×13) transformation matrix. The ground-state wave function is expressed as:

$$\Psi = \det|(K^2)(L^8)B_1\bar{B}_1B_2\bar{B}_2B_3\bar{B}_3B_4\bar{B}_4| \quad (11)$$

where (K^2) and (L^8) indicate $(1s\bar{1}\bar{s})$ and $(2s\bar{2}\bar{s}2p_x\bar{2}\bar{p}_x2p_y\bar{2}\bar{p}_y2p_z\bar{2}\bar{p}_z)$ respectively, and where B_i are the BO's defined in Eq. (6).

In Fig. 2 the total energy is given as a function of λ^2. We find the minimal energy to be −290.1267 a.u. when λ^2 is 0.48; this value is not very different from that of CH_4. The total energy is, however, considerably higher than that of the SC–LCAO–MO result, −290.1690 a.u.

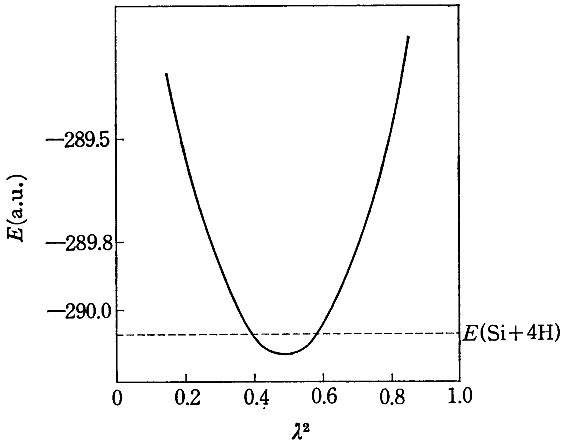

Fig. 2. The total energy of SiH_4 as a function of λ^2. The dotted line is the energy of four atoms (E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

MBO Calculation

By using the orthonormalized orbitals, b_i and h_i, obtained in the previous section, two BO's, B_i and $\tilde{B}_i$, are defined as follows:

$$B_i = \sqrt{1-\lambda^2}\, b_i + \lambda h_i \quad (12)$$

$$\tilde{B}_i = \sqrt{1-\mu^2}\, b_i + \mu h_i, \quad (13)$$

from which we construct the electron-pair function of the *i*th bond as Eq. (14):

$$(B_i\tilde{B}_i) = N[\det|B_i\bar{\tilde{B}}_i| + \det|\tilde{B}_i\bar{B}_i|] \quad (14)$$

where N is a normalization constant. The total wave functions of the ground state are given by Eqs. (15) and (16) for CH_4 and SiH_4 respectively:

$$\Psi_m = \det|(K^2)(B_1\tilde{B}_1)(B_2\tilde{B}_2)(B_3\tilde{B}_3)(B_4\tilde{B}_4)| \quad (15)$$

$$\Psi_s = \det|(K^2)(L^8)(B_1\tilde{B}_1)(B_2\tilde{B}_2)(B_3\tilde{B}_3)(B_4\tilde{B}_4)|. \quad (16)$$

Equation (14) reflects the concept of the "different orbitals for different spins"; and the total energy expressions for CH_4 and SiH_4 become a little more complicated because of the overlap between B_i and $\tilde{B}_i$, which is given as $\sqrt{(1-\lambda^2)(1-\mu^2)}+\lambda\mu$.

The dependence of the total energy on the parameters, λ^2 and μ^2, is shown in Figs. 3 and 4 for each molecule. The best pairs of the parameters, λ^2 and μ^2, are 0.74 and 0.19, and 0.78 and 0.20, which give the total energies of −40.1621 and −290.1809 a.u. for CH_4 and SiH_4 respectively. The lowering of the total energy from the SC–LCAO–MO result is bigger in CH_4 than in SiH_4. However, the lowering from the BO calculation is about the same for both molecules.

In Table 3 the results are summarized, along with the results of other calculations for the sake of comparison.

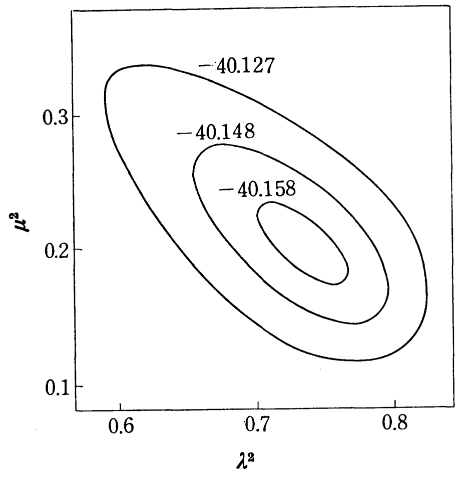

Fig. 3. The contour map of the total energy of CH_4 (in a.u.).

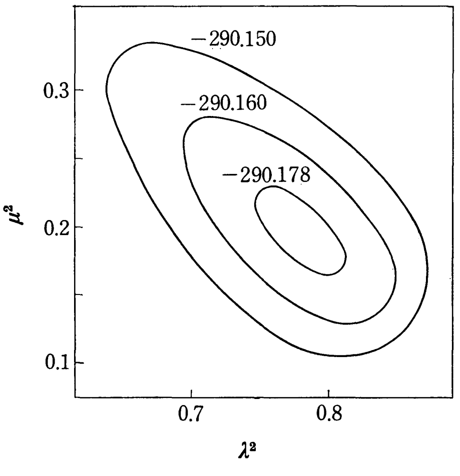

Fig. 4. The contour map of the total energy of SiH_4 (in a.u.).

TABLE 3. TOTAL ENERGY FOR CH_4 AND SiH_4 (IN a.u.)

	CH_4	SiH_4
SC–LCAO–MO (Present)	−40.1130	−290.1690
SC–LCAO–MO	−40.1140$^{a)}$	−290.4250$^{b)}$
OC–SCF–MO$^{d)}$	−39.8660$^{c)}$	−290.1024$^{c)}$
BO Appro.	−40.1074 (λ^2=0.46)	−290.1267 (λ^2=0.48)
MBO Appro.	−40.1621 (λ^2=0.74, μ^2=0.19)	−290.1809 λ^2=0.78, μ^2=0.20)
Experiment	−40.522	−292.141

a) Ref. 13.
b) Ref. 19 (The best atom orbital exponents were used for the Si atom).
c) Ref. 17.
d) One-Center Basis Set SCF-MO's.

Discussion

Tsuchida and Ohno[4] discussed the degree of localization for the two basic AO's of NH_3, which correspond to the basic AO's given in Eqs. (3) and (4) for CH_4 in our calculations. They calculated the self-Coulomb integral $(\chi\chi|\chi\chi)$[23] as the measure of the localization for the atomic orbital, χ. In our orthonormalized and original AO's, the self-Coulomb integrals are:

$$(hh|hh) = 0.8432 \text{ a.u.}$$

$$(HH|HH) = 0.7500 \text{ a.u.}$$

for CH_4, and:

$$(hh|hh) = 0.8722 \text{ a.u.}$$

$$(HH|HH) = 0.7500 \text{ a.u.}$$

for SiH_4. We can see that the orthonormalized AO's are more localized than the original AO's in both molecules.

In the MO theory, as is well known, a wave function given by a single Slater determinant is invariant with respect to the unitary transformation among the doubly-filled MO's. Moreover, we can construct, from the MO's in Tables 1 and 2, the equivalent orbitals,[24–27] ϕ_i, which may be considered as localized orbitals along the ith C–H or Si–H bond. For example, ϕ_2 of SiH_4 may be expressed as follows:

$$\phi_2 = \frac{1}{2}(3a_1 + 2t_{2,x} + 2t_{2,y} + 2t_{2,z}),$$

where other MO's are assumed to form purely the inner shells of the Si atom, not entering into the chemical bond, and are neglected. Rewritten in terms of original AO's, the equivalent orbital is:

$$\phi_2 = 0.027(1s) - 0.096(2s) + 0.324(3s) - 0.073(2p) + 0.268(3p) + 0.864(H_2) - 0.163(H_1 + H_3 + H_4).$$

Comparing the above equivalent orbital with the corresponding bond orbital, B_2, at the optimum parameter:

$$B_2 = 0.021(1s) - 0.079(2s) + 0.301(3s) - 0.055(2p) + 0.287(3p) + 0.521(H_2) - 0.034(H_1 + H_3 + H_4),$$

we can see that the two orbitals, ϕ_2 and B_2, are very similar; this is the same in the case of the CH_4 molecule. It is notable that we can get such similar orbital by entirely different approaches. Such a similarity of the two orbitals has already been shown in NH_3.[4]

The BO calculation gives a higher total energy than does the SC–LCAO–MO calculation, but the MBO calculation gives a lower one in both molecules if the same basis set is used. In SiH_4, as is shown in Eq. (9), the 2s and 2p AO's are fixed as inner shells and are not allowed to take part in the binding. The gross atomic populations of the 2s and 2p AO's resulting from the SC–LCAO–MO calculation are smaller than

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[25] G. G. Hall and J. E. Lennard-Jones, *ibid.*, **202**, 155 (1950).
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[27] G. G. Hall, *ibid.*, **202**, 336 (1950). About the localized orbitals, see also K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962) and C. Edmiston and K. Ruedenberg, *ibid.*, **35**, 457 (1963).

2. This seems to be the reason why the energy lowering from the SC–LCAO–MO results by the MBO method is smaller in SiH_4. In the MBO calculation we take into account the electron correlation between the different spins, α and β, to some extent. However, no such consideration is taken into account in the BO calculation. The optimum values of λ^2 and μ^2 are considerably different from that of λ^2 in the BO for both the molecules. This is also clearly reflected in the B_i and $\tilde{B}_i$ orbitals, given in Eqs. (12) and (13). These orbitals for SiH_4 are as follows:

$$B_2 = 0.014(1s) - 0.064(2s) + 0.035(3s) - 0.031(2p) + 0.087(3p) + 0.901(H_2) - 0.022(H_1+H_3+H_4),$$

$$\tilde{B}_2 = 0.025(1s) + 0.087(2s) + 0.527(3s) - 0.073(2p) + 0.452(3p) + 0.110(H_2) - 0.052(H_1+H_3+H_4).$$

The energy lowering from the BO approximation should be regarded as resulting from this intrabond correlation.

To summarize briefly, we can obtain, without self-consistent iterative calculations, total energies comparable to or slightly better than the SC–LCAO–MO results. And the optimum polarization parameters, in the BO method, take about the same value in CH_4, SiH_4, NH_3, and H_2O. It may be considered that the above obtained values are useful as the optimum polarization parameters for the covalent X–H bond of other molecules.

We are now preparing the application of the BO method to the excited states of CH_4.[28]

The authors wish to express their hearty thanks to Professor K. Ohno for his valuable discussions.

The molecular integrals were calculated on the HITAC 5020E Computer at the University of Tokyo Computer Centre, using the library program written by Professor H. Taketa. The authors are very grateful to him for his helpful communications about the use of the program (Y4/TC/AD05; Molecular Integral over CGTO).

The rest of the calculations were carried out on the NEAC 2200 Model 700 Computer at the Tohoku University Computer Center and on the HIPAC 103 Computer at Hirosaki University.

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[28] The anti-bonding BO's are defined as $A_i=\lambda b_i-\sqrt{1-\lambda^2}h_i$