# Bond Orbital Calculations on the Methane and Silane Molecules. II. Vertical Transition Energies of the Lower Singlet-Excited States of $CH_4$

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The vertical singlet-transition energies of $CH_4$ were calculated using the BO method. Two types of basis sets, minimal and extended, were employed. The vertical transition energy of the lowest singlet state of $CH_4$ was found to be 9.1 eV using the extended-basis set. This transition is assigned to a Rydberg-type transition in agreement with experiments. The other lower excited-states of $CH_4$ may also be assigned to Rydberg transitions. The main features of the present BO calculations do not differ greatly from those of other extended-basis MO calculations. The total energy of the ground state is discussed briefly.

In previous bond orbital (BO) calculations1) for the methane and silane molecules, the total energies of the ground states were calculated in this, as well as the ordinary SCF-LCAO-MO, method and the polarization parameters were approximately equal to those of the O–H and N–H bonds in the water2) and ammonia3) molecules, respectively. It appears interesting to investigate how well excited states are expressed by the BO method. Among the many properties of the excited molecular states our interest here is mainly in the lowest vertical transition energies for the present BO calculations. The total energy of the ground state of $CH_4$ will be discussed briefly.

Recently, extended-basis MO calculations are frequently carried out on the electronic structure and spectra of medium-sized molecules using Gaussian-type orbitals (GTO) as atomic orbitals (AO).4–12) These calculations have succeeded in explaining the electronic spectra of organic molecules, especially Rydberg-type transitions. The present authors have already calculated the vertical transition energies of $CH_4$ using the MO method,13) and found that the lowest excited state of $CH_4$ can be assigned to a transition of an electron from the $1t_2$ to the 3s-like Rydberg MO's in agreement with the electron-impact experiments of Harshbarger and Lassetre.14) Here BO calculations for the vertical transition energies of methane obtained using two basis sets (*i.e.*, minimal and extended-basis sets) are presented. BO-type calculations have already been performed by Klessinger and McWeeny15) using the group-function method with minimal Slater-type AO (STO) as the basis set. They discussed only two excited states, $A_1$ and $T_2$, which were described by linear combinations of four locally-excited configurations (excitons), with the results not in quantitative agreement with experiment.

In this study other excited states which can also be constructed from other types of electron promotion (*vide infra*) were investigated. The molecular geometry is assumed to be $T_d$ and the bond distance is fixed at $R(C\text{–}H)=2.05$ a.u.16) The STO are used as the basis AO, with the orbital exponents:

$$\delta_{1s}(C) = 5.7,\ \delta_{2s}(C) = \delta_{2p}(C) = 1.625,$$
$$\delta_{3s}(C) = \delta_{3p}(C) = 0.4388, \text{ and } \delta_{1s}(H) = 1.2.$$

These values were obtained from Slater's rules, except for $\delta_{1s}(H)$. All molecular integrals were calculated on the HITAC 8800/8700 Computer at the University of Tokyo Computer Centre, using the library program written by Taketa (Y4TC/AD05; Molecular Integrals over CGTO), where the molecular integrals were calculated over the composite GTO's.17) The CI calculations were carried out on the NEAC 2200 Model 700 Computer at the Tohoku University Computer Centre.

## Method of Calculations

In previous BO studies, the original non-orthogonal basis set,

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

where $H_i$ is the $i$th hydrogen 1s AO, was transformed into the orthonormalized basis set,

$$\mathbf{b} = (1s, b_1, h_1, b_2, h_2, b_3, h_3, b_4, h_4), \tag{2}$$

using the procedure of McWeeny and Ohno.2) 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 orbitals obtained were orthonormalized according to Löwdin's method. The orthonormalized orbitals, $b_i$ and $h_i$, were used to construct the bond orbitals (BO) for the $i$th bond, thus

$$B_i = \lambda^2 h_i + \sqrt{1-\lambda^2}\, b_i, \tag{3}$$

where $\lambda$ is a variational parameter. Now we assume the following antibonding BO ($A_i$) for constructing the excited state of $CH_4$,

$$A_i = \mu^2 b_i - \sqrt{1-\mu^2}\, h_i. \tag{4}$$

In order to maintain orthogonality between the ground and excited states, we make the assumption that the variational parameters, $\lambda$ and $\mu$, in Eqs. 3 and 4 are identical, such that $\lambda^2=\mu^2=0.46$, the optimum value for the ground state of $CH_4$, throughout the present calculations.1) The number, and types of electron promotion taken into account will be discussed below in detail.

*Extended-basis Calculations*: The extra-valence AO, the 3s and 3p orbitals of the carbon atom, were added to the minimal-basis set. In the calculations, the following suppositions were made. First, the bonding BO are the same as those of the minimal-basis calculations. Second, the pseudo-antibonding BO are expressed by only the extra-valence AO, thus

$$A_i = \frac{1}{2}(3\mathrm{s} \pm 3\mathrm{p_x} \pm 3\mathrm{p_y} \pm 3\mathrm{p_z}), \tag{5}$$

where the 3s and 3p AO are orthonormalized to the inner and valence shell AO of the C atom using the Schmidt procedure, and the signs are chosen to form directed hybridized orbitals toward to the $i$th H atom, as in the case of $\mathrm{b}_i$ in Eqs. 3 and 4. Finally, we neglect the overlap integrals between the $A_i$ and the hydrogen 1s AO, *i.e.*, $S(A_i, B_i)=0$,[20] to insure orthogonality for the $A_i$ and $B_i$. The form of the pseudo-antibonding orbitals is of great advantage to constructing symmetry adapted basis functions, and should be regarded as virtually equivalent orbitals.

*Wavefunctions of the Excited States*: We can consider many types of electron promotion from the bonding orbitals ($B_i$) to the antibonding or pseudo-antibonding orbitals ($A_i$). The excited electronic configurations arising from one- and two-electron promotion are taken into account in the CI calculations. The types of electron promotion actually considered are

$$\{(B_i)^2\} \longrightarrow \{(B_i)(A_j)\}, \qquad (16)$$
$$\{(B_i)^2\} \longrightarrow \{(A_j)^2\}, \qquad (16)$$
$$\{(B_i)^2\} \longrightarrow \{(A_i)(A_j)\}, \quad i \neq j, \qquad (12)$$
$$\{(B_i)^2\} \longrightarrow \{(A_k)(A_l)\}, \quad i \neq k \neq l, \qquad (12)$$
$$\{(B_i)^2(B_j)^2\} \longrightarrow \{(B_i)(B_j)(A_i)^2\}, \quad i \neq j, \qquad (12)$$

and

$$\{(B_k)^2(B_l)^2\} \longrightarrow \{(B_k)(B_l)(A_i)^2\}, \quad i \neq k \neq l, \qquad (12)$$

where an electron promotion, such as $\{(B_i)^2(B_j)^2\} \rightarrow \{(B_i)(B_j)(A_i)^2\}$ means that two electrons in the bonding BO, $B_i$ and $B_j$, are excited to the vacant antibonding or pseudo-antibonding BO ($A_i$) at the same time and the other doubly-occupied orbitals remain unchanged. The numbers in parenthesis are the possible ways of exciting the electron from four bonding BO to four antibonding or pseudo-antibonding BO.

The symmetry-adapted basis functions of the excited states are easily obtained by taking appropriate linear combinations of the above excited configurations. From the fact that the direct product $(\mathrm{A_1+T_2})\otimes(\mathrm{A_1+T_2})$ is $\mathrm{2A_1+E+T_1+3T_2}$, for example, we can take the following combinations of four singly-excited configurations as one of the CI basis functions for the states $\mathrm{A_1}$ and $\mathrm{T_2}$

$$\Psi(\mathrm{A_1\ or\ T_2}) = c_1\phi(B_1 \rightarrow A_1) + c_2\phi(B_2 \rightarrow A_2) + c_3\phi(B_3 \rightarrow A_3) + c_4\phi(B_4 \rightarrow A_4), \tag{6}$$

where the symbol A is used to denote both the symmetry species and pseudo-antiboding BO, although being careful to avoid confusion. The final excited-state wavefunction will be expressed as a linear combination of these symmetry-adapted basis functions.

## Results and Discussion

The vertical transition energies of the lower excited states are given in Table 1, along with other MO calculations and experimental results. The total enrgy of the ground state of $CH_4$ is improved considerably by the configuration interaction. The results of the CI are shown in Table 2, where the results indicate the extent that individual excited configurations contribute to the improvement of the total energy. In the minimal-basis calculations, the doubly-excited configurations, such as $(B_i)^2 \rightarrow (A_j)^2$, are most affected by the CI calculations. Especially, the energy lowering due only to local configurations, *i.e.*, $(B_i)^2 \rightarrow (A_i)^2$ is calculated to be −0.0535 a.u., which amounts to about 88% of the entire energy decrease. This results from inclusion of intra-bond electron correlation. This can be compared with the result (0.0517 a.u.) of previous modified BO calculations,[1] where electron correlation between orbitals of two different spins (different orbitals for different spins) were included. In the extended-basis calculations, on the other hand, the singly-excited configurations make exclusively dominant contributions to the decrease of the total energy. As for the results of the minimal-basis calculations, the energy decrease due only to local configurations, *i.e.*, $(B_i)^2 \rightarrow (B_iA_i)$, is very great (−0.0323 a.u.), which amounts to about 86% of the total energy decrease.

TABLE 2. ENERGY DECREASE DUE TO CI (a.u.)

| Excited configuration | Minimal basis | Extended basis |
|---|---|---|
| $(B_i)^2 \rightarrow (B_iA_j)$ | −0.0026 | −0.0376 |
| $(B_i)^2 \rightarrow (A_j)^2$ | −0.0550 | −0.0001 |
| Others | −0.0035 | −0.0000 |
| Total | −0.0611 | −0.0377 |
| Total energy | −40.1658 | −40.1451 |

Turning our attention now to the predicted excited states, the symmetry of the calculated lowest excited-state, as seen from Table 1, is $T_2$ in all cases except for the minimal-basis MO calculations. In spite of the

TABLE 1. VERTICAL TRANSITION ENERGIES (eV)

| State | Minimal basis | | | | Extended basis | | | | | Obsd[f] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (I)[a] | (II)[b] | MO[c] | GF[d] | (I) | (II) | MO[c] | EOM[e] | CI[e] | | |
| $1T_2$ | 20.52 | 17.43 | 23.78 | 21.11 | 9.37 | 9.11 | 11.62 | 10.24 | 10.76 | 9.7 | 10.3 |
| E | 21.97 | 22.56 | 21.93 | | 13.37 | 13.28 | 12.49 | 11.72 | 12.40 | | |
| $2T_2$ | 26.08 | 26.49 | 24.08 | | 13.44 | 13.29 | 12.50 | 11.68 | 12.47 | 11.7 | |
| $1A_1$ | 27.40 | 27.79 | 27.65 | 28.11 | 14.52 | 14.36 | 13.06 | 12.38 | 13.55 | | |
| $T_1$ | 27.67 | 29.26 | 21.50 | | 18.89 | 18.89 | 12.54 | 11.77 | 12.43 | | |
| $3T_2$ | 33.47 | 33.76 | | | 21.95 | 21.63 | 23.67 | | | | |
| $2A_1$ | 36.21 | 36.04 | | | 23.50 | 23.38 | 27.25 | | | | |

a) Single-excitation CI. b) Double-excitation CI. c) See Ref. 13. d) See Ref. 15. e) See Ref. 11. f) See Ref. 18.

fact that the $T_2$ state participates in an electronically-allowed transition, the vertical transition energies calculated using the minimal-basis set are too high in comparison with the experimental results, and moreover exceed the ionization potential.[18] This is common for non-empirical calculations using the minimal-basis set.[10,15] The situation, however, is changed drastically by introducing into the basis set the extra-valence AO of the C atom. The lowest excited state is calculated to be 9.4 and 9.1 eV above the ground state for cases (I) and (II), respectively (see footnotes to Table 1). The symmetry of this state is that of the dipole-allowed $T_2$ state for both calculations. The agreement with experiment is fairly good. Williams and Poppinger have calculated the transition energies of $CH_4$ using the CI and EOM methods, for which they also used the extra-valence 3s and 3p AO of the C atom as bases.[11] As is seen from Table 1, their results show almost the same tendency as the present BO calculations with respect to the transition energies, but there are some differences for the relative ordering of the calculated excited states. The BO results do not differ in main features from the MO results, although it is of note that the BO lowest $T_1$ state is considerably higher than that for the MO calculations.

In the extended-basis BO calculations, the results of CI with both singly- and doubly-excited configurations give lower transition energies than do those including only single excitations. For the minimal-basis BO calculations, on the other hand, inverse results are obtained, except for only two states ($1T_2$ and $2A_1$). This appears to conflict with the conventional SCF-LCAO-MO CI results that the doubly-excited CI give higher vertical transition energies than do the singly-excited CI, because of the improvement of the ground-state total energy for the former CI calculations. This may be understood from the BO-CI results shown in Table 2.

It is interesting to examine the nature of the lowest excited state. It has already been shown, for MO calculations,[13] that the lowest vacant MO ($3a_1$) resembles the 3s AO of the C atom which is orthogonalized to the 2s and 1s AO using Schmidt procedure, and the lowest singlet excited-state is assigned to the Rydberg transition, *i.e.*, from the triply degenerate $2t_2$ MO to the above 3s-like MO. In the present BO calculations, this $T_2$ state is expressed as

$$\begin{aligned} {}^1\Psi(T_2) = {} & 0.212\{\phi(B_1\to A_1)+\phi(B_2\to A_2) \\ & -\phi(B_3\to A_3)-\phi(B_4\to A_4)\} \\ & +0.173\{\phi(B_1\to A_2)+\phi(B_2\to A_1) \\ & -\phi(B_3\to A_4)-\phi(B_4\to A_3)\} \\ & +0.294\{\phi(B_1\to A_3)+\phi(B_2\to A_4) \\ & -\phi(B_3\to A_1)-\phi(B_4\to A_2)\} \\ & +0.294\{\phi(B_1\to A_4)+\phi(B_2\to A_3) \\ & -\phi(B_3\to A_2)-\phi(B_4\to A_1)\} \\ & +\text{doubly-excited configurations,} \end{aligned}$$

where the $\phi(B_i\to A_j)$ denote the excited singlet configurations arising from one-electron promotion from the $B_i$ to the $A_j$ orbitals. The lowest excited state is not expressed only by local excitation. The contribution of the doubly-excited configurations to this state is small.

It is seen that the lower excited states of $CH_4$ are not explained by the valence-shell transitions using the minimal-basis calculations, but can be understood to be Rydberg-type transitions obtained using the extended-basis calculations. This agrees with the results of the extended-basis MO calculations.[13] Here, no consideration was made of the interaction between the Rydberg and valence-shell transitions. However, more extended-basis MO calculations will be presented elsewhere,[19] in which the mixing of the above two types of transitions will be discussed.

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