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MO Calculations of the Rydberg Transitions of the Methane Molecule

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The vertical transition energies of both the Rydberg and valence-shell type transitions of CH_4 were calculated by the use of the *ab initio* SC-LCAO-MO method. We used Slater-type AO's as the basis AO's and added the extra-valence AO's (3s, 3p, 4s, and 4p) of a carbon atom to the minimal-basis set in order to express the Rydberg MO's. From the limited CI calculations, the mixing expressed in terms of the orthogonalized AO's between the Rydberg and valence-shell transitions was shown to be little. The lowest two absorption bands near 9.7 and 11.7 eV were identified as a 3s-like Rydberg transition with a 3p-like one and a 4s-like Rydberg transition with a 4p-like one respectively. The total energy and Mulliken population analysis were also calculated and compared with the results of the minimal-basis calculations.

The studies of the molecular Rydberg states, though not many, have been done continuously for a long time from both experimental and theoretical points of view.[1–15] Recently the Rydberg states of the methane molecule, as well as of water[5,9,15,16] and ethylene[12,16,17] molecules, have been studied in detail because of its simple molecular form. Methane has a diffuse but entirely structureless band system, with a maximum at 9.7 eV in its far ultra-violet absorption spectra.[8] Mulliken[1] identified this band as a $1t_2 \rightarrow 3s$ (Rydberg orbital) transition, using the united atom model. However, another assignment of the valence-shell transition, $1t_2 \rightarrow 2t_2$, is possible. Katagiri and Sandorfy,[18] in fact, carried out P-P-P-type semi-empirical calculations and obtained reasonable values of the transition energies for several *n*-alkanes. Ohmichi *et al.*[19] made modified CNDO calculations of several saturated compounds. They identified the absorption spectra of methane as being due to the valence-shell transitions, in agreement with the Katagiri and Sandorfy results. In 1971 Salahub and Sandorfy[13] carried out CNDO-type calculations with an extended-basis set (RCNDO), in which they used these extra-valence atomic orbitals: 3s and 3p AO's, for a carbon atom and 2s and 2p AO's for a hydrogen atom. The results show that the contribution of the Rydberg orbital to the first excited state of CH_4 is very low. From these semi-empirical calculations, it seems likely that the first band of CH_4 can be explained as the valence-shell transition. Pauzat *et al.*,[20] on the other hand, carried out non-empirical GTO-basis calculations of the ionization and transition energies of this molecule. They used a diffuse molecular orbital (Rydberg MO), as Salahub and Sandorfy did in their RCNDO calculations. The result for the first excited state gave features different from those of Salahub and Sandorfy in its Rydberg character. Williams and Poppinger also carried out non-empirical calculations of CH_4 and H_2O by means of the Equations of Motion and the configuration interaction (CI) method; they obtained a good agreement with the Pauzat *et al.* calculations.

From the experiments on the electron-impact spectra, Harshbager *et al.*[23] assigned the first band to the $1t_2 \rightarrow 3a_1$ (carbon 3s-like MO) Rydberg transition, which is split by Jahn-Teller distortion into two peaks, 9.7 eV and 10.3 eV. Furtheremore, they discussed the band near 11.7 eV and assigned it to the Rydberg transition from $1t_2$ to the carbon 4s-like MO. In our work we used, in order to clarify the nature of the excited states of CH_4, the extra-valence AO's, 3s, 3p, 4s, and 4p AO's of a carbon atom in addition to the minimal-basis set. The Slater-type AO's were used for these AO's. All the following orbital exponents of the STO's except the hydrogen 1s AO's are obtained from Slater's rules: $\delta_{1s}=5.7$, $\delta_{2s}=\delta_{2p}=1.625$, $\delta_{3s}=\delta_{3p}=0.4833$, and $\delta_{4s}=\delta_{4p}=0.3625$ for the carbon atom, and $\delta_{1s}=1.2$ for the hydrogen atom. The symmetry of the molecule is assumed to be T_d, and the nuclear distance is fixed as $R(C\text{–}H)=2.05$ a.u.

Calculation and Discussion

The ordinary SC-LCAO-MO calculations are performed for the ground state by the use of the extended-basis set (minimal-basis set plus the extra-valence 3s, 3p, 4s, and 4p AO's of a carbon atom). All the molecular integrals are calculated by using the library program of the University of Tokyo Computer Centre (Y4/TC/ADO5), where the molecular integrals are calculated over the composite GTO's, so we expanded all s-type STO's by 8-terms of the GTO's and the 2p, 3p, and 4p STO's by 6, 6, and 4-terms of GTO's respectively.[27]

The orbital exponents of used AO's are not optimized; *i.e.*, they are fixed as Slater's values. Hosoya[25] calculated the orbital exponents of the carbon Rydberg AO's, *i.e.*, 3s, 3p, and 3d, by optimizing the one-electron energy. He expanded the Rydberg orbitals in terms of several STO's and thus obtained the values of 0.55 and 0.465 for 3s and 3p STO's respectively, which contribute mainly to the optimized Rydberg orbitals. These values are not very different from Slater's values. This shows that, for the orbital exponents of the extra-valence AO's we may use the values obtained from Slater's rules as the first approximation. The calculated SC-LCAO-MO's, both occupied and unoccupied, are shown in Table 1, along with the orbital and total energies. The predicted total energy of the ground state is lower than that of our previous minimal-basis calculations by only 0.0154 a.u.[21] This shows that the employment of the extended-basis set does not affect the total energy greatly. The resulting virtual MO's, however, turn out to be useful in the calculations of the transition energies, as will be shown below.

The gross atomic and bond populations found by Mulliken population analysis are as follows:

Table 1. The MO's and total energy of CH_4

Orbital energy and MO ε_i (a.u.)	1s	2s	3s	4s	2p	3p	4p	H
$-11.2869\,(1a_1)$	0.9953	0.0277	0.0000	0.0002	0.	0.	0.	−0.0058
$-0.9460\,(2a_1)$	−0.2050	0.6817	−0.0576	0.0355	0.	0.	0.	0.1588
$-0.5547\,(1t_2)$	0.	0.	0.	0.	0.5863	0.0372	−0.0193	0.2841
$0.0095\,(3a_1)$	0.0097	−0.0484	0.0002	0.9997	0.	0.	0.	0.0054
$0.0181\,(2t_2)$	0.	0.	0.	0.	−0.0135	−0.1878	1.1321	0.0022
$0.0608\,(4a_1)$	0.0584	−0.2422	1.5605	−1.1581	0.	0.	0.	−0.0212
$0.1049\,(3t_2)$	0.	0.	0.	0.	−0.2099	1.5695	−1.0389	0.1027
$0.6382\,(4t_2)$	0.	0.	0.	0.	1.1242	0.2167	−0.1202	0.6723
$0.8347\,(5a_1)$	0.1928	−1.7567	−0.5338	0.3168	0.	0.	0.	0.7704
Total energy				−40.1284 a.u.				

$$n(\mathrm{C}) = 6.553,\ n(\mathrm{H}) = 0.862,\ n(\mathrm{C\text{-}H}) = 0.784,$$

and

$$n(\mathrm{H\text{-}H}) = -0.042.$$

Our previous minimal-basis calculations, on the other hand, gave the following results:

$$n(\mathrm{C}) = 6.539,\ n(\mathrm{H}) = 0.865,\ n(\mathrm{C\text{-}H}) = 0.784,$$

and

$$n(\mathrm{H\text{-}H}) = -0.042.$$

There is little difference. The extra-valence AO's of the carbon atom seem to have no effect in the C–H binding. If we use the extra-valence AO's of the hydrogen atom also, an increase in the bond population may be expected.

Table 2. Vertical transition energies (eV)

Symmetry[d)]	Minimal	Extended	CI	Pauzat[a)]	Klessinger[b)]
T_2		12.37 (12.20)[c)]	11.61 (11.40)	10.87 (10.53)	
A_1		13.29 (13.27)	12.27 (12.27)	12.18 (11.45)	
T_2		13.30 (13.30)	12.57 (12.43)	11.86 (11.70)	
E		13.32 (13.32)	12.01 (11.87)	11.93 (11.65)	
T_1		13.33 (13.33)	12.66 (12.66)	11.96 (11.70)	
T_2		12.88 (12.87)	13.56 (13.51)		
T_2		13.32 (13.08)	13.95 (13.86)		
E		13.44 (13.23)	14.70 (14.58)		
T_1		13.88 (13.37)	13.98 (13.98)		
A_1		14.04 (13.35)	14.92 (14.92)		
T_1	21.50 (21.28)	21.55 (21.23)	21.61 (21.29)	22.43 (20.21)	
E	21.93 (20.78)	22.32 (21.23)	22.37 (21.33)	23.21 (22.15)	
T_2	23.78 (21.65)	28.38 (25.83)	28.38 (25.99)	27.41 (25.33)	
T_2	24.08 (18.80)	23.73 (18.70)	23.84 (18.80)	25.62 (20.21)	21.11
A_1	27.65 (17.03)	27.58 (17.44)	27.72 (17.62)	28.46 (17.15)	28.11

a) From Table 5 in Ref. 20. b) Ref. 22. c) The parentheses in this table indicate the transition energies of the triplet states. d) The transitions are classified into three types of transitions; the first five transitions are from $1t_2$ to $3a_1$ or $2t_2$ MO's; the second five ones are from $1t_2$ to $4a_1$ or $3t_2$ MO's, and the remaining transitions are from $1t_2$ to $5a_1$ or $4t_2$ MO's.

The vertical transition energies are calculated by means of Eq. 1, using the virtual orbital approximation

$$\Delta E^{1,3}(i \to j) = \varepsilon_j - \varepsilon_i - (J_{ij} - K_{ij}) \pm K_{ij}, \qquad (1)$$

where ε_i, J_{ij} and K_{ij} are the orbital energies and the Coulombic and exchange integrals respectively, and where the plus sign of the last term holds for the singlet, and the minus sign for the triplet. The results are shown in Table 2, along with those of other calculations. In the case of the minimal-basis set, the vertical transition energy of the lowest excited state is calculated to be about twice the experimental value. Moreover, this value is higher than the ionization potential. These are common in other *ab initio* minimal-basis calculations.[20,22)] The symmetry of the calculated lowest-excited-state is T_1, which is electronically forbidden. On the other hand, the extended-basis calculations bring in another profile of the predicted transition energies. The lowest value for the singlet state appears at 11.61 and 12.37 eV above the ground state with and without CI respectively; this agrees with the experiments fairly well. The symmetry of this state is T_2, which is an allowed transition. The excited states considered to be due to the valence-shell transitions are found at almost the same positions as in the minimal-basis calculations. The relative ordering of the predicted excited states is not necessarily the same in all types of methods and basis sets, but so long as we use the extended-basis set the lowest excited state can be calculated to be T_2 symmetry.[26)] Pauzat *et al.*[20)] calculated the vertical transition energies by taking into account the Rydberg orbitals, which were constructed by orthogonalizing them to the inner SCF-MO's by the Schmidt procedure. We have already used the carbon 3s, 3p, 4s, and 4p Rydberg AO's as the starting-basis ones, along with the minimal-basis set, in the calculations of the ground state. Therefore, the Rydberg orbitals are assumed to be the virtual SC-LCAO-MO's, and then they are automatically orthonormalized to the inner MO's. It is interesting that the virtual $3a_1$

MO has a strong resemblance to the 4s′ AO which is orthogonalized to the carbon inner 1s and 2s AO's, while the $4a_1$ MO is also like the 3s′ AO which is orthogonalized to the 4s′ AO as follows:

$$3s' = 1.553(3s) - 1.155(4s) - 0.286(2s) + 0.063(1s)$$

$$4a_1 = 1.561(3s) - 1.158(4s) - 0.242(2s) + 0.058(1s)$$

and

$$4s' = 1.014(4s) - 0.028(2s) + 0.006(1s)$$

$$3a_1 = 1.000(4s) - 0.048(2s) + 0.010(1s)$$

These correspondences hold between the $2t_2$ MO and the 4p′ AO, and the $3t_2$ MO and the 3p′ AO respectively: the 3p′ and 4p′ AO's are the orthonormalized AO's, like the above-mentioned 3s′ and 4s′ AO's. The other two virtual MO's, $4t_2$ and $5a_1$, are mainly constructed from the hydrogen 1s and carbon valence AO's.

The results of the CI calculations shown in Table 2 are obtained by means of a limited single-excitation CI. The lowering of the lowest excitation energy is considerable, and the mixing among the excited states seems to be large. Here let us examine six electronically allowed transitions in detail. Three of them (φ_1, φ_2, and φ_3) are one-electron transitions from the $1t_2$ to the $3a_1$, $4a_1$, and $5a_1$ MO's, while the others (φ_4, φ_5, and φ_6) are the transitions from the $1t_2$ to the $2t_2$, $3t_2$, and $4t_2$ MO's respectively. The CI results exhibit the following configuration mixings and transition energies:

$$^1\Psi_1 = 0.588\varphi_1 + 0.807\varphi_2 + 0.058\varphi_3 \quad \Delta E = 11.61\ \text{eV}$$

$$^1\Psi_2 = 0.809\varphi_1 - 0.586\varphi_2 - 0.043\varphi_3 \quad \Delta E = 13.56\ \text{eV}$$

$$^1\Psi_3 = 0.003\varphi_1 - 0.072\varphi_2 + 0.997\varphi_3 \quad \Delta E = 28.38\ \text{eV}$$

$$^1\Psi_4 = 0.683\varphi_4 + 0.726\varphi_5 - 0.075\varphi_6 \quad \Delta E = 12.57\ \text{eV}$$

$$^1\Psi_5 = 0.730\varphi_4 - 0.679\varphi_5 + 0.104\varphi_6 \quad \Delta E = 13.95\ \text{eV}$$

$$^1\Psi_6 = 0.075\varphi_4 + 0.073\varphi_5 - 0.995\varphi_6 \quad \Delta E = 23.84\ \text{eV}$$

for the singlet excited states. We showed previously that there was a likeness between the virtual MO's and the orthogonalized carbon extra-valence AO's, so we can estimate the Rydberg character of the above excited states in terms of the 3s′, 3p′, 4s′, and 4p′ orthogonalized AO's. The contribution of these AO's to each state is calculated approximately as follows:

$$^1\Psi_1 \approx 0.947(3s') - 0.226(4s')$$

$$^1\Psi_2 \approx 0.237(3s') + 0.965(4s')$$

$$^1\Psi_4 \approx 1.010(3p') + 0.012(4p')$$

$$^1\Psi_5 \approx 0.031(3p') - 1.008(4p')$$

From these coefficients of the orthogonalized AO's, four states, $^1\Psi_1$, $^1\Psi_2$, $^1\Psi_4$, and $^1\Psi_5$, are considered to be mainly constructed by the transitions of a $1t_2$ electron to 3s′, 4s′, 3p′, and 4p′, that is the Rydberg MO's, respectively. The remaining two states, $^1\Psi_3$ and $^1\Psi_6$, may be understood as valence-shell types (2s and 2p). We can say, from the above CI results and discussion, that the configuration mixing between the valence-shell and Rydberg transitions does not occur in these excited states of the methane molecule. For the six triplet states which correspond to the above six singlet excited states, the similar configuration mixings given below are obtained:

$$^3\Psi_1 = 0.547\varphi_1' + 0.832\varphi_2' + 0.093\varphi_3' \quad \Delta E = 11.42\ \text{eV}$$

$$^3\Psi_2 = 0.837\varphi_1' - 0.544\varphi_2' - 0.058\varphi_3' \quad \Delta E = 13.51\ \text{eV}$$

$$^3\Psi_3 = 0.002\varphi_1' + 0.109\varphi_2' - 0.994\varphi_3' \quad \Delta E = 25.99\ \text{eV}$$

$$^3\Psi_4 = 0.624\varphi_4' + 0.775\varphi_5' - 0.097\varphi_6' \quad \Delta E = 12.43\ \text{eV}$$

$$^3\Psi_5 = 0.781\varphi_4' - 0.619\varphi_5' + 0.087\varphi_6' \quad \Delta E = 13.86\ \text{eV}$$

$$^3\Psi_6 = 0.008\varphi_4' - 0.130\varphi_5' - 0.991\varphi_6' \quad \Delta E = 18.80\ \text{eV}$$

where the triplet functions, φ_i', are used instead of φ_i. The nature of each triplet state is almost the same as that of the corresponding singlet excited states.

With respect to these transition energies, it is found that the calculated singlet-triplet separation is very small for the Rydberg transitions, but it is quite large for the valence-shell transitions. The experimental values of the singlet-triplet separation are about 1 eV.[24] In order to explain the experimental values, we may need moderate diffuse orbitals for the triplet excited states.

Table 3. Comparison with experiments (eV)

State	Transition type	Calcd	Exptl[a]
$^1\Psi_1$	$1t_2 \longrightarrow 3s'$	11.61	9.7, 10.3
$^1\Psi_4$	$1t_2 \longrightarrow 3p'$	12.57	
$^1\Psi_2$	$1t_2 \longrightarrow 4s'$	13.56	11.7
$^1\Psi_5$	$1t_2 \longrightarrow 4p'$	13.95	

a) Ref. 23.

The vertical transition energies of the four lowest allowed-transitions are summarized in Table 3, along with the experimental values. We may assign the band at 9.7 eV to the $1t_2 \rightarrow 3s'$ Rydberg transition ($^1\Psi_1$): this conflicts with the semi-empirical calculations, but agrees with other extended basis non-empirical calculations. Similarly the band at 11.7 eV is assigned to the $1t_2 \rightarrow 4s'$ Rydberg transition ($^1\Psi_2$) by a comparison with the experimental and calculated energy separation. Two states, $^1\Psi_4$ and $^1\Psi_5$, will overlap with the above two bands respectively. No discussions of the oscillator strength for each allowed transition and the vibronic interactions of the forbidden transitions is given here, so the above assignments of the absorption bands of CH_4 are somewhat qualitative, but they do confirm Hashbarger and Lassetre electron-impact experiments.[23]

The calculations were carried out on the HITAC 8700/8800 Computer at the University of Tokyo Computer Centre. The authors are very grateful to Professor Hiroshi Taketa for his helpful communications about the use of the program (Y4/TC/ADO5: Molecular Integrals over CGTO).

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