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Ab initio Calculation of Some Low-Lying Electronic Excited States of Methane

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The energies of some low-lying electronic excited states of methane are calculated by using wave functions built up in terms of plane waves modulated by multicenter Gaussian factors. The wave functions of the various states are evaluated by a two steps iterative process. In the first step, each excited orbital is determined while keeping all other rigid; in the second, rearrangement effects are introduced. Final results are in good agreement with experimental data and allow to enhance an assignement hypothesis for the first electronic transitions.

Key words: Methane, excited states of ~

Introduction

Although many theoretical calculations on the electronic ground state of methane have been performed [1, 2], relatively poor attention has been paid to its excited states [3–8]. From the united atom theory, Mulliken qualitatively stated electronic structures for both ground and first excited states [9]. Katagiri and Sandorfy [3] discussed about first electronic transition using semiempirical Pariser and Parr type calculations. More recently, Pauzat, Ridard and Levy [7] studied transitions energies and the first ionization potential by an *ab initio* calculation using a multicenter Gaussian basis set and calculating the energies of various states by a second order perturbation method. Their results are in good agreement with experiments, and evidentiate a strong Rydberg character for the first allowed electronic transition. Although the perturbation method employed by these authors appears in this case to be adequate to the purpose, we considered worthwhile to make a calculation of methane first excited electronic states energies, following a scheme very close to the independent particle model. This way, in fact, allows a more immediate and intuitive visualisation of the various phenomena occuring in the physical process. The basis set we have employed is similar to the Pauzat's one, but it represents more accurately the wave function in the space regions close to the nuclei and far from the carbon atom.

Basis Functions

The basis functions we have chosen, consists of plane waves modulated by a proper Gaussian factor [10]:

$$\chi(\ell, \boldsymbol{n}, \boldsymbol{r}) = \mathcal{N} \exp(-(\pi^2/8\ell^2)r^2 + i(\pi/\ell)\boldsymbol{n} \cdot \boldsymbol{r}) = \mathcal{N} \exp(-\alpha r^2 + i\boldsymbol{N} \cdot \boldsymbol{r})$$

Table 1. Functions employed in the various basis sets

	Type	Center	Symmetry	ℓ	Basis sets												
					1	2	3	4	5	6	7	8	9	10	11	12	13
1	*s*	C	A_1	0.01								+	+	+	+	+	+
2	*s*	C	A_1	0.02							+	+	+	+	+	+	+
3	*s*	C	A_1	0.04						+	+	+	+	+	+	+	+
4	*s*	C	A_1	0.08					+	+	+	+	+	+	+	+	+
5	*s*	C	A_1	0.12				+	+	+	+	+	+	+	+	+	+
6	*s*	C	A_1	0.18			+	+	+	+	+	+	+	+	+	+	+
7	*s*	C	A_1	0.26		+	+	+	+	+	+	+	+	+	+	+	+
8	*s*	C	A_1	0.37	+	+	+	+	+	+	+	+	+	+	+	+	+
9	*s*	C	A_1	0.54		+	+	+	+	+	+	+	+	+	+	+	+
10	*s*	C	A_1	0.78			+	+	+	+	+	+	+	+	+	+	+
11	*s*	C	A_1	1.13		+	+	+	+	+	+	+	+	+	+	+	+
12	*s*	C	A_1	1.63	+	+	+	+	+	+	+	+	+	+	+	+	+
13	*s*	C	A_1	2.41		+	+	+	+	+	+	+	+	+	+	+	+
14	*s*	C	A_1	3.57			+	+	+	+	+	+	+	+	+	+	+
15	*s*	C	A_1	5.28				+	+	+	+	+	+	+	+	+	
16	*s*	C	A_1	7.81											+		
17	*s*	C	A_1	11.00											+		
18	*p*	C	T_2	0.26						+	+	+	+	+			+
19	*p*	C	T_2	0.37					+	+	+	+	+	+	+	+	+
20	*p*	C	T_2	0.54				+	+	+	+	+	+	+	+	+	+
21	*p*	C	T_2	0.78			+	+	+	+	+	+	+	+	+	+	+

22	*p*	C	T_2	1.13		+	+	+	+	+	+	+	+	+	+	+	+
23	*p*	C	T_2	1.63	+	+	+	+	+	+	+	+	+	+	+	+	+
24	*p*	C	T_2	2.41		+	+	+	+	+	+	+	+	+	+	+	+
25	*p*	C	T_2	3.57			+	+	+	+	+	+	+	+	+	+	+
26	*p*	C	T_2	5.28				+	+	+	+	+	+	+	+	+	
27	*p*	C	T_2	7.81											+		
28	*p*	C	T_2	11.00											+		
29	*d*	C	T_2	0.75										+			+
30	*d*	C	T_2	1.25									+	+	+	+	+
31	*d*	C	T_2	2.00										+	+	+	+
32	*d*	C	T_2	4.40											+	+	+
33	*d*	C	T_2	10.00											+		
34	*f*	C	A_1	1.25									+	+	+	+	+
35	*f*	C	A_1	2.50										+	+	+	+
36	*f*	C	A_1	5.00											+		
37	*f*	C	A_1	9.00											+		
38	*s*	H	A_1, T_2	0.20						+	+	+	+	+	+	+	+
39	*s*	H	A_1, T_2	0.50					+	+	+	+	+	+	+	+	+
40	*s*	H	A_1, T_2	1.00				+	+	+	+	+	+	+	+	+	+
41	*s*	H	A_1, T_2	1.67	+	+	+	+	+	+	+	+	+	+	+	+	+
42	*s*	H	T_2	2.40				+	+	+	+	+	+	+	+	+	+
43	*s*	H	T_2	4.00					+	+	+	+	+	+	+	+	
44	*p*	H	T_2	1.50										+			+
45	*s*	CH	A_1, T_2	1.10										+			+

Considering the behaviour of these functions near $\mathbf{r}=\mathbf{0}$, we denote respectively by *s,p,d,f*-type orbitals the following combinations:

$$\begin{aligned}
s &= \mathcal{N}\exp(-\alpha r^2)\,,\\
p_x &= \mathcal{N}\exp(-\alpha r^2)\sin N_x x\,,\\
d_{xy} &= \mathcal{N}\exp(-\alpha r^2)\sin N_x x \sin N_y y\,,\\
f_{xyz} &= \mathcal{N}\exp(-\alpha r^2)\sin N_x x \sin N_y y \sin N_z z\,.
\end{aligned}$$

The used parameters have been obtained by optimizing a single function approximation, along the McWeeny's procedure [11], for the lowest level of every employed symmetry. We have then extended the ℓ range so as to keep the overlap between two functions less than 0.9. The parameters of the functions employed in our calculations are reported in Table 1; the wave function is nearly completely expanded within a 10 ÷ 12 a.u. sphere.

Ground State and Virtual Levels

Methane ground state is represented in the single-particle approximation by the well known structure $(1a_1)^2(2a_1)^2(1t_2)^6$. Since our interest is to obtain a wave function which approaches as close as possible the Hartree-Fock (H.F.) one, it seems to be worthwhile to discuss separately the basis functions employed for the various molecular orbitals. As regards the first orbital $1a_1$, we started solving the C^{4+} ion problem. Starting from the optimized function with $\ell = 0.37$, and expanding step by step the basis set, we did not find any appreciable energy changes after the first nine functions of Table 1 had been employed. The energy value so obtained coincides with the value reported by Clementi in terms of a Slater basis [12], while it is slightly better than the Huzinaga's one [13] (he used a 5 GTO set). A similar procedure has been carried out for carbon 2*s* and 2*p* as well as hydrogen 1*s* orbitals, starting in each case from the common optimized value $\ell = 1.67$. Energy values obtained from the various basis sets are reported in Table 2. We can see that, in order to obtain a good energy value for the ground

Table 2. SCF energies from various basis sets

Basis set	Energy (a.u.)
1	−34.511
2	−37.782
3	−39.109
4	−39.828
5	−40.085
6	−40.178
7	−40.188
8	−40.189
9	−40.2067
10	−40.2125
11	−40.2064
12	−40.2063
13	−40.2115

state, the introduction in the basis set of functions with very high orbital exponents ($\ell = 0.01$, i.e. $\alpha = 12337$) is needed. In fact, from the energy point of view, an accurate description of the electron behaviour in proximity of the nuclei is very important. As far as excited levels are concerned, on the contrary, functions of this kind are no longer necessary. The value of -40.1891 a.u., given by the basis set 8, is the limit value for the energy obtainable in terms of carbon *s* and *p* and hydrogen *s* functions. The addition of carbon *d* and *f* and hydrogen *p* functions gives an improvement of -0.0234 a.u. We point out that *d* and *f* functions which are relevant for the ground state are relatively concentrated, and do not bear a strong resemblance with *d* and *f* orbitals for the first excited states of carbon atom.

Since our interest is turned to study excited states, it is worthwhile to keep an eye on the behaviour of the orbital energies of both occupied and first virtual levels. It is well known that H.F. virtual solutions display a continuous spectrum [14]; therefore, if the excited states are developed in terms of virtual orbitals, a basis set which furnishes a sufficiently tick series of them is needed.

Excited States

In the independent particle model, first excited states derive from a $3a_1 \leftarrow 1t_2$ transition leading to a T_2-type state, and from a $2t_2 \leftarrow 1t_2$ transition, leading to A_1, E, T_1 and T_2 states. Only the transitions leading to a T_2 state are allowed. As a rough approximation, these states could be described by suitable symmetry combinations [15] of detors built up from the ground state replacing a single occupied $1t_2$ spinorbital by a virtual H.F. one (Single Transition Approximation) [16]. Although this approximation lends itself to an intuitive physical interpretation of the excitation process, it provides numerical results which are only qualitatively correct, even though the basis functions are potentially suited for describing the involved excited states. This is mainly due to the following reasons:

a) The H.F. virtual orbitals correspond to solutions which are more closely related to the negative ion than to the true excited state problem.

b) The transition of one electron to an upper level involves a not negligible rearrangement energy of the other electrons.

All these problems are automatically solved by using H.F. open shell equations for the excited states; there are, nevertheless, remarkable difficulties in considering, in the most general case, orthogonalization conditions with the ground state [17]. For this reason, and in order to better analyze the underlying physics, we preferred to solve the problem following the steps outlined in a) and b).

The first step of our method involves therefore the minimization of the energy from a linear combination of determinants in which a t_2-type spinorbital has been substituted by a virtual one. The other levels are unchanged; the orthogonality of the states so obtained with respect to the H.F. one is automatically satisfied. The energy values obtained by this scheme for basis 11 can be found in Table 3. In the second column the orbital energies associated with the virtual a_1 levels to be added one at a time are reported; the third column collects the transition energies to a T_2 state arising from promotion of the kind $3a_1 \leftarrow 1t_2$, $3a_1$ being a linear combination of the first N virtual SCF levels. Convergency looks

Table 3. Behaviour of the transition energies with respect to the number of introduced virtual orbitals and their orbital energies (st step, basis 11; all energies in atomic units)

N	$\varepsilon^{(a_1)}$	$\Delta E(T_2)$	$\varepsilon^{(t_2)}$	$\Delta E(A_1)$	$\Delta E(E)$	$\Delta E(T_1)$	$\Delta E(T_2)$
1	0.0130	0.4575	0.0202	0.4722	0.4711	0.4721	0.4701
2	0.0613	0.4287	0.0411	0.4719	0.4709	0.4718	0.4696
3	0.0698	0.4287	0.0715	0.4645	0.4575	0.4593	0.4578
4	0.1849	0.4148	0.1861	0.4645	0.4573	0.4590	0.4562
5	0.2509	0.4148	0.2060	0.4644	0.4556	0.4571	0.4530
6	0.4979	0.4112	0.3408	0.4639	0.4547	0.4563	0.4529
7	0.7754	0.4112	0.4618	0.4635	0.4536	0.4552	0.4510
8	1.2174	0.4109	0.5813	0.4635	0.4535	0.4551	0.4509
9	1.5124	0.4108	1.1280	0.4633	0.4533	0.4548	0.4506
10	2.7015	0.4108	1.2656	0.4633	0.4533	0.4548	0.4505

very good. Entries in columns 4, 5, 6, 7, and 8 have analogous meaning to 2 and 3 for the $2t_2 \leftarrow 1t_2$ transitions. The virtual orbitals we have found actually constitute a discrete set of solutions from the continuum of positive energy eigenfunctions of the H.F. operator. In order to see how this continuous set is approximated by our basis 11, in Fig. 1 the transition energy values (columns 3, 5, 6, 7

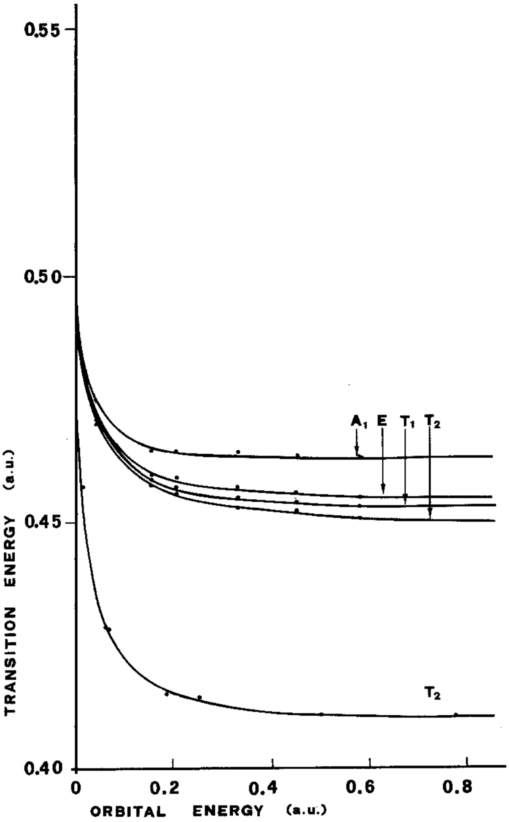

Fig. 1. Transition energy versus orbital energy of levels added (1st step, basis 11)

in Tab. 3) have been plotted against the orbital energies of added virtual levels. The interaction with the first continuum portion rapidly decreases the energy of the states above and, from the behaviour of the curves, it appears that the eigenvalues range which significantly contributes is $0 \div 0.3$ a.u.

In the second step, we take into account the rearrangement effect of the underlying orbitals. Let us consider a determinant

$$\Psi = (n!)^{-\frac{1}{2}} \sum_{\mathscr{P}} (-)^{\mathscr{P}} \mathscr{P}[\varphi_1(1)\,\varphi_2(2)\ldots\varphi_n(n)]\,.$$

If the terms of higher order than first are neglected, we have:

$$\Psi + \delta\Psi \cong \Psi + (n!)^{-\frac{1}{2}} \sum_{j} \sum_{\mathscr{P}} (-)^{\mathscr{P}} \mathscr{P}[\varphi_1(1)\ldots\delta\varphi_j(j)\ldots\phi_n(n)]\,.$$

If the orbital variations, $\delta\varphi_i$, are expanded in terms of the available virtual levels, the orthogonality of these excited states with respect to the fundamental one is warranted, even if this should not be assured by symmetry. In Table 4 we have reported the influence of the various "polarizations" on the excited states energy. It is to be pointed out that we neglected the variations $\delta(1a_1)$ which reasonably furnishes a very small contribution. Energy effects arising from the rearrangement of the $1t_2$ and $2a_1$ orbitals are shown in Fig. 2. The largest contribution comes from $1t_2$ orbitals, probably because they lodge altogether five electrons. The energy improvement is very similar for all of considered states, an average lowering of 0.046 a.u. being recognizable. The next rearrangement of the $2a_1$ orbital produces a more modest lowering of 0.0074 a.u. The polarization of the excited levels gives now an improvement of only 0.0006 a.u., so that a repetition of the polarization cycle is not necessary. Being these effects nearly constant for the various states, the relative positions of such states can be estimated, with a good degree of approximation, by starting from the rigid inner shell assumption. It is to be remarked, in fact, that the correlation energy change for the considered excitations is reasonably constant. All of this is not unexpected if one considers that the excited electron moves at a very large distance from the carbon atom, so that the physical situation of the remaining electrons is intermediate between CH_4^+ ion and neutral molecule.

Table 4. Polarization effects on the transition energies (second step, basis 11)

Transition	State	ΔE^a	ΔE^b	ΔE^c
$a_1 \leftarrow t_2$	T_2	0.3679	0.3602	0.3596
$t_2 \leftarrow t_2$	T_2	0.4029	0.3956	0.3951
$t_2 \leftarrow t_2$	T_1	0.4050	0.3979	0.3973
$t_2 \leftarrow t_2$	A_1	0.4199	0.4127	0.4121
$t_2 \leftarrow t_2$	E	0.4061	0.3989	0.3984

[a] Only $1t_2$ orbitals polarized.

[b] $1t_2$ and $2a_1$ orbitals polarized.

[c] $1t_2$, $2a_1$ and $3a_1$ – or $2t_2$ – orbitals polarized.

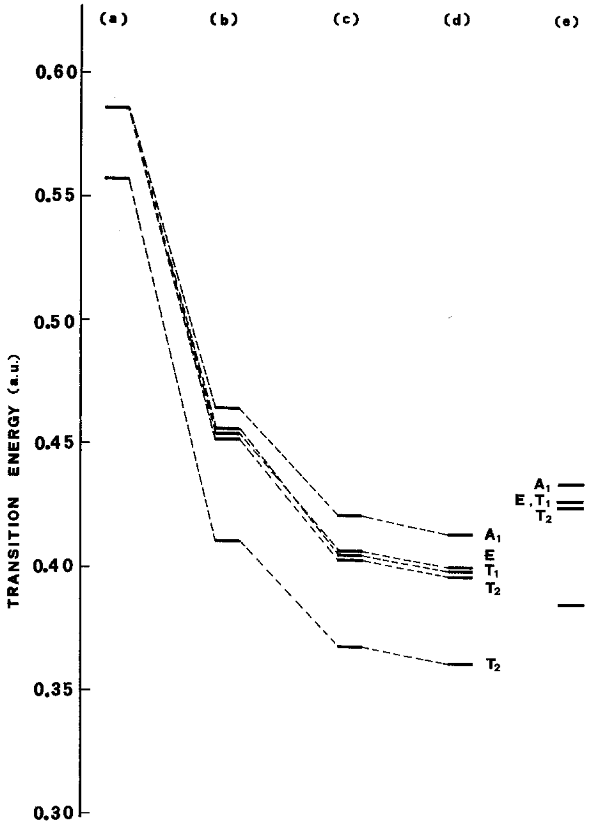

Fig. 2. Transition energy diagram: a as difference of orbital energies. b rigid inner shell approximation. c only $1t_2$ orbitals polarized. d $1t_2$, $2a_1$ and $3a_1$ orbitals polarized. e Ref. [7]

Rydberg Character of Transitions

We think it is not easy to define the Rydberg character of an excited orbital when, as in the present work, extended basis sets are used. As a matter of fact, the recent definition given by Mulliken [18, 19] takes an evident meaning when the representation of the ground state is made in terms of a minimal set of atomic orbitals, also optimized. Several generalized definitions are possible, the utility and significance of which we are unable to express. We can just point out that in our experience the basis functions which are of importance in building up excited orbitals are different from the basis functions needed for a good description of the fundamental state orbitals. Actually, any electron in a methane excited level spends most of its time in a space region which is substantially different from that where it would move if allocated in the ground state. In order to show more clearly this fact, we have reported in Table 5 the average values $\langle r^2\rangle^{\frac{1}{2}}$ for several orbitals. Starting from Mulliken's formulae for $r_{\max}$ and n^* [19], and putting our $\langle r^2\rangle$ value equal to that obtained by using a single 3s Slater orbital,

$$\langle r^2_{\mathrm{SL}}\rangle = (n^*/2Z)^2\,[\Gamma(2n^*+3)/\Gamma(2n^*+1)]\,,$$

Table 5. $\langle r^2\rangle^{\frac{1}{2}}$ values in a.u. for various orbitals

Level	$\langle r^2\rangle^{\frac{1}{2}}$	Level	$\langle r^2\rangle^{\frac{1}{2}}$
$1a_1$	0.3126	$1t_2$	2.1829
$2a_1$	1.8928	$2t_2$	13.4729
$3a_1$	11.6777	$2t_2$[b]	8.3041
$3a_1$[a]	6.1613	$2t_2$[c]	7.5822
		$2t_2$[d]	7.6277
		$2t_2$[e]	7.5293

[a] After 1st step, from a $3a_1 \leftarrow 1t_2$ transition.

[b] After 1st step, from a $2t_2 \leftarrow 1t_2$ transition resulting in an A_1 state.

[c] As above, E state resulting.

[d] As above, T_1 state resulting.

[e] As above, T_2 state resulting.

the following values for $3a_1$ orbital of the first excited state results:

$$n^* = 2.55, \qquad Z = 1.37, \qquad r_{\max} = 4.8 .$$

The $r_{\max}$ value evidentiates that the excited orbital is substantially external to the hydrogen nuclei skeleton, as it is expected for a Rydberg type orbital.

Comparison with Experimental Data

In a recent work, Koch and Skibowski [20] published an U.V. methane spectrum where two peaks at 9.6 and 10.4 eV clearly appear. The comparison with our results leads reasonably to assign both of them to the two allowed excitations to a T_2 state, which we estimate at 9.73 and 10.70 eV respectively. Our interpretation contrasts with the current one, which assigns the spectrum portion under 11 eV to a single T_2-type transition, corresponding to the lowest value we calculate. In view of the quality of the basis set employed and the regular behaviour of the energy in the various steps of the excitation process, considering also that the interaction between the two T_2 calculated states is reasonably very small, we can hope that the suggested assignment is not a bold one.

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