Theoret. chim. Acta (Berl.) 21, 287—300 (1971)
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# An Investigation of the $^1B_1$ Excited States of Water

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Received November 24, 1970

The first seven $^1B_1$ excited states of water are investigated within the framework of the single centre method. Energies, wave-functions and electronic densities are found using one basis set of 25 Slater type orbitals and one of 40 orbitals (both with non-integer principal quantum numbers). All singly excited configurations of $^1B_1$ symmetry are taken into account. For each state the orbital parameters ($n$'s and $\zeta$'s) are carefully optimized. The energy differences between neighboring excited states are, when the comparison can be made, in good agreement with experiment as is also the major contributing configuration of each state. Particular emphasis is placed on the electronic rearrangement that occurs during excitation and this is explicitly brought out by the contour maps of the electronic density. These maps show "satellite-clouds" in the excited states.

Die ersten sieben $^1B_1$-Zustände von Wasser werden mittels der Einzentrenmethode untersucht. Energien, Wellenfunktionen und Elektronendichten werden auf Grund je eines Basissatzes von 25 bzw. 40 Slater-Funktionen mit nicht-ganzzahligen Exponenten bestimmt. Dabei werden alle einfach angeregten $^1B_1$-Konfigurationen mit einbezogen und für jeden Zustand die Orbitalparameter sorgfältig optimalisiert. Die Energiedifferenzen zwischen benachbarten Zuständen sind in den Fällen, in denen der Vergleich mit dem Experiment möglich ist, richtig. Besondere Bedeutung wird den Elektronenumlagerungen beigemessen, die während der Anregung auftreten; sie werden in den Konturen-Bildern, die die Satellitenwolken in den angeregten Zuständen zeigen, wiedergegeben.

Les sept premiers états excités $^1B_1$ de l'eau sont étudiés dans le cadre de la méthode à un seul centre. Les énergies, les fonctions d'onde et les densités électroniques sont trouvés successivement dans des bases de 25 et de 40 orbitales de type Slater (dans les deux cas avec des nombres quantiques principaux non entiers). Toutes les configurations monoexcitées de symétrie $^1B_1$ sont prises en compte. Les paramètres orbitaux ($n$ et $\xi$) sont soigneusement optimisés pour chaque état. Lorsque la comparaison avec l'expérience peut être faite on trouve des différences correctes entre les énergies d'état excités voisins, ainsi qu'une bonne identification des configurations essentielles correspondantes. On insiste particulièrement sur le réarrangement électronique qui se produit au cours de l'excitation et qui est explicitement révélé par les cartes d'isodensité. Ces cartes présentent des «nuages satellites» dans les états excités.

## Introduction

In this paper we investigate the seven lowest lying $^1B_1$ electronic states of $H_2O$ using the single centre method, that is to say a multiconfiguration wave-function composed of Slater type orbitals (STOs) centred on the oxygen nucleus. Our main interest is the character of each state rather than its energy. For a general review of previous work on the excited states of water, the reader is referred to a previous publication by the authors on the $^1A_1$ states [9]. For the $^1B_1$ states Goddard *et al.* [1] have used the LCAO SCF framework with Gaussian type orbitals but rather than using for the excited state the virtual orbitals that naturally arise in such a treatment, they have used so-called "improved virtual orbitals" found from a modified Hartree-Fock Hamiltonian with the self Coulomb and exchange terms removed. It should be noted that the "core" is frozen in these calculations and that the ground state geometry is used for all states.

Krauss *et al.* [2], using a nuclear centred Gaussian basis set, have looked at the lowest lying $^1B_1$ excited state of water and found that, for the ground state geometry, this state lies 6.5 eV above the ground state. Horsley and Fink [3] using Gaussian lobe orbitals in an SCF calculation with Nesbet's symmetry and equivalence restrictions found the lowest $^1B_1$ state (in the ground state geometry) to be 7.9 eV above the ground state. La Paglia [4] and Murrell *et al.* [5] have both used perturbation treatments; the former starting from the Hartree-Fock Rydberg orbitals for oxygen and the latter from the neon Hartree-Fock orbitals. In both cases the agreement with experiment was fair. Lin and Duncan [6] have performed a single centre calculation and in spite of a number of approximations [frozen core, poor basis orbitals, single-configurational wavefunctions and an approximate Hamiltonian (molecular puff)] have obtained quite good results.

Experimental information on the $^1B_1$ states of water can be found in Herzberg's book [7]. The values given there correspond to the onset of absorption and therefore to excited states in their equilibrium geometry (which is unlikely to be the ground state geometry).

We have carried out all our calculations on the $^1B_1$ states with a bond length of 1.91 a.u. and bond angle of 107°. These are the appropriate experimental values for the second $^1B_1$ state. We have kept this geometry constant in order to have a fixed framework in which to compare the wavefunctions corresponding to the different states. The nuclear repulsion energy for this fixed geometry is 8.7026 a.u.

## Method and Results

The basis sets consist of oxygen-centred Slater type orbitals with non-integer $n$ values:

$$\psi_i = (2\zeta_i)^{n_i+1/2}[(2n_i)!]^{-1/2} r^{n_i-1} e^{-\zeta_i r} S_{l_i,m_i}$$

$$S_{l_i,m_i} = \begin{cases} \Theta_{l_i,m_i}(\theta)\cos(m_i\phi)/\pi^{1/2} & m_i > 0 \\ \Theta_{l_i,m_i}(\theta)/(2\pi)^{1/2} & m_i = 0 \\ \Theta_{l_i,m_i}(\theta)\sin(-m_i\phi)/\pi^{1/2} & m_i < 0 \end{cases}$$

where $\Theta_{l,m}$ are associated Legendre polynomials normalized to unity. Several basis sets of different size were tried for the $^1B_1$ states and the most satisfactory one in terms of time and accuracy is listed in Table 1, it consists of 25 orbitals: five $s$-type, seven $p$-type, eight $d$-type and five $f$-type. All the results in this paper are for this basis set unless stated otherwise. Each orbital is Schmidt orthogonalized to all the orbitals which have the same angular dependence and appear higher in the list.

With this basis set a wavefunction was constructed of 26 configurations each being related to the Slater determinant:

$$|\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\bar{\psi}_3\psi_4\bar{\psi}_4\psi_5\bar{\psi}_5|$$

(a bar indicates spin $\beta$ and no bar spin $\alpha$).

The 26 configurations were produced by the replacement of one orbital in this determinant, while maintaining $^1B_1$ symmetry. For each configuration we use the notation $(i/j)$ with $i \leq 5$ where, for example, (2/6) signifies the combination:

$$[|\psi_1\bar{\psi}_1\psi_6\bar{\psi}_2\psi_3\bar{\psi}_3\psi_4\bar{\psi}_4\psi_5\bar{\psi}_5| + |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_6\psi_3\bar{\psi}_3\psi_4\bar{\psi}_4\psi_5\bar{\psi}_5|]/2^{1/2}$$

We will refer to the basic orbitals, $\psi_1$ to $\psi_5$, as core orbitals and to the rest as peel orbitals.

The linear coefficients which multiply these configurations in the total wavefunction were found through the variational method by solving the usual secular equation. The roots of this equation correspond to upper bounds on the $^1B_1$ excited states of $H_2O$. For each root we separately optimized the non-linear parameters using the Method of Pattern Search [8]. In actual practice it was found to be faster to optimize $n_i$ and $n_i/\zeta_i$ rather than $n_i$ and $\zeta_i$. Great care was taken to ensure that these parameters were truly optimum. Because of this optimization on each root, the wavefunctions are not orthogonal [9].

The whole calculation was completely automatic, requiring only the selection of basis set and configurations, and was carried out on an IBM 360/65 computer using single precision arithmetic. We believe our energies, on this basis, to be good to within ±0.001 a.u.

Table 1. *Basis set*

| Orbital number ($i$) | $l_i$ | $m_i$ |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 0 | 0 |
| 3 | 1 | 0 |
| 4 | 1 | 1 |
| 5 | 1 | −1 |
| 6 | 0 | 0 |
| 7 | 1 | 0 |
| 8 | 1 | −1 |
| 9 | 2 | 0 |
| 10 | 2 | −1 |
| 11 | 2 | 2 |
| 12 | 2 | −2 |
| 13 | 0 | 0 |
| 14 | 1 | 0 |
| 15 | 1 | −1 |
| 16 | 2 | 0 |
| 17 | 2 | −1 |
| 18 | 2 | 2 |
| 19 | 2 | −2 |
| 20 | 3 | 0 |
| 21 | 3 | −1 |
| 22 | 3 | 2 |
| 23 | 3 | −2 |
| 24 | 3 | −3 |
| 25 | 0 | 0 |

Table 2. *Energy spacings between neighboring excited $^1B_1$ states of water*[a]

| | Improved virtual orbital[b] | This work | Experimental[c] |
|---|---|---|---|
| $^1B_1-7$<br>$^1B_1-6$ | | 0.22 | |
| $^1B_1-6$<br>$^1B_1-5$ | | 0.26 | |
| $^1B_1-5$<br>$^1B_1-4$ | 0.36 | 0.16 | |
| $^1B_1-4$<br>$^1B_1-3$ | 0.75 | 0.56 | |
| $^1B_1-3$<br>$^1B_1-2$ | 0.61 | 0.35 | 1.0 |
| $^1B_1-2$<br>$^1B_1-1$ | 2.79 | 3.26 | 3.33 |

[a] Results are given in eV.

[b] Ref. [1], we have given only those values which correspond directly to the states investigated in this paper.

[c] Ref. [7], we have taken the energy levels which correspond to the start of absorption and therefore to excited states having an equilibrium geometry, i.e. $T_0$ values.

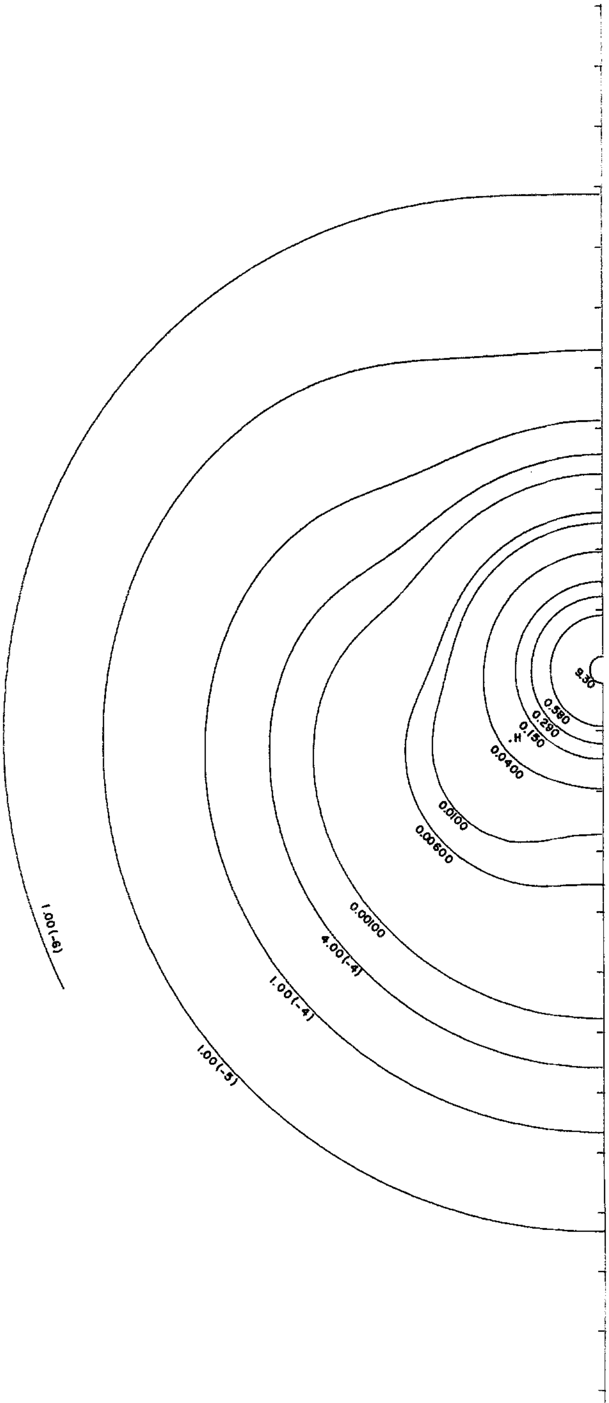
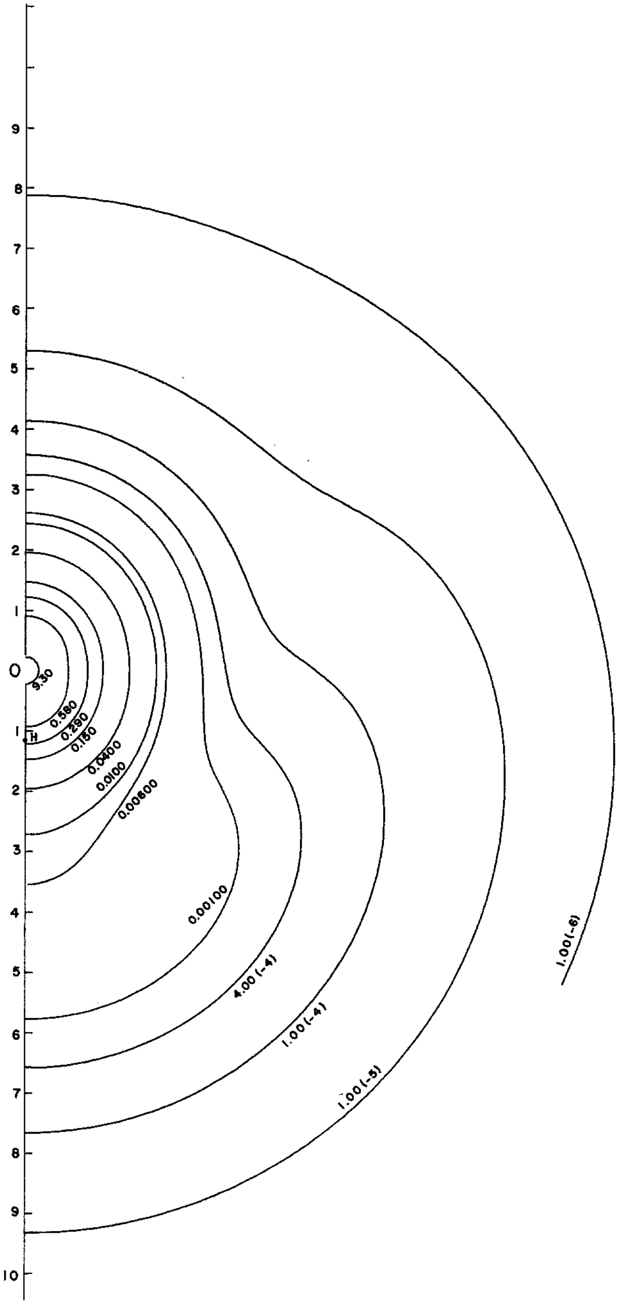


Fig. 1. Contour maps of the electron density in the molecular plane (left hand side) and in the symmetry plane at 90° to the molecular plane (right hand side) for the $^1B_1 - 1$ state of water using the basis set of Table 1 with additional $g$ and $h$ orbitals. The scale is in a.u.


9
8
7
6
5
4
3
2
1
O
1
H
2
3
4
5
6
7
8
9
10
9.30
0.580
0.290
0.150
0.0400
0.0100
0.00800
0.00100
4.00(-4)
1.00(-4)
1.00(-5)
1.00(-6)

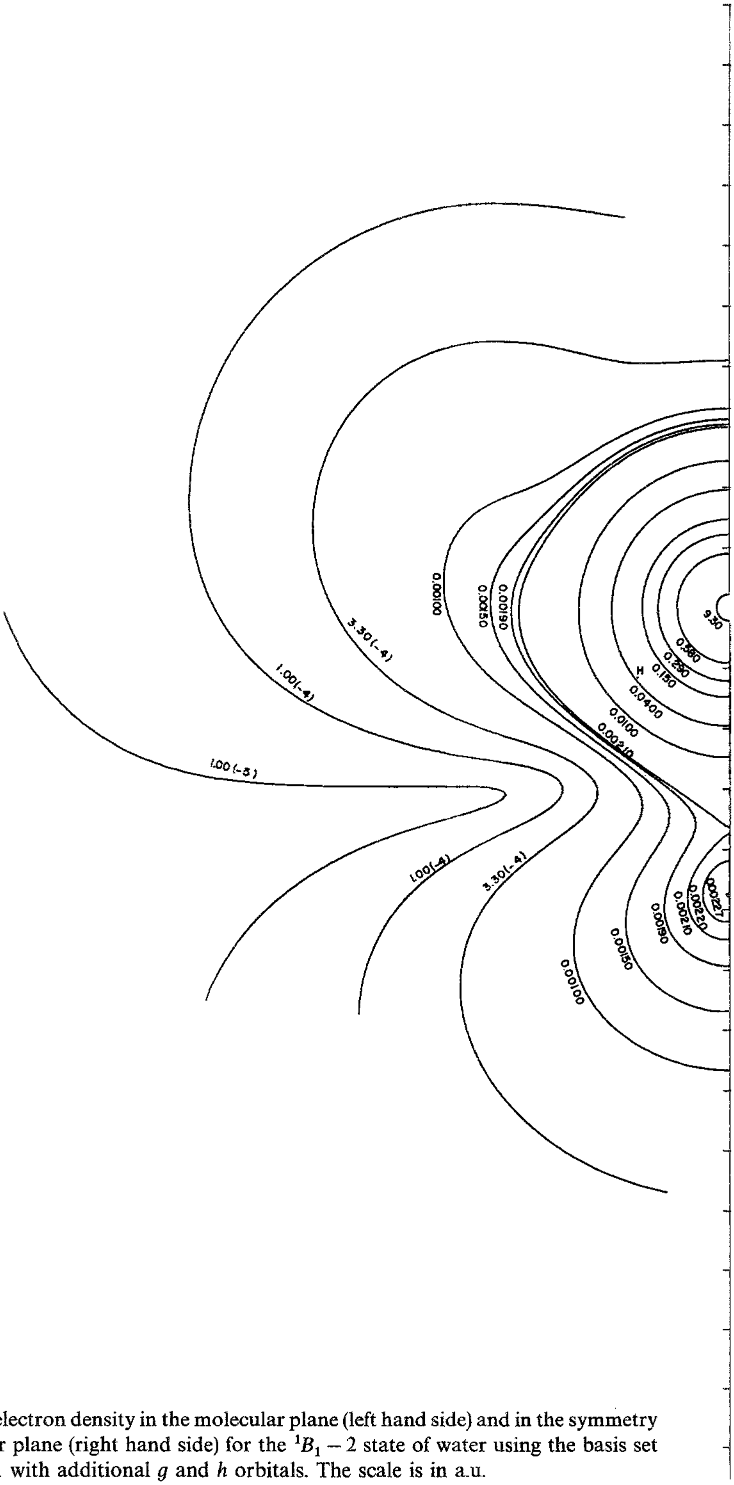
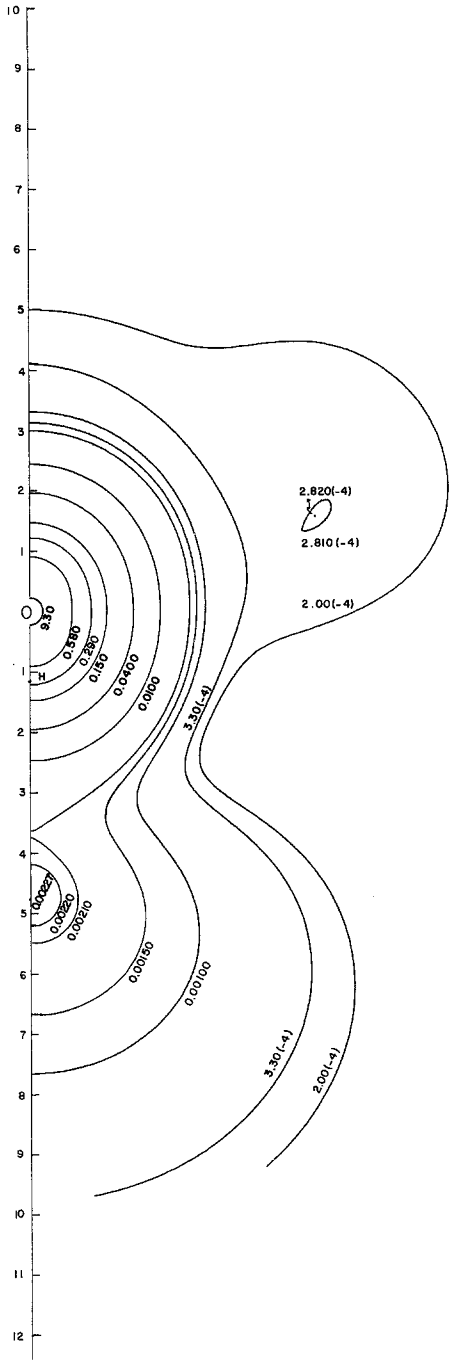


Fig. 2. Contour maps of the electron density in the molecular plane (left hand side) and in the symmetry plane at 90° to the molecular plane (right hand side) for the $^1B_1 - 2$ state of water using the basis set of Table 1 with additional $g$ and $h$ orbitals. The scale is in a.u.


10
9
8
7
6
5
4
3
2
1
O
9.30
0.580
0.290
0.150
0.0400
0.0100
3.30(-4)
2.820(-4)
2.810 (-4)
2.00(-4)
1
H
2
3
4
5
6
7
8
9
10
11
12
0.00227
0.00220
0.00210
0.00150
0.00100
3.30(-4)
2.00(-4)

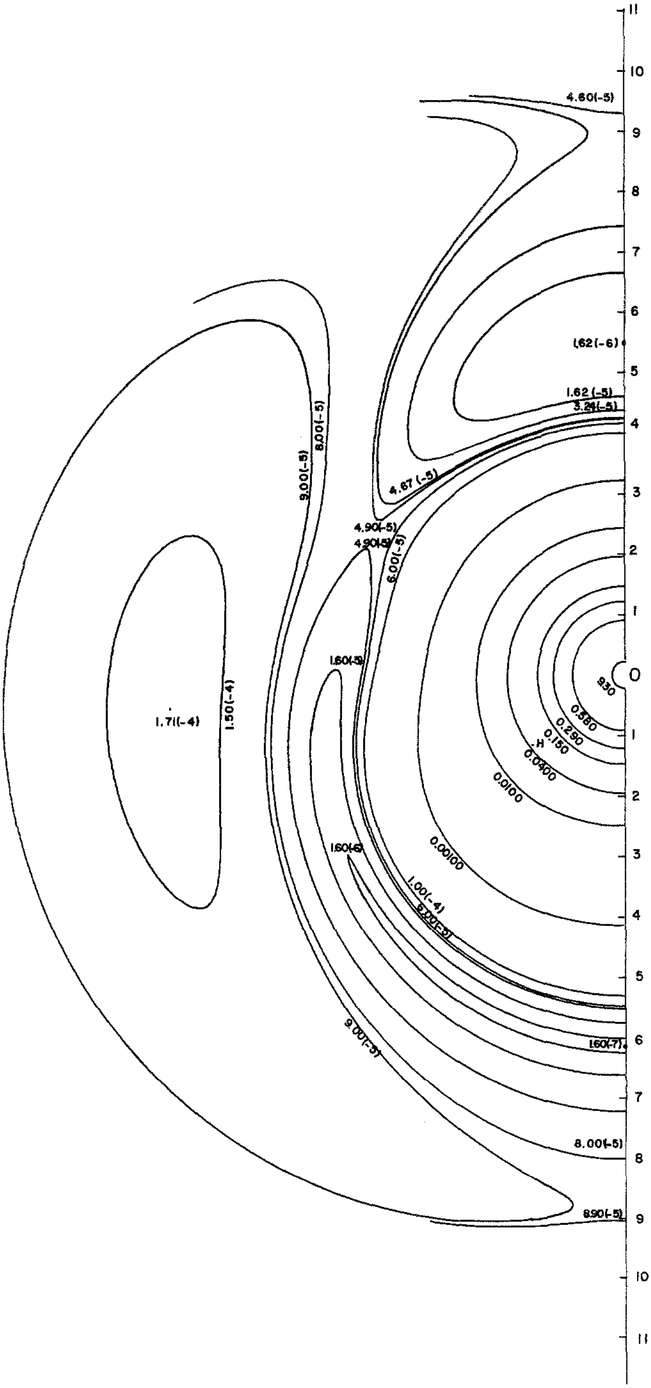


Fig. 3. Contour map of the electron density in the molecular plane for the $^1B_1 - 3$ state of water using the basis set of Table 1 with additional $g$ and $h$ orbitals. The scale is in a.u.

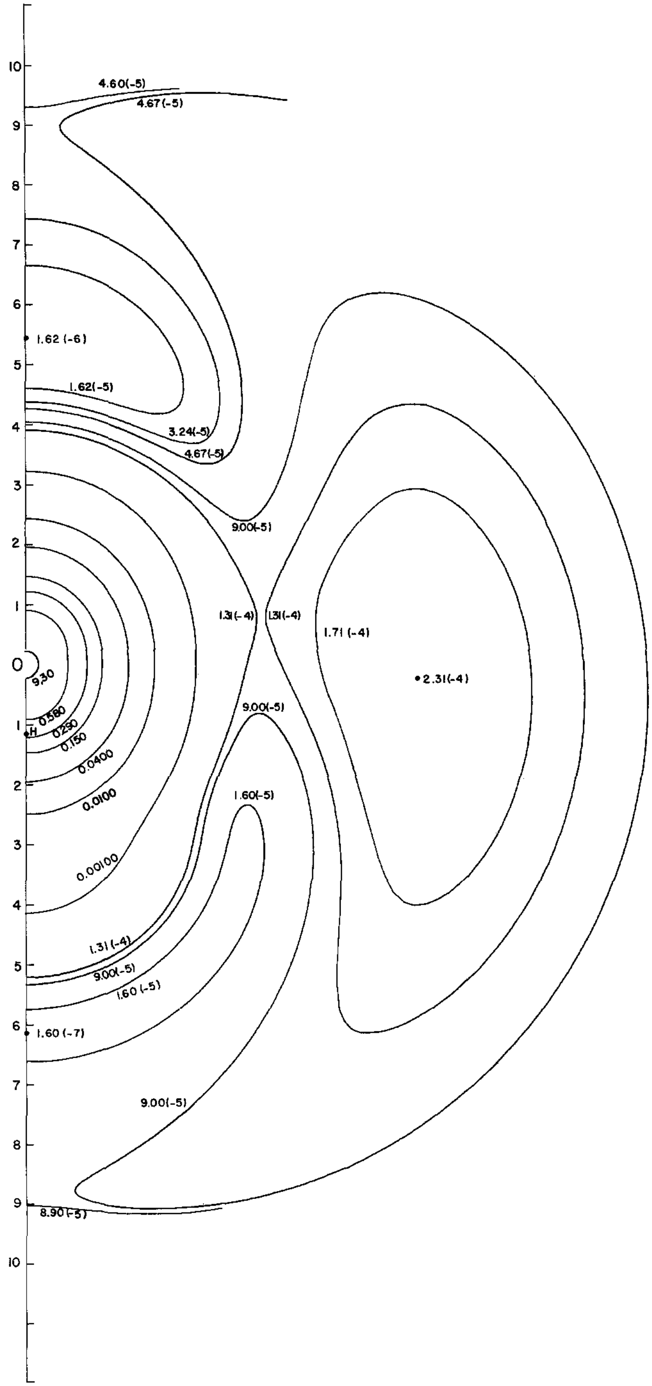


Fig. 4. Contour map of the electron density in the symmetry plane at 90° to the molecular plane for the $^1B_1 - 3$ state of water using the basis set of Table 1 with additional $g$ and $h$ orbitals. The scale is in a.u.

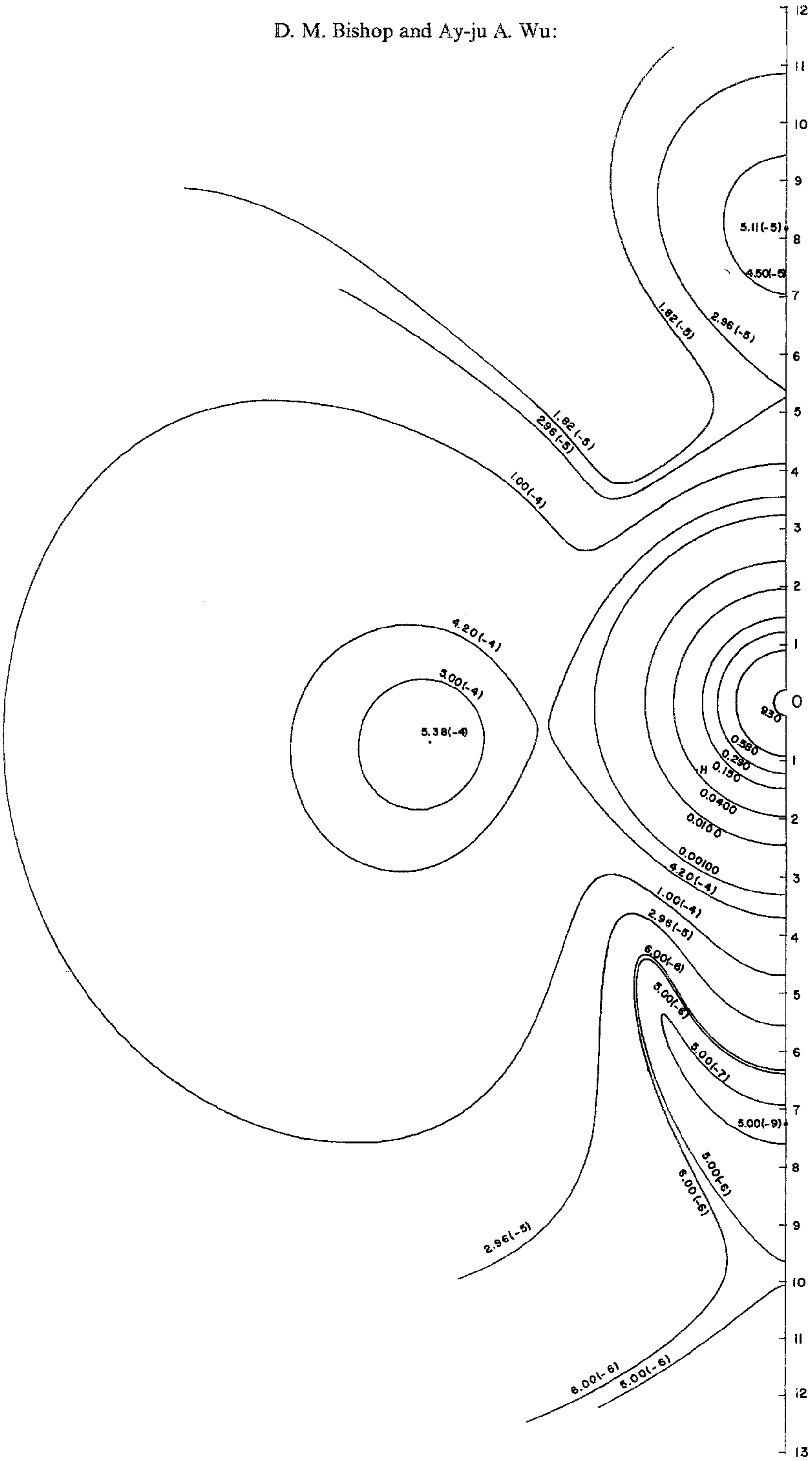


Fig. 5. Contour map of the electron density in the molecular plane for the $^1B_1 - 4$ state of water using the basis set of Table 1. The scale is in a.u.

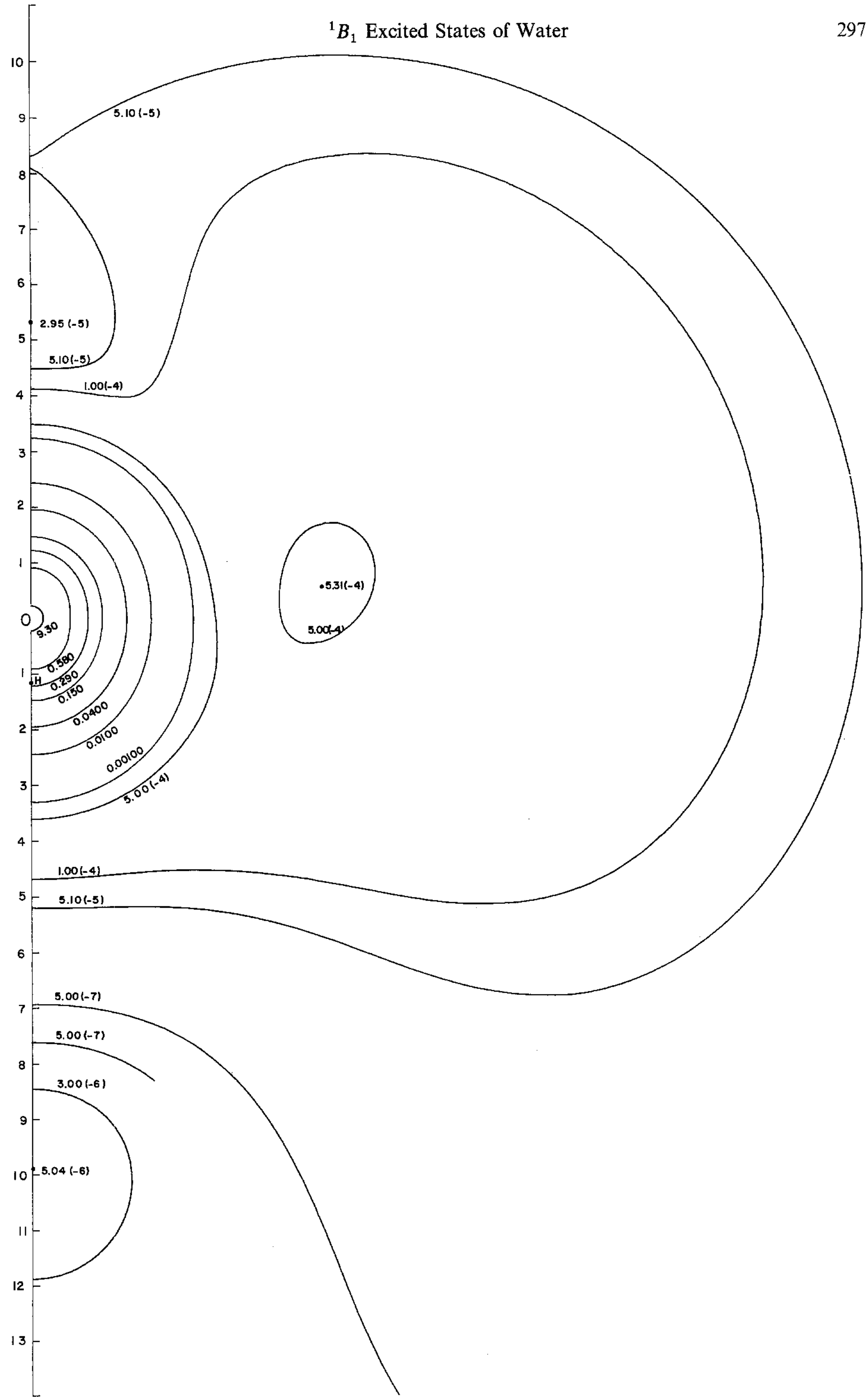


Fig. 6. Contour map of the electron density in the symmetry plane at 90° to the molecular plane for the $^1B_1 - 4$ state of water using the basis set of Table 1. The scale is in a.u.

In Tables 2 and 3 we summarize the important results for the seven lowest roots. These correspond to the seven lowest $^1B_1$ excited states which are labelled $^1B_1 - n(n = 1, 2 \ldots 7)$.

In Figs. 1–6 we display the contour maps of the electron density in the molecular plane and in the symmetry plane at 90° to the molecular plane for the first four $^1B_1$ states of water. The units are electrons/$a_0^3$ and the scale is in $a_0$ measured from the oxygen nucleus. For the lowest three states, the plots are for a basis set which is larger than that in Table 1, by the addition of $g$ and $h$ orbitals (7 $g$-type and 8 $h$-type leading to a 46 configurational wavefunction). For the plots in the symmetry plane at 90° to the molecular plane, the "H" indicates the projection of the two hydrogen nuclei onto the symmetry plane.

## Discussion

In Table 2 we show the energy spacings between neighboring states for the seven lowest $^1B_1$ excited states of $H_2O$ as found by experiment [7], Goddard's "improved virtual orbital method" [1], and by our method. The experimental values relate to excited states in their equilibrium geometries, Goddard's values are for the ground state geometry and ours for the known geometry of the second $^1B_1$ excited state, i.e. bond length = 1.91 a.u. and bond angle = 107°. We believe that our geometry choice is closer to reality than Goddard's and probably explains the fact that our value of the energy difference between the first and second $^1B_1$ states (3.26 eV) is in good agreement with the experimental difference (3.33 eV). As in Ref. [9], we prefer to make comparisons within the excited states rather than with the $^1A_1$ ground state. By doing this we are comparing wavefunctions which use the same basis set and for which the functions describing the bonding electrons are of comparable accuracy.

Though the absolute energies of these $^1B_1$ states are only in fair agreement with experiment, their order when combined with the $^1A_1$ states (see Ref. [9]) is in complete agreement with experiment [7]. Furthermore, as was found for the $^1A_1$ states, the leading configuration type is in agreement with molecular orbital predictions. In Table 3 we list the leading configurations together with the $n$ and the $n/\zeta$ values for the important peel orbitals. The $n/\zeta$ values which are a measure of the distance of the excited electron from the oxygen nucleus increase as one goes up the series in agreement with expectation. It is seen from this Table that there is considerable electronic reorganization in going from one state to the next, this also shows up dramatically in the contour maps of the electron density.

As was true for the $^1A_1$ states we are again able to determine the symmetry of the orbitals which describe the electron being excited simply by looking at the $n/\zeta$ values. The orbitals with large $n/\zeta$ values all have the same symmetry ($a_1$). However, if this fact is to be used to determine the symmetry of the orbitals of excitation it is necessary, as was done in this work, to optimize the energy very carefully.

The above points are visually brought out by the contour maps of the electron density in the molecular plane and the plane at 90° to it and bisecting the H–O–H angle. These maps are shown in Figs. 1–6. They show that there is considerable

Table 3. *Leading configurations and corresponding peel orbitals in the $^1B_1$ states of water*

| State | Leading configurations | Weight (%) | Peel orbital number | $n$ | $n/\zeta$ |
|---|---|---|---|---|---|
| $^1B_1-1$ | (5/6) | 65.9 | 6 | 2.0 | 3.0 |
| | (5/7) | 28.0 | 7 | 2.9 | 3.4 |
| $^1B_1-2$ | (5/7) | 48.2 | 7 | 3.7 | 6.7 |
| | (5/9) | 29.9 | 9 | 4.0 | 7.1 |
| | (5/6) | 17.0 | 6 | 2.8 | 6.2 |
| $^1B_1-3$ | (5/6) | 69.3 | 6 | 4.0 | 8.9 |
| | (5/14) | 14.6 | 14 | 6.5 | 8.5 |
| | (5/13) | 11.0 | 13 | 7.0 | 4.0 |
| $^1B_1-4$ | (5/11) | 91.9 | 11 | 4.0 | 10.0 |
| | (5/14) | 4.5 | 14 | 6.9 | 9.3 |
| $^1B_1-5$ | (5/9) | 64.2 | 9 | 3.6 | 10.3 |
| | (5/14) | 12.4 | 14 | 6.8 | 9.3 |
| | (5/7) | 10.4 | 7 | 3.6 | 4.6 |
| | (5/20) | 7.4 | 20 | 7.0 | 9.6 |
| $^1B_1-6$ | (5/14) | 77.0 | 14 | 6.8 | 18.3 |
| | (5/16) | 7.1 | 16 | 6.2 | 7.0 |
| | (5/13) | 6.2 | 13 | 7.2 | 5.4 |
| | (5/9) | 4.6 | 9 | 3.9 | 10.9 |
| $^1B_1-7$ | (5/11) | 68.1 | 11 | 4.7 | 19.9 |
| | (5/18) | 28.9 | 18 | 4.4 | 7.7 |

reorganization between one state and the next and that compared with the ground state plot the electronic density is much more spread out. The distinction between the $^1A_1$ and $^1B_1$ excited states is clearly shown by comparing the plots in the molecular plane, whereas for the $^1A_1$ states the contours are almost circular, for the $^1B_1$ states, they are decidedly not. For most of these states the maps are quite complex and show several "satellite clouds", however in Figs. 5 and 6 the predominance of the peel orbital no. 11 ($d_{x^2-y^2}$) in the $^1B_1-4$ state is quite apparent.

We hope to carry out further calculations on the excited states of water, this paper being only the first step. In particular, we hope to be able to determine the potential surfaces of these states.

*Acknowledgements.* We gratefully acknowledge the financial support of this work by the National Research Council of Canada. We are indebted to Dr. Thomas W. Dingle of the University of Victoria who wrote much of the basic programming during his stay at the University of Ottawa. We thank the Computing Centre of the University of Ottawa for granting us the large amount of computing time necessary to carry out this project and the enthusiastic cooperation of the Centre's staff. In particular we thank Mr. Rich Kado for technical assistance in computing and Mr. Len Fleming in machine plotting. We also gratefully acknowledge the technical assistance of Mrs. Bertha Fuller of IBM.

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