

# ***Ab Initio* Valence Bond Calculations of the Ground and First Two Singlet Excited States of H<sub>4</sub> Molecule**

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Através da teoria da ligação de valência, utilizando resultados de cálculos *ab initio* com uma base mínima e com uma base estendida, realizaram-se cálculos de interação de configurações com o propósito de determinar a energia eletrônica dos três primeiros estados de singleto, para diferentes geometrias da molécula de H<sub>4</sub>. Os cálculos mostram com uma base STO-3G, um segundo estado excitado ligado (S<sub>2</sub>), com a geometria piramidal trigonal. Além disso, os resultados confirmam que a geometria piramidal trigonal, prevista pelo modelo de Ionicidade Máxima do Estado Excitado e possuindo a mínima energia para o estado S<sub>2</sub>, tem energia mais baixa que as estruturas planares correspondentes. Este último resultado também concorda com o resultado de um cálculo MRD-CI publicado anteriormente.

*Ab initio* valence bond calculations in a minimal and extended gaussian basis set, plus full configuration interaction calculations, have been performed for some different geometries of H<sub>4</sub> molecule. Results for the three lowest singlet electronic states are reported. These calculations show that the trigonal pyramidal geometry has the second excited state (S<sub>2</sub>) bounded, even when we use the STO-3G basis set. Our results (with 4-31G basis set) also show that the trigonal pyramidal geometry, which has been predicted for the energy minimum in the S<sub>2</sub> state by the Maximum Ionicity of the Excited State model, is lower in energy than the corresponding planar structures. This last result is also confirmed by MRD-CI results reported previously.

**Key words:** *valence bond; electronic energy; (geometry) H<sub>4</sub> molecule.*

## **Introduction**

The potential energy surface of the H<sub>4</sub> system is repulsive in the ground state, except for the possible existence of the van der Waals minima. The *ab initio* valence bond (VB) calculation<sup>1,2</sup>, using a minimum basis set (STO-3G) and configuration interaction (CI) calculations<sup>3,4</sup>, have predicted the existence of a bound H<sub>4</sub> complex in the second excited singlet state (S<sub>2</sub>). These theoretical calculations<sup>1-4</sup> cover only highly symmetrical structures and do not include arbitrary points on the 6-dimensional surface, then, the geometry of the H<sub>4</sub> molecule in the S<sub>2</sub> state has not been established by these two calculations.

Recently, Nicolaides *et al.*<sup>5,6</sup> have shown that the pyramidal geometry, which has been predicted for the energy minimum in the S<sub>2</sub> state on the basis of the recently proposed Maximum Ionicity of the Excited State (MIES) model (to be described later), has a lower energy than the corresponding planar structure. The prediction of this model (MIES) on H<sub>4</sub> was supported by the results of MRD-CI calculations, where

the authors<sup>5,6</sup> used the atomic orbital basis set 5s/3s of Dunning<sup>7</sup>, augmented with p-type functions for polarization (exponent 0.7) and s-type diffuse function (exponent 0.025).

In this paper we present results of VB calculations, complete within a minimal (STO-3G) and an extended (4-31G) basis set, at various geometries of H<sub>4</sub>. The results obtained with the 4-31G basis set confirm that the lowest energy minimum for the second excited singlet state occurs at the trigonal pyramidal geometry.

## **Model**

The MIES model suggests that<sup>5,6,8,9</sup> if one of the reacting molecules can exist in a MIES then unbound polyatomic systems can in fact form stable compounds in excited states, with geometries characterized by absence of crossing with the ground state.

This scheme is formulated around the idea that one of the constituent products becomes excited vibronically to a stretched H<sub>2</sub><sup>\*</sup> B<sup>1</sup>Σ<sub>u</sub><sup>+</sup> state, and a charge transfer occurs, yielding a MIES at 4.0 Bohr<sup>10</sup>. This state can be bound

electrostatically and via small overlap effects to the nonreactive singlet ground state H<sub>2</sub>X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>. A singlet excited state for the compound system is formed, whose geometry of minimum energy is obtained by considering the following three steps: i) the geometry of the "positive ion complex", ii) the "geometry of maximum ionicity" and iii) the overlap and the volume effects of the molecule added to the MIES. In the case of H<sub>4</sub>, we take the geometry of the positive ion H<sup>+</sup> as an equilateral triangle with side of 1.65 Bohr<sup>11</sup>, and the fourth H atom is then placed above the centre of the triangle, at a distance of about 4.0 Bohr, which is the maximum ionicity distance of the B<sup>1</sup>Σ<sub>u</sub> state of H<sub>2</sub><sup>10</sup>. The resulting geometry is trigonal pyramidal, and its stability is verified by our calculations as can be seen in the following section.

## Results and discussion

*Ab initio* valence bond calculations in a minimal and an extended gaussian basis set plus full CI calculations have been performed here at various geometries of the H<sub>4</sub> molecule.

The hydrogen basis set employed in these calculations is formed by a minimum (STO-3G) and an extended basis set (4-31G), where the minimal and the extended basis set consists of 1 and 2 functions for the H atom, respectively. Our calculations use the "Gaussian 70" computer program<sup>12</sup>, where our s-exponents are defined. It was used an IBM 4381 computer.

First of all, *ab initio* SCF MO calculations of the H<sub>4</sub> molecule were performed and then the overlap and the one and two-electron integrals derived from these calculations were used to make a full CI VB calculation for various geometries of H<sub>4</sub>. For the STO-3G and the 4-31G basis set, 20 and 336 singlet structures are used in our full CI VB calculations, respectively.

The geometries used for the H<sub>4</sub> system in this work are indicated in Fig. 1. In Fig. 1(a) the fourth H atom is placed above the center of the equilateral triangle formed by the other three H atoms, i. e., at an angle of 90° with the plane. Geometry with  $\phi = 0^\circ$  gives rise to the "kite" shape, (b), of Gerhartz *et alii*. In the calculations, the ring dimension ( $r$ ) and the distance of the fourth hydrogen from the centre of the ring ( $R$ ) (Fig. 1(a)), were varied in order to determine which geometry would give minimum energy with respect to these two coordinates. For the calculations of the planar structure of Fig. 1(b), when we use a STO-3G basis set, the side of the equilateral triangle ( $r$ ) is considered constant and the distance of the fourth H atom varies in order to obtain the

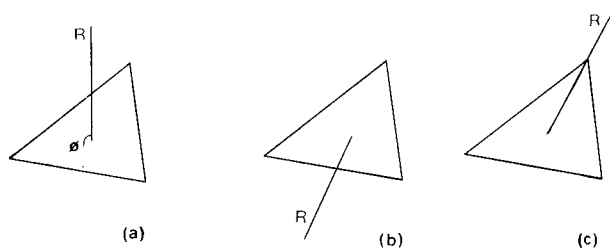


Figure 1. Geometries of H<sub>4</sub> molecule

optimum geometry for  $\phi = 0^\circ$ . When we work with a 4-31G basis set, the calculation of the total energy (geometry 1(b)) is obtained with the same values (of  $r$  and  $R$ ) of the optimum geometry of Fig. 1(a). In Fig. 1(c) we have a planar geometry with  $\phi = 180^\circ$ ; this is the geometry also used by Junsen and Staemmler<sup>13</sup>. In addition, calculations with the square geometry given by Goddard and Csizmadia<sup>3,4</sup> have been made.

For a trigonal pyramidal geometry in C<sub>3v</sub> symmetry, the ground (S<sub>0</sub>) and S<sub>2</sub> states have <sup>1</sup>A' symmetry, while the first excited state (S<sub>1</sub>) has <sup>1</sup>A". For a planar geometry (Fig. 1(b)), all three states have <sup>1</sup>A' symmetry<sup>6</sup>.

In order to test the theoretical model described in the last section, we have carried out a full CI VB calculation using a STO-3G and a 4-31G basis set for the three lowest singlet states, around the anticipated stable geometry.

In Fig. 2 we plot the H<sub>4</sub> ground and S<sub>2</sub> singlet surfaces as a function of  $R$  and  $r$  for the trigonal pyramidal geometry, where we have used a STO-3G basis set. Other potential energy surfaces, with different values of  $r$  (e.g.  $r=1.74$  and  $1.82$  Bohr), do not appear in Fig. 2 because they nearly coincide with the potential energy surface for  $r=1.78$  Bohr. The minimum energy of the S<sub>2</sub> state occurs at  $R = 3.2$  Bohr and  $r = 1.78$  Bohr, where the calculated total energies are -1.78505, -1.78503 and -1.67234 Hartree for S<sub>0</sub>, S<sub>1</sub> and S<sub>2</sub> states, respectively. In this figure a bound S<sub>2</sub> state can be observed using a minimal basis set, even though the potential energy surface is repulsive in the ground state.

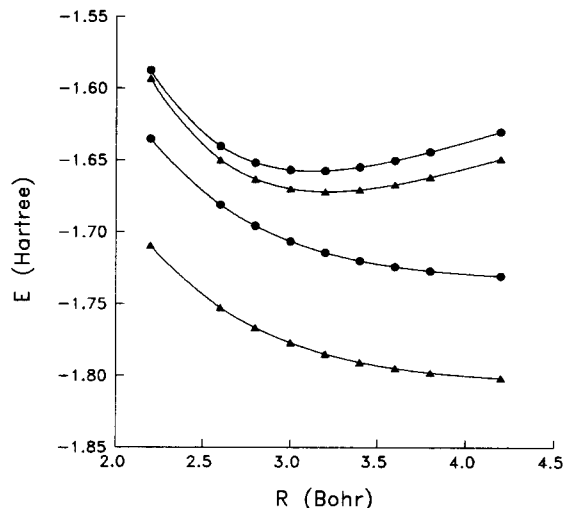


Figure 2. Potential energy surfaces (in Hartree) obtained with a STO-3G basis set, for the ground and the first excited states of A' symmetry of H<sub>4</sub> with a trigonal pyramidal geometry.  $R$  is the distance of the fourth H from the center of the H<sub>3</sub> triangle of side  $r$ . ( $\bullet \rightarrow r = 1.58$  Bohr,  $\blacktriangle \rightarrow r = 1.78$  Bohr,  $\blacksquare \rightarrow r = 1.78$  Bohr)

In Table 1, we show the total energies (obtained from full CI VB calculations, using a STO-3G basis set) of the first three singlet states of H planar structure of Fig. 1(b), with  $r=1.78$  Bohr and with different values for the distance of the fourth H atom from the center of the ring. The minimum energy of the S<sub>2</sub> state (-1.61463 Hartree) occurs at  $R = 4.7$  Bohr. From this table we also can notice that this excited state is bound for this planar structure.

**Table 1** Total energies (Hartree), obtained by a full CI VB calculation with a STO-3G basis set, of the first three singlet states of  $H_4$  for planar structures (Fig. 1(b)), for different values of the fourth H atom ( $R$  distance) from the center of the ring of side  $r = 1.78$  Bohr.

R(Bohr)	3.0	3.5	4.0	4.5	4.7	5.0	5.5
E(S <sub>0</sub> )	-1.91501	-1.88468	-1.85360	-1.83063	-1.82418	-1.81703	-1.81031
E(S <sub>1</sub> )	-1.79920	-1.80246	-1.80417	-1.80499	-1.80519	-1.80531	-1.80546
E(S <sub>2</sub> )	-1.44705	-1.54134	-1.59140	-1.61198	-1.61463	-1.61451	-1.60757

Furthermore, we have also calculated, using a minimal basis set, the total energies of the first three singlet states of  $H_4$ , with the structure shown in Fig. 1(c) and the dimensions reported<sup>13</sup>. The energies -1.85784, -1.75678 and -1.56376 Hartree, were obtained for  $S_0$ ,  $S_1$  and  $S_2$ , respectively. Finally, by using the square geometry with a side of 2.2 Bohr<sup>3,4</sup> within the same minimal basis set, we have total energies of -1.96364, -1.81310 and -1.72140 Hartree for the first three singlet states, respectively.

From all these results it is possible to observe that when we use a minimal basis set the minimum energy of the S state occurs for the square geometry.

We can also see from our results with the trigonal pyramidal geometry that even when we use the STO-3G basis set, the  $S_2$  state minimum energy occurs when the  $R$  and  $r$  values are not very different from the values anticipated by the theoretical model.

Recently, by working within the VB theory and using only the covalent structures of some systems and a set of optimized atomic orbitals, we have obtained results for the total energies of some compounds (e.g.,  $H_4$  molecule) that are approximately equal to the full CI calculations.

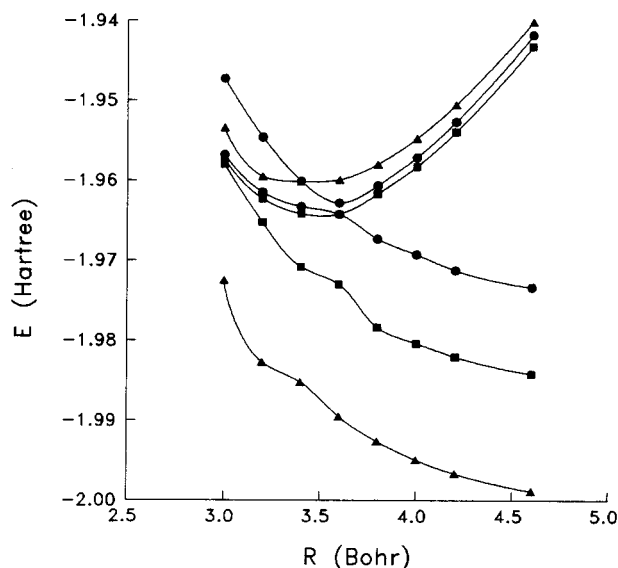
Fig. 3 shows the potential energy surfaces for the ground and first excited state of  $^1A'$  symmetry of  $H_4$  with the geometry of a trigonal pyramid.  $R$  is the distance of the fourth H atom from the center of the  $H_3$  triangle of side  $r$ . In this case, we have used a 4-31G extended basis set and have made a full CI VB calculation to obtain these surfaces. The minimum energy of the  $S_2$  state occurs for  $R = 3.6$  Bohr and  $r = 1.58$  Bohr. These results confirm the theoretical predictions made in the last section. The differences between our results and the theoretical model ( $R = 4.0$  Bohr,  $r = 1.65$  Bohr) are approximately equal to the differences between the predictions and the results of MRD-CI calculations<sup>5,6</sup> ( $R = 3.8$  Bohr,  $r = 1.70$  Bohr) made with the basis set described in the first section of this paper. We should point out that the basis set used by Nicolaides *et alii.*<sup>6</sup> is more complete than the 4-31G basis set. They used only the main configurations, and consequently, have not made full CI calculation as reported here. From our calculations it also can be seen that on changing from a minimal to an extended basis set, the optimum values of  $R$  and  $r$  approach the expected values of the theoretical model. Thus, the choice of a basis set and a full CI calculation are both very important to obtain results in accordance with the prediction values of the last section.

Besides, from Fig. 3 we see that even with the 4-31G basis set, all the potential energy surfaces are repulsive in the

ground state, in accordance with the case of polyatomic systems composed of "nonreactive" closed shell singlet molecular fragments. On the other hand, Nicolaides *et alii.*<sup>5,6</sup> with their MRD-CI calculations, have obtained a bound ground state for  $H_4$  when  $r \leq 1.70$  Bohr.

As can be noted from Fig. 3, there is a region of avoided crossing between the ground and the  $S_2$  states in the same symmetry. The point of the closest approach of the two states occurs at  $r = 1.52$  Bohr and  $R = 3.6$  Bohr.

All the results that we present below were obtained with a full CI VB calculation, where we have used a 4-31G basis set. The total energies of the first three singlet states of the "kite" shape are indicated Fig. 1(b), where we have used  $R = 3.6$  Bohr and  $r = 1.58$  Bohr, are -2.06717, -1.97584 and -1.81480 Hartree, respectively. For the geometry of Fig. 1(c), with the dimensions reported in Ref. [13], the total electronic energies are -2.06739, -1.98970 and -1.84780 Hartree for  $S_0$ ,  $S_1$  and  $S_2$ , respectively. Finally, the total energies of the square geometry with side of 2.2 Bohr are -2.06329, -1.97201 and -1.93414 Hartree for the first three singlet states, respectively.



**Figure 3.** Potential energy surfaces (in Hartree) obtained with a 4-31G basis set, for the ground and second excited states of  $H_4$  at the geometry of trigonal pyramid.  $R$  is the distance of the fourth H from the center of the  $H_3$  triangle of side  $r$ . (● →  $r = 1.52$  Bohr, ■ →  $r = 1.58$  Bohr, ▲ →  $r = 1.70$  Bohr)

From the above results, we observe that on the contrary to what occurs with the STO-3G basis set, where the square geometry gives the minimum energy to the S<sub>2</sub> state, in the 4-31G basis set the minimum energy of the S<sub>2</sub> state is obtained with the trigonal pyramidal geometry (-1.96422 Hartree). This last result is in accordance with the MRD-CI calculations<sup>5,6</sup> and the MIES model.

In Table 2 we compare the total energies of the three lowest singlet states of trigonal pyramidal H<sub>4</sub> system obtained in this and in some previous studies. Earlier calculations using a larger basis set have given larger values of r and R in comparison with our CI VB results, that were made with a 4-31G basis set. All calculations have predicted the same order of states but the energy differences between states vary for the different levels of calculation. The MRD-CI<sup>5,6</sup> calculations yield lower total energies for all three states than do our results.

**Table 2** Total energies (Hartree) of the three lowest singlet states of trigonal pyramidal H<sub>4</sub> as calculated with various correlated wavefunctions.

Energy	STO-3G	4-31G	Ref <sup>5,6</sup>
	full-CI	full-CI	
E(S <sub>0</sub> )	-1.78505	-1.97302	-2.04606
E(S <sub>1</sub> )	-1.78503	-1.97301	-2.04603
E(S <sub>2</sub> )	-1.67234	-1.96422	-2.04601

The differences between the energies of the various states are revealing. The energy difference between the first excited and the ground states is approximately equal for the three calculations. On the other hand, while the energy differences between S<sub>1</sub> and S<sub>2</sub> states obtained with the minimal basis set is very large in comparison with those obtained elsewhere<sup>5,6</sup>, these differences are significantly reduced with the use of the 4-31G basis set. With the STO-3G basis set E(S<sub>2</sub>)-E(S<sub>1</sub>) = 70.71 kcal/mol, whereas the 4-31G basis set E(S<sub>2</sub>)-E(S<sub>1</sub>) = 5.51 kcal/mol. Also<sup>5,6</sup>, E(S<sub>2</sub>)-E(S<sub>1</sub>) = 0.01 kcal/mol.

## Conclusions

The calculated electronic energies resulting from this work, even considering the minimum basis set, confirm the existence of a bound S<sub>2</sub> state of H<sub>4</sub> molecule, corresponding to the trigonal pyramidal geometry. On the other hand, in this same basis set, a square geometry gives the lowest energy for the S<sub>2</sub> state, in disagreement with predictions of the MIES model.

Our *ab initio* VB calculations, which are complete within an extended basis set (4-31G), are in accordance with various MRD-CI results obtained for the H<sub>4</sub> structures considered here. According to our results the square geometry gives the lowest energy among all the planar structure results that we have considered. These calculations also show that the trigonal pyramidal geometry, which has been predicted for the minimum energy in the S<sub>2</sub> state on the basis of MIES model,

has a lower energy than either the corresponding planar structures or a square geometry, when we use the 4-31G basis set. Therefore, we conclude that it is necessary to use an extended basis set in order to obtain results that are in accordance with the MIES model.

The main qualitative difference between our CI VB extended basis set calculations and the MRD-CI<sup>5,6</sup> calculations, for a trigonal pyramidal geometry, is that our results give an unbound ground state for all values of r, while the Nicolaides *et alii*.<sup>5,6</sup> calculations give a bound state only for r ≤ 1.70 Bohr, in the H<sub>4</sub> molecule.

The principal contribution of this work is the predicted existence of a bound excited S<sub>2</sub> state for trigonal pyramidal H<sub>4</sub> molecule using modest (STO-3G and 4-31G) basis set and CI VB. A bound S<sub>2</sub> state has already been predicted by other workers<sup>5,6</sup> using sophisticated calculations and the MIES model.

## References

1. W. Gerhartz, R. D. Poshusta and J. Michl, *J. Am. Chem. Soc.* **98**, 6427 (1976).
2. W. Gerhartz, R. D. Poshusta and J. Michl, *J. Am. Chem. Soc.* **99**, 4263 (1977).
3. J. D. Goddard and I. G. Csizmadia, *Chem. Phys. Lett.* **43**, 73 (1976).
4. J. D. Goddard and I. G. Csizmadia, *Chem. Phys. Lett.* **64**, 219 (1979).
5. C. A. Nicolaides, G. Theodorakopoulos and I. D. Petsalakis, *J. Chem. Phys.* **80**, 1705 (1984).
6. G. Theodorakopoulos, I. D. Petsalakis and C. A. Nicolaides, *J. Mol. Structure (THEOCHEM)* **149**, 23 (1987).
7. C. A. Nicolaides and A. Zdzetsis, *J. Chem. Phys.* **80**, 1900 (1984).
8. C. A. Nicolaides, I. D. Petsalakis and G. Theodorakopoulos, *J. Chem. Phys.* **81**, 748 (1984).
9. T. H. Dunning Jr, *J. Chem. Phys.* **55**, 716 (1971).
10. W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **45**, 509 (1966).
11. C. E. Dykstra and W. S. Swope, *J. Chem. Phys.* **70**, 1 (1979).
12. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, H. B. Schlegel, D. J. Defrees and J. A. Pople, "Gaussian 70", Quantum Chemistry Program Exchange, Indiana University.
13. M. Jungen and V. Staemmler, *Chem. Phys. Lett.* **103**, 191 (1983).
14. (a) R. McWeeny, *Theor. Chim. Acta* **73**, 115 (1988) (b) R. McWeeny and F. E. Jorge, *J. Mol. Structure (THEOCHEM)* **46**, 459 (1988).
15. (a) F. E. Jorge, *Rev. Bras. Fisica* **19**, 281 (1989) (b) F. E. Jorge and R. N. Suave, *Rev. Bras. Fisica* **20**, 84 (1990) (c) F. E. Jorge, *Rev. Bras. Fisica* **21**, 72 (1991).