

***Ab Initio* Valence Bond Calculations of the Total Electronic Energies of the H₄ Molecule**

Francisco Elias Jorge

*Departamento de Física, Universidade Federal do Espírito Santo,
29060-900 Vitória - ES, Brazil*

Received: 8 March, 1993; 8 June 1994

Através da teoria da ligação de valência, utilizando resultados de cálculos *ab initio* com as bases STO-3G e 4-31-G, realizaram-se cálculos de integração de configurações com o fim de determinar a energia de alguns estados eletrônicos da molécula de H₄. Nossos resultados mostram que os três estados de singleto de mais baixa energia têm mínimos com respeito a dissociação em quatro átomos de hidrogênio, quando a molécula de H₄ tem geometria de um losango. Além disso, trabalhando com essa mesma geometria e com a base STO-3G, verifica-se que, para determinados estados eletrônicos de simetria ³B_{2u} ou ³B_{3u} usando somente as respectivas estruturas covalentes decada estado, a energia total é aproximadamente igual à energia correspondente a um cálculo completo de interação de configurações. Obtem-se estes resultados somente quando usamos um conjunto de orbitais atômicos completamente otimizado.

Ab initio valence bond calculations with a STO-3G and a 4-31G basis set, plus full configuration interaction calculations, have been performed for the lozenge geometry of the H₄ molecule to determine the total electronic energy of some states. Our results show that even when the correspondent minimum energies of the three lowest singlet states, obtained with these two basis, are different, the correspondent lengths of the lozenge side of these three energy values are approximately equal. In addition, using *only* a STO-3G basis set, we conclude that for some states of the symmetry ²B_{2u} and ³B_{3u} with covalent structures, the total energy is approximately equal to the energy obtained in the full-CI calculation only when a fully optimized set of atomic orbitals is used.

Keywords: *valence bound, eletronic energy, optimized atomic orbitals, H₄ molecule*

Introduction

The ground state potential of the four hydrogen atom system is repulsive, except for the possible existence of van der Waals minima. The excited states of H₄ are of interest for several reasons, including the fact that this system provides the simplest model for bimolecular photochemical processes¹⁻⁵, such as energy and charge transfer, excimer formation and photocycloadditions.

The *ab initio* valence bond (VB) calculation^{1,2}, using a minimum basis set (STO-4G) and configuration interaction (CI) calculations^{3,4}, has predicted the existence of some bounded states for some geometries of the H₄ molecule. As these results are restricted to a very limited number of geometries, Goddard and Csizmadia^{3,4} think it necessary to study new geometries.

Rubinstein and Shavitt⁵ have studied the lozenge geometry of the H₄ molecule using a double zeta CI calcula-

tion. However, their calculations are limited because they have studied only three states (¹B_{1g}, ³B_{1g}, ¹A_g) and have kept the angle ϕ (see Fig.1) constant with a value of 70°.

Goddard⁶ was the first to use optimized atomic orbitals (AOs) in VB theory to calculate the total electronic energies of some molecules. Cooper *et al.*⁷ generalized this method and developed the spin-coupled VB theory, where the atomic orbitals are expanded on a basis set, and all the variational parameters are simultaneously optimized to minimize the energy.

Recently, a different approach was used to describe the molecular electronic structure of some states^{8,9}. In this case, only the mutual overlap of the nearest-neighboring orbitals are increased, and it is shown that when these modified orbitals are used, the full CI limit may be closely obtained by using only a small number of structures. The definition of these modified orbitals is not recent, since they were employed by Coulson and Fisher¹⁰, and later by Mueller

and Eyring¹¹, but their use was restricted due to problems of non-orthogonality.

In this initial study of the H₄ molecule with lozenge geometry, the total energies of some electronic states have been calculated; we have used an *ab initio* VB calculation, complete within a STO-3G and a 4-31G basis set. The optimum lozenge geometry of H₄ is obtained by minimizing the total energy of the first singlet excited state. Our results indicate that the three lowest singlet states of a lozenge arrangement show a minimum with respect to the dissociation into four hydrogen atoms. These results are also compared to the results obtained by Rubinstein and Shavitt⁵.

Also, we will see in the Results and Discussion section, using *only* a STO-3G basis set, that with covalent structures it is necessary to use a fully optimized set of atomic orbitals in order to obtain an energy (for some states) comparable to the energy obtained in the full-CI calculation.

Theory

The method used in the present calculations is fully described elsewhere^{8,9} and is briefly presented here, and the discussion is valid *only* for the STO-3G basis set.

The total energies of some states, in a lozenge geometry of the H₄ molecule (D_{2h} point group), are calculated in this work. Our VB calculation includes only four electrons and four **non-orthogonal** atomic orbitals, with 20 singlet and 15 triplet structures¹².

Figure 1 shows the H₄ molecule, where each 1s non-orthogonal AO is denoted by

$$a_1, a_2, a_3, a_4 \quad (2.1)$$

An appropriate combination of the original AOs is

$$\begin{aligned} a_1' &= a_1 + \lambda(a_2 + a_4) + \nu a_3 \\ a_2' &= a_2 + \lambda(a_1 + a_3) + \mu a_4 \\ a_3' &= a_3 + \lambda(a_2 + a_4) + \nu a_1 \\ a_4' &= a_4 + \lambda(a_1 + a_3) + \mu a_2 \end{aligned} \quad (2.2)$$

where each modified orbital has been expanded in terms of the complete set basis, and λ, ν, μ are numerical parameters that may be varied in order to minimize the energy. To enhance only the mutual overlap of the nearest-neighbor-

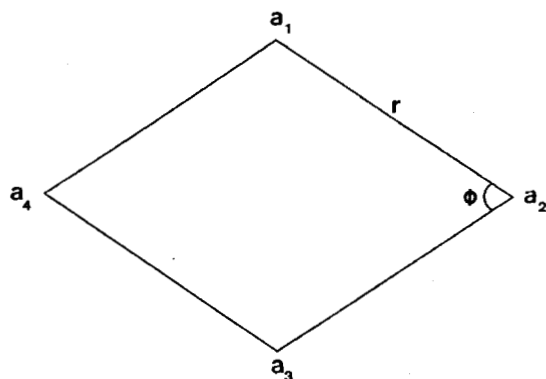


Figure 1. The lozenge geometry of an H₄ molecule.

ing^{8,9} orbitals, we make ν and μ equal to zero in eq. 2.2. In this case the modified orbitals are reduced to

$$\begin{aligned} a_1'' &= a_1 + \lambda(a_2 + a_4) \\ a_2'' &= a_2 + \lambda(a_1 + a_3) \\ a_3'' &= a_3 + \lambda(a_2 + a_4) \\ a_4'' &= a_4 + \lambda(a_1 + a_3) \end{aligned} \quad (2.3)$$

The use of the modified orbitals of eq. 2.3, instead of eq. 2.2, reduces the computational labor, but in general the energies obtained with eq. 2.2 are lower than those obtained with eq. 2.3 (see Ref. 8).

Results and Discussion

To argue in favor of employing a minimum basis set (STO-3G) in an initial study of the H₄ molecule with lozenge geometry, we recall the studies of Michl *et al.*^{1,2} of a large number of geometries of H₄ that were calculated with a STO-4G basis set.

They predicted a bound excimer state of H₄ that was later confirmed by the results of an *ab initio* CI calculation of Goddard and Csizmadia^{3,4} using an extended basis set. Furthermore, in a recent *ab initio* VB calculation, using both a minimal and an extended basis set plus CI calculations¹³, our results confirm the predictions of Nicolaides *et al.*^{14,15}, that the trigonal pyramidal geometry of the H₄ molecule has the singlet second excited state bounded.

Ab initio VB calculations in a minimal and an extended gaussian basis set plus full CI calculations have been performed here for the lozenge geometry of the H₄ molecule.

The hydrogen basis set we have employed is formed by a minimal (STO-3G) and an extended basis set (4-31G), consisting of 1 and 2 functions for the H atom, respectively. Our calculations use the "Gaussian 70" computer program¹⁶, with 1.24 (STO-3G basis set) and 1.20 and 1.15 (4-31G basis set), for the values of the s-exponent.

First of all, *ab initio* SCF MO calculations of the H₄ 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 the lozenge geometry of the H₄ molecule. For the STO-3G and the 4-31G basis set, 20 and 336 singlet structures, respectively, have been used in our full CI VB calculations.

To obtain the optimum geometry of a lozenge H₄ molecule we first make the lengths of the lozenge sides (see Fig. 1) equal to 2.50 Bohr, a result obtained for the best square geometry of H₄ with the STO-3G basis set. Then, the angle ϕ (in Fig. 1) is varied in order to obtain a minimum energy for the first singlet excited state, the only one among the three lowest singlet states that shows a minimum depending on the angle ϕ . The best angle is found to be 65°

In Fig. 2 we plot the potential energy surfaces of the three lowest singlet states (r is the length of the lozenge side), with a STO-3G basis set, for the lozenge geometry ($\phi = 65^\circ$, see Fig. 1) of the H₄ molecule. These three singlet

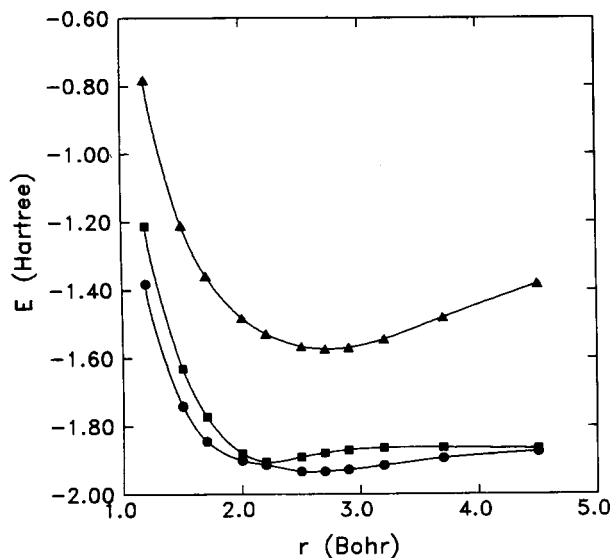


Figure 2. Potential energy surfaces (in Hartree) obtained with a STO-3G basis set, for the three lowest singlet states of a lozenge H₄ geometry. r is the length of the lozenge side.

● → ¹B_{1g}, ■ → ¹A_{1g}, ▲ → ¹B_{2g}

states show local minima for side lengths in the range $r = 2.20$ to 2.70 Bohr, close to the best geometry of a lozenge (with $\phi = 65^\circ$) H₄ molecule, which is obtained when r is equal to 2.50 Bohr. In the limit of an infinite lozenge the ground state approximates the four ground state hydrogen atoms ($E(\text{this work}) = -1.86633$ Hartree). The first excited state, which presents a minimal with this geometry, tends to the same dissociation products as the ground state. The second excited state is much higher in energy and its dissociation product is different from the other two states. The minimum energies of the ¹B_{1g} (-1.93322 Hartree), ¹A_g (-1.90553 Hartree) and ¹A_g^{*} (-1.57367 Hartree) states occur for the values 2.50 , 2.20 and 2.70 Bohr, respectively.

Figure 3 shows the potential energy curves for the three lowest singlet states of the H₄ molecule of Fig. 1, using the 4-31G basis set. The results indicate that the three lowest singlet states show minima with respect to dissociation into four hydrogen atoms.

The minimum energies of the ¹B_{1g} (-2.04772 Hartree), ¹A_g (-2.04222 Hartree) and ¹A_g^{*} (-1.82533 Hartree) states occur for the values 2.50 , 2.30 and 2.70 Bohr, respectively. We have seen that similar values of r (2.50 (¹B_{1g}), 2.20 (¹A_g) and 2.70 Bohr (¹A_g^{*})) are obtained for the minimal energies of these states when we used the STO-3G basis set, even when the energy eigenvalues of the corresponding states are different. Rubinstein and Shavitt⁵, using the same approach mentioned in section 1, have obtained the minimum energies for ¹B_{1g} (-2.06065 Hartree) and ¹A_g (-2.04001 Hartree) at r equal to 2.57 and 2.25 Bohr, respectively. We can see from these results that the r values, of the minimum energies of the ¹B_{1g}

Table 1. Total energies (in Hartree) obtained using a STO-3G basis set, of the four lowest electronic states in a lozenge geometry* of the H₄ molecule, within different approaches.

Symmetry of the state	Number of structures	Approach (theory)	Total energy (Hartree)
³ B _{1g}	3	eq. 2.1	-1.80500
	3	eq. 2.3	-1.88566
	3	eq. 2.2	-1.88733
	Full-CI: 15		-1.89083
¹ B _{1g}	2	eq. 2.1	-1.88925
	2	eq. 2.3	-1.91251
	2	eq. 2.2	-1.91315
	Full-CI: 20		-1.91458
³ B _{2u}	3	eq. 2.1	-1.64983
	3	eq. 2.3	-1.66852
	3	eq. 2.2	-1.67918
	Full-CI: 15		-1.68061
³ B _{3u}	3	eq. 2.1	-1.60764
	3	eq. 2.3	-1.63854
	3	eq. 2.2	-1.64202
	Full-CI: 15		-1.64440

* See Fig. 1, $r = 2,50$ Bohr and $\phi = 65^\circ$

and ¹A_g states, are approximately equal in the three different approaches.

Total energies (in Hartree) of the four lowest electronic states in a lozenge geometry (with $r = 2.50$ Bohr and $\phi = 65^\circ$) of the H₄ molecule using only a STO-3G basis set and the equations 2.1, 2.2 and 2.3, are tabulated in Table 1. For the purpose of comparison, the energies of the full-CI calculations are also presented.

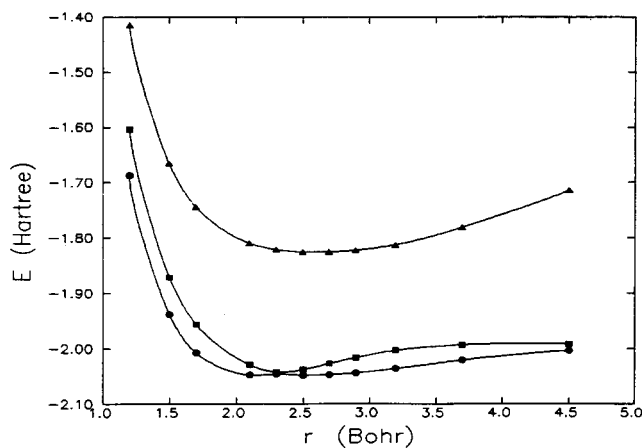


Figure 3. Potential energy surfaces (in Hartree) obtained with a 4-31G basis set, for the three lowest singlet states of a lozenge H₄ geometry. r is the length of the lozenge side.

● → ¹B_{1g}, ■ → ¹A_g, ▲ → ¹A_g^{*}

It can be seen from Table I that the total energies of all electronic states (${}^3B_{1g}$, ${}^1B_{1g}$, ${}^3B_{2u}$ and ${}^3B_{3u}$ symmetries) obtained with eq. 2.1 are higher than the corresponding energies obtained with the full-CI calculation. The difference between the total energies predicted by eqs. 2.2 and 2.3 is approximately 0.001 Hartree for the ground state (${}^3B_{1g}$ symmetry) and the first excited state (${}^1B_{1g}$ symmetry), when we use only the covalent structures of each state. Also, they are approximately equal to the corresponding energies obtained with the full-CI calculation.

For the ${}^3B_{2u}$ state the difference between the energies obtained with the full-CI calculation and with eq. 2.3, using only the covalent structures (where the optimum value of the parameter λ is 0.10) is of the order of 0.012 Hartree. This difference is high compared to the difference obtained for the ${}^3B_{1g}$ and ${}^1B_{1g}$ states, with the same atomic orbitals set of eq. 2.3 and the full CI calculation. Thus, in this case, the energy obtained with this method is not satisfactory. We remind the reader that similar calculations using modified atomic orbitals of the type of eq. 2.3 have given good results for other molecules (see Jorge *et al.*^{8b,9a}), where the electronic states had a different symmetry than ${}^3B_{2u}$. However, if we substitute these modified orbitals by the fully optimized set of atomic orbitals of eq. 2.2, the difference is reduced to 0.001 Hartree, even using the same structures as the previous calculations. This last difference is about ten times smaller than the first one. The reason for this discrepancy is that, for this state, the total energy value depends more on the bonds between non-adjacent orbitals (a_2a_4 , see Fig. 1) than in the case of the other states analyzed above.

The difference between the energies obtained with eq. 2.2 for the ${}^3B_{3u}$ state, using only the covalent structures of this state, and the full-CI calculation (Table 1) is about two times smaller than the difference between the energies obtained with eq. 2.3 and the full-CI calculation. Once more, we see that it is necessary to use the fully optimized set of atomic orbitals to obtain the value of the energy which is approximately equal to the value obtained by a full-CI calculation.

The wave functions of states ${}^3B_{2u}$ and ${}^3B_{3u}$, using only the triplet covalent structures, are respectively

$${}^3\psi_{2u} = a_1 a_2 a_3 a_4 (\alpha(s_2) \beta(s_4) - \beta(s_2) \alpha(s_4)) \alpha(s_1) \alpha(s_3)$$

$${}^3\psi_{3u} = a_1 a_2 a_3 a_4 (\alpha(s_1) \beta(s_3) - \beta(s_1) \alpha(s_3)) \alpha(s_2) \alpha(s_4)$$

where α and β represent the spin functions. From these equations we clearly see that the pairing of spins is made between non-adjacent electrons. This is the reason that these states depend on a fully optimized set of atomic orbitals (eq. 2.2).

4. Conclusions

For the lozenge geometry of the H_4 molecule the results for the three lowest singlet states obtained with the STO-3G

and 4-31G basis set are very similar. The two basis set show that the three states present minimal energy with respect to dissociation into four hydrogen atoms. Even when the correspondent minimum energies obtained with the two basis set are different, the correspondent r values of these energy values are approximately equal.

In addition, we conclude that for the ${}^3B_{2u}$ and ${}^3B_{3u}$ states (when we use a STO-3G basis set), the total energy (with covalent structures) is approximately equal to the energy obtained in the full-CI calculation, only when we use a fully optimized set of atomic orbitals. In these cases, the numerical parameters (ν and μ) that appear in the modified orbitals (eq. 2.2) are necessarily different from zero, because these states depend on the bonds between non-adjacent orbitals. Such a conclusion is equally applicable to other molecules subjected to the same type of situation.

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. M. Rubinstein and I. Shavitt, *J. Chem. Phys.* **51**, 2014 (1969).
6. W. A. Goddard, *Phys. Rev.* **157**, 73,81 (1967).
7. D. L. Cooper, J. Gerratt and M. Raimondi, *Nature* **323**, 699(1986).
8. a) R. McWeeny, *Theoret. Chim. Acta*, **73**, 115 (1988)
b) R. McWeeny and F. E. Jorge, *J. Mol. Structure (THEOCHEM)* **42**, 1459 (1988).
9. 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).
10. C. A. Coulson and I. Fisher, *Phil. Mag.* **40**, 306 (1949).
11. C. A. Mueller and H. Eyring, *J. Chem. Phys.* **19**, 1495 (1951).
12. R. McWeeny, *Proc. Roy. Soc., Ser. A* **227**, 228 (1955)
13. F. E. Jorge, *J. Braz. Chem. Soc.* **4**, 26 (1993).
14. C. A. Nicolstates, G. Theodorakopoulos and I. D. Petsalakis, *J. Chem. Phys.* **80**, 1705 (1984).
15. G. Theodorakopoulos, I. D. Petsalakis and C. A. Nicolaidis, *J. Mol. Structure (THEOCHEM)* **149**, 23 (1987).
16. 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.