

# NON-EMPIRICAL APPROXIMATE CALCULATIONS FOR THE GROUND STATES OF $H_2$ AND $H_3$ INCLUDING COMPLETE CONFIGURATION INTERACTION

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Calculations are reported for the ground states of  $H_2$  and  $H_3$  in which the original atomic orbital basis is transformed to a symmetrically orthonormal atomic orbital basis. Complete configuration interaction is carried out and the results are shown to be in good agreement with ab initio calculations.

## 1. Introduction

Although the development of high-speed computers brings ab initio calculations within the reach of many laboratories, the search for approximate theories is still a matter of importance, especially for large molecules and in cases where many different nuclear configurations have to be calculated, e.g., potential energy surfaces.

In this note we present some calculations with an approximate method, described recently [1] in which a minimal basis of symmetrically orthonormal atomic orbitals is used and all integrals are evaluated non-empirically.

In the present work we extend the method with inclusion of complete configuration interaction (CI). To make a complete CI treatment tractable, calculations have been performed in a minimal STO basis for  $H_2$  and  $H_3$ .

For these systems minimal basis set ab initio calculations have been reported by McLean et al. [2] and by Ransil et al. [3] which makes a direct comparison possible.

## 2. Method

If we represent the original atomic orbital (AO) basis and the symmetrically orthonormal atomic orbital (OAO) basis by the row vectors  $\chi$  and  $\lambda$  respective-

ly, the following relation holds [4,5]:

$$\lambda = \chi S^{-1/2}, \quad (1)$$

where  $S$  is the overlap matrix in the AO basis. Using this relation together with a Ruedenberg expansion [6], whereby two-centre charge densities are expressed as linear combinations of one-centre densities, Roby [1] showed that all multi-centre repulsion integrals in the OAO basis containing two-centre charge densities are eliminated, the remaining repulsion integrals being equal to the corresponding integrals in the AO basis. If a minimal basis set is used, this is equivalent to the NDDO approximation [1,7].

The resulting method may then be classified as a non-empirical NDDO method. Its accuracy depends on the accuracy of the Ruedenberg expansion truncated to a minimal basis set, which in our calculations for  $H_2$  and  $H_3$  consists of one 1s STO on each centre. The method involves:

(a) calculation of the core hamiltonian matrix in the OAO basis by [4]:

$$H^\lambda = S^{-1/2} H^x S^{-1/2}; \quad (2)$$

(b) the electron repulsion integrals in the OAO basis left after the NDDO approximation are set equal to the corresponding integrals calculated in the AO basis. This is the only integral approximation made in the method. In order to calculate  $H^\lambda$  we need the matrices  $S^{-1/2}$  and  $H^x$ . The matrix  $S^{-1/2}$  is found as follows [5]:

$$SU = UD, \quad S^{-1/2} = UD^{-1/2}U^\dagger \quad (3)$$

where  $U$  is a unitary matrix and  $D$  a diagonal matrix. The matrix  $D^{-1/2}$ , which is also diagonal, is the inverse of the positive square root of  $D$ :

$$(D^{-1/2})_{ii} = (D_{ii})^{-1/2}. \quad (4)$$

In fact there is a choice of sign in every element of  $D^{-1/2}$ , but in order to get a physically satisfactory situation it is necessary to choose always the same sign [8].

The matrix elements of  $H^x$  are evaluated using Roothaan's formulae [9]. The three-centre nuclear attraction integrals, which occur in the case of  $H_3$ , are calculated to within an accuracy of about  $10^{-5}$  au by replacing each STO by a linear combination of 6 gaussian type orbitals [10].

In addition our calculations include complete CI. The performance of these CI calculations is facilitated if simple approximate MO's are used instead of SCF MO's since this should not affect the final results of a complete CI calculation [11] whereas the computation time is considerably reduced and convergence difficulties are avoided. The approximate MO's which we use in our CI calculations are the eigenvectors of the core hamiltonian matrix  $H^\lambda$ .

### 3. Results and discussion

Calculations were first carried out by setting the orbital exponents ( $\zeta$ ) equal to the Slater atomic values. These calculations are designated as I.

In subsequent calculations (designated as II) this restriction was removed and the orbital exponents were allowed to vary.

In the case of linear symmetric  $H_3$  this variation

was done in two distinct calculations, one (IIa) using the same orbital exponent for the three H atoms and another (IIb) in which the orbital exponent of the middle atom ( $\zeta_m$ ) and that of the outer atoms ( $\zeta_o$ ) was varied independently.

Table 1 summarizes the results for  $H_2$  whereas the results for  $H_3$  are shown in table 2. For comparison the corresponding ab initio results reported by McLean et al. [2] and by Ransil et al. [3] are also given. As may be seen from the tables the results of the present work are in good agreement with the ab initio calculations, especially in the case of  $H_2$ , though the correspondence in total energies comes out somewhat less satisfactory if CI is included.

For  $H_3$  the deviations in total energies are more pronounced and consequently, the calculated barrier height  $\Delta E$  of the reaction  $H_2 + H \rightarrow H + H_2$  — which is a small difference between large numbers — differs relatively much from the ab initio values.

The less satisfactory results of the CI calculations may be understood from a consideration of the repulsion integral approximation formulated in section 2, because this procedure underestimates the one-centre integrals and overestimates the two-centre integrals in the OAO basis by about 10% [12]. From the energy expressions for  $H_2$  without and including CI,

$$E(\text{SCF}) = 2H_{11}^\lambda + \frac{1}{2}[(11|11) + (11|22)] + 2H_{12}^\lambda + 1/R, \quad (5)$$

$$E(\text{CI}) = 2H_{11}^\lambda + \frac{1}{2}[(11|11) + (11|22)] - \{(2H_{12}^\lambda)^2 + \frac{1}{4}[(11|11) - (11|22)]^2\}^{1/2} + 1/R, \quad (6)$$

it is clear that if the difference between one-centre and two-centre integrals — which appears only in eq. (6) — comes out too small the resulting energy is too high.

Table 1  
Comparison of results for  $H_2$  a)

Method	Code b)	$R$ (au)	$E$ (au)	$-\epsilon_1$ (eV) c)	$\zeta$
ab initio d)	I	1.61 (1.66)	-1.099 (-1.119)	15.9	1.00 (1.00)
this work	I	1.60 (1.64)	-1.101 (-1.107)	16.0	1.00 (1.00)
ab initio d)	II	1.38 (1.42)	-1.128 (-1.148)	16.1	1.20 e) (1.19) e)
this work	II	1.39 (1.42)	-1.130 (-1.136)	16.2	1.20 e) (1.20) e)

a) The values in parentheses refer to the CI calculations.

b) See text; c) orbital energy; d) ref. [2]; e) optimized orbital exponent.

Table 2  
Comparison of results for linear symmetric  $H_3$  including CI

Method	Code <sup>a)</sup>	$R$ (au) <sup>b)</sup>	$E$ (au)	$\Delta E$ (au) <sup>c)</sup>	$\xi$
ab initio <sup>d)</sup>	I	2.05	-1.597	0.022	1.00
this work	I	2.15	-1.539	0.068	1.00
ab initio <sup>d)</sup>	II	1.92	-1.609	0.039	1.10 <sup>e)</sup>
this work	IIa	2.00	-1.549	0.087	1.10 <sup>e)</sup>
this work	IIb	1.97	-1.554	0.082	1.03 ( $\xi_o$ ) <sup>e)</sup> 1.23 ( $\xi_m$ ) <sup>e)</sup>

a) See text; b) neighbour internuclear distance at saddle point; c)  $\Delta E = E(H_3) - E(H_2 + H)$ ; d) ref. [3]; e) optimized orbital exponent.

Though we used in our calculations the same number of electron repulsion integrals as in the CNDO method, the present results are clearly superior. The orbital energy for  $H_2$  calculated with CNDO/2 is 20.8 eV [13] which is much greater than the values given in table 1. Moreover the binding energies calculated with CNDO/2 for  $H_2$  and  $H_3$  are much too large, being 0.197 au [13] and 0.210 au [14] respectively, which means that  $H_3$  is erroneously predicted to be more stable than  $H_2 + H$ .

#### 4. Conclusions

The results of our calculations indicate that the present method using a minimal basis set is able to reproduce the ab initio results quite well, but it is important to note that at equilibrium distances the inclusion of CI in the present method has almost no effect on the total energies.

Obviously, the accuracy in total energies is not good enough to make a quantitative correct prediction of such a small quantity as the barrier height. For that purpose extension of the basis set would be appropriate. An interesting feature of the present method is the possibility of orbital exponent optimization. In this respect the method is markedly different from CNDO/2 or other semi-empirical theories, where such optimization is not possible.

It can be concluded that the present non-empirical NDDO method shows much promise for the predic-

tion of bond distances, though it remains to be seen what the results are when heavier atoms are involved.

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#### References

- [1] K.R. Roby, Chem. Phys. Letters 11 (1971) 6; 12 (1972) 579.
- [2] A.D. McLean, A. Weiss and M. Yoshimine, Rev. Mod. Phys. 32 (1960) 211.
- [3] V. Griffing, J.L. Jackson and B.J. Ransil, J. Chem. Phys. 30 (1959) 1066.
- [4] P.-O. Löwdin, J. Chem. Phys. 18 (1950) 365.
- [5] P.-O. Löwdin, Advan. Quantum Chem. 5 (1970) 185.
- [6] K. Ruedenberg, J. Chem. Phys. 19 (1951) 1433.
- [7] J.A. Pople, D.P. Santry and G.A. Segal, J. Chem. Phys. 43S (1965) 129.
- [8] P.A.M. Dirac, Quantum mechanics (Oxford Univ. Press, London, 1958) p. 41.
- [9] C.C.J. Roothaan, J. Chem. Phys. 19 (1951) 1445.
- [10] W.J. Hehre, R.F. Stewart and J.A. Pople, J. Chem. Phys. 51 (1969) 1657.
- [11] R. McWeeny and B.T. Sutcliffe, Methods of molecular quantum mechanics (Academic Press, New York, 1969) p. 56, 168.
- [12] D.B. Cook, P.C. Hollis and R. McWeeny, Mol. Phys. 13 (1967) 553.
- [13] J.A. Pople and D.L. Beveridge, Approximate molecular orbital theory (McGraw-Hill, New York, 1970) p. 89.
- [14] S. de Jong, unpublished results.