Double Orbital Exponent SCF Functions for H_2O, NH_3, CH_4[*]

CARLA GUIDOTTI and ORIANO SALVETTI

Istituto di Chimica Fisica, Università degli Studi di Pisa

The results of an investigation on best double orbital exponents for Hydrogen in H_2O, NH_3, CH_4 are reported. An error analysis for calculations with extended basis sets is presented. This analysis is based on the hypothesis that the errors on the integrals are small so that it is possible to use statistical methods.

Introduction

Some recent works on the electronic structure of atoms [1, 2] have shown that SCF energies very near to the Hartree-Fock limit can be obtained by replacing each Slater orbital of the basis set by two Slater orbitals with suitable orbital exponent ζ. This kind of calculations have been accomplished on linear molecules also: A. D. McLean and M. Yoshimine [3] used such double-ζ orbitals with a larger basis set to take account of polarization effects.

For molecules containing hydrogen atoms, "best atomic double-ζ" criterion breaks down for the H atom itself: on the other hand using double-ζ for H also is requested by a balancing criterion of basis atomic functions [4].

The aim of this work is to ascertain whether double-ζ orbitals can be used generally in molecules containing OH, NH and CH bonds and to find out what kind of errors on the energy values can arise from the inaccuracy of basic integrals.

General Relationships and Computational Errors

The first problem to be tackled was the determination of the best couple of ζ values for H. We tried to do this by carrying out a calculation in which each H atom was described by 5 $1s$ orbitals with $\zeta = 0.9$, 1.15, 1.4, 1.65, and 1.9. Though our SCF program worked always in double precision, however the process did not converge and the energy values were several atomic units wrong. To explain this fact we thought necessary to ascertain the influence of integral evaluation errors on the SCF energy.

Be C the matrix of the coefficients of occupied molecular orbitals with $C^\dagger SC = 1$ where S is the overlap matrix. The energy is given by

$$E = \text{tr}\left[D(2H + G)\right]$$

with $D = CC^\dagger$,

$$H_{rs} = \int \chi_r^*(\mu)\, h(\mu)\, \chi_s(\mu)\, d\tau_\mu,$$
$$G_{rs} = \sum_{pq} D_{pq} I_{pq}^{rs}, \tag{1}$$

$$I_{pq}^{rs} = 2 \int \chi_r^*(\mu) \chi_s(\mu) \frac{1}{r_{\mu\nu}} \chi_p^*(\nu) \chi_q(\nu)\, d\tau_\mu\, d\tau_\nu - \int \chi_r^*(\mu) \chi_q(\mu) \frac{1}{r_{\mu\nu}} \chi_p^*(\nu) \chi_s(\nu)\, d\tau_\mu\, d\tau_\nu$$

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where μ are the spatial variables of electron μ, $h(\mu)$ is the one electron Hamiltonian operator on electron μ and χ_r is a basic atomic function on the center r.

The integrals I_{pq}^{rs} and H_{rs} are not exact: hence the energy E given by (1) is affected by an error δE, which on the other hand depends also upon C. For a given C, the most probable value of δE can be determined by statistical methods, by supposing that the errors of the integral values are casual and small, hence not correlated to the signs of the elements of the C matrix. The error δE calculated in this way is certainly less than the one relative to the whole iterative procedure, for C itself depends upon the values of the integrals and E goes towards a minimum.

By the following analysis we calculate the error δE relative to the final C, independently from the possibility of an error on C itself. C is taken as rigorously orthonormal. This can be verified by calculating

$$\eta = (CC^\dagger)\,S(CC^\dagger) - C(C^\dagger SC)\,C^\dagger,$$

In our calculation η_{max} may not be greater than 10^{-12}. The above property is not easily attainable: if the order of the matrix is about 30 and the overlap integrals are relatively high, the accuracy may be so poor to invalidate the results completely.

By differentiating (1) we get:

$$\delta E = 2 \sum_{pq} D_{pq}\,\delta H_{qp} + \sum_{pq}\sum_{rs} D_{pq}D_{rs}\,\delta I_{pq}^{rs} \tag{2}$$

where δH_{qp} and δI_{pq}^{rs} are the probable errors on the one and two electron integrals. Rigorously, δE should be calculated by the relationship

$$|\delta E| = 2 \sum_{pq} \left|D_{pq}\,\delta H_{qp}\right| + \sum_{pq}\sum_{rs} \left|D_{pq}D_{rs}\,\delta I_{pq}^{rs}\right|$$

but this brings certainly a too high value of δE, for in this case the elements of D and the errors on the integrals should be of the same sign. On the contrary, D will depend essentially on the values of I_{pq}^{rs} and H_{pq} and not on their errors. If these errors are casual, their average will be zero, hence

$$\overline{\delta E^2} = \varepsilon'^2 \sum_{pq} D_{pq}^2 + \varepsilon''^2 \sum_{pq}\sum_{rs} D_{pq}^2 D_{rs}^2 = \varepsilon'^2 \sum_{pq} D_{pq}^2 + \varepsilon''^2 \left(\sum_{pq} D_{pq}^2\right)^2 \tag{3}$$

where ε'^2, ε''^2 are the standard deviations of the one and two electron integrals respectively. Generally the accuracy of the one electron integrals is much higher than that of two electron integrals: therefore the first term of (3) can be neglected and (3) can be written

$$\overline{\delta E^2} = \varepsilon''^2 \left(\sum_{pq} D_{pq}^2\right)^2, \qquad s = |\delta E| = \varepsilon'' \sum_{pq} D_{pq}^2 \tag{4}$$

When, as a consequence of the choice of the basis orbitals, some elements of C are greater than 1 and the number of basis functions is high, δE can become quite large. δE given by (4) has been assumed to be an approximate value of the error on the energy evaluation.

Results and Conclusions

Slater type orbitals with Clementi's orbital exponents ζ [1] for C, N and O were used as basis functions. For H atoms all the combinations of two $1s$ orbitals with $\zeta = 0.9$, 1.15, 1.4, 1.65, and 1.9 were considered. The whole set of ζ values is

reported in Table 1. In every case a set of 14 basis orbitals for H_2O, 16 for NH_3 and 18 for CH_4 was employed. Self-consistency was achieved by a Roothaan iterative procedure [5].

Table 3 shows the values of the energies of the three molecules for all the couples of ζ and the errors calculated by relation (4) with $\varepsilon'' = 5 \cdot 10^{-6}$. The energy

Table 1. *Orbital exponents for double-ζ basis set for C, N, O, H*

	C	N	O	H
$1s$	5.23090	6.11863	7.06227	0.9
$1s'$	7.96897	8.93843	10.10850	1.15
$2s$	1.16782	1.39327	1.62705	
$2s'$	1.82031	2.22157	2.62158	
$2p$	1.25572	1.50585	1.65372	
$2p'$	2.72625	3.26741	3.68127	
$1s''$				1.4
$1s'''$				1.65
$1s''''$				1.9

Table 2. *Coordinates of different atoms* (a.u.)

	O	H_1	H_2	N	H_1	H_2	H_3	C	H_1	H_2	H_3	H_4
X	0.	a	$-a$	0.	c	$-1/2 \cdot c$	$-1/2 \cdot c$	0.	e	$-e$	e	$-e$
Y	0.	0.	0.	0.	0.	$+\sqrt{3}/2 \cdot c$	$-\sqrt{3}/2 \cdot c$	0.	e	$-e$	$-e$	e
Z	0.	b	b	0.	d	d	d	0.	e	e	$-e$	$-e$

$a = 1.436208$ $c = 1.783245$ $e = 1.193625$

$b = 1.102041$ $d = 0.720487$

Table 3. *Total energies and evaluated errors* (a.u.)

ζ_1	ζ_2	CH_4		NH_3		OH_2	
0.9	0.9	-40.0381	$\pm 0.0^3 2$	-56.0290	$\pm 0.0^4 1$	-75.8917	$\pm 0.0^4 5$
0.9	1.15	-40.1822	$\pm 0.0^3 3$	-56.1632	$\pm 0.0^3 3$	-76.0003	$\pm 0.0^3 3$
0.9	1.4	-40.1821	$\pm 0.0^4 5$	-56.1666	$\pm 0.0^4 5$	-76.0039	$\pm 0.0^4 4$
0.9	1.65	-40.1744	$\pm 0.0^4 4$	-56.1633	$\pm 0.0^4 3$	-76.0018	$\pm 0.0^4 2$
0.9	1.9	-40.1624	$\pm 0.0^4 4$	-56.1556	$\pm 0.0^4 3$	-75.9961	$\pm 0.0^4 1$
1.15	1.15	-40.1667	$\pm 0.0^3 1$	-56.1392	$\pm 0.0^4 7$	-75.9723	$\pm 0.0^4 4$
1.15	1.4	-40.1834	$\pm 0.0^4 6$	-56.1678	$\pm 0.0^4 7$	-76.0052	$\pm 0.0^4 8$
1.15	1.65	-40.1813	$\pm 0.0^4 5$	-56.1666	$\pm 0.0^4 4$	-76.0043	$\pm 0.0^4 2$
1.15	1.9	-40.1790	$\pm 0.0^4 6$	-56.1642	$\pm 0.0^4 3$	-76.0022	$\pm 0.0^4 2$
1.4	1.4	-40.1773	$\pm 0.0^4 7$	-56.1590	$\pm 0.0^4 5$	-75.9975	$\pm 0.0^4 3$
1.4	1.65	-40.1845	$\pm 0.0^3 2$	-56.1675	$\pm 0.0^3 1$	-76.0054	$\pm 0.0^4 6$
1.4	1.9	-40.1848	$\pm 0.0^3 1$	-56.1669	$\pm 0.0^4 8$	-76.0048	$\pm 0.0^4 4$
1.65	1.65	-40.1374	$\pm 0.0^4 5$	-56.1423	$\pm 0.0^4 4$	-75.9875	$\pm 0.0^4 3$
1.65	1.9	-40.1841	$\pm 0.0^3 8$	-56.1660	$\pm 0.0^3 7$	-76.0052	$\pm 0.0^3 2$
1.9	1.9	-40.0780	$\pm 0.0^4 4$	-56.0809	$\pm 0.0^4 4$	-75.9611	$\pm 0.0^4 2$
minimal basis set		-40.1141[a]		-56.0058[d]		-75.6807[e]	
more elaborated		-40.180[b]		-56.201[e]		-76.034[e]	
basis set		-40.198[e]				-76.042[f]	
experimental		-40.525[e]		-56.588[e]		-76.483[e]	

    [a] See Ref. [6]. – [b] See Ref. [7]. – [e] See Ref. [8]. – [d] See Ref. [9]. – [e] See Ref. [10]. – [f] See Ref. [11].

values of the best ζ couples are in italic. It should be noticed that around the minimum the dependence of the energy upon ζ_1, ζ_2 is very low; hence we did not look for the couple corresponding to the absolute minimum. In the lowest rows of Table 3 the literature values of "minimal basis set" calculations and with very large basis sets are reported. The differences of our calculations with these latter ones are 0.014, 0.033, 0.037 a.u. for CH_4, NH_3, and H_2O respectively. The energy values are quite good but not completely satisfactory. We think that it is necessary to extend the basis set to take account of the different molecular symmetries.

However we think to have shown that with large basis set calculations an accurate error analysis should be made, because even when two-electron integrals are evaluated very accurately it is easy to get incorrect energy values.

In fact, while in the calculations reported in Table 3 the errors are reasonably small (10^{-3}, 10^{-4} a.u.), with three $1s$ functions for each H atom these errors become decidedly larger (10^{-1}, 10^{-2} a.u.) and with five $1s$ functions rise to several atomic units so that the calculations lose their meaning.

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Dr. Carla Guidotti
Istituto di Chimica Fisica
Università degli Studi di Pisa
Pisa / Italia