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GF Calculation with Minimal and Extended Basis Sets for H_2O, NH_3, CH_4 and H_2O_2

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A method is proposed for applying the theory of generalized group functions to SCF–GF calculations with large basis sets. A simple procedure for localising the SCF–MO's resulting from a standard SCF calculation is described, with applications to H_2O, NH_3, CH_4 and H_2O_2. Results compare quite favourably with those obtained by the usual GF method. It is shown that when basis functions are the SCF–MO's and there are only two functions per group, the GF approach is practically equivalent to a configuration interaction treatment where only double excitations within the groups are considered.

Es wird eine Methode zur Anwendung von verallgemeinerten Gruppenfunktionen auf SCF–GF-Rechnungen mit großen Basissätzen vorgeschlagen. Ferner wird ein einfaches Verfahren zur Lokalisierung von SCF–MO's angegeben und auf H_2O, NH_3, CH_4 und H_2O_2 angewendet. Die Resultate sind denen üblicher GF-Methoden ähnlich. Wenn als Basisfunktionen SCF-Funktionen, und zwar nur zwei je Gruppe, angewendet werden, ist der GF-Ansatz praktisch einer CI-Rechnung mit maximal Zweifachanregungen äquivalent.

On propose une méthode pour appliquer la théorie des fonctions de groupes généralisés à des calculs SCF GF dans des bases de grande dimension. Un procédé de localisation simple est décrit, il permet de localiser les orbitales SCF ordinaires et est appliqué à H_2O, NH_3, CH_4 et H_2O_2. Les résultats obtenus sont comparables à ceux fournis par la méthode GF ordinaire. Lorsque les fonctions de base sont les O.M. S.C.F. et qu'il n'y a que deux fonctions par groupe, la méthode GF est pratiquement équivalente à une interaction de configuration où seules seraient prises en considération les diexcitations à l'intérieur des groupes.

1. Introduction

The theory of generalised group functions [1, 2, 3] has been successfully applied to self-consistent group calculations on some polyatomic molecules with a minimal basis set of STO's [4, 5, 6]. The results were superior to those obtained by the standard SCF method.

A difficulty in extending such GF approach to larger basis sets is, that the construction of the localized orbitals through the optimum hybrids, from which they might be formed, involves a choice which is by no means unique. Various procedures for constructing optimum hybrids in the case of minimal basis sets (see, for instance, Ref. [7], where a full bibliography is given) have been proposed.

A different and convenient approach is to look for a procedure of localization of the SCF-MO's obtained by standard SCF calculations. In fact, the ground state orbitals and their virtual counterparts constitute an orthonormal set which satisfy one of the fundamental conditions for a GF calculation in its more simple

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scheme. Therefore, such a set needs only to be suitably localized by an unitary matrix and collected in groups to be used within a GF approach.

In the present paper some localization procedures are reported together with some applications for a variety of molecules, using minimal and more extended basis sets. Some of the molecules studied here had not been treated previously by the GF method.

In most cases, basis integrals were used which had already been evaluated for other purposes: the relative computer programs have been described elsewhere [8]. The GF programs were written by the authors for the 7090-IBM computer of the University of Pisa.

All calculations were carried out for the experimental distances and angles, the z axis being always the axis with the highest symmetry.

In the future, the same approach described in this paper will be employed with larger basis sets.

2. Description of Calculation

A. Method

The basic theory has been outlined in Refs. [3] and [4] and the same notations and formalism will be used here.

The effective Hamiltonian for the N_R electrons of group R in the field of all other groups is defined as

$$\mathscr{H}^R_{\mathrm{eff}}(1,2,\ldots,N_R) = \sum_{i=1}^{N_R} \mathrm{h}^R_{\mathrm{eff}}(i) + \tfrac{1}{2} {\sum_{i,j=1}^{N_R}}' 1/r_{ij} \tag{1}$$

where

$$h^R_{\mathrm{eff}}(1) = h(i) + \sum_{S(\neq R)} (J^S(i) - K^S(i)) \tag{2}$$

is an effective one-electron Hamiltonian and J^S, K^S the coulomb and exchange operators for the S-groups electrons [4].

For a group R in state r, described by the N_R-electrons group function ϕ_{Rr}, the energy in the field of all others group is given by

$$H^R_{\mathrm{eff}}(rr) = \frac{\langle \phi_{Rr} | \mathscr{H}^R_{\mathrm{eff}} | \phi_{Rr} \rangle}{\langle \phi_{Rr} | \phi_{Rr} \rangle} \tag{3}$$

while the total energy is

$$E_0 = \sum_R H^R_{\mathrm{eff}}(rr) - \tfrac{1}{2} {\sum_{R,S}}' \{J^{RS}(rr,ss) - R^{RS}(rr,ss)\} = \tfrac{1}{2} \sum_R \{H^R(rr) + H^R_{\mathrm{eff}}(rr)\}\,. \tag{4}$$

For the energy and all other molecular properties given by simple formulae such as (4), it is necessary that groups R and S are "strong orthogonal" [4]: this condition may be achieved by constructing the group function ϕ_{Rr} from an orthonormal set of orbitals and by not allowing any orbital to belong to different groups. Usually, a Löwdin orthogonalization of the atomic orbital set is accomplished [4, 5, 6]. The present approach is instead to start from the SCF-MO's which are authomatically orthonormal.

It is then necessary to localize them and some methods are described in the following paragraph.

B. *Localized Orbitals for* GF *Calculations*

Many localization procedures have been proposed in literature, notably the ones reported in Refs. [9] and [10]. Three different methods have been used here, whose most general one has been put forward by Boys [11] and will be referred to as [Loc. (1)]. It needs the handling of the one-electron dipole moment integrals only and is based essentially upon the following procedure.

Let $\{\varphi_1, \varphi_2, \ldots, \varphi_j, \ldots, \varphi_m, \ldots, \varphi_n\}$ be a set of MO's, whose first m are occupied. For these m orbitals, the method looks for a minimum of the sum of the mean square deviations of their charge densities from their centers of gravity, i.e.,

$$\sum_{j=1}^{m} \langle f_j|(\bar{r}-\bar{r}_{0j})^2|f_j\rangle = \text{minimum value}$$

where

$$\bar{r}_{0j}=\langle f_j|\bar{r}|f_j\rangle \quad \textit{and} \quad \{f_1, f_2, \ldots, f_m\}=\{\varphi_1, \varphi_2, \ldots, \varphi_m\}\,\boldsymbol{U}\,,$$

with $\boldsymbol{U}^\dagger \boldsymbol{U}=\boldsymbol{I}, \boldsymbol{I}$ being the identity matrix. Starting from some approximate values of the centers of gravity of the occupied orbitals, the process is repeated iteratively by determining at each cycle a matrix $\boldsymbol{U}^{(n+1)}$ such that

$$F^{(n+1)}=\sum_{j=i}^{m} \langle f_j^{(n+1)}|(\bar{r}-\bar{r}_{0j}^{(n)})^2|f_j^{(n+1)}\rangle \leqq F^{(n)}$$

where

$$r_{0j}^{(n)}=\langle f_j^{(n)}|\bar{r}|f_j^{(n)}\rangle\,, \qquad \{f^{(n)}\}=\{\varphi\}\,\boldsymbol{I}\,\boldsymbol{U}^{(1)}\,\boldsymbol{U}^{(2)}\ldots\boldsymbol{U}^{(n)}=\{f^{(n-1)}\}\,\boldsymbol{U}^{(n)}\,.$$

As for the $(n-m)$ virtual ones, they are employed to obtain orbitals localized on the centers of gravity, $\bar{r}_{0j}$ (which do not change any longer), of the occupied ones. At first, a set of $l_{\text{I}} \leqq m$ virtual orbitals are localized on the corresponding ground state orbitals by achieving the condition

$$\sum_{j=1}^{m} \delta_j^{\text{I}}\langle g_{\text{I}j}|(\bar{r}-\bar{r}_{0j})^2|g_{\text{I}j}\rangle = \text{minimum value}$$

where

$$\{g_{\text{I}}\}=\{\varphi_{m+1}, \varphi_{m+2}, \ldots, \varphi_n\}\,V_{\text{I}}\,, \qquad \text{with} \qquad V_{\text{I}}V_{\text{I}}^\dagger=\boldsymbol{I}^{l_{\text{I}}}$$

and δ_j^{I} is 1 or 0 according with the fact that a virtual orbital has to be localized or not on the orbital φ_j at the stage I, i.e., $\sum_j \delta_j^{\text{I}}=l_{\text{I}}$.

Subsequently, the new quantity

$$\sum_{j=1}^{m} \delta_j^{\text{II}}\langle g_{\text{II}j}|(\bar{r}-\bar{r}_{0j})^2|g_{\text{II}j}\rangle$$

is minimised, where $\{g_{\text{II}}\}=\{\varphi_{m+l+1}, \ldots, \varphi_n\}\,V_{\text{II}}$, $(V_{\text{II}}V_{\text{II}}^\dagger=\boldsymbol{I}^{(l_{\text{II}})})$. Again $\delta_j^{\text{II}}=1, 0$ and $\sum_j \delta_j^{\text{II}}=l_{\text{II}}\leqq l_{\text{I}}$; furthermore, if $\delta_j^{\text{I}}=0$, also $\delta_j^{\text{II}}=0$ and so on. This symbol δ

has been introduced only to allow for the facts that a different number of virtual orbitals may be localized at each stage and may be wanted to be localized on each occupied one.

In the cases of H_2O and NH_3 another procedure has also been used [Loc. (2)]. From the MO's of symmetry $(2a_1)$ and $(3a_1)$, two new vectors have been formed, pointing towards the positive and negative side of the z axis, by rotation through an angle α. By mixing them with the orbitals of symmetry (b) (for H_2O) and of symmetry (e) (NH_3), the bond hybrids and the lone pairs have been obtained. The angle α has been determined by minimising the content of h in the lone pairs. As for the virtual orbitals, they are completely determined by symmetry for the cases of minimal basis sets. In the case of H_2O with a double ζ on the $1s$ of oxygen [set (b)] the orbital $(5a_1)$ has been assigned to the inner shell group.

Finally, a third method [Loc. (3)] has been used for H_2O [set (b)]. It consists in rotating the $(2a_1)$ and $(3a_1)$ MO's to form two new vectors as above, one of which is taken to be such to form with $(1b_2)$, at the origin, an angle equal to the valence angle (105°).

By using the GF approach, a full configuration interaction is then allowed within the two-electron group R, whose group function is described by the N_R localized one-electron functions r_i.

3. Results and Discussion

The basis sets and the results of the SCF and GF calculations for H_2O, NH_3, CH_4 and H_2O_2 at four configurations (0°, 120°, 150°, 180°), are reported in Table 1. For H_2O (a) the orbital exponents are the same as in the case III of Ref. [5], while for all other molecules they were taken from Ref. [12]. In the case of H_2O (b), the ζ's are "best atom" ζ's [13], but for ζ_H and the two ζ_{1s} of oxygen. ζ_H has been determined by minimizing the energy of H_2O for a minimal basis set [14], while the two ζ_{1s} of oxygen were determined by keeping the lower ζ, which is the best atom ζ [13] as a constant, and by varying the second value in order to get a minimum for the energy of O^{+6}. The energy values obtained by this procedure vary very little for $\zeta_2 > 11$: hence the choice of this value for ζ_2.

The SCF energies of H_2O_2 agree well with those reported by Palke and Pitzer [15] although the orbital exponents are slightly different: no energy minimum at intermediate angles is found. The quantity Δ, i.e., the decrement of energy, relatively to the SCF, is ~ 0.064 a.u. for all 4 configurations and, of course, the internal rotation potential curve obtainable by the GF values is parallel to the SCF one. The cis-trans energy difference is 0.0204 a.u. for the SCF and 0.0203 a.u. for the GF calculation, while $E\,(120°) - E\,(180°)$ is 0.0018 a.u. and 0.0017 a.u. respectively.

Also for all other molecules, the energy values are lower than the corresponding SCF and usual GF ones. The decrement of energy, Δ, depends upon the number of groups in which some correlation is allowed for, upon the type of such groups, and upon the localization procedure. The dependence upon the first two factors is shown by the fact that, for H_2O_2, Δ is the same for all configurations, but is much greater than for H_2O (b) and NH_3, all having three partially correlated groups. On the other hand, Δ is almost the same for H_2O (a) and (b), where there

Table 1. SCF *and* GF *energies of* H_2O [(*a*) *and* (*b*)], NH_3, CH_4 *and* H_2O_2 *(4 configurations)* [Loc. (1)]

Molecules and orbital exponents	Method of calculation	Energies (a.u.)			
		Total electron.	Total (electr. + nucl.)	Δ	$\frac{2\text{ Kin. En.}}{\text{Pot. En.}}$
$H_2O^{(a)}$ ζ_O: $1s = 7.6579$ $2s = 2.2458$ $2p_z = 2.2266$ $2p_x = 2.2266$ $2p_y = 2.2266$ ζ_H {$1s = 1.30$	SCF	−84.88877	−75.70232	−0.03501	−1.00104
	GF	−84.92378	−75.73733		−1.00094
$H_2O^{(b)}$ ζ_O: $1s = 7.658$ $1s = 11.000$ $2s = 2.2461$ $2p_z = 2.22625$ $2p_x = 2.22625$ $2p_y = 2.22625$ ζ_H {$1s = 1.28$	SCF	−84.90202	−75.71561	0.03544	−1.00311
	GF	−84.93747	−75.75105		−1.00314
NH_3 ζ_N: $1s = 6.70$ $2s = 1.925$ $2p_z = 1.925$ $2p_x = 1.925$ $2p_y = 1.925$ ζ_H {$1s = 1.267$	SCF	−67.93973	−56.00448	−0.04665	−1.00304
	GF	−67.98638	−56.05113		−1.00304
CH_4 ζ_C: $1s = 5.716$ $2s = 1.625$ $2p_z = 1.625$ $2p_x = 1.625$ $2p_y = 1.625$ ζ_H {$1s = 1.28$	SCF	−53.49876	−40.11287	−0.05803	−1.00233
	GF	−53.55679	−40.17090		−1.00254
H_2O_2 180° I ζ_O: $1s = 7.6482$ $2s = 2.2597$ $2p_z = 2.2145$ $2p_x = 2.2145$ $2p_y = 2.2145$ ζ_H {$1s = 1.2675$	SCF	−186.9596	−150.2231	−0.0643	−0.99823
	GF	−187.0239	−150.2874		−0.99824
H_2O_2 150° II	SCF	−186.9635	−150.2229	−0.0642	−0.99824
	GF	−187.0277	−150.2871		−0.99824
H_2O_2 120° III	SCF	−186.9748	−150.2213	−0.0644	−0.99823
	GF	−187.0391	−150.2857		−0.99824
H_2O_2 0° IV	SCF	−187.0515	−150.2027	−0.0644	−0.99813
	GF	−187.1159	−150.2671		−0.99816

are 2 and 3 such groups, respectively. The dependence of Δ upon the localization procedure is shown in Table 2, where the results of the calculations on H_2O (a) and (b) and NH_3 are reported. The group properties, such as $H^R_{\mathrm{eff.}}$ and electric dipole moment, appear to be much affected by the localization procedure, while the total energies and the total electric dipole moment are less.

The from zero different components of the electric dipole and the quadrupole moments of all molecules here considered are reported in Tables 3 and 4. The differences between the SCF and GF values are small and show that the electron distribution for a given basis does not change noticeably going from an SCF to a GF treatment. The fact, that the one-electron density matrix does not vary too much from cycle to cycle of iterations in the GF process, is shown also from the smallness of the coefficients of the determinants corresponding to the single excitations.

Therefore, it is of some interest to compare the results of the GF approach with those which would be obtained by a configuration interaction treatment with double excitations only. Such comparison gives also a clue for a better understanding of the physical meaning of Δ, when the ortho-normal set of orbitals used with the GF approach are the SCF-MO's.

For each group R constituted by only two basis orbitals r_1 and r_2 the group function ϕ_R will be given by (dropping the suffix r for the state)

$$\phi_R = \sum_{i=1}^{3} C_i^R \varphi_i^R \tag{5}$$

where

$$\varphi_1^R = \frac{1}{\sqrt{2}} \mathscr{A}(r_1 \bar{r}_1); \qquad \varphi_2^R = \frac{1}{2} \mathscr{A}[(r_1 \bar{r}_2) - (\bar{r}_1 r_2)]; \qquad \varphi_3^R = \frac{1}{\sqrt{2}} \mathscr{A}(r_2 \bar{r}_2).$$

The matrix of the 3×3 secular problem to be diagonalized at the first cycle of iteration of the GF approach, is of the form

$$\begin{vmatrix} H^R_{\mathrm{eff}_{11}} & 0 & H^R_{\mathrm{eff}_{13}} \\ 0 & H^R_{\mathrm{eff}_{22}} & H^R_{\mathrm{eff}_{23}} \\ H^R_{\mathrm{eff}_{31}} & H^R_{\mathrm{eff}_{32}} & H^R_{\mathrm{eff}_{33}} \end{vmatrix}$$

where $H^R_{\mathrm{eff}_{ij}} = \langle \varphi_i^R | \mathscr{H}^R_{\mathrm{eff}} | \varphi_j^R \rangle$. $\mathscr{H}^R_{\mathrm{eff}}$ is given by (1) and is calculated with the density matrix arising from the SCF calculation: therefore, at the first cycle of iteration, the energy E_0, calculated by the GF approach, i.e.,

$$E_0 = \tfrac{1}{2} \sum_R \{H^R(r\,r) + H^R_{\mathrm{eff}}(r\,r)\} \tag{6}$$

coincides with the SCF energy.

The elements $H^R_{\mathrm{eff}_{13}} = (r_1 r_2 \,|\, r_1 r_2)$ and $H^R_{\mathrm{eff}_{23}}$ are smaller than the diagonal ones: the decrement of energy, relatively to E_0, due to the group R, can then be calculated, up to the second order, by the perturbation method as

$$\delta_R = \frac{|H^R_{\mathrm{eff}_{13}}|^2}{(H^R_{\mathrm{eff}_{11}} - H^R_{\mathrm{eff}_{33}})} \tag{7}$$

Table 2. *Comparison of results obtained by the three different localization procedures described in Sect. 2 (a.u.)*

			$H_2O^{(a)}$		$H_2O^{(b)}$			NH_3	
			Loc. (1)	Loc. (2)	Loc. (1)	Loc. (2)	Loc. (3)	Loc. (1)	Loc. (2)
Total energy			−75.73733	−75.74240	−75.75105	−75.76579	−75.75804	−56.05113	−56.05378
Δ			− 0.03501	− 0.04008	− 0.03544	− 0.05018	− 0.04243	− 0.04665	− 0.04930
$H_{\text{eff}}^{\text{inner shell}}$			−45.65125	−45.84035	−45.69889	−45.90196	−45.89493	−35.12999	−35.22603
$H_{\text{eff}}^{\text{bond}}$			− 2.47414	− 2.04598	− 2.46921	− 2.03795	− 2.56839	− 2.23234	− 2.04974
$H_{\text{eff}}^{\text{lone pair}}$			− 2.23869	− 2.46420	− 2.25219	− 2.48742	− 2.00028	− 1.83699	− 2.11792
Group dip. moment[a] (a.u.)	bond	x	1.6935	1.3190	1.6891	1.3072	1.7494	− 2.2419	− 1.9812
		z	− 1.3265	− 1.0928	− 1.3249	− 1.0815	− 1.2943	0.9254	0.9633
	lone pair	y	0.9966	1.2471	1.0008	1.2548	0.8724	0	0
		z	0.5938	0.3528	0.5918	0.3370	0.5575	− 1.3582	− 1.4685
Total electr. dip. moment		z	− 1.4664	− 1.4806	− 1.4674	− 1.4896	− 1.4743	1.4216	1.4223

[a] Dipole moment components of groups equivalent to the one under consideration can be obtained by symmetry. To get the right value of the total electron dipole moment it is necessary to add the small value of the inner shell group moment.

Table 3. *Electric dipole and quadrupole moments of* H_2O [(a) *and* (b)], NH_3 *and* CH_4 [Loc. (1)] (a.u.)

		Dipole moment[a]		Quadrupole moment					
		Z		X^2		Y^2		Z^2	
		SCF	GF	SCF	GF	SCF	GF	SCF	GF
$H_2O^{(a)}$	electr.	-1.4494	-1.4664	- 7.1376	- 7.1975	- 4.4938	- 4.4968	- 6.0238	- 6.0607
	total	0.7547	0.7377	- 3.0122	- 3.0721	- 4.4938	- 4.4968	- 3.5948	- 3.6317
$H^2O^{(b)}$	electr.	-1.4576	-1.4674	- 7.1804	- 7.2140	- 4.5220	- 4.5242	- 6.0555	- 6.0764
	total	0.7465	0.7367	- 3.0550	- 3.0886	- 4.5220	- 4.5242	- 3.6265	- 3.6474
NH_3	electr.	1.4106	1.4216	- 9.0014	- 9.0504	- 9.0014	- 9.0504	- 6.9675	- 6.9827
	total	-0.7583	-0.7473	- 4.2777	- 4.3267	- 4.2777	- 4.3267	- 5.3994	- 5.4146
CH_4	electr.	0	0	-11.4942	-11.5285	-11.4942	-11.5285	-11.4942	-11.5285
	total	0	0	- 5.7952	- 5.8295	- 5.7952	- 5.8295	- 5.7952	- 5.8295

[a] 1 a.u. $= 4.8025 \cdot 10^{-10}$ u.e.s. charge $\times 0.52917 \cdot 10^{-8}$ cm $= 2.5413$ Debye.

Table 4. *Electric dipole and quadrupole moments of* H_2O_2 (I: 180°; II: 150°; III: 120°; IV: 0°) [Loc. (1)] (a.u.)

		Dipole moment[a]		Quadrupole moment							
		Z		X^2		XY		Y^2		Z^2	
		SCF	GF	SCF	GF	SCF	GF	SCF	GF	SCF	GF
H_2O_2 (I)	electr.	0	0	-11.9578	-12.0663	3.5489	3.6077	-43.6481	-43.7068	- 8.0353	- 8.0373
	total	0	0	- 5.5571	- 5.6656	-1.9751	-1.9163	- 7.8029	- 7.8616	- 8.0353	- 8.0373
H_2O_2 (II)	electr.	-0.6019	-0.6114	-11.7016	-11.8025	3.4371	3.4936	-43.6541	-43.7127	- 8.2967	- 8.3056
	total	0.3242	0.3147	- 5.7296	- 5.8305	-1.8987	-1.8422	- 7.8089	- 7.8675	- 7.8679	- 7.8768
H_2O_2 (III)	electr.	-1.1728	-1.1912	-10.9948	-11.0752	3.1001	3.1499	-43.6677	-43.7261	- 9.0217	- 9.0496
	total	0.6162	0.5978	- 6.1942	- 6.2746	-1.6838	-1.6340	- 7.8224	- 7.8808	- 7.4215	- 7.4494
H_2O_2 (IV)	electr.	-2.4103	-2.4417	- 8.0379	- 8.0384	0	0	-43.7475	-43.8057	-12.0903	-12.1854
	total	1.1676	1.1362	- 8.0379	- 8.0384	0	0	- 7.9022	- 7.9604	- 5.6896	- 5.7847

[a] 1 a.u. $= 4.8025 \cdot 10^{-10}$ u.e.s. charge $\times 0.52917 \cdot 10^{-8}$ cm $= 2.5413$ Debye.

and the total decrement, Δ, as a sum over the groups in which some correlation is allowed for, i.e.,

$$\Delta = E^{(2)} = \sum_R \delta_R .$$

So Δ appears to have the same addictive properties as E_0.

From the above treatment it is clear that the GF approach, when the basis functions are the SCF-MO's and there are only two functions per group, is practically equivalent to a configuration interaction treatment in which only doubly excited states would be considered: in fact, the coefficients C_2^R corresponding to single excitations are always very small.

For example, in the case of H_2O (b), the determinants to be taken in consideration should be

$$\Psi_0 = \frac{1}{\sqrt{10}} \mathscr{A}(K, \bar{K}, B_1, \bar{B}_1, B_2, \bar{B}_2, L_1, \bar{L}_1, L_2, \bar{L}_2),$$

$$\Psi_1 = \frac{1}{\sqrt{10}} \mathscr{A}(K', \bar{K}', B_1, \bar{B}_1, B_2, \bar{B}_2, L_1, \bar{L}_1, L_2, \bar{L}_2),$$

$$\Psi_2 = \frac{1}{\sqrt{10}} \mathscr{A}(K, \bar{K}, B_1', \bar{B}_1', B_2, \bar{B}_2, L_1, \bar{L}_1, L_2, \bar{L}_2),$$

$$\Psi_3 = \frac{1}{\sqrt{10}} \mathscr{A}(K, \bar{K}, B_1, \bar{B}_1, B_2', \bar{B}_2', L_1, \bar{L}_1, L_2, \bar{L}_2).$$

In fact, the diagonalization of the determinant

$$\begin{vmatrix} H_{00} & H_{01} & H_{02} & H_{03} \\ H_{10} & H_{11} & 0 & 0 \\ H_{20} & 0 & H_{22} & 0 \\ H_{30} & 0 & 0 & H_{33} \end{vmatrix}$$

where $H_{K\lambda} = \langle \Psi_K | \mathscr{H} | \Psi_\lambda \rangle$, gives almost the same result for the ground state energy as the coresponding GF calculation, the difference being a few units on the sixth significant figure.

By the perturbation method, the energy up to the second order is given by

$$E = E_0 + E^{(2)} = E_0 + \sum_\lambda \frac{|H_{0\lambda}|^2}{(H_{00} - H_{\lambda\lambda})}$$

and it is easy to verify that

$$H_{0\lambda} = H^R_{\mathrm{eff}_{13}} \quad \text{and} \quad (H_{00} - H_{\lambda\lambda}) = (H^R_{\mathrm{eff}_{11}} - H^R_{\mathrm{eff}_{33}})$$

where λ refers to the determinant describing the double excitation relative to the substitution of orbital r_1 with r_2 in the group R.

The results of Table 2 can be explained now on the basis of (5), (6) and (7). In the case of H_2O (b), for example, the Δ obtained with Loc. (1) is lower than that with Loc. (2) and (3) for the higher value of $(H^R_{\mathrm{eff}_{11}} - H^R_{\mathrm{eff}_{33}})$ in the bond, owing to a too high contribution of the two 1s oxygen orbitals to the excited bond orbital B_1', while $H^R_{\mathrm{eff}_{13}} = (B_1 B_1' \mid B_1 B_1')$ is almost the same in all cases.

The two values of Δ in the cases of Loc. (1) and Loc. (2) may be split in their components δ_R which are given by, respectively

$$\delta_{\text{inner shell}} = -0.0114; \quad \delta_{\text{bond}} = -0.0120, \qquad [\text{Loc. (1)}]$$

and

$$\delta_{\text{inner shell}} = -0.0103; \quad \delta_{\text{bond}} = -0.0200. \qquad [\text{Loc. (2)}]$$

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