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Relationes

GF Calculations for Some Tricyclic Molecules: C_3H_6, C_3H_4, C_2H_4NH, C_2H_4O and C_2H_4S

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Wave functions expressed as antisymmetrized products of strongly orthogonal geminals have been evaluated for some three membered ring molecules. GF results are compared with previously computed SCF-MO results, obtained employing the same atomic basis. Transferability features of bonds and inner shells are shown.

1. Introduction

Recently, many calculations have been carried out on a number of chemically interesting polyatomic molecules, such as the tricyclic compounds cyclopropane, cyclopropene, aziridine, oxirane and thiirane [1–10].

The reason for this is that now *ab-initio* computations are possible with a reasonable expenditure of computer time; it is therefore appealing to try and see whether it is possible to explain some of the main characteristics, particularly the chemical reactivity, of the above compounds.

From a qualitative point of view an interpretation of both structure and chemical behaviour of the examinated molecules has already been given [1, 10].

The energies are in some cases only a few tenths of an atomic unit from the Hartree-Fock limit [5, 6]; however, other interesting observables such as dipole moments are often far from experimental values.

To go beyond the Hartree-Fock limit in such calculations is still very expensive because of the large number of electrons involved; however, the use of SCF–GF wave functions [11, 12] can involve a small amount of additional computing.

It is well known that the GF method improves the energy values significantly with respect to the SCF–MO method; moreover these improvements appear to be an additive property of each group [11–12].

When SCF–MO wave functions are computed using a minimal basis set, they generally are rather different from the true HF solutions, and these differences may cause noticeable changes in the first order density matrices. In such cases it is therefore interesting to find out whether the GF treatment modifies the conclusions already reached within the SCF–MO frame-work.

Concepts, such as bonds, lone pairs and inner shells provide a convenient model for the understanding of molecular phenomena and the interpretation of chemical experience. Much effort [13, 18, 20, 24] has been directed to the well known problem of "transferability" of these entities from one molecule to another.

It is known that the method of Group Functions (GF) [15–17] leads to group wave functions and group expectation values from which one may ascertain the degree of transferability of a given bond, inner shell or lone pair.

2. Molecules, Geometries and Orbitals

The molecules treated were cyclopropane, cyclopropene, aziridine, oxirane and thiirane.

The nuclear geometries close to experimental values, and orientation of the frame of reference are given in Ref. [10].

Minimal basis sets of Slater type functions with "best atom ξ's" were employed at most atomic centers: exceptions being the sulfur atom in thiirane in which additional $3d$ functions ($\xi = 1.7$) and hydrogen atoms bonded to carbon and nitrogen on which functions with ξ values of 1.2 and 1.3 were used, respectively.

The occupied MO's calculated by the LCAOMO–SCF procedure have been localized according to Boys criterion [13]. The virtual MO's have been transformed in order to obtain functions with minimal dispersion around the center of gravity of the occupied localized orbitals and, in this way, were localized in the same spatial regions [11].

Since the localization criteria are rather arbitrary, results obtained depend upon the localization criteria chosen. Two different localizations for the geminals connected with C=C double bond in cyclopropene were carried out. Boys' criterium and the above mentioned localization process for virtual orbitals, lead to the formation of so called "banana" bond functions (β) while another type of localization defined by:

$$\sigma = \sqrt{2}/2(\beta_1 + \beta_2) \qquad \sigma' = \sqrt{2}/2(\beta'_1 + \beta'_2)$$
$$\pi = \sqrt{2}/2(\beta_1 - \beta_2) \qquad \pi' = \sqrt{2}/2(\beta'_1 - \beta'_2)$$

leads to more usual type functions of σ and π symmetry.

In the above formulas the prime signifies "excited" functions, while the subscripts 1 or 2 indicate that the "banana" function is localized, for the most part, above or below the molecular plane, respectively.

Table 1 reports the distribution of localized orbitals per group in the series of molecules treated. The number of localized orbitals per group is determined by characteristics of the basis, by molecular symmetry and physical reasoning.

In the case of the thiirane molecule, for example, the SCF–MO process leads to twelve virtual symmetry MO's; four a_1, two a_2, four b_1, and two b_2 respectively. From these twelve, five (two a_1, one a_2, one b_1 and one b_2) are for the most part respectively $3d_{z^2}$, $3d_{x^2-y^2}$, $3d_{yz}$, $3d_{xz}$, $3d_{xy}$ in character. Because of this predominantly atomic orbital character (associated with the S atom) it was decided to use these functions to describe the lone pair groups of the S atom rather than to attempt a description of the C–S bonds, despite the fact that these virtual orbitals are highly diffuse and therefore tend to "spread out" also in the vicinity of the

Table 1. *Distribution of localized orbitals in the groups*

Molecules group	C_3H_6	C_3H_4	C_2H_4NH	C_2H_4O	C_2H_4S
Kc	1	1	1	1	1
Kx	—	—	1	1	1
C–C	2	2	2	2	2
C–H	2	2	2	2	2
C–X	—	—	2	2	2
X–H	—	—	2	—	—
L.P.	—	—	1	1	3

C atoms. Linear combinations of a_1 and b_2 orbitals as well as of a_2 and b_1 lead to two virtual localized functions for each lone pair. With the remaining orbitals one may construct, a function localized on the C–C bond (b_1 symmetry), a function localized on each of the C–S bonds (combination of a_1 and b_1) and a function for each C–H bond (a_1, b_1, a_2, and b_2 combination).

Many quantities, such as the coefficients of the localized orbitals, or expectation values such as $\langle r \rangle$ have not been given here because of the extensive tabulation required.

Some of these quantities have been given previously by Ref. [10]. It is interesting to note that in every case the ring bond localized functions are bent and lie outside the ring (i.e. their center of gravity) rather than on straight lines between atoms.

The problem of satisfying molecular symmetry for the localized group functions has been mentioned previously [12]. The problem seems especially acute when one attempts to transform virtual MO's to localized functions. Thus slight asymmetry might be introduced, but it does not appear to materially affect the overall results.

3. Results and Discussion

With the exception of the dipole moment of thiirane, Table 2 shows that those quantities which depend upon the first order density matrix show little or no variation from those predicted from an SCF–MO treatment with the same basis.

It is particularly interesting that there should be such small differences between these computed quantities for the cyclopropene molecule. In fact with SCF calculations the π MO's are almost exclusively determined by symmetry, while the GF treatment allows a considerable mixing between the $|\pi'\pi'|$ and $|\pi\pi|$ configurations for the group function description of π electrons. Thus it leads to a more flexible description of the C=C bond with an anomalously good energetic improvement per group, due to great change in the first order density matrix (Tables 3–4). Table 3 shows that the total energy improvements, Δ, are practically identical, for example, in the case of C_3H_6 and C_3H_4 (σ/π), even if the total number of groups is 12 and 11 respectively.

Table 2. *Ground state one-electron quantities*

Molecules		C_3H_6	$C_3H_4(\sigma/\pi)$	$C_3H_4(\beta)$	C_2H_4NH	C_2H_4O	C_2H_4S
μ	SCF[d]	0	0.3388	0.3388	1.7676	1.1896	0.8357
(Debye)	GF	0	0.3368	0.3434	1.7285	1.1312	0.5572
	Exptl.	0	0.454	0.454[a]	1.89[b]	1.88[c]	1.84[a]
$\langle x^2\rangle$	SCF[d]	62.3711	83.7142	83.7142	69.0449	59.9798	178.0810
(a.u.)	GF	62.4299	83.8114	83.8159	69.0933	59.9529	177.4877
$\langle y^2\rangle$	SCF[d]	32.0694	20.6650	20.6650	28.1708	24.7751	30.7890
	GF	32.2136	20.6689	20.6904	28.3049	24.8777	30.9441
$\langle z^2\rangle$	SCF[d]	62.3711	48.9600	48.9600	60.0551	58.7400	64.2653
	GF	62.4299	49.1238	49.0855	60.1273	58.8526	64.3870

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[d] Ref. [10].

Table 3. SCF, GF *and* CI–GF *molecular energies*

Molecules		C_3H_6	$C_3H_4(\sigma/\pi)$	$C_3H_4(\beta)$	C_2H_4NH	C_2H_4O	C_2H_4S
Total energy (a.u.)	SCF[a]	−116.7516	−115.4973	−115.4973	−132.6582	−152.3689	−474.5159
	GF	−116.8638	−115.6097	−115.5998	−132.7652	−152.4668	−474.6197
	Δ	− 0.11223	− 0.11240	− 0.10249	− 0.10706	− 0.09790	− 0.10379
	CI–GF	−116.8894	−115.6440	−115.6356	−132.7909	−152.4880	−474.6465
	Exptl.	−117.944	−116.668	−116.668	−133.993	−153.856	−477.846
$\frac{-2\,\text{Kin.en.}}{\text{Pot.en.}}$	SCF[a]	0.9923	0.9922	0.9922	0.9943	0.9951	0.9981
	GF	0.9926	0.9925	0.9925	0.9945	0.9952	0.9981

[a] From Ref. [10].

Table 4. *Group energy improvements*

	C_3H_6	$C_3H_4(\beta)$	$C_3H_4(\sigma/\pi)$	C_2H_4NH	C_2H_4O	C_2H_4S
C–H	−0.0124	−0.0115 −0.0127	−0.0115 −0.0127	−0.0119	−0.0125	−0.0129
C–C	−0.0126	−0.0126	−0.0126	−0.0117	−0.0120	−0.0118
C–X	—	—	—	−0.0153	−0.0180	−0.0109
X–H	—	—	—	−0.0163	—	—
C=C	—	−2 × 0.0144	(−0.0069 − 0.0317)	—	—	—
Lone pair	—	—	—	—	—	−0.0113

In Table 3 are reported the total molecular energies computed with the SCF, GF and GF–CI methods as well as the experimental values for purposes of comparisons.

The GF–CI treatments reported were limited only to all possible double group excitation configurations [12].

The group improvement energies reported in Table 4 were obtained as the difference in total energies for a group wave function in which only one group was determined variationally, the others being held fixed to the SCF–MO's electronic density, and a comparable SCF–MO wave function.

A comparison of the quantity Δ, the difference between the GF energies, in which all the groups shown in Table 4, are determined variationally, and the SCF energies, and the sum of the energy improvements due to each respective group reported in Table 4 shows the usual good agreement [11, 12].

There are a number of possible quantum mechanical approaches to the interpretation of bonds, lone pairs, and inner shells [19, 21–24]. Perhaps the most commonly employed technique is the localization of MO's such that they describe the electron pair distribution in the bond, lone pair or inner shell region.

In general, the MO's arising from LCAO–MO–SCF treatment are delocalized over the molecular framework and hence must be localized by a physically appropriate linear transformation. Unfortunately, there are an infinite number of such transformations so that an unique description is not possible.

Using the GF method one obtains in a natural way, as eigenfunctions of an effective group Hamiltonian, wave functions for all groups of localized electrons. The corresponding group eigenvalues provide a useful means of judging the degree of transferability of energetically dependent characteristics of a given group from one molecule to another.

For example, if one has effective group hamiltonians differing by a constant (such as is the case in which the difference of the potential due to changes in molecular environment is almost constant in the region of an electron group), then the group eigenfunctions remain unchanged.

Thus all "shape-dependent" quantities such as kinetic energy or electronic moments also remain constant and only the group energy eigenvalues will be different.

In Table 5 are reported the group energy eigenvalues of some three membered ring compounds as well as a number of previously unpublished results for some molecules containing similar electron groups. These latter were computed using bases of 39, 29, 27 and 16 STO's for CH_4, NH_3, H_2O and C_2H_4 respectively [12]. Variation of a given group eigenvalue evident in this table depends upon changes in the basis set employed as well as physical reasons such as changes in the molecular environment of the group. Passing from minimal bases to very large bases in the NH_3, CH_4 and H_2O molecules one notes maximal variations in the eigenvalues of 2%, most cases being less than 1%. In the same Table 5 are listed the C–C and C–H bond group kinetic energies.

The overall results of Table 5 do indeed support the transferability of bonds and inner shells even if one allows a bond distance range of variation of the order of 5%. Furthermore, the effective group hamiltonian matrix elements over the 3 possible detors [12] for the aziridine and oxirane molecules, in which

Table 5. *Group kinetic energy and group effective Hamiltonian lowest eigenvalues (a.u.)*

Molecules	Group	C_3H_6	$C_3H_4(\sigma/\pi)$	$C_3H_4(\beta)$	C_2H_4NH	C_2H_4O	C_2H_4S	CH_4	C_2H_4	NH_3	H_2O
Group kinetic energy	C–H	1.818	1.822 1.829	1.822 1.829	1.811 1.819	1.828	1.822				
	C–C	2.235	2.230	2.230	2.276	2.271	2.278				
Lowest eigenvalues of effective Group Hamiltonian	C–H	− 2.051	− 2.029	− 2.029	− 2.065 − 2.041	− 2.079	− 2.069	− 2.005	− 2.032		
	C–C	− 2.004	− 2.031	− 2.030	− 2.062	− 2.076	− 2.107				
	N–H				− 2.316					−2.314	
	lone pair				− 1.951	− 2.463				−1.843	−2.327
	k shell (carbon)	−26.218	−26.277	−26.279	−26.259	−26.318	−26.269	−25.984	−26.070		

Table 6. C–C *effective groupy Hamiltonian matrix elements*

	H_{11}	H_{12}	H_{22}	H_{13}	H_{23}	H_{33}
C_2H_4NH	−2.051	0.000	−1.133	0.138	−0.002	−0.439
C_2H_4O	−2.064	0.000	−1.155	0.139	−0.000	−0.472

comparable basis sets and bond lengths were used for the C–C bond, are in substantial agreement (Table 6).

The all important transferability feature of bonds and inner shells seems due to the form of the effective group hamiltonian, containing contributions from the molecular total hamiltonian, which remain unchanged from one molecule to another, as well as much less important contributions which depend upon molecular environments, and also upon basis employed, and hence differ from case to case. It is conjectured that the relative unimportance of these latter terms is a result of a non-fortuitous cancellation of opposing nuclear and electronic effects.

Finally results presented in Tables 3 and 4 for a GF treatment of cyclopropene confirm the observation of Klessinger [14] that GF constructed with functions of σ and π symmetry provide a better (energywise) description of C=C double bond in ethylene than with comparable "banana" functions. Moreover this superior bond description is preserved even when some "intergroup" correlation is included by means of the previously mentioned GF–CI treatment.

4. Conclusions

The GF results presented here are in substantial agreement with previously published SCF–MO results obtained employing the same atomic basis [10]. However, the GF method allows a more satisfactory approach to molecular quantum mechanical problems in terms of the traditional concepts of chemistry such as bonds, inner shells and lone pairs, which, with the exception of lone pair groups, display some transferable properties.

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