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COLOPHON

The attached paper is another in my series of experiments to see how long it takes me to re-build electronic versions of my published early papers as properly re-typeset 'PDF Normal' rather than just as a bitmap scan.

This particular paper appeared in the journal "Chemical Physics Letters" (Elsevier) in 1975. The canonical published version is available online (to subscribers, or for one-off purchase) as a scanned bitmap PDF via: <http://www.sciencedirect.com/>

The text was acquired by scanning the paper from an offprint and then using Readiris OCR on the resulting TIFF files. The paper was then re-typeset using UNIX *troff* suite to set up the correct typeface (Times) and to get the line and page breaks as accurate as possible. The tables were re-set using the *tbl* pre-processor for *troff*.

The time taken to build this paper (over several lunchtimes ...) to a reconstituted 'final draft' form was about 4 hours.

FLOATING s- AND p-TYPE GAUSSIAN ORBITALS

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The advantages of including a small number of p-type gaussian functions in a floating spherical gaussian orbital calculation are pointed out and illustrated by calculations on molecules which previously have proved to be troublesome. These include molecules such as F_2 with multiple lone pairs and C_2H_2 with multiple bonds. A feature of the results is the excellent correlation between the orbital energies and those of a double zeta calculation reported by Snyder and Basch.

1. Introduction

Since its introduction by Frost [1] and its adaptation by others (Preuss [2], Blustin and Linnett [3], Christoffersen [4], Ford et al. [5]) the floating spherical gaussian orbital form of wave function has proved to be a vivid and versatile addition to the armory of theoretical methods. In its original form the minimum number of spherical gaussian was used to set up a determinantal wave function and, to compensate for this small basis set, the positions and exponents of all functions were optimized.

Unfortunately not all molecules have models of this type which are numerically stable so constraints were introduced to prevent close functions from coalescing. This feature detracts from the purity of the appeal to optimization as determining molecular structure and does not completely avoid the problems of numerical accuracy. This situation can be remedied by introducing p-type gaussians as the limit functions produced by the coalescence. The stability of the calculation is dramatically improved.

Results are given here for H_2O , H_2O_2 , HF, F_2 , C_2H_2 , CH_3OH , CH_2CCH_2 and CH_3CCH_3 , in their experimental geometries, to illustrate the effectiveness of this solution. The total energies represent about 95% of the molecular orbital energies. The extent to which the orbital energies correlate with those of an exact Hartree-Fock calculation is often taken [6] as a mea-

sure of the balance of the basis set. The correlations here are excellent.

2. Limit functions

When two FSGO's are used to describe the lone pairs of the oxygen atom in a molecule they float towards one another. There is now considerable evidence (Hylton [11]) that the optimum separation in circumstances like this is zero. Because the overlap matrix becomes singular as the functions coalesce (Ford and Hall [7]) the energy calculation becomes numerically unstable. One way of avoiding this situation is to introduce a new basis function. Thus the two basis functions

$$\phi_1 = e^{-\alpha(r+\delta r)^2}, \quad \phi_2 = e^{-\alpha r^2},$$

are replaced by their sum and differences. In the limit the sum becomes ϕ_2 but the difference becomes the p-type derivative function

$$\phi_3 = \nabla\phi_2 = r e^{-\alpha r^2}.$$

By symmetry, ϕ_2 and ϕ_3 have vanishing overlap integral so that the singularity in the overlap matrix disappears. The introduction of a p-type gaussian directed along the line of centres of the previous functions will then give a much more stable molecular model.

For a fluorine atom with 3 lone pairs two p-type

functions directed at right angles will be needed to span the set of possible coalescences. The double bond is now most easily described in terms of σ and π functions with the latter represented by p-type gaussians. There will be some advantage for most molecules in introducing the complete set of p functions (p_x, p_y, p_z) since this spans all possible directions that may be required.

In principle these p functions should be allowed to float freely through the molecule to optimize the energy. Practical calculation has shown, however, that they usually optimize on or very close to the nuclei so that it is more economical in terms of parameters to fix them on the nuclei. The FSGO's that remain in the basis set can now be optimized more freely than before since the cause of their instability has been removed.

3. Molecular models

The introduction of p functions into the basis complicates the calculations in several respects. Additional procedures are required to label the functions, to classify the integrals and to evaluate the auxiliary functions $F_1(x)$ and $F_2(x)$. Within the OPIT system these modifications have been implemented without major reprogramming (Brailsford and Schnuelle [12]). The restriction has been imposed that all p functions should be parallel to one of the coordinate axes. This eliminates the need for procedures to handle integrals of certain kinds. For multiply bonded and conjugated molecules the restriction is immaterial since it is already a desired feature of the model.

To illustrate the extended range of molecules which can now be easily modelled some selected examples have been calculated. They fall into three classes:

(a) *Containing O atoms.* The oxygen atom is modelled using two spherical gaussians on the nucleus together with a set of p-type functions (p_x, p_y, p_z). Its bonds to other atoms are represented by spherical gaussians floating along the internuclear axes. Details of these functions are given in table 1. The location of bond s functions is given as a fraction of the bond length.

The p functions are allowed to have different exponents. The smallest exponents arise when the p functions lie in the direction of the bisector of the bonding angle at the oxygen atom. The largest exponents

Table 1
Parameters for models of O containing molecules

Exponents location	H ₂ O ₂	H ₂ O	CH ₃ OH	
s ₁ on O	84.4549	83.9328	83.9069	
s ₂ on O	12.3511	12.2692	12.2652	
p on O	bisector	0.4714	0.4315	0.4419
	lone pair	0.7023	0.5601	0.5445
		2.3964	3.3871	3.2355
s on OH	0.5485	0.5705	0.5533	
Os/OH	0.3253	0.5362	0.3967	

correspond to p functions in the plane of the oxygen bonds but perpendicular to the previous ones. These functions are helping to describe the bonds which are also described by s functions in the bond directions. Because of this flexibility these s functions shrink closer to the oxygen nucleus and make some contribution to the description of the non-bonding electrons. The substantial differences in the exponents of the p functions shows that although the angular functions span spherical symmetry the radial functions optimize so that there is no invariance around the atom.

The exponents of the s functions are very similar from molecule to molecule though small systematic trends can be observed across the table.

(b) *Containing F atoms.* The fluorine atom is also modelled using two s functions and a set of p functions on the nucleus. In addition there is one s function on the HF axis and one at the mid-point of F₂. The parameter values are given in table 2.

Table 2
Parameters for models of F containing molecules

Exponents location	HF	F ₂	
s ₁ on F	108.4639	103.1813	
s ₂ on F	15.9287	15.1370	
p on F	p _x , p _y	1.0683	1.3756
	p _z	0.3931	0.3226
s on HF	0.8104	0.3852	
Fs/FX	0.0863	0.5	

The exponents of the p-functions are smallest when these are directed along the bonds (p_z). The F atom in HF appears to be attracting its s electrons more strongly than the F atom in F₂ but its lone-pair p elec-

Table 3
Parameters for models of CC containing molecules

Exponents location	CH ₂ =C=CH ₂		CH=CH	CH ₃ -C≡CH		
s ₁ on C	45.8725	46.0934	45.9374	45.8317	45.9501	45.9501
s ₂ on C	6.6288	6.6618	6.6392	6.6226	6.6407	6.6407
p _x , p _y on C	0.3178	0.4171	0.3829		0.3824	0.3824
s on C		0.4401	0.4551		0.3831	0.4538
s on CH	0.3768		0.3865	0.3638		0.3844
Cs/CC		0.4801 ^{a)}	0.5		0.4792 ^{a)}	0.5027 ^{a)}
Cs/CH	0.6082		0.5865	0.5985		0.5896

^{a)} C_s measured from central C

trons less strongly. This may be due to the much closer approach of the s function in the HF bond.

(c) *Containing multiple CC bonds.* Double or triple CC bonds are now described in a more conventional way using p_x and p_y functions normal to the internuclear axis for the π bonds and an s function on the axis for the σ bond. There are two s functions on the C nucleus and one on each CH bond axis. The exponents for the C≡C in CH₃CCH have been constrained to be equal. The parameter values are given in table 3.

The optimal parameter values for these molecules are much closer to one another than for the earlier molecules. Nevertheless some trends can be observed such as the rise in the s₁ exponent with the fall in the number of H neighbours.

4. Energy results

The total energies calculated for all these molecules are shown in table 4 together with those given by Snyder and Basch [8] using double zeta wavefunctions. From these results it is apparent that the use of p functions is slightly less successful for the molecules containing F atoms than for the remainder since these have energies close to 95% of the double zeta value.

It has been argued by Mulliken [6] that an approximate wave function can produce reasonable values for molecular properties only if the basis set is balanced. One measure of this balance is the relation between the corresponding orbital energies and those of a Hartree-Fock wave function [9]. For FSGO wave functions it has been found [10] that the valence orbital energies correlate very well with those of an ac-

Table 4
Comparison of total energies (in hartrees)

	This paper	Snyder and Basch	%
H ₂ O	-72.3329	-76.0035	95.17
H ₂ O ₂	-143.2892	-150.7373	95.06
CH ₃ OH	-109.6062	-115.0059	95.30
HF	-94.2205	-100.0150	94.20
F ₂	-184.2382	-198.6932	92.72
CH ₂ CCH ₂	-110.9419	-115.8203	95.79
CHCH	-73.6012	-76.7919	95.85
CH ₃ CCH	-110.8995	-	-

Table 5
Approximate linear relation between orbital energies

	a	b	Correlation coefficient
H ₂ O	1.01395	0.27853	0.99984
H ₂ O ₂	1.00311	0.28355	0.99981
CH ₃ OH	0.99707	0.15583	0.99979
HF	1.01235	0.36947	0.99976
F ₂	1.03123	0.29860	0.99954
CH ₂ CCH ₂	0.99009	0.10729	0.99992
CHCH	0.98669	0.12825	0.99993

curate wave function. In table 5 a similar correlation with the Snyder and Basch orbital energies EDZ in the form

$$\epsilon = a\epsilon_{DZ} + b$$

is reported for each molecule.

The correlation coefficients for the regressions are remarkably high and this shows that the linear relation is closely obeyed for each molecule. The regression

coefficient a remains close to unity. As is to be expected, it becomes greater than one for the poorer calculations as indicated by the percentages in table 4. The constant b increases with the inclusion of an O or F atom in the molecule.

5. Discussion

The molecules considered above have been selected as ones for which the original Frost FSGO model was either numerically unstable or singular. The introduction of a limited number of p functions has eliminated this difficulty. None of these molecular models exhibited any tendency to numerical instability. Since a cusp function on each heavy nucleus has been used in addition to the bond functions the results compare more directly with those of Ford et al. [5] than with Frost. In both calculations it is significant that the total energies are close to 95% of the Hartree-Fock results.

The models of bonding that this treatment supports are still recognisable as simple classical models. The major distinction from the Frost model is that the multiple bond is described using σ and π orbitals and the multiple lone pairs are similarly resolved into s and p orbitals.

The correlation coefficients between the orbital energies of these models and those of the double zeta

energies are not less than 0.9995. This demonstrates the balance of the basis set and suggests that other predicted properties will exhibit similar correlations.

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