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THE FLOATING SPHERICAL GAUSSIAN ORBITAL (FSGO) MODEL OF MOLECULAR STRUCTURE

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Abstract. The floating spherical gaussian orbital (FSGO) model uses localized closed-shell orbitals for arriving at geometries and energies for singlet ground electronic states for atoms and molecules. The orbitals are allowed to interpenetrate—change positions with respect to the orbital exponent and the space coordinates of the orbital centre.

The FSGO model is *ab initio* with no semi empirical parameters involved. The results obtained through this method are interpretable in terms of the classical Lewis 'electron pair' structures, and the method is, therefore, intuitively appealing to the chemist's viewpoint.

In molecules, the 'electron pair' representation for bonding and nonbonding electrons has been extensively used in chemistry. Lewis first pictured two atoms being held together by a pair of electrons. Since then, the concept of the 'electron-pair bond' has become so popular and well-established in chemistry that it is now an integral part of our chemical vocabulary. However, the 'Lewis representation' of molecular structure leaves much to be desired because it does not exhibit some important electromagnetic properties of molecules. Furthermore, the Lewis picture *per se* was entirely qualitative in nature with no quantum mechanical postulates involved. The theory tells us that 'electron pairs' are responsible for bonding but it does not explain why it should be so.

The floating spherical gaussian orbital (FSGO) model recently established by Frost[1] retains the basic idea of an 'electron-pair bond' similar to that of Lewis and in addition has the special merit of furnishing quantitative information as regards the geometry and energies of molecules. On the whole, the FSGO model has made a reasonably successful attempt to quantify the Lewis theory of chemical bonding.

Prior to the FSGO model, attempts had been made from time to time to put the 'electron pair' model on a semiquantitative and quantitative footing. These attempts include the charge cloud model of Kimball and his associates[2] which was later developed and modified by the authors of the chemical bond approach (CBA) project[3] and others.[4] A similar approach to the charge cloud model was used by Bent[5] in the development of the tangent sphere model. The valence shell electron pair repulsion (VSEPR) model in its present form has been developed by Gillispie and Nyholm[6] and is being extensively used in a qualitative way to determine some important molecular geometrics. By and large these models are empirical and semiempirical in nature and do not involve the use of quantum mechanical postulates. The FSGO model, on the other hand, is *ab initio* with no semiempirical parameters involved. The results obtained by this method are interpretable in terms of classical Lewis 'electron pair' structures, and the method is, therefore, intuitively appealing to the chemist's viewpoint.

Gaussian Type Orbitals vs Slater Type Orbitals. The gaussian orbitals have been extensively used by many authors to calculate energies and geometries of atoms[7] and molecules.[8–10] In most calculations the SCF–MO scheme has been applied for gaussian type orbitals. These orbitals have the general form

$$= r^{n+1} e^{-\alpha r^2}$$

where α is the variation parameter and n takes on values 0,1,2....They differ from the Slater type orbitals (STO) in their property of decaying to zero much more quickly, particularly for large internuclear distances. This of course is obvious from the plots in Fig. 1 where $e^{-\alpha r^2}$ is gaussian and $e^{-\alpha r}$ represents an STO. Furthermore, the gaussian type orbitals (GTO) have no well defined 'cusps' and are, therefore, a poor approximation for an atomic orbital at small internuclear distance (Fig.1). For a more accurate representation of atomic orbitals, however, linear combinations of several spherical gaussians are usually taken. This means that for accurate energy calculations in GTO's many more integrals are needed as compared to STO's. This difficulty is counterbalanced by the fact that integrals involving gaussians are much easier to evaluate as compared to Slater type integrals. Nevertheless, the 'cusp effect' on the nuclei is only of secondary importance as regards energy calculations. According to Hellman–Feynmann theorem the 'charge pile up' between the nuclei is the major effect.

Both normalized and unnormalized gaussians are useful for energy and geometry calculations. All necessary integrals for the unnormalized gaussian have been given by Boys[11] and in greater detail by Shavitt[12] while Preuss and Whitten formulas for normalized spherical gaussians are given elsewhere.[13]

The Frost Model. The Frost model which uses FSGO for the calculation of energies and geometries for various atomic and molecular systems[14] is now described in some detail.

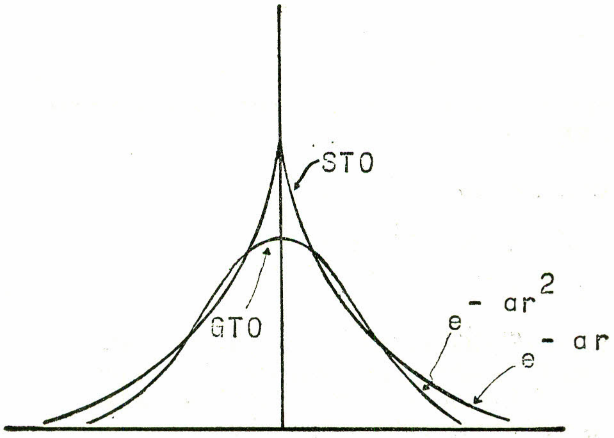

Fig. 1. Plots of the gaussian type orbitals (e^{-ar2}) vs the Slater type orbitals (e^{-ar}). Note the lack of 'cusp' in GTO as compared to STO.

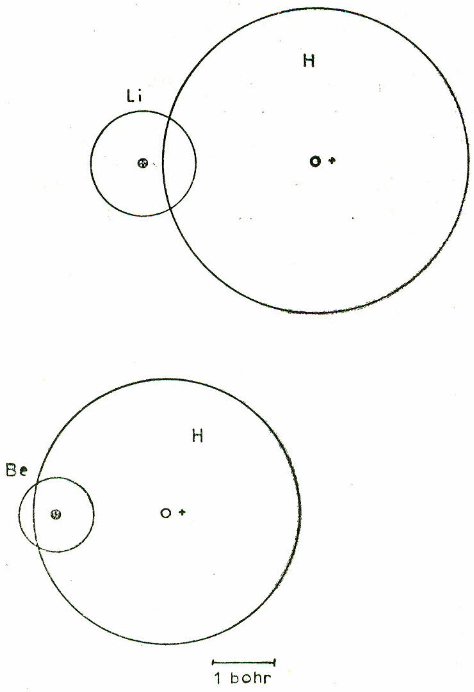

Fig. 2. Nuclear and orbital positions and orbital radii for LiH and BeH+. Orbital sizes are drawn to scale with their centres marked as 0.

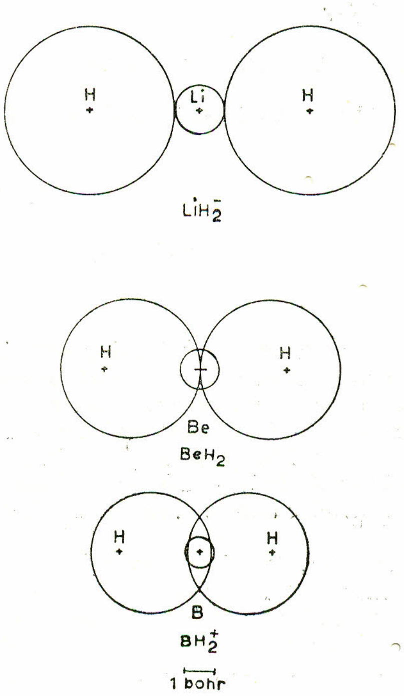

Fig. 3. Positions of localized orbitals in BeH_2 series, drawn to scale.

The FSGO model uses localized closed shell orbitals and hence is capable of giving energies and geometries for singlet ground electronic states. The method differs from the conventional charge cloud model and other electrostatic models in the sense that here the orbitals are allowed to interpenetrate-change positions with respect to the orbital exponent and the space coordinates of the orbital centre.

The results obtained with the help of the FSGO method for common diatomic and polyatomic molecules agree with our knowledge derived from other sources. For example, LiH molecule turns out to be predominantly ionic in nature containing Li^+ and H^-. A comparision of LiH and BeH^+ shows the effect of the nuclear charge on the size of the orbitals (Fig. 2).

Ab initio calculations (with obvious symmetry) for the isoelectronic triatomic (LiH_2^-, BeH_2 and BH_2^+) lead to a linear configuration. The nuclear positions for these molecules are shown in Fig. 3, and these are in no way different than the Lewis representations or the tangent sphere diagrams except that in the FSGO model the electrons clouds are allowed to diffuse. The calculations including the lone-pair orbitals, the inner shell orbitals and the bonding-pair orbitals exhibit behaviour similar to the one predicted by the tangent sphere and valence shell electron pair repulsion (VSEPR) models. For example, the VSEPR model works on the basis of the assumption that lone-pairs occupy greater space around the central nucleus than the bonding pairs. This turns out to be the case in the FSGO calculations. Pictorial representations for molecules containing lone-pairs are given in Fig. 4 and 5. The model is perhaps too naive to give quantitative estimates of energies for molecular systems as good as the SCF–MO scheme, for example, in spite of its simplicity, the model predeicts remarkably well the trends in reproducing observable properties and molecular geometrics in chemical systems. The following statement by the author in ref. 14 spells out the objectives of the model clearly.

> The purpose of such models is not to obtain an accurate solution of the Schroedinger wave equation but rather to develop a relatively simple scheme of calculation that will reproduce the major trends in the electronic and geometrical

structure of molecules and possibly give alternate and perhaps improved concepts for understanding chemical phenomenon. The calculations are to be strictly *ab initio* with no semiempirical parameters involved.

In this gcal the author appears to have well succeeded as the discussion in the following pages shows.

In the first series of papers the FSGO model is explained in some detail[14] and results are discussed for LiH. The energy calculations for atomic (He, Be) and molecular (H_2,He_2^{++}, HeH^+, H_3^+, H_4^{++}, HeH^-, BeH^+) systems are described in paper II. Paper III describes energies and geometries of many molecules of which BH_3, CH_4, NH_3,

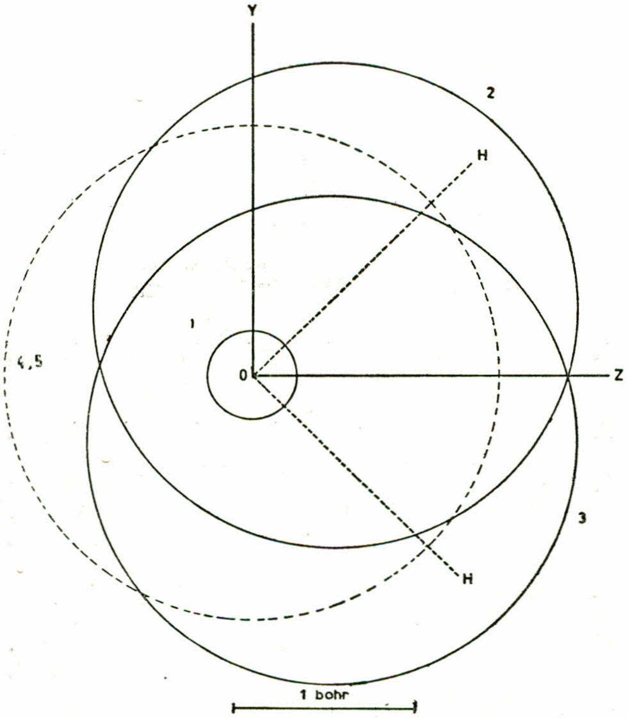

Fig. 4. The structure of the water molecule as predicted by the FSGO model. The solid circles represent bonding-pairs while the dashed circle indicate lone-pairs up and down the plan of the nuclei.

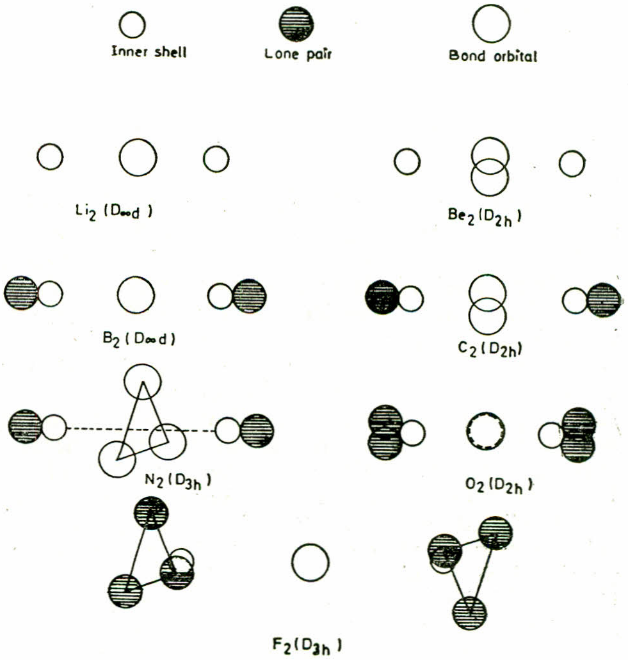

Fig. 5. The geometries for first row homonuclear diatomic molecules as predicted by the FSGO model. The dashed and solid circles in O_2 represent bonding-pairs up and down the plan of the diagram.

TABLE 1. FSGO MODEL CALCULATION DATA FOR VARIOUS MOLECULAR SYSTEMS.

System	Bond length (Bohrs)		Negative total *E* (Hartrees)		Bond angle[i]	
	FSGO	Experimental[d,e,i] or accurate calculation	FSGO	Accurate non-relativistic	FSGO	Observed
H_2	1.474	1.398	0.9559	1.174		
Li_2	5.304	5.051	12.2817	14.8717[a]		
N_2	2.034	2.075	92.0592	108.9956[b]		
O_2(singlet)	2.031	2.318	126.3735	149.5683[c]		
CH_4	2.107	2.066	33.992	40.198[f]		
NH_4^+	1.876		47.893			
NH_3	1.910(A—H)	1.913	47.568		87.6°(HAH)	106.6°
H_2O	1.666(A—H)	1.809	64.288		88.4°(HAH)	104.5°
$C_2H_6(D_3d)$	2.837(C—C)	2.900	67.005	79.0979[g]	110.7(C—C—H)	
	2.116(C—H)	2.053			108.2(H—C—H)	109.1°
$C_2H_4(D_2h)$	2.554(C=C)	2.527	65.835	78.0012[h]	120.7(C—C—H)	
	2.081(C=H)	2.053			118.7(H—C—H)	117.3°
C_2H_2	2.295(C≡C)	2.278	64.678	76.7916[h]		
	2.039(C—H)	2.002				

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HF and their isoelectronic molecules are of special interest. Hydrocarbons are treated in paper IV for which the model predicts particularly accurate geometries and energies. In a second series of papers, double spherical gaussian orbitals are used instead of only one (paper VI). The use of double guassians does not change the overall geometries but improves somewhat the energies. Paper VIII and IX discuss the structure of second row hydride and first and second row diatomic molecules, respectively.

The results for some of the well-known molecules using gaussians are given in Table 1. These results have been compared with similar parameters obtained through other models in the following discussion.

The FSGO model gives molecular energies which are generally 80–85% of the Hartree–Fock values, and the bond distances are off by a few per cent. The bond angles in H_2O and NH_3 are low by about 17%. The angle predicted by the FSGO model in H_2O and NH_3 are 88.4° and 87.6° respectively as compared to the experimental values of 104.5° for H_2O and 106.6° for NH_3. The use of double gaussian improves somewhat the bond lengths, bond angles, and molecular energies so that the energies approach values which are generally 96% of the Hartree–Fock values and most bond length values are predicted within 5.8%. For second row hydrides (not given in the table) the bond lengths are predicted with an average deviation of 3% and the bond angles are: PH_3 (90.9°) as compared to the experimental value of 93.2°; and H_2S (87.7°) as compared to the experimental value of 92.2°. The H—C—H angles in hydrocarbons are predicted with an accuracy of better than 1%.

Recently, the FSGO model has been used[15] in the analysis of energy terms involved in determining the geometry of the water molecule. The total energy E_T has been broken down to smaller components namely, the electron repulsion terms (VEE), the nuclear attractions terms (VNN) and the kinetic energy terms (TE).

From the data obtained for these energy terms as a function of the H–O–H angle, it has been shown that if the difference in electron repulsion (VEE) and the nuclear repulsion (VNN) terms are added together, they almost exactly cancel out the changes in nuclear attraction (VEN) terms. This leaves behind only the kinetic energy (TE) terms to account for the geometric variations in the water molecule. Now this idea does not entirely fall in line with the arguments used by other models in explaining molecular geometries. For example, the VSEPR and the tangent sphere models use electrostatic repulsions between electron pairs (or their size) as a fundamental deriving force to optimize geometric configurations. The idea of kinetic energy in determining geometric shapes in molecules is comparatively a recent one. It has been previously used by Schmidtke and Preuss[16] who showed that angular dependence of AH_2 and AH_3 type molecules could be reproduced by using a Hamiltonian that only contained the one electron terms: kinetic energy and electron nuclear attraction. Recently, Allen[17] has analysed the relationship between molecular shape and various energy components and is of the opinion that lone-pair and bond-pair interactions manifest themselves through a size-Pauli exclusion effect rather than charge density and concludes that shape does not follow directly from simple electrostatics which agrees with the findings of the FSGO method.

Other workers have also used floating gaussian orbitals for molecular energy and geometry computations.[18]

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