

**Analysis of Energy Terms Affecting the Geometry of the
BeH₂ and Water Molecules. A Classical Interpretation
of the Floating Spherical Gaussian Orbital Model of
Molecular Structures.**

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Summary: The energy terms arising in the calculations of BeH₂ and H₂O molecules by the FSGO method are analysed as a function of the bond angle in order to gain insight into the reasons for the particular equilibrium configurations. The analysis is made in terms of symmetrically orthogonalized orbitals so as to exclude three and four-orbital electron repulsion terms.

Introduction

Multiple Floating Spherical Gaussian Orbital (FSGO) sets were used to calculate bond distance and energy terms involved in the formation of the H₂ molecule [1]. The Gaussian sets included as much as five orbitals containing cusp, concentric and non concentric functions. It was shown that the FSGO-model for H₂ molecule was capable of reproducing the bond distance with almost complete accuracy and the energy value well within 5% accuracy.

Here we have picked up two typical not-so-simple molecules namely BeH₂ and H₂O for FSGO calculation. These molecules may easily be seen as a natural extension of the simple H₂-molecule treatment, in so far as BeH₂ being triatomic linear containing two bonding-pairs and no lone-pair while H₂O molecule being bent and containing two bonding-pairs and two lone-pairs. To make the FSGO calculations more telling the total energy terms in the computer programme have been broken down into electronic kine-

tic energy terms (T_e), electron-electron repulsion terms (V_{ee}), nuclear repulsion terms (V_{NN}) and electron-nuclear attraction terms (V_{eN}).

The FSGO model predicts energies and geometries of molecules using localized, closed shell, singlet ground state configuration. Its results, therefore, are interpretable in terms of 'Lewis electron pair' model which justifies the piecemeal energy contributions to the total energy to be split up into (T_e), (V_{NN}), (V_{ee}) and (V_{eN}) terms as described earlier. To keep the above described model in view the electron energy terms have been looked at in terms of inner shell electrons (s), bonding-pairs electrons (bp), lone-pairs electrons (lp) and interactions between them. By using symmetrically orthogonalized orbitals three and four centre electronic terms are made to vanish. Thus the results obtained by using orthogonal localized orbitals have been compared with simple semi-quantitative models such as the tangent [2] sphere and the valence shell

electron pair repulsion (VSEPR) [3] models.

In BeH_2 and H_2O , the geometry of the molecules is commonly explained by bringing into play the electron-pair interactions. The inner shell electrons being dormant, the bonding and lone pair interactions count. With this in mind the FSGO calculations have been done using orthogonal localized orbitals for BeH_2 and H_2O molecules. The FSGO calculations for various simple systems have been done by various authors [4-7].

The results have been interpreted in terms of classical Lewis "electron pair" structures and the method is therefore intuitively appealing to the Chemists' viewpoint. It would be seen that in the discussion, results are compared with simplified nonquantitative models such as the tangent sphere and the valence shell electron pair repulsion (VSEPR) models. In addition to these crude models, the FSGO model has been compared with simple molecular orbital pictures and energy-level correlation diagrams that have been used by many authors to arrive at the qualitative features of molecular geometry. As will be seen in the discussion, the MO model was initiated by Mulliken and used by Walsh to analyse the geometrical shape of simple molecules, especially the angular dependence.

Symmetric Orthogonalized Orbitals for BeH_2 and H_2O :

Transformation of nonorthogonal orbitals ϕ_i into symmetrically orthogonalized orbitals X_i is achieved by a nonunitary transformation converting the overlap matrix to the unit matrix. Lowdin [8] has shown such transformations for a determinantal wave function of $2n$ orbitals all with parallel

spin. Such transformations are therefore applicable to molecules such as BeH_2 and H_2O .

For a closed-shell case the transformation from the original non-orthogonal orbitals ϕ_i to an orthogonal set X_i may be carried out by the following formula given in matrix notation:

$$X = \phi T^{\frac{1}{2}} \quad \text{-----(1)}$$

where $T = S^{-1}$ is the inverse overlap matrix and X and ϕ are row vectors of the corresponding orbitals. S and T are assumed to be real. The

$$\int X^* X_i dv = [i|i],$$

may then be transformed to give

$$\sum_i [i|i] = \sum_i \sum_j \sum_k (j|k) (T^{\frac{1}{2}})_{ij} (T^{\frac{1}{2}})_{ik} = \sum_{j,k} (j|k) T_{jk} \quad (2)$$

$$\text{where } (j|k) = \int \phi_j^* \phi_k dv$$

In the same way

$$\sum_{i,j} [ij|jj] = \sum_{k,l,p,q} (k|l|pq) T_{kl} T_{pq} \quad (3)$$

and

$$\sum_{i,j} [ij|ji] = \sum_{k,l,p,q} (k|l|pq) T_{kq} T_{lp} \quad (4)$$

where

$$(k|l|pq) = \int \phi_k^*(1) \phi_l(1) \phi_p^*(2) \phi_q(2) r_{12}^{-1} dv_1 dv_2 \quad (5)$$

Brackets here involve orthogonal orbitals while parentheses refer to integrals over non-orthogonal orbitals.

Electronic energy may be evaluated as

$$E_{el} = 2 \sum_{j,k} (j|k) T_{jk} + \sum_{k,l,p,q} (k|l|pq) [2T_{kl} T_{pq} - T_{kq} T_{lp}] \quad (6)$$

and the total energy as

$$E = E_{el} + \sum_{\mu < \nu} \frac{Z_{\mu} Z_{\nu}}{r_{\mu\nu}}$$

after adding the internuclear repulsion energy.

Each symmetrically orthogonalized orbital has a negative lobe projected towards the adjacent nucleus. This can be shown by expansion of equation (1). For the H_2O molecule, orthogonalized OH bonding orbital contour and orthogonalized lone pair contour diagrams are shown in Figures 1 and 2 respectively as drawn by the computer calculated using previously determined parameters [9].

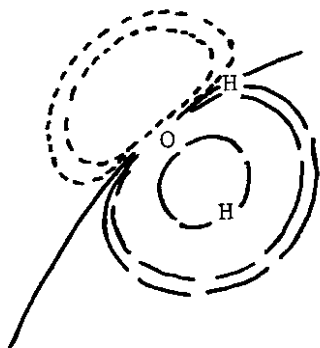


FIG.1

Fig.1: Orthogonalized OH bonding orbital contour diagram.

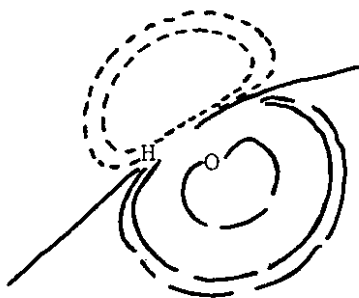


FIG.2

Fig.2: Orthogonalized lone pair orbital contour diagram.

It is seen here that the negative lobe in the bonding pair (and lone pairs) is smaller as compared to their positive counterparts. Furthermore,

the values for orbital coefficients for BeH_2 and H_2O (Tables I and II respectively) for symmetrically orthogonalized orbitals indicate that negative contributions to the bond orbitals/lone pair orbitals from other orbitals are comparatively small. The main effect of orthogonalization is therefore to compress more tightly the original gaussians about their central nuclei. This is a good thing because orthogonalization makes the gaussians relatively more localized and hence more susceptible to physical interpretation.

*Calculations for BeH_2 and H_2O
Molecules Using Symmetric
Orthogonalized orbitals:*

The computer programme used here is known as LOCO-GR and was developed in the U.S. It is available in Chemistry Department, Northwestern University, USA.

For BeH_2 computer calculations, approximate coordinates, orbital radii and orbital exponents were fed into the computer and the energy was allowed to minimize with respect to these. The calculations are therefore ab initio with no semi-empirical parameters involved. The calculations were then repeated at various angles being fixed. In the ground state the BeH_2 molecule shows liner geometry with a minimum energy of -13.214 a.u. when the HBeH angle is exactly 180° . The present and previous calculations [9] using gaussians agree that the $\text{Be}-\text{H}$ bond length is 2.669 a.u with inner shell and bonding pair radii being 0.510 a.u and 2.108 a.u respectively (Fig. 3).

In case of the H_2O molecule, it was assumed to have C_{2v} symmetry with the z axis as the C_2 axis bisecting

Table-1: The geometry of the beryllium hydride molecule
coefficients for symmetrically orthogonalized orbitals

orbital/angle	180°	170°	160°	150°	140°	130°
S	1.00994 ^{a)}	1.00992	1.00987	1.00979	1.00968	1.00952
	-0.05552	-0.05545	-0.05521	-0.05480	-0.05421	-0.05341
	-0.05552	-0.05545	-0.05521	-0.05480	0.05421	-0.05341
bp	-0.05552	-0.05545	-0.05521	-0.05480	-0.05421	-0.05341
	1.01146	1.01166	1.01231	1.01351	1.01548	1.01858
	-0.06412	-0.06521	-0.06854	-0.07435	-0.08302	-0.09511
bp	-0.05552	-0.05545	-0.05521	-0.05480	-0.05421	-0.05431
	-0.06412	-0.06521	-0.06854	-0.07435	-0.08302	-0.09511
	1.01146	1.01166	1.01231	1.01351	1.01548	1.01858

(a) In each section the successive coefficients are for the original inner shell and bonding pair gaussians, respectively.

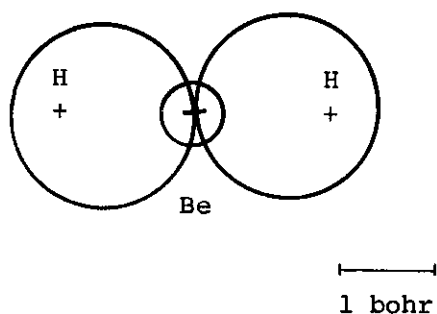


FIG.3 ORBITALS AND COORDINATES FOR THE BeH_2 MOLECULE.

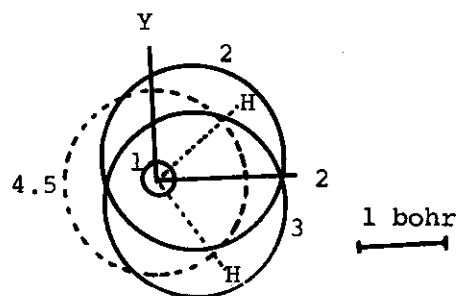


FIG.4 ORBITALS AND COORDINATES FOR THE H_2O MOLECULE.

1. Inner shell (S)
- 2.3. Bonding pairs (bp)
- 4.5. Lone pairs (lp)

the H-O-H angle. The nuclei lie in the y,z plane with the oxygen nucleus at the origin (Figure 4). The inner shell at oxygen has a fixed radius of 0.24 Bohr. The bonding pairs lie on the O-H bond axis with their centre at a fixed distance of 0.34 of the O-H bond distance towards the oxygen nucleus. (This turns out to be the distance from the centre of the bonding electron pair to the oxygen nucleus

when energy is minimized with respect to all parameters in the H_2O molecule [9]). To seek further simplification in the energy analysis, the O-H bond lengths are fixed at 1.66927 a.u irrespective of bond angle. Furthermore, the lone pairs are held fixed at a

Table-II: Coefficients for symmetrically orthogonalized orbitals
(Geometry of H₂O molecule)

Orbital/Angle	80	90	100	110	120
S	1.01874 ^a	1.01877	1.01880	1.01885	1.01890
	-0.00705	-0.00634	-0.00536	-0.00402	-0.00221
	-0.00705	-0.00634	-0.00536	-0.00402	-0.00221
	-0.06091	-0.06161	-0.06255	-0.06381	-0.06550
	-0.06091	-0.06161	-0.06255	-0.06381	-0.06550
bp	-0.00705	-0.00634	-0.00536	-0.00402	-0.00221
	2.14681	2.10852	2.10987	2.14771	2.22209
	-0.35563	-0.18651	-0.02731	0.13210	0.30045
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
bp	-0.00705	-0.00634	-0.00536	-0.00402	-0.00221
	-0.35563	-0.18651	-0.02731	0.13210	0.30045
	2.14681	2.10852	2.10987	2.14771	2.22209
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
1p	-0.06091	-0.06161	-0.06255	-0.06381	-0.06550
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	5.57554	5.62523	5.68684	5.76328	5.85827
	-3.87490	-3.82520	-3.76360	-3.68715	-3.59216
1p	-0.06091	-0.06161	-0.06255	-0.06381	-0.06550
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	-0.61019	-0.66694	-0.73700	-0.82357	-0.93069
	-3.87490	-3.82520	-3.76360	-3.68715	-3.59216
	5.57554	5.62523	5.68684	5.76328	5.85827

(a) In each section the successive coefficients are for the original inner shell, bonding and lone pair spherical gaussians, respectively.

distance of 0.1 Bohr up and down the x-axis. This follows from the calculation in reference [9] where energy minimization with respect to all parameters 'blows up' because of the tendency of the two lone pairs to coalesce. If the x coordinate for two lone pairs is allowed to vary, the overlap between the lone pair orbitals increases and the integral approaches unity. This makes the overlap matrix singular with the result that the increase overlap matrix 'blows up'. The way around this difficulty is to hold constant the x coordinate for the lone pair. Furthermore, it has been

shown [9] that $x = \pm 0.1$ yields good results.

The energy minimization calculations were repeated at different angles holding fixed all other parameters. This enables one to calculate the changes in various energy contributions such as, electronic repulsion energy (V_{ee}), electron nuclear attraction energy (V_{en}), nuclear repulsion energy (V_{nn}) and kinetic energy (T_e) as a function of the bond angle. Table IV contains all the energy contributions which add up to give the total

Table-III: Various energy components for the BeH_2 molecule
(Energy in atomic units, Hartree)

Energy/angle	180°	170°	160°	150°	140°	130°
Electron repulsion						
(2-Orb.)						
S - bp	3.4484	3.4478	3.4460	3.4428	3.4380	3.4374
bp - bp	0.9146	0.9176	0.9267	0.9418	0.9631	0.9844
(1-Orb.)						
S	2.2096	2.2096	2.2096	2.2095	2.2095	2.2094
bp	1.0780	1.0781	1.0785	1.0709	1.0799	1.0811
VEE	7.6506	7.6531	7.6608	7.6731	7.6905	7.7123
Nuclear attraction						
S	-26.5776	-26.5774	-26.5770	-26.5764	-26.5754	-26.5741
bp	-20.6825	-10.6837	-10.6905	-10.7020	-10.7183	-10.7398
VEN	-37.2591	-37.2611	-37.2675	-37.2784	-37.2937	-37.3139
Nuclear repulsion						
VNN	3.1847	3.1854	3.1876	3.1913	3.1967	3.2041
Kinetic energy						
S	11.7556	11.7553	11.7542	11.7524	11.7497	11.7462
bp	1.4539	1.4545	1.4564	1.4597	1.4648	1.4725
TE	13.2095	13.2198	13.2106	13.2121	13.2145	13.2187
Total	-13.2143	-13.2128	-13.2085	-13.2019	-13.1920	13.1788

energy as the angle in H_2O molecule varies at intervals of 10° from 80° to 120° .

Discussion and Conclusion

In table III are listed electron repulsion (VEE), nuclear attraction (VEN), nuclear repulsion (VNN), kinetic energy (TE) and total energy terms for all the electrons and nuclei involved in BeH_2 molecular energy and geometry computation. The inner shell(s) seems to be inactive; more significant changes occur in 2-orbital bp-bp interactions, bp-nuclear interactions and to a lesser extent in the kinetic energy terms for all electron pairs. Nuclear-Nuclear repulsion energy also changes significantly, in line with the previous observation regarding H_2O molecule. The changes

in different energy terms as a function of the bond angle listed in table III are by no means dramatic, yet they contain the relevant information if looked into a little more carefully. It is seen that there is an increase in kinetic energy going from linear to the bent configuration, which has been explained in the next paragraph.

At equilibrium distances for any molecule, the energy analysis to make sense, the Virial Theorem should be obeyed. The Virial theorem states that $E = -T = V/2$. Here V is the average potential energy and T the average kinetic energy. It is observed that at equilibrium and in its vicinity (HBeH angles being 180° & 170°), E values are -13.2143 and -13.2128 respectively, while their corresponding kinetic energy values are 13.209 & 13.2198 respectively. For BeH_2 the agreement

Table-IV: Various energy components for the H_2O molecule
(energy in a.u., Hartrees)

	80°	90°	100°	110°	120°
Electron repulsion					
(2-orb)					
(S-bp)	6.3856	6.3877	6.3838	6.3713	6.3467
(S-lp)	7.3321	7.3383	7.3459	7.3551	7.3659
(bp-bp)	2.3005	2.2571	2.2068	2.1488	2.0818
(bp-lp)	9.2307	9.2453	9.2605	9.2760	9.2909
(lp-lp)	2.3412	2.3440	2.3465	2.3479	2.3475
(1-orb)					
S	4.6666	4.6666	4.6666	4.6666	4.6667
bp	1.7466	1.7448	1.7440	1.7452	1.7494
lp	1.7298	1.7346	1.7399	1.7457	1.7514
VEE	35.7331	35.7184	35.6940	35.6566	35.6003
Nuclear attraction					
S	-108.8803	-108.8806	-108.8812	-108.8824	-108.8842
bp	-32.0468	-31.9583	-31.8539	-31.7292	-31.5775
lp	-33.4999	-33.5353	-33.5808	-33.6384	-33.7090
VEN	-174.4270	-174.3742	-174.3159	-174.2500	-174.1707
Nuclear repulsion					
VNN	10.0510	10.0086	9.9760	9.9507	9.9309
Kinetic energy					
S	53.9035	53.9061	53.9092	53.9130	53.9177
bp	5.1239	5.0846	5.0485	5.0186	4.9988
lp	5.3401	5.3750	5.4207	5.4812	5.5617
TE	64.3675	64.3657	64.3784	64.4128	64.4782
Total	-64.2854	-64.2815	-64.2675	-64.2299	-64.1613

with the Virial theorem is therefore just fair near equilibrium. However, for HBeH angles being 140° & 130° , the agreement with the virial theorem is not good, which is understandable since the molecule is far from equilibrium. It is due to this factor that the interpretation angle for BeH_2 molecules becomes somewhat obscure and should therefore be handled with care.

The overall picture of BeH_2 resembles closely the electrostatic models of Bent [2] and Gillespie [3]. The detailed energy analysis, however, as shown in table III reveals

that this indeed is not the case. Electrostatic models such as mentioned above and others [10,11] explain molecular geometries in terms of interactions between electron pairs (bonding and lone pairs) which turns out to be too simple to be true. The apparent fallacy of such models lies in neglecting nuclear-nuclear, nuclear-electronic and kinetic energy effects, which in many molecules may play the dominating role.

The water molecule obeys the virial theorem [12] like BeH_2 molecule. The Virial theorem is obeyed in cases where a scale factor is a variation

parameter [13]. In the present calculations energy computations have been carried out as a function of the bond angle with other parameters fixed, hence agreement with the virial theorem is not expected to be good. The deviations from the virial theorem (less than 1%) remains more or less the same for most H-O-H angles.

The FSGO picture developed here may usefully be compared with Walsh [14] diagrams for molecules of the type AH_2 with the difference that the FSGO model in its simplest form does not use p-type orbitals to represent electron pairs; (although it can easily be done). Walsh's rules that predict molecular geometries for various electronic states have been presented by some authors as originating from no theory [15]. According to Walsh diagram for H_2O , the $2a_1$ bent configuration lies higher than the linear $26g$ configurations, but the lone pairs in the relative energies of the lone pairs in $a_1-\pi_u$ orbitals determine the bent structure in the H_2O molecule. This conclusion agrees with the VSEPR and other models. The curves in the Walsh diagram may be compared with energy values obtained by the FSGO model.

The Walsh representation for molecules has been given a valence bond meaning by Takahata, Schnuelle, and Parr [16], which resembles somewhat the electrostatic picture given by other authors [2,3,17]. The TSP model represents the H_2O molecule as $H^-O^{2+}H^-$ where each H atom is given a closed shell of electrons. According to the TSP model the molecule achieves its most symmetric configurations if no electrons remain after giving closed shell configuration to ligands. On the other hand if there are electrons left over, the molecule distorts to a less symmetric configuration. Coulombic

repulsion between the ligands keep the molecule in its most symmetric form while the left over electron at the central atom make it less so by hybridizing $2S-2P$ orbitals at the central atom. The degeneracy of the $2S$ and $2P$ electrons will make the affect as a second-order Jahn-Teller effect.

The TSP calculation gives a value of 102° for the bond angle in the H_2O molecule as compared to the experimental value of 104.5° . This may be compared with the FSGO value of 88.4° reference [4] and values 103° and 104° obtained by Thompson [10]. It is observed that although the FSGO model gives a comparatively less accurate bond angle value, it has the advantage of furnishing additional quantum mechanical (piecemeal) information which most electrostatic models do not.

Other energy analysis schemes for geometric interpretation of molecular structure have been used by some authors. For example, Allen [18] breaks up the total energy (E_T) of a system into two broad categories namely the repulsive part (TE , VNN , VEE) and the attractive part (VEN). The geometric changes in molecules and barriers to such changes are visualized by Allen as repulsive or attractive dominant. Clementi [19] using a bond energy analysis scheme decomposes the total energy of molecular systems into one-, two-, three-, and four-center contributions and gives explanation in terms of these contributions.

The analysis of energy terms used in the present paper is a step towards better understanding of the nature of forces involved in determining the shape of the BeH_2 and H_2O molecules, taking each term as an independent contributor. It has been shown that if symmetric orthogonalized gaussians are used (one gaussian for each electron pair bond or a lone pair to deter-

mine the angle dependence of the two molecules, the change in geometry can almost entirely be explained on the basis of variations in the kinetic energy terms for the bonding orbitals and the lone pair orbitals).

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