ANALYSIS OF ENERGY TERMS AFFECTING THE GEOMETRY OF THE BERYLLIUM HYDRIDE MOLECULE CALCULATED THROUGH THE FLOATING SPHERICAL GAUSSIAN ORBITAL MODEL OF MOLECULAR STRUCTURE

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Abstract. The energy terms arising in the floating spherical guassian orbital (FSGO) model calculation of BeH_2 molecule have been analysed as a function of the bond angle using symmetric orthogonalized orbitals. This helps exclude three — and four orbital electron repulsion terms making the results interpretable in terms of some well known electron pair repulsion models.

The energy terms arising in the floating spherical gaussian orbital (FSGO) model calculation used for water molecule have been previously analysed as a function of the bound angle.[1] Since the FSGO model predicts energies and geometries of molecules using localized, closed shell, singlet ground state configurations, its results are interpretable in terms of 'Lewis electron pair' model. Therefore, the piecemeal energy contributions to the total energy were split up as electronic repulsion (VEE), nuclear attraction (VEN), nuclear repulsion (VNN) and kinetic energy (TE) terms. Of these terms the electronic repulsion (VEE) contains interactions such as the inner shell(s)—bonding pair (bp), inner shell-lone pair (lp), bonding pair-bonding pair, bonding pair-lone pair and lone pair-lone pair for 2-orbital terms and inner shell, bonding pair and lone pair for 1-orbital terms. By using symmetrically orthogonalized orbitals the three and four centre electronic terms are made to vanish. Thus the results obtained by using orthogonal localized orbitals have been compared with simplified semi-quantitative models such as the tangent sphere[2] and the valence shell electron pair repulsion (VSEPR)[3] models.

In water the geometry of the molecule is commonly explained by bringing into play the electronic interactions between pairs of electrons. Since inner shell electrons here do not contribute much, bonding and lone pairs essentially determine the geometry. It was considered worthwhile, on the basis of the above argument, to look into a simple molecule in which only bonding pairs are present so that the lone pairs effects may be 'sorted out'. With this in mind, the 'FSGO' model' has been used here to compute various electronic and nuclear interactions for the BeH_2 molecule using orthogonal localized orbitals.

Each localized spherical gaussian orbital function is represented mathematically by the expression :

$$\Phi_i\,[r] = (\frac{2}{\pi\,\rho_i{}^2})^{3/4}\ \exp\left[-(r/\rho)^2\right] \quad (1)$$

which contains variable 'orbital radius' ρ_i The orbitals represented in equation (1) are nonortho-gonal and hence require a complex energy expression because they involve three and four orbital interactions. For orthogonal orbitals X_i, only two orbital interactions count and the energy expression has been given by Lowdin.[4]

$$E_{el} = 2\Sigma_i\,[i/i] + \Sigma_{i,j}\{\,2\,[ii/jj] - [ij/ji]\,\} \quad (2)$$

Summations are from 1 to n unless otherwise indicated ;

$$[i/i] = \int x_i^* h\,x_i\ dv \quad (3)$$

are one electron integrals involving the one electron. Hamiltonian operator :

$$h = -\tfrac{1}{2}\nabla^2 - \sum_\nu^N \frac{Z_\nu}{r_\nu} \quad (4)$$

Here z_ν is the atomic number of nucleus ν and r_ν the distance of the electron from that nucleus. N is the number of nucleii;

$$[ij/kl] = \int x_i^*(1) \times_j(1) x_k^*(2) \times_l(2)\,(1/r_{12})\,dv_1 dv_2 \quad (5)$$

are the two electron repulsion integrals. Equation (2) is obtained from :

$$E_{el} = \int \Psi^* H\Psi\,dT_1 \ldots\ dT_{2n}$$

with the total Hamiltonian

$$H = \sum_{i=1}^{2n} h_i + \sum_{i<j} \gamma_{ij}^{-1} \quad (6)$$

and

$$\Psi = 1/\sqrt{(2n)\,!}\ \det(x_1\bar{x_1}x_2\bar{x_2}\ldots x_n\bar{x_n})$$

Transformation from Nonorthogonal to Symmetric Orthogonalized Orbitals. The transformation from the nonorthogonal orbitals Φ_i to symmetrically orthogonalized orbitals X_i is achieved through a nonunitary transformation which converts the overlap matrix to the unit matrix. Such transformation has been shown by Lowdin[4] for

determinantal wave function of 2n orbitals all with paralled spins. The transformation, for a closed shell case, from the nonorthogonal orbitals Φ_i to an orthogonal set Xi may be carried out by the following formula given in matrix notation :

$$X = \Phi \, T^{\frac{1}{2}} \tag{7}$$

where $T = S^{-1}$ is the inverse overlap matrix and X and Φ are row vectors of the corresponding orbitals. Both S and T are assumed to be real. The integrals in equation (3) may then be transformed to give :

$$\sum_i [i/i] = \sum_i \sum_j \sum_k (j/k) (T^{\frac{1}{2}})_{ij} (T^{\frac{1}{2}})_{ik} = \sum_{j,k} (j/k) T_{jk} \tag{8}$$

where

$$(j/k) = \int \Phi_j^* \, h \, \Phi_k \, dv$$

In the same way

$$\sum_{i,j} [ii/jj] = \sum_{k,l,p,q} (kl/pq) T_{kl} T_{pq} \tag{9}$$

and

$$\sum_{i,j} [ij/ji] = \sum_{k,l,p,q} (kl/pq) T_{kq} T_{lp} \tag{10}$$

where

$$(kl/pq) = \int \Phi_k^*(1) \Phi_l(1) \Phi_p^*(2) \Phi_q(2) r_{12}^{-1} dv_1 \, dv_2 \tag{11}$$

(Parentheses refer to integrals over non-orthogonal orbitals while the brackets involve orthogonal orbitals).

The electronic energy becomes :

$$E_{el} = 2 \sum_{j,k} (j/k) T_{jk} + \sum_{k,l,p,q} (kl/pq)$$
$$[2 \, T_{kl} \, T_{pq} - T_{kq} T_{lp}] \tag{12}$$

The total energy is then given by

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

After adding the internuclear repulsion energy.

Orbital Coefficients and geometries for Symmetrically Orthogonalized Orbitals. In the ground state the BeH$_2$ molecule shows linear geometry with the minimum energy of -13.214 a.u. when the H Be H angle is exactly 180°. The present and previous calculations[5] using FSGO agree that the Be—H bond length is 2.669 e.u with inner shell and bounding pair radii being 0.510 a.u. and 2.108 a.u. respectively, Fig. 1.

Coefficients for symmetrically orthogonalized orbitals are shown in Table 1. The coefficient have been evaluated for BeH$_2$ geometries when the H Be H angle is varied from 180° to 130° with successive intervals of 10° between each geometry. The data on coefficients for inner shell(s) and bonding pair (bp) orbitals indicate that the negative contribution from the other orbitals to the inner
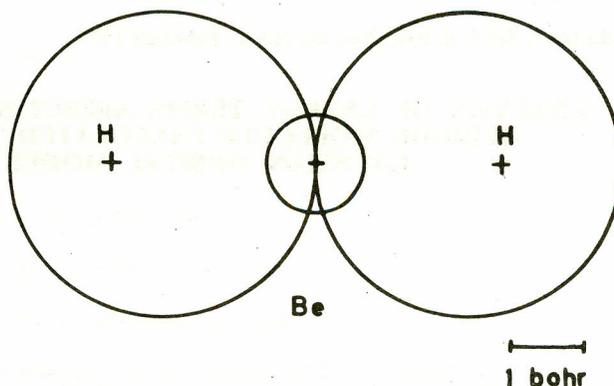
Fig. 1. Orbitals and coordinates for the BeH$_2$ molecule.

shell and bonding pair orbital is rather small. In most cases, it is not more than 5% and remains more or less the same with changing geometries.

For 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, almost *ab intio* with no semi-empirical parameters involved. The calculations were then repeated at various angles being fixed.

Discussion

In Table 2 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 Be H$_2$ 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$_2$O molecule. The changes in different energy terms as a function
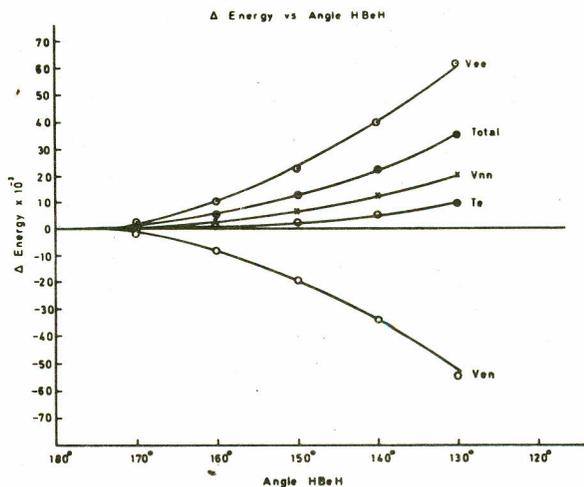
Fig. 2. Plot showing $\triangle$E as a function of angle variation for various energy factors.

TABLE 1. COEFFICIENTS FOR SYMMETRICALLY ORTHOGONALIZED ORBITALS.

Orbital/angle	180°	170°	160°	150°	140°	130°
	a)					
S	1.00994	1.00992	1.00987	1.00979	1.00068	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.

TABLE 2. 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	—10.6815	—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

of the bond angle listed in Table 2 are by no means dramatic, yet they contain the relevant information if looked into a little more carefully. For this purpose, differences in energies ($\triangle$ Energy) between two consecutive points is plotted in Fig. 2, taking energies for the linear configuration (180°) to be at point zero. Fig. 2 shows that the nuclear attraction terms become more minus with the bond distortion from linear to a bent configuration while all other terms (VEE, VNN, TE and total energy) increase. This perhaps may best be explained by assuming that a bent structure for the BeH$_2$ molecule brings into play more markedly the nuclear - electron attraction interactions which are absent when the nuclei and electrons are far apart. Also, the same factor which is responsible for a favourable (low energy) VEN

term makes VNN and VEE more repulsive since now the nuclear-nuclear and electron - electron interactions become more dominant. It is seen that there is an increase in kinetic energy going from linear to the bent configuration. The role of kinetic energy, however, is relatively more difficult to explain.

At equilibrium distances for any molecule, the energy analysis to make sense, Virial theorem should be obeyed. Virial theorem states that $E = -\bar{T} = \bar{V}/2$. Here $\bar{V}$ is the average potential energy and $\bar{T}$ the average kinetic energy. It is observed that at equilibrium and in its vicinity (H Be H angles being 180° and 170°), E values are — 13.2143 and -13.2128 respectively while their corresponding kinetic energy values are 13.209 and 13.2198 respectively. For BeH$_2$, the agreement with the

Virial theorem is therefore just fair near equilibrium. However, for H Be H angles being 140° and 130°, the agreement with the Virial theorem is not good, which is understable since the molecule is far from equilibrium. It is due to this factor that the interpretation of the analysis of energy terms as a function of the bond angle for BeH_2 molecule becomes somewhat obscure and should therefore be handled with care.

At first sight, the overall picture of BeH_2 molecule developed here resembles closely the electrostatic models of Bent[6] and Gillespie.[7] The detailed energy analysis, however as shown in Fig. 2 and Table 2 reveals that this indeed is not the case. Electro-static models such as mentioned above and others[8][9] explain molecular geometries in terms of interactions between electron pairs (all 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 domineering part. An alternate approach to molecular geometry has been used by Pauling,[10] Strong and others.[11] In this approach radius ratios and size effects are assumed to give guidelines to final answers.

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