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The Calculation of Valence Angles for H_2O and NH_3 Using the Maximum Overlap Principle

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A new approximate method for the determination of the valence bond angles for MX_k-type molecules, based on the maximum overlap principle, is proposed. The valence bond angles are determined from the conditions of maxima of the "total bonds strength". The method has been used to calculate the valence angles and the hybrid orbitals for the water, and the ammonia molecule, respectively. The calculated valence bond angles for both molecules are about 2° too high with respect to experimental equilibrium values. Also the best hybrid orbitals using the Golebiewski simplified method were calculated.

Eine neue Näherungsmethode für die Bestimmung der Valenzwinkel für Moleküle vom Typ MX_k wird vorgeschlagen, die sich auf das Prinzip der maximalen Überlappung gründet. Die Valenzwinkel werden aus der Forderung nach einem Maximum der „Gesamtbindungsstärke" abgeleitet. Die Methode wird zur Berechnung der Valenzwinkel und der Hybridorbitale von H_2O und NH_3 angewendet. Die berechneten Valenzwinkel sind für beide Moleküle etwa 2° zu hoch gegenüber den experimentellen Gleichgewichtswerten. Die besten Hybridorbitale werden entsprechend der vereinfachten Methode von Golebiewski berechnet.

On propose, sur la base du principe du recouvrement maximum, une nouvelle méthode approchée pour la détermination des angles des liaisons de valence des molécules de type MX_k. Ces angles sont déterminés à partir des conditions de maxima de la «force totale de liaison». La méthode a été utilisée pour calculer les angles de valence et les orbitales hybrides de l'eau et de l'ammoniac. Les valeurs obtenues sont supérieures d'environ 2° aux valeurs expérimentales. Les meilleures orbitales hybrides de ces deux molécules ont été aussi calculées par la méthode simplifiée de Golebiewski.

Introduction

The prediction of bond angles, in general, has to be carried out with approximate methods which suggest plausible structures rather than give definite demonstrations of structure. Unfortunately, accurate calculations are tedious and very complicated, and only a few have been carried out. Comparatively considerable calculations have been reported in literature on the H_2O molecule [2–7]. Obtained results are summarized in Table 1. The NH_3 molecule has received also much attention from a number of authors [6–11], who used different approaches and obtained results with different degrees of accuracy (Table 2).

From the review contained in the Table 1 and 2 it follows that the used methods lead, however, to long computations. It is preferable to compute valence bond angles by methods which are less obvious but which are easier to use.

Pauling and Sherman [1] have shown for a one electron bond that its energy varies considerably with force of the hybrid in the direction of the bond. Many

Table 1. *Calculated values and experimental equilibrium bond angle for* H_2O

Reference	Method of calculation	Number and type of basic functions	Bond angle
Present calculation	Maximum overlap method	5 STAO's 3 on O and 1 on each H	107°10′
Coulson[a]	Non-localised orbitals	p_x and p_y on O h_1 and h_2 of the H	90°
Duncan[b]	Method of localised orbitals	s and p on O and h_a and h_b on H	120.2°
Boys[c]	Single-determinant one-center SCF-CI	linear combination of determinants corresponding to thirty configurations	96°
Frost[d]	Model of floating localised orbitals	Spherical GTO's	88°
Pople[e]	CNDO method	5 STAO's with 3 on O and 1 on each H	107.1°
Pople[f]	INDO method	5 STAO's with 3 on O and 1 on each H	108.6°
Experimental[g]			104°45′

[a] Ref. [2]. – [b] Ref. [3]. – [c] Ref. [4]. – [d] Ref. [5]. – [e] Ref. [6]. – [f] Ref. [23]. – [g] Ref. [7].

Table 2. *Calculated values and experimental equilibrium bond angle for* NH_3

Reference	Method of calculation	Number and type of basis functions	Bond angle
Present calculation	Maximum overlap method	7 STAO's with 4 on N and 1 on each H	109°35′
Higuchi[a]	Approximate polycenter SCF-MO	8 STAO's with 5 on N and 1 on each H	108°
Kaplan[b]	Single-determinant polycenter SCF-MO	8 Hartree-Fock AO's, 5 on N and 1 on each H	106°47′
Moccia[c]	Single-determinant one-center SCF-MO	21 STAO's with l up to 3	110°2′
Joshi[d]	Single-determinant one center SCF-MO	25 STAO's with l up to 5	109.34°
Frost[e]	Model of floating localised orbitals	Spherical GTO's	88°
Pople[f]	CNDO method	7 STAO's with 4 on N and 1 on each H	106.7°
Pople[g]	INDO method	7 STAO's with 4 on N and 1 on each H	109.7°
Experimental[h]			106°47′

[a] Ref. [8]. – [b] Ref. [9]. – [c] Ref. [10]. – [d] Ref. [11]. – [e] Ref. [5]. – [f] Ref. [6]. – [g] Ref. [23]. –– [h] Ref. [7].

objections can be raised to Pauling's [1, 12] concept of the strength of a hybrid. For example Maccoll [13] has observed that the strength of a hybrid bond orbital as defined by Pauling and the C–C(σ) bond dissociation energy does not always increase in the same order. Therefore Maccoll has proposed the use of the overlap integral between a hybrid orbital and the orbital characterising the other atom of the bond.

In the present paper a new approximate maximum overlap method for the determination of the bond angles for polyatomic molecules is proposed.

Calculations and Results

a) Calculations: The General Method

Because bond overlap is very sensitive to the angle of deviation between the hybrid forming a bond and the straight atom-atom line, and because this angle does not depend strongly on the particular choise of atomic orbitals, or atomic overlap integrals employed, the method of maximum overlap seems suitable for the determination of bond valence angles in molecules.

Let us assume that we know the approximate geometrical configuration of the molecule of a type MX_k and also any set of linearly independent orthonormal atomic orbitals $\varphi_1, \ldots, \varphi_n$ of the central atom, M, and $\Theta_1, \ldots, \Theta_k$ a set of atomic orbitals of the ligands. Murrell [14] suggested to look for the k best hybrid orbitals of the central atom M,

$$\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_k \end{pmatrix} = A \begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_n \end{pmatrix} = \begin{pmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & & \vdots \\ a_{k1} & \cdots & a_{kn} \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_n \end{pmatrix} \tag{1}$$

(where $n \geqq k$) such that the sum of all "bond strength"

$$\sum_{i=1}^{k} \langle \Theta_i | \psi_i \rangle = \operatorname{tr} S_1 \tag{2}$$

is a maximum. The matrix S_1 in Eq. (2) is given by the formula:

$$S_1 = \begin{pmatrix} \langle \Theta_1 | \psi_1 \rangle & \cdots & \langle \Theta_1 | \psi_k \rangle \\ \vdots & & \vdots \\ \langle \Theta_k | \psi_1 \rangle & \cdots & \langle \Theta_k | \psi_k \rangle \end{pmatrix} = \begin{pmatrix} \langle \Theta_k | \varphi_1 \rangle & \cdots & \langle \Theta_k | \varphi_n \rangle \\ \vdots & & \vdots \\ \langle \Theta_k | \varphi_1 \rangle & \cdots & \langle \Theta_k | \varphi_n \rangle \end{pmatrix} A^{\mathrm{T}} = S A^{\mathrm{T}} . \tag{3}$$

A simple method of constructing ψ_i was developed by Lykos and Gilbert [15] and independently and differently by Golebiewski [16].

The calculations are carried out within the framework of the Golebiewski simplified maximum overlap method. In the practical applications of the maximum overlap principle for the determination of bond valence angles in molecules, we need the explicit formulae for overlap integrals between the s, p, and d orbitals proposed by Golebiewski [17]. For example, all overlap integrals $\langle \Theta_i | \varphi_j \rangle$ used in the present paper, can be expressed in terms of the angular co-ordinates of the center of ligands $\sigma - \Theta_i$-type orbitals in the following form:

$$\begin{aligned} \langle \Theta | s \rangle &= S_{\sigma s}(X)\,, \\ \langle \Theta | p_x \rangle &= S_{\sigma p}(X) \sin v_x \cos \phi_x\,, \\ \langle \Theta | p_y \rangle &= S_{\sigma p}(X) \sin v_x \sin \phi_x\,, \\ \langle \Theta | p_z \rangle &= S_{\sigma p}(X) \cos v_x\,. \end{aligned} \tag{4}$$

In these formulae v_x and ϕ_x mean the angular co-ordinates of the atom X, on which the Θ-orbital is centered. The standard overlap integrals $S_{\sigma s}(X)$ and $S_{\sigma p}(X)$ depend still on bond length and the nature of both atoms. They can be evaluated if one knows the radial parts of the orbitals. Following the Golebiewski procedure we construct the overlap integral matrix $\boldsymbol{S}$ and in the next step the matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$, where $\boldsymbol{S}^{\mathrm{T}}$ is transposed. If λ is a scalar parameter, and $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ is a square matrix of the order $k \leqq n$ and $\boldsymbol{I}$ the unit matrix of the same order, then we get the eigenvalues from the characteristic matrix of $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$

$$\boldsymbol{K}(\lambda) = [\lambda \boldsymbol{I} - \boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}] \tag{5}$$

we get by solution of the characteristic equation

$$\lambda^n + c_1 \lambda^{n-1} + c_2 \lambda^{n-2} + \cdots + c_n = 0 \tag{6}$$

where c_k are functions of the elements of $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ and are defined as

$$c_k = (-1)^k S_k \tag{7}$$

where S_k is the sum of all head minors of order k which appears in the matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$. For the sum, $\lambda_1, \lambda_2, \ldots, \lambda_n$, of the characteristic roots it is known that

$$\lambda_1 + \lambda_2 + \cdots + \lambda_n = \mathrm{tr}\,(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})\,. \tag{8}$$

For a given geometrical configuration and a given set of orbitals $\varphi_1, \varphi_2, \ldots, \varphi_n$, the "total bonds strengths", E, is given by the formula

$$E = \mathrm{tr}\,(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{1/2} = \lambda_1^{1/2} + \lambda_2^{1/2} + \cdots + \lambda_n^{1/2}\,. \tag{9}$$

The bond strength, E, according to Eq. (8) is a function of only $(n-1)$ independent variables, λ_i, i.e. $E = E(\lambda_1, \lambda_2, \ldots, \lambda_{n-1})$. The condition that, E, should be a maximum is given by

$$\mathrm{d}E = \frac{\partial E}{\partial \lambda_1}\mathrm{d}\lambda_1 + \frac{\partial E}{\partial \lambda_2}\mathrm{d}\lambda_2 + \cdots + \frac{\partial E}{\partial \lambda_{n-1}}\mathrm{d}\lambda_{n-1} = 0 \tag{10}$$

where $\mathrm{d}\lambda_1, \mathrm{d}\lambda_2, \ldots, \mathrm{d}\lambda_{n-1}$ are independent and not zero. To determine the "best" characteristic roots, λ_i, the "total bonds strength" must now be maximized with respect to all of them, independently and simultaneously. This leads to the equations:

$$\frac{\partial E}{\partial \lambda_i} = 0 \quad \text{for all } i \quad (i = 1, 2, \ldots, n-1)\,. \tag{11}$$

Our problem is now in principle solved. We need only to evaluate the "best" characteristic roots of the system of Eq. (11) to obtain the eigenvalues of $(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{1/2}$, which are numerically equal to the orbital energies of the LCAO-MO method

[17], necessary and sufficient conditions for determination of the equilibrium bond angles in molecules then follow from them. The "total bonds strength" may be considered as a parameter on the basis of which we can speak about the stability of a molecule. A direct solution of the characteristic Eq. (6), for ligands more than $k > 3$, would be (aggravatingly) tedious and difficult. One can use symmetry properties to obtain the non-variational eigenvalues of SS^T in a much more simple way.

b) Results: H_2O, NH_3 *as Examples*

H_2O *Molecule*

We illustrate our method on the example of the H_2O and NH_3 molecules. The most familiar angular triatomic molecule is water, H_2O. We can conveniently derive the molecular orbitals and bond angle for the H_2O molecule by placing the oxygen atom at the origin of an xyz co-ordinate system. The two hydrogens are placed in the xz plane, as shown in Fig. 1. It is convenient to bend each hydrogen the same angle from the z axis, so that the z axis bisects v. The valence orbitals involved are $2s$ and $2p_x$, $2p_y$, and $2p_z$ for oxygen and $1s$ for hydrogen. The $2p_y$ is available for bonding, but hydrogens do not have σ valence orbitals in the ground electronic state [18].

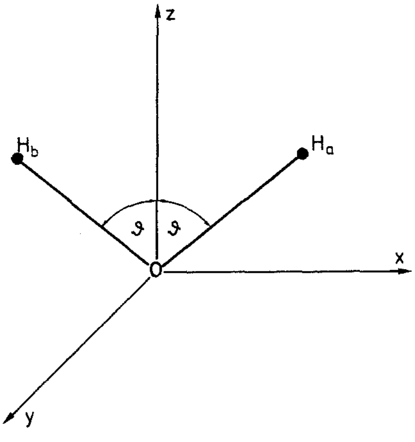

Fig. 1. Co-ordinate system for H_2O

The spherical co-ordinates of hydrogen atom are $H_a(r_{O-H_a}, v, \phi = 0°)$ $H_b(r_{O-H_b}, v, \phi = 180°)$. Using the following set of atomic orbitals, the atomic overlap integrals matrix becomes:

$$R = \begin{array}{c} \\ 2s \\ 2p_x \\ 2p_z \end{array} \begin{array}{c} \begin{array}{cc} 1s_a \quad\quad & \quad\quad 1s_b \end{array} \\ \begin{pmatrix} S_{\sigma s} & S_{\sigma s} \\ S_{\sigma p}\sin v & -S_{\sigma p}\sin v \\ S_{\sigma p}\cos v & S_{\sigma p}\cos v \end{pmatrix} \end{array}. \tag{12}$$

In the Golebiewski method [17] the matrix R^T, which has k rows and n columns is noted by S.

The symmetric and real overlap matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ will then be

$$\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}} = \begin{pmatrix} S_{\sigma s}^2 + S_{\sigma p}^2 & S_{\sigma s}^2 + S_{\sigma p}^2 \cos 2v \\ S_{\sigma s}^2 + S_{\sigma p}^2 \cos 2v & S_{\sigma s}^2 + S_{\sigma p}^2 \end{pmatrix} \tag{13}$$

where $S_{\sigma s} = \langle \mathrm{O}\ 2s | \mathrm{H}\ 1s_x \rangle$, $S_{\sigma p} = \langle \mathrm{O}\ 2p_n | \mathrm{H}\ 1s_x \rangle$, ($x = a$ or b and $n = x$ or y) represent overlap integrals between appropriate atomic orbitals.

The eigenvalues of the characteristic matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ (13) are

$$\lambda_1 = \alpha + \beta \qquad \lambda_2 = \alpha - \beta\,,$$

$$\lambda_1 + \lambda_2 = \operatorname{tr}(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}) = 2\alpha$$

where $\alpha = S_{\sigma s}^2 + S_{\sigma p}^2$ and $\beta = S_{\sigma s}^2 + S_{\sigma p}^2 \cos 2v$.

The variational procedure for maximizing the "total bonds strength" of the H_2O molecule:

$$E = \lambda_1^{1/2} + \lambda_2^{1/2}$$

then leads to following best eigenvalues of the matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$: $\lambda_1 = \lambda_2 = \alpha > 0$. From this follows that $\beta = 0$, or

$$-\cos 2v = \cos(180^\circ - 2v) = \frac{S_{\sigma s}^2}{S_{\sigma p}^2}\,. \tag{14}$$

The overlap integrals are all calculated explicitly using formulas given by Mulliken *et al.* [19]. The hydrogen-oxygen bond length is 0.960 Å [7]. These values lead to the following atomic overlap integrals $S_{\sigma s} = 0.238$ and $S_{\sigma p} = 0.438$. This would make the angle between the O–H bonds in water equal to 107°10′, as compared with the experimental equilibrium value 104°45′ [7].

NH_3 *Molecule*

A familiar example of a trigonal-pyramidal molecule is NH_3. The three hydrogens H_a, H_b and H_c, from which H_c is apart from the xz plane, form the base of a trigonal pyramid that has the nitrogen at the apex with the hydrogen H_a and H_b which lie in the plane xz. Each N–H_a and N–H_b makes angles $v_a = v_b = v$ with z and N–H_c makes an angle v_c with z co-ordinate (Fig. 2). The spherical co-ordinates of hydrogen atoms are $H_a(r_{\mathrm{N-H}_a}, v, \phi_a = 0^\circ)$, $H_b(r_{\mathrm{N-H}_b}, v\ \phi_b = 180^\circ)$ and $H_c(r_{\mathrm{N-H}_c}, v_c, \phi_c = 90^\circ)$. Bonding in NH_3 involves the hydrogens $1s$ valence orbitals and the nitrogen $2s$, $2p_x$, $2p_y$ and $2p_z$ valence orbitals. We construct the following overlap matrix

$$\boldsymbol{R} = \left(\begin{array}{cccc} & 1s_a & 1s_b & 1s_c \\ 2s & S_{\sigma s} & S_{\sigma s} & S_{\sigma s} \\ 2p_z & S_{\sigma p}\cos v & S_{\sigma p}\cos v & S_{\sigma p}\cos v_c \\ 2p_y & 0 & 0 & S_{\sigma p}\sin v_c \\ 2p_x & S_{\sigma p}\sin v & -S_{\sigma p}\sin v & 0 \end{array}\right). \tag{15}$$

For the matrix product $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ we have

$$\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}} = \begin{pmatrix} S_{\sigma s}^2 + S_{\sigma p}^2 & S_{\sigma s}^2 + S_{\sigma p}^2 \cos 2v & S_{\sigma s}^2 + S_{\sigma p}^2 \cos v \cos v_c \\ S_{\sigma s}^2 + S_{\sigma p}^2 \cos 2v & S_{\sigma s}^2 + S_{\sigma p}^2 & S_{\sigma s}^2 + S_{\sigma p}^2 \cos v \cos v_c \\ S_{\sigma s}^2 + S_{\sigma p}^2 \cos v \cos v_c & S_{\sigma s}^2 + S_{\sigma p}^2 \cos v \cos v_c & S_{\sigma s}^2 + S_{\sigma p}^2 \end{pmatrix} \tag{16}$$

where $S_{\sigma s} = \langle \mathrm{N}\ 2s|\mathrm{H}\ 1s_x\rangle$ and $S_{\sigma p} = \langle \mathrm{N}\ 2p_n|\mathrm{H}\ 1s_x\rangle$ ($n = x$ or y or z and $x = a$ or b or c) are overlap integrals between appropriate atomic orbitals.

The eigenvalues of the characteristic matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$ are

$$\lambda_1 = \alpha - \beta \qquad \lambda_{2,3} = \alpha + \beta/2 \pm 1/2(\beta^2 + 8\gamma^2)^{1/2} \tag{17}$$

and

$$\lambda_1 + \lambda_2 + \lambda_3 = \mathrm{tr}(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}) = 3\alpha \tag{18}$$

where $\alpha = S^2_{\sigma s} + S^2_{\sigma p}$, $\beta = S^2_{\sigma s} + S^2_{\sigma p}\cos 2v$, and $\gamma = S^2_{\sigma s} + S^2_{\sigma p}\cos v \cos v_c$.

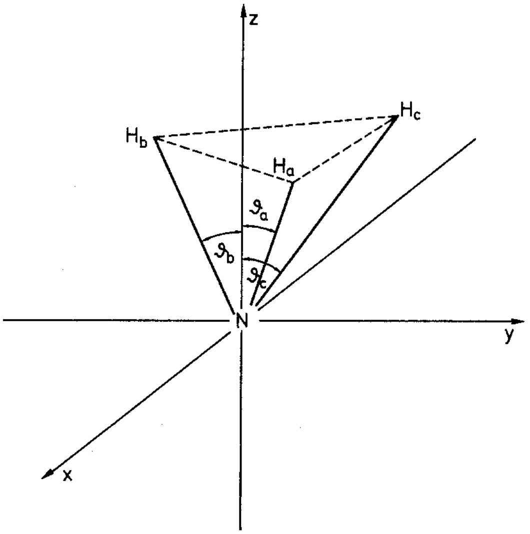

Fig. 2. Co-ordinate system for NH_3

It is now required to find the value of v and v_c that makes the energy of the system a minimum, and hence the "total bonds strength" a maximum. The variational procedure for maximizing the "total bonds strength" of NH_3 molecule

$$E = \lambda_1^{1/2} + \lambda_2^{1/2} + \lambda_3^{1/2} \tag{19}$$

then leads to following "best" eigenvalues of the matrix $\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}}$, which are $\lambda_1 = \lambda_2 = \lambda_3 = \alpha > 0$ and hence $\beta = 0$, and also $\gamma = 0$. This means that

$$\cos 2v = -S^2_{\sigma s}/S^2_{\sigma p} \tag{20}$$

$$\cos v_c = -(2)^{1/2} S^2_{\sigma s}/S^2_{\sigma p}(S^2_{\sigma p} - S^2_{\sigma s})^{1/2}\,. \tag{21}$$

The hydrogen-nitrogen bond length used is 1.014 Å [7] and the overlap integrals are: $S_{\sigma s} = 0.286$ and $S_{\sigma p} = 0.491$. From Eq. (20) for $2v$ we have 109°35′, and this is bond angle H_a–N–H_b and from Eq. (21) for v_c it follows that $v_c = 126°15'$. Bond angles H_a–N–H_c are determined on the basis of scalar product of vectors defined by their co-ordinates: $x_a = r_{\mathrm{N–N}}\cos(90° - v)$, $y_a = 0$, $z_a = r_{\mathrm{N–H}}\cos v$, $x_b = -r_{\mathrm{N–H}} \cdot \cos(90° - v)$, $y_b = 0$, $z_b = r_{\mathrm{N–H}}\cos v$, $x_c = 0$, $y_c = r_{\mathrm{N–H}}\cos(90° - v)$, $z_c = r_{\mathrm{N–H}}\cos v_c$.

We may write

$$\cos(\mathrm{H}_a\text{–N–}\mathrm{H}_c) = \cos(\mathrm{H}_b\text{–N–}\mathrm{H}_c) = \cos v \cos v_c = -S^2_{\sigma s}/S^2_{\sigma p} = -0.3351\,. \tag{22}$$

This theory leads to calculated equilibrium bond angles 109°35′ which are in reasonable agreement with the experimental.

Best Hybrid Orbitals for H_2O and NH_3

Now we find the best hybrid orbitals for the molecule H_2O by the Golebiewski simplified method [17]. The best hybrid orbitals are expressed in the form

$$\{\psi\} = A\{\varphi\} = \boldsymbol{S}\boldsymbol{S}^{\mathrm{T}-1/2}\boldsymbol{S}\{\varphi\} \tag{23}$$

where A is the matrix of the best linear transformation coefficients; $\{\psi\}$ and $\{\varphi\}$ are column matrices. For the matrix $(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{-1/2}$ we have

$$(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{-1/2} = \begin{pmatrix} (S^2_{\sigma s}+S^2_{\sigma p})^{-1/2} & 0 \\ 0 & (S^2_{\sigma s}+S^2_{\sigma p})^{-1/2} \end{pmatrix}. \tag{24}$$

The best hybrid orbitals are obtained according to Eq. (23), for calculated valence angle for H_2O $2v = 107°10'$ it follows:

$$\begin{aligned} \psi_1 &= 0.478s + 0.707p_x + 0.522p_z\,, \\ \psi_2 &= 0.478s - 0.707p_x + 0.522p_z\,. \end{aligned} \tag{25}$$

The "total bonds strength" for the H_2O molecule is:

$$E = (\mathrm{tr}\,\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{1/2} = 2(S^2_{\sigma s}+S^2_{\sigma p})^{1/2} = 0.9968\,.$$

The diagonal elements of E have been chosen positive to ensure the maximum value of the trace [16].

Similarly as for H_2O the best hybrid orbitals are defined also for NH_3 molecule by Eq. (23), where

$$(\boldsymbol{S}\boldsymbol{S}^{\mathrm{T}})^{-1/2} = \begin{pmatrix} (S^2_{\sigma s}+S^2_{\sigma p})^{-1/2} & 0 & 0 \\ 0 & (S^2_{\sigma s}+S^2_{\sigma p})^{-1/2} & 0 \\ 0 & 0 & (S^2_{\sigma s}+S^2_{\sigma p})^{-1/2} \end{pmatrix}. \tag{26}$$

For the angles calculated in this paper for best hybrid orbitals we have

$$\begin{aligned} \psi_1 &= 0.508s + 0.503p_x + 0.712p_z\,, \\ \psi_2 &= 0.508s - 0.503p_x + 0.712p_z\,, \\ \psi_3 &= 0.508s + 0.516p_y - 0.703p_z\,. \end{aligned} \tag{27}$$

The "total bonds strength" for the NH_3 molecule is: $E = 1.7046$.

Discussion

Volkov and Dyatkina [20], also used a method of maximum overlap in order to find stable configuration of molecules UF_2 and UF_3. Maksić, Klasinc and Randić [21] succesfully applied the maximum overlap method to the calculation of the hybridization in high strained small ring molecules. The most important feature of the method used here is that it maximizes directly the "total bonds strength", without using the other conditions. Mulliken [22] has examined the bonding energy and the overlap integrals in some depth. Mulliken has drawn attention to the fact that the values of this integrals depend strongly on the particular form of explicit functions used to represent an orbital, and that, for example a function of Slater's and a self-consistent field function lead to different results. In the present paper the calculated equilibrium valence angles for H_2O and NH_3 are about 2° too high with respect to experimental values. A better agreement with experimental values could be expected with Clementi or some other more realistic wave functions. It is possible to draw a comparison between the maximum overlap and the more elaborate other methods. Bond angles of smaller polyatomic molecules have been calculated by Pople and Segal [23] using the MO-LCAO-SCF method with zero-differential overlap approximation. In the light of their results the success of the present calculation is very astonishing. However, their methods employ semi-empirical bond parameters which are adjusted to experimentally known properties of other, usually diatomic molecules. In this way large classes of more or less similar molecules can be calculated sometimes with rather high accuracy. Valence angles for more accurate methods, such as mentioned semi-theoretical methods in the Tables 1 and 2, or even more accurate sophisticated approaches, may not easily yield results. From this point of view our method based on the maximum overlap principle appears to be particularly useful for determination of the stable configuration of molecules.

From the obtained results it follows that according to the variation principle of quantum mechanics, the individual AO's composing a hybrid AO in a molecule should be adjusted in such a way as to maximize the "total bonds strength". A good example is that the improvement of the H_2O and NH_3 molecule valence bond angles and hybrid wave function by using $2s-2p\sigma$ hybrid AO's instead of pure $p\sigma$ AO's.

It is intended to extend calculations of the type used here to other symmetrical triatomic AB_2 and tetratomic AB_3 molecules.

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