

## Dipole Correlation of the Electronic Structures of the Conformations of Water Molecule Evolving Through the Normal Modes of Vibrations Between Angular ( $C_{2v}$ ) to Linear ( $D_{\infty h}$ ) Shapes

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**Abstract:** In order to settle the issue of equivalence or non-equivalence of the two lone pairs of electrons on oxygen atom in water molecule, a quantum chemical study of the dipole correlation of the electronic structure of the molecule as a function of conformations generated following the normal modes of vibrations between the two extreme conformations,  $C_{2v}$  ( $\angle\text{HOH}$  at  $90^\circ$ ) and  $D_{\infty h}$  ( $\angle\text{HOH}$  at  $180^\circ$ ), including the equilibrium one, has been performed. The study invokes quantum mechanical partitioning of molecular dipoles into bond moment and lone pair moment and localization of delocalized canonical molecular orbitals, CMO's into localized molecular orbitals, LMO's. An earlier suggestion, on the basis of photoelectron spectroscopy, that one lone pair is in p-type and the other is in s-type orbital of O atom of water molecule at its equilibrium shape, and also the qualitative "Squirrel Ears" structure are brought under serious scrutiny. A large number of conformations are generated and the charge density matrix, dipole moment of each conformation is computed in terms of the generated canonical molecular orbitals, CMO's and then Sinanoğlu's localization method is invoked to localize the CMO's of each conformation and the quantum mechanical hybridizations of all the bonds and lone pairs on O center are evaluated in terms of the localized molecular orbitals. Computed data demonstrate that the electronic structures i.e. two bond pairs and two lone pairs and its hybridization status of all conformations of water molecule are straightforward in terms of the LMO's. It is further revealed that the pattern of orbital hybridization changes continuously as a function of evolution of molecular shape. The close analysis of the generated LMO's reveals that one lone pair is accommodated in a pure p orbital and another lone pair is in a hybrid orbital in almost all conformations. One more important result of the

present study is that, with the physical process of structural evolution from close angular shape to the linear transition state, the length of the  $\sigma$  (O–H) decreases and its strength increases as a monotone function of reaction coordinates. The bond length is shortest and the strength is largest at the transition state of structural inversion. Result of structural effect of the present study during the evolution of molecular conformations is quite consistent with the result of a very refined calculation that one physically significant feature of force field that the stretching force constants at the linear geometry are considerably larger than their equilibrium counter parts. The variation of bond strength and the hybridization of s and p orbitals on O atom center to form the  $\sigma$  (O–H) bond as a function of evolution of conformations is in accordance with Coulson's prediction. The total dipole moment of all conformations is partitioned into the contribution from bonds and lone pairs and correlated in terms of the computed hybridization in lone pairs. The analysis of the variation of dipole moment as a function of angular to linear structural evolution reveals that the dipole moment of H<sub>2</sub>O molecule is not due to the bond moments only but a significant contribution comes from a lone pair. It is strongly established that the dipole moment of water molecule at and around the equilibrium geometry is not due to the bond moments only and the major part of the molecular dipole comes from the contribution of lone pair electrons. This necessitates the accommodation of a lone pair of electrons in a hybrid orbital on O atom. The computed LMO's webbed with partitioned molecular dipole reveal that one lone pair is in a pure p-type orbital and the other lone pair is in a hybrid of s and p, and not in a pure s type orbital as suggested on the basis of photoelectron spectra. The possibility of qualitative "Squirrel Ears" structure is also ruled out. The problem of equivalence or non-equivalence of the two lone pairs of the O atom in water seems to have been finally resolved by the present quantum chemical calculation. An attempt of locating the origin of barrier to the physical process of inversion of water molecule is made in terms of energy partitioning method. It is found that the dipole can be used as a descriptor for the elucidation of electronic structure of molecules.

**Key words:** Atomic dipole; hybridization; lone pair; localized orbitals; energy partitioning; barrier to inversion.

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## 1. Introduction

Water, H<sub>2</sub>O, is one of the most indispensable ingredients for the creation of life on this planet. The triatomic molecule has an angular ( $C_{2v}$ ) shape in the equilibrium form and it may, following normal modes of vibration, evolve to linear ( $D_{\infty h}$ ) transition state for inversion. The charge rearrangement during the formation of H<sub>2</sub>O molecule from its elements leads to the accumulation of net negative charge on the oxygen atom and net positive charge on hydrogen atoms, which are not placed symmetrically. This pattern of charge distribution creates a permanent dipole in the molecule although the charge of the whole molecule is zero [1]. The water molecules aggregate in vapour, liquid and solid

states through the hydrogen bonding. The mechanism of water aggregation is a notoriously complex problem. The molecular mechanism of protein folding is a major unsolved problem in biology. The elucidation of the mechanism of protein folding is to decipher the final stage of genetic information [2]. The mechanism of protein folding or the base pairing in the DNA helix fundamentally depends upon the mechanism of hydrogen bonding. Many remarkable properties of liquid water are largely due to the high density of hydrogen bonds. The hydrogen bond network in liquid water rearranges and follows an ultra fast dynamics [3,4,5]. There are attempts of modeling the hydrogen bonding in liquid water within molecular dynamics [6].

It seems that each and every modeling of the structure of liquid water presupposes a symmetric environment around oxygen atom [7]. One popular model of water is that of ice-like hydrogen bonded structure [8,9,10]. The open structure of ice seems to have been correlated in terms of the hydrogen bonding through two lone-pairs and two hydrogen atoms on each oxygen atom [11].

This tetrahedral aggregation around oxygen atom has a precursor electronic structure of the water molecule that the oxygen atom is  $sp^3$  hybridized with two lone-pairs and bond pairs of electrons directed along the apices of the tetrahedron. This electronic structure of water molecule is deeply implanted in the minds of chemists and physicists. A further simplified picture of the above structure of water molecule is known a “Rabbit Ears”[12] or “Squirrel Ears”[13]. Although Pauling [14] himself pleaded for the impossibility of  $sp^3$  hybridization in O atom, VSEPR model [15-17] was invoked to correlate the “Rabbit Ear” structure of the molecule. But recently it has been pointed out by Laing [12] and Sweigart [18], on the basis of photoelectron spectral data, that the two lone pairs on O atom of water molecule are not equivalent rather one lone pair resides in pure p while the other lone pair is in a s-type orbitals [12,18]. This implies that the two lone pairs of electrons of the O atom of water molecule are not accommodated in an  $sp^3$  or any other type hybrid orbitals. It transpires that a quantum theoretical quest for the electronic structure of water molecule is required to settle the issue of equivalence or non- equivalence and the hybridization status of the lone pairs on O atom

### *1.1 Dipole moment as a probe of the electronic structure of water molecule.*

Water molecule is one of the most widely studied chemical systems. Innumerable theoretical and experimental reports of investigations of the water aggregates have appeared in the scientific literature. Its dipole moment is quite high. Levine [19] has summarized results of some important theoretical calculations, and the computed and experimental dipole moments of water molecule. It can be predicted easily that the dipoles of hetero-atomic molecules are due to the bond moments. Coulson [20] and Dewar [21] have argued at length that the major part of the dipole moments of molecules with lone pairs has its origin from lone pair moments. They [20,21] have pointed out that the dipole due to the charge distribution in a pure s or pure p orbital vanishes identically to zero because of symmetry, but the hybridization or mixing of s and p orbitals at various proportions induces asymmetry in charge distribution leading to the creation of high dipole moment. Thus the lone pair moment arises from the asymmetry of the charge distribution when the electrons are accommodated in such hybrid orbitals. In the above premise, it may be argued that the bond moments are usually small and can be offset by symmetry of the shapes of the molecules. Thus it may be argued that molecules with lone pairs of

electrons should have high dipole moments [20, 21,22] and the total dipole of hetero-atomic molecules with lone pairs should have two components –bond moment and lone pair moment-

$$\mu = \mu_{\text{chg}} + \mu_{\text{hyb}} \quad (1)$$

The bond moments arise from the charge density distribution on atomic sites in a molecule and the lone pair moment arises from the asymmetry of charge distribution in hybrid orbitals.

The permanent high dipole moment of water molecule cannot be correlated in terms of bond moment only because, if the experimental dipole moment ( $\mu_{\text{R}}$ ) [19] of water molecule is resolved into bond moments by the formula

$$\mu_{\text{R}} = \sqrt{2} \mu_{\text{b}} (1 + \cos \theta) \quad (2)$$

where  $\theta$  is the valence angles and  $\mu_{\text{b}}$  is the bond moment and  $\mu_{\text{R}}$  is the resultant molecular dipole moment, the bond moment becomes 1.745D and charge density on each H atom is 0.6208 a.u and that on O atom is 6.7584 a.u. It is apparent that such a charge distribution is unrealistic as because the chemical properties abundantly testify that water is not as acidic as would be predicted by the this hypothetical charge distribution. It, therefore, transpires that the lone pair(s) of O atom has a definite contribution to the dipole moment of water molecule. We [22] have recently found that dipole moment can be a descriptor of electronic structure of molecules containing lone pair electrons. The hybridization status of lone pair is straightforward in quantum mechanical localized molecular orbitals and the dipole partitioning can ascertain the contribution of lone pairs into molecular dipoles. The lone pair component of molecular dipole and the hybridization status of lone pair are complementary to each other [22]. Thus we can argue that the dipole moment can be used as descriptor of charge density distribution and the hybridization status in lone pairs of electrons in molecules.

However, the electronic structure in terms of the lone pair, bond pair and hybridization is the contribution of Valence Bond Theory, VBT evolved with time due to the seminal work of Lewis and Pauling [14,23]. Pauling's [14] hybridization is a local perturbation under chemical response when valence orbitals of the responding atoms get blended just prior to the event of bond formation. In the Pauling's scheme of hybridization and structural correlation, however, there is one serious drawback that the model is environment independent and does not take into account the nature of ligands attached to a central atom. Bent [24, 25], however, supplemented the work of Pauling by qualitatively incorporating the effect of change of environment around the atom, the site of hybridization. In may be further pointed out that Pauling's hybridization was designed for fixed geometries and if the molecular shape evolves during some physical process, there is no whisper, in this model, to evaluate the changes in hybridization during such continuous evolution of shapes of the molecules

The present day theoretical apparatus of studying the molecular electronic structure is some formalism either based on the method of Hartree-Fock-Roothaan and it's numerous variants [26] or the density functional theory, DFT due to Kohn and co-workers [27,28]. However, it is strongly felt that DFT is an approximate theory and its final form suitable for application is yet to be developed [29].

The molecular functions generated in terms of Hartree-Fock-Roothaan's formalism [26] are called canonical molecular orbitals, CMO's or spectroscopic molecular orbitals, SMO's [13]. The concept of lone pair and bond pair completely vanishes in such calculations. But the lone pair is almost a reality

and indispensable in the theory of electronic structure of molecules. Scientists are recently trying to obtain structures analogous to the valence bond scheme from the computed MO wave functions. Many workers, exploiting the freedom of unitary transformation in Hartree-Fock space, have developed methods to generate molecular orbitals known as localized molecular orbitals, LMO's that restores the concept of lone pair and bond pair in a quantum mechanical way. More recently scientists are engaged to reproduce reliable electronic structure by transferring the results of ab initio calculation in the language of resonance theory [30,31]. The important methods of transforming CMO's to the LMO's are summarized by Pipek et al [32] and Liu et al [33]. An alternative view of generating the localized bond concept in quantum chemistry is natural bond orbitals [34,35].

We [22, 36–38] have found that the hybridizations of lone pairs and bond pairs are straightforward in the LMO's generated from CMO's by unitary transformation. We have also tested the efficiency of the method of localization suggested by Sinanoğlu [39,40] that the method is fast, efficient and requires less computer time. Sinanoğlu himself demonstrated that the hybridization computed in terms of the LMO's generated through his method was in good agreement with experimental predictions. There is one more advantage of the method of Sinanoğlu in elucidating the electronic structure. We have found [36, 37] that the unambiguous quantum mechanical hybridization can be evaluated in terms of the generated LMO's of molecular conformations that evolve during the physical process of inversion of molecules. Thus we see that the lone-pair and bond pair and unambiguous hybridization in any shape of a molecule can be conveniently computed quantum mechanically. The CMO's can be utilized first to evaluate observables like charge distribution and dipole moment and thereafter these delocalized orbitals are localized to generate lone pair and bond pairs by suitable unitary transformation upon the CMO's –and the unambiguous hybridizations can be easily evaluated in terms of the generated LMO's. We, therefore, bring the suggestion that [12,18] one lone pair resides in pure p-type and the other lone pair resides in pure s type orbital of O atom and also the qualitative “Squirrel Ears” structure of water molecule under serious scrutiny. To settle the problem whether the lone pairs of electrons on the oxygen atom of water molecule are accommodated in a pure or a hybrid orbital, we propose to exploit conveniently the method of dipole correlation of electronic structure recently suggested by us [22]. We want to proceed a bit more. The water molecule occurs in angular shape ( $C_{2v}$ ) in the equilibrium geometry and evolves, following the normal modes of vibrations, to linear form ( $D_{\infty h}$ ), the transition state for inversion. It may be pointed out that the magnitude of barrier to the linearity of water is quite high [41,42]. It has been opined by many workers that the stretching frequency of the ‘O–H’ bond of water molecule both in ground and excited vibrational levels is worthy of investigation [3,4,5,6]. We therefore propose to optimize and evaluate the ‘O–H’ bond strength at each conformation generated theoretically. The bond energy can be conveniently evaluated invoking the energy partitioning technique of Fischer and Kollmar [43]. We have already demonstrated that the energy partitioning approach is a meaningful venture in locating the origin of barrier to the physical process of inversion [36,37] and intra molecular rotation [44,45] of molecules. We have, therefore, taken up a detailed study of the dipole correlation of the electronic structure of the conformations, including the equilibrium one, of water molecule between angular to linear shapes.

## 2. Method of Computation

We start with a very close  $\angle\text{HOH}$  angle and then the molecule is allowed to evolve theoretically following the normal mode of vibration till the linear transition state is reached. We adopt the GOT, the geometry optimization technique in this study. The approximate SCF–MO method of Pople and Co-workers [46,47] is invoked to optimize the length of O–H bond at each conformation and then the CMO's are generated at optimized geometry and the charge density distribution and dipole moment are calculated. The CMO's are then transformed into the LMO's by invoking the Sinanoğlu's method of localization and the unambiguous quantum mechanical hybridization on the oxygen atom center is determined for each conformation.

### 2.1 Localization and Computation of hybridization

The general scheme of localization may be written in equation (3) below:

$$L = TC \quad (3)$$

Where L is the localized set and C is the canonical set of molecular orbitals, and T is the unitary matrix which converts a set canonical or delocalized molecular orbitals into localized molecular orbitals. T is suitably chosen by different methods of localization. We have invoked the algorithm developed by Sinanoğlu [39,40].

In order to analyze the bonding and the nature of atomic hybrids used by various atoms to form bonds and lone pairs in a molecule, the LMO belonging to a central atom is extracted from the generated full LMO neglecting the vanishingly small off-center contributions i.e., delocalized tails. Since generated LMO's are orthonormal, the truncated LMO's – the bond and lone pair LMO's are no longer normalized. The extracted LMO's are therefore renormalized before the hybridizations on O center are computed. To ensure normalization of the hybrid orbitals and renormalization of the truncated LMO's, we adopt the following procedure:

$$\phi_{(\text{hybrid})} = a(2s) + b(2p) \quad (4)$$

Now we ensure that

$$a^2 + b^2 = 1 \quad (5)$$

and

$$2p = b_1(2p_x) + b_2(2p_y) + b_3(2p_z) \quad (6)$$

with

$$b_1^2 + b_2^2 + b_3^2 = 1 \quad (7)$$

However, detailed calculation shows that the nature of the s-p atomic hybrids is simply found from the ratio of the square of the coefficients of 2s orbital and the sum of the square of the coefficients of 2p orbitals in the LMO's.

## 2.2 Computation of molecular dipole and its partitioning into bond and lone pair moments

The permanent quantum mechanical electric dipole moment,  $\mu$  of the molecule whose electronic state is given by  $\psi_{el}$  is

$$\mu = \int \psi_{el}^* d_{op} \psi_{el} d\tau \quad (8)$$

where  $d_{op}$  is the quantum mechanical operator of dipole moment. The electric dipole moment operator,  $d_{op}$  for a molecule includes summation over both the electronic and nuclear charges.

$$d_{op} = \sum_i (-e r_i) + \sum_{\alpha} Z_{\alpha} e r_{\alpha} \quad (9)$$

where  $r_{\alpha}$  is the vector from the origin to the nucleus of atomic number  $Z_{\alpha}$  and  $r_i$  is the vector to the electron  $i$ .

Since the second term in eqn 9 is independent of the electronic coordinates, we have

$$\mu = \int \psi_{el}^* \left\{ \sum_i (-e r_i) \right\} \psi_{el} d\tau + \sum_{\alpha} Z_{\alpha} e r_{\alpha} \int \psi_{el}^* \psi_{el} d\tau \quad (10)$$

$$= -e \int (\psi_{el})^2 \sum_i r_i d\tau + e \sum_{\alpha} Z_{\alpha} r_{\alpha} \quad (11)$$

Because of the indistinguishability of the electrons, we can write this expression as

$$\mu = -e N \int (\psi_{el})^2 r_i d\tau + e \sum_{\alpha} Z_{\alpha} r_{\alpha} \quad (12)$$

where  $N$  is the number of electrons in the molecule and  $r_i$  is the position vector of electron  $i$ . Introducing the electronic probability density,  $\rho(x,y,z)$ , we write

$$\mu = -e \iiint \rho(x, y, z) r dx dy dz + e \sum_{\alpha} Z_{\alpha} r_{\alpha} \quad (13)$$

The equation 13 gives the electric dipole moment for a continuous charge distribution. Now expanding  $\rho$  in terms of the molecular orbitals and then expanding the molecular orbitals, in turn, in terms of the atomic orbitals according to LCAO-MO SCF scheme and invoking the necessary approximations of the Pople's method [46,47], the molecular dipole moments are obtained as a sum of two components as already mentioned above:

$$\mu = \mu_{chg} + \mu_{hyb} \quad (1)$$

- 1)  $\mu_{chg}$ , a contribution from net atomic charge densities
- 2)  $\mu_{hyb}$ , a contribution from atomic polarization or hybridization resulting from mixing of the 2s and 2p orbitals.

- 1) The component of dipole from net atomic charges

$$\mu_Q(z) = 2.5416 \sum_A Q_A z_A \text{ (debyes)} \quad (14)$$

where  $Q_A$  is the net charge on atom A and  $z_A$  is the appropriate Cartesian coordinate. The  $Q_A$  may be obtained from the following equation

$$Q_A = Z_A - P_{AA} \quad (15)$$

where  $P_{AA}$  is the gross electronic population on atom A and  $Z_A$  is the core charge.

2)  $\mu_{\text{hyb}}$ , the contribution from atomic polarization or hybridization:

$$\mu_{\text{sp}}(z) = - \sum_{\text{atoms}} P_{2s(A), 2pz(A)} \int \phi_{2s(A)} z \phi_{2pz(A)} d\tau \quad (16)$$

$$= -7.3370 \sum_{\text{atoms}} \zeta_A^{(-1)} P_{2s(A), 2pz(A)} \quad (17)$$

where  $\zeta_A$  is the orbital exponent of the orbital centered on atom A;  $\phi$ 's are atomic orbitals and P's are elements of corresponding density matrix. The hydrogen atoms are excluded from the summation for obvious reason.

Thus the two components of the dipole moment stated above may be labeled as dipole due to hybridization ( $\mu_{\text{hyb}}$ ), equations 16 and 17, and dipole due to net charge on atomic sites ( $\mu_{\text{chg}}$ ), eqn 14. The sum of these two components is the molecular dipole  $\mu$  already mentioned in eqn. 13 above. Thus the quantum mechanical theory of molecular dipoles suggests that high dipole moment originate from the lone pair electrons accommodated in hybrid orbitals with induced asymmetry of charge distribution.

The localization technique of Sinanoğlu [39,40] works within the framework of approximate SCF formalism of Pople and co-workers [46,47]. The molecular dipole partitioning into bond and hybridization components can be easily envisaged in Pople's approximate SCF method. It may be further noted that a large number workers [48-54] have verified that dipole moments computed through above formulation invoking Pople's approximate SCF method is quite consistent with experiment. Relying upon Pople's suggestion that the total energy of a molecule can be partitioned into one and two center components, Fischer and Kollmar [43] decomposed the total energy into meaningful physical components. The algorithm is laid down below in short.

The total CNDO energy of a system can be written as sum of one center and two-center terms as follow:

$$E = \sum_A E_A + \sum_A \sum_{A < B} E_{AB} \quad (18)$$

where  $E_A$  are monatomic terms and  $E_{AB}$  are diatomic terms.

The monatomic terms  $E_A$  and the diatomic terms  $E_{AB}$  can be further broken down into physically meaningful components as follows: The superscripts characterize the physical nature of the energy terms.

$$E_A = E_A^U + E_A^J + E_A^K \quad (19)$$

where  $E_A^U$ ,  $E_A^J$  and  $E_A^K$  are total monatomic orbital energy, electron-electron repulsion energy and non-classical exchange energy respectively.

$$E_{AB} = E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N \quad (20)$$

where  $E_{AB}^R$  is the contribution of the resonance integrals to the energy of A-B bond and is the principal feature of covalent bond,  $E_{AB}^V$  signifies the total potential attraction of all electrons of A in the field of the nucleus of B plus those of B in the field of the nucleus of A,  $E_{AB}^J$  estimates the total electron-electron repulsion energy between two centers- A and B, while  $E_{AB}^N$  stands for nuclear repulsion and  $E_{AB}^K$  defines the total exchange energy arising out of quantum mechanical exchange effect between electrons of A and B and is an important quantity in the physical process of chemical bonding.

In view of the above noted cluster of added advantages, we have invoked the approximate SCF method of Pople and Co-workers [46,47] in this study. Standard parameters [47] and STO basis sets are used. The overlap and coulomb integrals are computed through the explicit analytical formulae laid down by Roothaan [55].

### 3. Results and Discussion

The computed results are presented in Tables 1–8 and for better visualization, results are drawn in Figures 1–7. Analyzing the computed localized molecular orbitals for each conformation we see that the valence bond electronic structure of water molecule is perfectly reproduced in the present calculation. The LMO's corresponding for each conformation consists of two bond pairs corresponding to two  $\sigma$  (O–H) bonds and two lone pairs on O atom. The two bond pairs are perfectly equivalent. Hence we have reported only one LMO corresponding to each  $\sigma$  (O–H) bond and two lone pairs of each conformation in Table-1. The quantum mechanical hybridizations of bond and lone pairs are computed invoking eqn. 4 in terms of the LMO's in Table-1 for all the conformations of water molecule and are presented in Table-2. The variation of the length and the energy of the  $\sigma$  (O–H) bond and the hybridization on O-atom forming the bond as a function of  $\angle$ HOH angles are reported in Table 3. The gross atomic charge densities on O and H sites, the dipole moment of the molecule along with its dissected components, the percentage of s-character of the hybrid lone pair are presented in Table 4. The decomposed energy components are presented in Tables-5–8. The energy of the  $\sigma$  (O–H) bond and the percentage of s-character of the hybrid of O forming this bond are plotted as a function of  $\angle$ HOH angles, the reaction coordinates, Q in Figure 1. The charge densities on atomic sites are plotted as a function of the reaction coordinates in Figure 2. The variations of the dipole moment with its dissected components of the water molecule are plotted as a function of the reaction coordinates in Figure 3. The lone-pair moment and percentage of s-character of the lone-pair hybrid are plotted as a function of reaction coordinates in Figure 4. The decomposed energy components are plotted as a function of the reaction coordinates in Figures 5 and 6. The electronic structure of the equilibrium geometry of the water molecule on the basis of the present calculation has been depicted in Figure 7.

### 3.1 The structural effect

We have already mentioned that the information relating to the variation of 'O–H' stretching frequency with molecular vibrations in ground and excited state is an important input in correlating many physical data relating to water [3,4,5,6]. From the results of this calculation it can be distinctly noticed that the length of the 'O–H' bond is decreasing and its strength is increasing as the molecule evolves in space from a close angular structure to the linear form. The increasing of stretching frequency and increase in the magnitude of energy of the 'O–H' bond measure the same physical effect. It is transparent from the results that the magnitude of 'O–H' bond energy is a monotone increasing function of the evolution of conformations of water molecule with the gradual opening of  $\angle$ HOH angle. This may be equivalently stated that the stretching frequency of 'O–H' bond is a monotone increasing function of the evolution of conformations of water molecule with the gradual opening of  $\angle$ HOH bond angle. It may be cited that a similar shortening of bond length and increasing of stretching frequency 'O–H' bond during the physical process of gradual opening of the  $\angle$ HOH angle was observed in a much more refined calculation of Schaefer III et al [42]. Evaluated quantum mechanical environment dependent hybridization as a function of structural evolution demonstrates that, at each stage of evolution of conformation, the molecule rehybridizes. Or in other words, the hybridization status of bond pair forming the 'O–H' bond and the lone pair is a continuous function of the physical process of evolution of the conformations of the molecule following the normal modes of vibration. It is further revealed from an analysis of Figure 1 that the profiles of magnitude of energy of the 'O–H' bond and the percentage of s-character of the hybrid forming the bond increase hand in hand with the reorganization of the molecular structure during the physical process of dynamic structural evolution from  $C_{2v}$  to  $D_{\infty h}$ .

Hence, the pattern of induced rehybridization on O center and the variation of the length and strength of the 'O–H' bond with the dynamic continuous change of conformation of the water molecule is in accordance with the prediction of Coulson [20]. We may further point out that the hybrid of O forming the  $\sigma$  (O–H) bond is  $sp^{0.67}$  for linear shape and not  $sp$  as may be envisaged in Pauling's model of hybridization for linear shape. Foster and Weinhold [56], by an NBO analysis, obtained a similar result on the pattern of hybridization in the linear structure of  $H_2O$  molecule. Thus the computed structural effect following the dynamic evolution of conformation of water molecule is consistent with experimental [3,4,5,6] and theoretical [42] observations relating to such process.

**Table 1.** Localized Molecular Orbitals, LMO's of H<sub>2</sub>O molecule at different  $\angle$ HOH angles ( $\theta$ ).  
(LMO's are shown horizontally and the AO's are shown vertically)

LMO's	$\theta = 90^\circ$			$\theta = 100^\circ$			$\theta = 104^\circ$			$\theta = 104.1^\circ$		
AO's	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>
O <sub>2s</sub>	0.2664	-0.0599	0.8540	-0.2898	0.8353	0.0000	-0.2995	0.8262	0.0000	-0.2996	-0.8261	0.0000
O <sub>2px</sub>	-0.5465	-0.0000	-0.0000	-0.5363	-0.0000	0.0000	-0.5328	0.0000	0.0000	0.5329	-0.0000	0.0000
O <sub>2py</sub>	-0.0000	0.9975	0.0700	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
O <sub>2pz</sub>	-0.4414	-0.0362	0.5155	0.4403	0.5497	0.0000	0.4392	0.5634	0.0000	0.4391	-0.5636	0.0000
H <sub>1s</sub> <sup>1</sup>	0.0249	-0.0000	-0.0000	-0.6591	-0.0000	0.0000	-0.6584	-0.0000	0.0000	-0.6584	0.0000	0.0000
H <sub>1s</sub> <sup>2</sup>	0.6595	0.0000	0.0000	-0.0074	0.0000	0.0000	-0.0011	-0.0000	0.0000	-0.0009	-0.0000	0.0000
LMO's	$\theta = 105^\circ$			$\theta = 110^\circ$			$\theta = 115^\circ$			$\theta = 120^\circ$		
AO's	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>
O <sub>2s</sub>	-0.3018	-0.8240	0.0000	-0.3145	-0.8111	0.0000	-0.3286	-0.7962	0.0000	-0.3431	-0.7802	0.0000
O <sub>2px</sub>	0.5321	0.0000	0.0000	0.5285	0.0000	0.0000	0.5249	0.0000	0.0000	0.5218	-0.0000	0.0000
O <sub>2py</sub>	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
O <sub>2pz</sub>	0.4388	-0.5666	0.0000	0.4362	-0.5849	0.0000	0.4326	-0.6050	0.0000	0.4279	-0.6256	0.0000
H <sub>1s</sub> <sup>1</sup>	-0.6582	0.0000	0.0000	-0.6569	0.0000	0.0000	-0.6551	0.0000	0.0000	-0.6530	0.0000	0.0000
H <sub>1s</sub> <sup>2</sup>	0.0005	0.0000	0.0000	0.0078	0.0000	0.0000	0.0150	0.0000	0.0000	0.0219	-0.0000	0.0000
LMO's	$\theta = 125^\circ$			$\theta = 130^\circ$			$\theta = 135^\circ$			$\theta = 140^\circ$		
AO's	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>
O <sub>2s</sub>	-0.3594	-0.7611	0.0000	-0.3773	-0.7387	0.0000	-0.3974	-0.7115	0.0000	-0.4190	-0.6803	0.0000
O <sub>2px</sub>	0.5189	-0.0000	0.0000	0.5161	-0.0000	0.0000	0.5136	-0.0000	0.0000	0.5112	-0.0000	0.0000
O <sub>2py</sub>	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
O <sub>2pz</sub>	0.4216	-0.6487	0.0000	0.4134	-0.6741	0.0000	0.4024	-0.7026	0.0000	0.3889	-0.7329	0.0000
H <sub>1s</sub> <sup>1</sup>	-0.6504	0.0000	0.0000	-0.6473	0.0000	0.0000	-0.6437	0.0000	0.0000	-0.6398	0.0000	0.0000
H <sub>1s</sub> <sup>2</sup>	0.0290	-0.0000	0.0000	0.0362	-0.0000	0.0000	0.0436	-0.0000	0.0000	0.0512	0.0000	0.0000
LMO's	$\theta = 145^\circ$			$\theta = 150^\circ$			$\theta = 155^\circ$			$\theta = 160^\circ$		
AO's	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>
O <sub>2s</sub>	-0.4431	-0.6423	0.0000	-0.4706	-0.5934	0.0000	-0.4997	0.0000	-0.5345	-0.5307	0.0000	-0.4596
O <sub>2px</sub>	0.5086	-0.0000	0.0000	0.5065	-0.0000	0.0000	0.5042	0.0000	0.0000	0.5023	0.0000	0.0000
O <sub>2py</sub>	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000
O <sub>2pz</sub>	0.3712	-0.7664	0.0000	0.3468	-0.8049	0.0000	0.3160	0.0000	-0.8452	0.2747	0.0000	-0.8881
H <sub>1s</sub> <sup>1</sup>	-0.6353	0.0000	0.0000	-0.6302	0.0001	0.0000	-0.6248	0.0000	-0.0000	-0.6192	0.0000	-0.0000
H <sub>1s</sub> <sup>2</sup>	0.0594	-0.0000	0.0000	0.0676	0.0000	0.0000	0.0763	0.0000	0.0000	0.0846	0.0000	0.0000
LMO's	$\theta = 165^\circ$			$\theta = 170^\circ$			$\theta = 175^\circ$			$\theta = 180^\circ$		
AO's	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>	$\sigma(\text{O-H})$	1.p.O <sup>1</sup>	1.p.O <sup>2</sup>
O <sub>2s</sub>	-0.5608	0.0000	-0.3692	-0.5876	0.0000	-0.2588	-0.6060	-0.1328	0.0000	0.6126	0.0000	0.0000
O <sub>2px</sub>	0.5004	0.0000	0.0000	0.4989	0.0000	0.0000	0.4981	-0.0000	0.0000	0.4977	0.0000	0.0000
O <sub>2py</sub>	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	1.0000	0.0000
O <sub>2pz</sub>	0.2229	0.0000	-0.9293	0.1575	0.0000	-0.9659	0.0811	-0.9911	0.0000	0.0000	0.0000	1.0000
H <sub>1s</sub> <sup>1</sup>	-0.6138	0.0000	-0.0000	-0.6092	0.0000	0.0000	-0.6060	0.0000	0.0000	-0.1054	0.0000	0.0000
H <sub>1s</sub> <sup>2</sup>	0.0926	0.0000	0.0000	0.0994	0.0000	0.0000	0.1038	0.0000	0.0000	0.6049	0.0000	0.0000

**Table 2.** The hybridization of the bond pair and lone pair on the O-center as a function of  $\angle\text{HOH}$  angles (in degrees).

$\angle\text{HOH}$ angle	Hybridization of bond pair	Hybridization of lone pair	$\angle\text{HOH}$ angle	Hybridization of bond pair	Hybridization of lone pair
90	$\text{sp}^{6.9}$	$\text{sp}^{0.36}$	135	$\text{sp}^{2.7}$	$\text{sp}^{0.97}$
100	$\text{sp}^{5.73}$	$\text{sp}^{0.43}$	140	$\text{sp}^{2.4}$	$\text{sp}^{1.2}$
104	$\text{sp}^{5.3}$	$\text{sp}^{0.46}$	145	$\text{sp}^2$	$\text{sp}^{1.4}$
104.1	$\text{sp}^{5.3}$	$\text{sp}^{0.46}$	150	$\text{sp}^{1.7}$	$\text{sp}^{1.8}$
105	$\text{sp}^{5.2}$	$\text{sp}^{0.48}$	155	$\text{sp}^{1.4}$	$\text{sp}^{2.5}$
110	$\text{sp}^{4.7}$	$\text{sp}^{0.52}$	160	$\text{sp}^{1.2}$	$\text{sp}^{3.7}$
115	$\text{sp}^{4.3}$	$\text{sp}^{0.59}$	165	$\text{sp}^{0.95}$	$\text{sp}^{6.3}$
120	$\text{sp}^{3.9}$	$\text{sp}^{0.62}$	170	$\text{sp}^{0.77}$	$\text{sp}^{13.9}$
125	$\text{sp}^{3.5}$	$\text{sp}^{0.71}$	175	$\text{sp}^{0.71}$	$\text{sp}^{55.6}$
130	$\text{sp}^{3.1}$	$\text{sp}^{0.83}$	180	$\text{sp}^{0.67}$	p

**Table 3.** The optimized length ( $\text{Å}$ ), energy (a.u.)  $E_{\text{O-H}}$ , of the  $\sigma$ -(O-H) and the percentage of s-character of the hybrid of O-atom forming the O-H bond as a function of  $\angle\text{HOH}$  angles (in degrees).

$\angle\text{HOH}$	O-H bond length	$E_{\text{O-H}}$	% of s-character of bond pair of O
90	1.035	-0.7361	12.66
100	1.030	-0.7487	14.86
104	1.029	-0.7526	15.85
104.1	1.029	-0.7526	15.9
105	1.029	-0.7534	16.1
110	1.027	-0.7574	17.5
115	1.026	-0.7610	18.9
120	1.025	-0.7638	20.41
125	1.024	-0.7665	22.2
130	1.023	-0.7691	24.4
135	1.021	-0.7720	27.03
140	1.020	-0.7746	29.4
145	1.020	-0.7774	33.3
150	1.017	-0.7813	37.04
155	1.016	-0.7852	41.7
160	1.013	-0.7898	45.5
165	1.012	-0.7940	51.2
170	1.011	-0.7979	56.5
175	1.010	-0.8007	58.3
180	1.010	-0.8015	60.0

**Table 4.** The charge densities on O atom,  $q(O)$  and H atom,  $q(H)$ , the dipole moment and its decomposed components into lone pair and bond pair moments, and the percentage of s-character of the hybrid orbital accommodating the lone pair of O as a function of  $\angle HOH$  angles (in degrees).

$\angle HOH$	$q(O)$	$q(H)$	Dipole Moment (D)	Bond Moment (D)	Lone pair Moment (D)	% of s-character of lone pair of O
90	6.2578	0.8711	2.2429	0.9063	1.3366	73.26
100	6.2623	0.8688	2.1497	0.8342	1.3155	69.79
104	6.2661	0.8669	2.1154	0.8097	1.3057	68.3
104.1	6.2662	0.8669	2.1147	0.8092	1.3055	68.3
105	6.2671	0.8664	2.1069	0.8039	1.3030	67.74
110	6.2739	0.8631	2.0646	0.7751	1.2895	65.8
115	6.2825	0.8587	2.0213	0.7483	1.2730	63.0
120	6.2926	0.8537	1.9740	0.7205	1.2535	61.5
125	6.3047	0.8476	1.9216	0.6922	1.2294	58.3
130	6.3186	0.8407	1.8613	0.6619	1.1994	54.5
135	6.3347	0.8326	1.7899	0.6284	1.1615	50.7
140	6.3522	0.8239	1.7046	0.5904	1.1142	45.5
145	6.3715	0.8142	1.6008	0.5474	1.0534	41.7
150	6.3929	0.8035	1.4722	0.4969	0.9753	35.7
155	6.4150	0.7925	1.3153	0.4385	0.8768	28.6
160	6.4376	0.7812	1.1224	0.3698	0.7526	21.3
165	6.4584	0.7708	0.8922	0.2909	0.6013	13.7
170	6.4761	0.7619	0.6207	0.2015	0.4192	6.7
175	6.4879	0.7561	0.3176	0.1033	0.2143	1.8
180	6.4920	0.7540	0.0000	0.0000	0.0000	0.00

### 3.2 Hybridization

The generated localized molecular orbitals at once reveal that two lone pairs on oxygen atom are not equivalent –one lone pair is in a pure p-type orbital in all conformations while the other lone pair is in an s-p hybrid in almost conformations. But the bond pairs are always s-p hybrids. But the computed data reveal one amazing pattern of change of hybridization of lone pair and bond pair on O atom center as a function of the physical process of  $C_{2v}$  to  $D_{\infty h}$  structural evolution of the molecule that the extents of contributions of s orbital into the two hybrids have mutually opposite trend of variation. In the lone pair hybrid, the percentage of s in the hybrid is more when the  $\angle HOH$  angle is smaller, and the contribution of the s-orbital to the hybrid is less when the  $\angle HOH$  angle is larger and is minimum at the  $D_{\infty h}$  form when the when the hybrid orbital accommodating lone pair becomes a pure p- type orbital. On the other hand, in case of bond pair, just opposite trend is observed. The contribution of s orbital in the hybrid of O atom forming the ‘O–H’ bond increases steadily with the opening of  $\angle HOH$  bond angle and becomes maximum at the transition state. The contribution of s into the hybrid accommodating lone pair decreases while that in hybrid forming the ‘O–H’ bond increases as the molecular structure evolves continuously from a close  $\angle HOH$  angles towards the transition state for inversion. Thus, as the molecule evolves in space by continuation of the normal modes of vibration by opening the  $\angle HOH$  angle to reach the structure of transition state for inversion, the percentage of s-character in the hybrid orbital accommodating lone pair electrons decreases steadily until the

hybridization vanishes completely into a pure p type orbital in the transition state. Thus the symmetry of the charge distributions in two lone pairs of O atom is equivalent only in the linear form and the lone pairs are now accommodated in pure p type orbitals. Now let us consider the hybridizations of all bond pair and lone pair of the molecule at the equilibrium geometry. A closer look at the Tables 1 and 2 reveals that one lone pair is in a pure p-type orbital and the other lone pair is in an s-p hybrid ( $sp^{0.46}$ ). The  $\sigma$ -(O-H) bonds are formed by  $sp^{5.3}$  hybrid orbitals of oxygen atom. Thus, the quantum mechanical hybridization in O atom at the equilibrium geometry of  $H_2O$  molecule is far from the  $sp^3$  type and the “squirrel ear” or “rabbit ear” is a myth and the environment around O atom is far from being symmetric as contemplated earlier. It may also be stated that the present quantum chemical calculation proves unequivocally that the lone pairs of O atom of water molecule are not accommodated in pure p and s type orbitals as suggested by Laing [12] and Sweigart [18]. We have noted that the percentage of s character of the hybrid lone pair is 73 when the  $\angle HOH$  angle  $90^\circ$ . It is further noted that the contribution of s into this hybrid increases with decreasing  $\angle HOH$  angle. But the chance of one of the lone pairs being s-type is completely ruled out because, although s character of this lone pair increases with decreasing  $\angle HOH$  angle, the barrier height is quite high and population of  $H_2O$  at this conformation is nearly 0.2% at 300K. The physical process of decreasing of  $\angle HOH$  angle may increase the percentage of s-character but there can be no population because of high energy of reorganization of structure. Hence such electronic structure of water molecule in which second lone pair is in pure s type orbital in addition to the one in a pure p-type orbital is highly improbable or unrealistic.

**Table 5.** The partitioning of the one-center energy (a.u.) on O-atom into its physical components.

$\angle HOH$ angle	$E^U$	$E^J$	$E^K$	$E_O$
90	-31.58767	16.18246	-2.18136	-17.58657
100	-31.59862	16.20565	-2.18183	-17.57480
104	-31.61243	16.22516	-2.18344	-17.57071
104.1	-31.61266	16.22546	-2.18347	-17.57067
105	-31.61634	16.23043	-2.18391	-17.56982
110	-31.64297	16.26535	-2.18724	-17.56486
115	-31.67830	16.31029	-2.19179	-17.55980
120	-31.72037	16.36259	-2.19726	-17.55504
125	-31.77149	16.42557	-2.20401	-17.54993
130	-31.83098	16.49839	-2.21196	-17.54455
135	-31.89983	16.58259	-2.22127	-17.53851
140	-31.97510	16.67408	-2.23160	-17.53262
145	-32.05862	16.77533	-2.24331	-17.52660
150	-32.15127	16.88867	-2.25649	-17.51909
155	-32.24723	17.00558	-2.27048	-17.51213
160	-32.34468	17.12527	-2.28491	-17.50432
165	-32.43543	17.23637	-2.29869	-17.49775
170	-32.51231	17.33083	-2.31056	-17.49204
175	-32.56366	17.39420	-2.31853	-17.48799
180	-32.58154	17.41610	-2.32135	-17.48679

**Table 6.** The partitioning of the one-center energy (a.u.) on H-atom into its physical components.

$\angle\text{HOH}$ angle	$E^U$	$E^J$	$E^K$	$E_H$
90	-0.55637	0.28454	-0.14227	-0.41410
100	-0.55495	0.28307	-0.14154	-0.41342
104	-0.55374	0.28185	-0.14092	-0.41281
104.1	-0.55372	0.28183	-0.14092	-0.41281
105	-0.55342	0.28152	-0.14076	-0.41266
110	-0.55127	0.27933	-0.13967	-0.41161
115	-0.54850	0.27654	-0.13827	-0.41023
120	-0.54528	0.27331	-0.13665	-0.40862
125	-0.54142	0.26945	-0.13472	-0.40669
130	-0.53696	0.26503	-0.13251	-0.40444
135	-0.53182	0.25998	-0.12999	-0.40183
140	-0.52625	0.25455	-0.12728	-0.39898
145	-0.52010	0.24864	-0.12432	-0.39578
150	-0.51323	0.24212	-0.12106	-0.39217
155	-0.50618	0.23551	-0.11776	-0.38843
160	-0.49898	0.22886	-0.11443	-0.38455
165	-0.49233	0.22279	-0.11140	-0.38094
170	-0.48668	0.21772	-0.10886	-0.37782
175	-0.48290	0.21435	-0.10718	-0.37573
180	-0.48160	0.21319	-0.10660	-0.37501

**Table 7.** The partitioning of the two-center bond energy ( $E_{\text{O-H}}$ ) (a.u.) into its physical component.

$\angle\text{HOH}$ angle	$E^J_{\text{O-H}}$	$E^N_{\text{O-H}}$	$E^V_{\text{O-H}}$	$E^K_{\text{O-H}}$	$E^R_{\text{O-H}}$	$E_{\text{O-H}}$
90	2.58453	3.06787	-5.44511	-0.23210	-0.71133	-0.73614
100	2.58869	3.08253	-5.45976	-0.23371	-0.72650	-0.74875
104	2.58656	3.08570	-5.46024	-0.23385	-0.73074	-0.75257
104.1	2.58639	3.08552	-5.45996	-0.23384	-0.73074	-0.75263
105	2.58535	3.08552	-5.45904	-0.23381	-0.73140	-0.75338
110	2.58170	3.09153	-5.46031	-0.23383	-0.73649	-0.75740
115	2.57411	3.09454	-5.45600	-0.23343	-0.74027	-0.76105
120	2.56493	3.09756	-5.45013	-0.23284	-0.74333	-0.76381
125	2.55345	3.10059	-5.44241	-0.23199	-0.74617	-0.76653
130	2.53982	3.10362	-5.43289	-0.23089	-0.74879	-0.76913
135	2.52546	3.10969	-5.42514	-0.22968	-0.75234	-0.77201
140	2.50764	3.11275	-5.41224	-0.22803	-0.75475	-0.77463
145	2.48586	3.11275	-5.39379	-0.22586	-0.75636	-0.77740
150	2.46654	3.12193	-5.38457	-0.22384	-0.76139	-0.78133
155	2.44276	3.12500	-5.36714	-0.22117	-0.76461	-0.78516
160	2.42161	3.13426	-5.35680	-0.21866	-0.77024	-0.78983
165	2.39873	3.13735	-5.34049	-0.21580	-0.77381	-0.79402
170	2.37940	3.14046	-5.32722	-0.21329	-0.77723	-0.79788
175	2.36691	3.14357	-5.31956	-0.21164	-0.77996	-0.80068
180	2.36200	3.14357	-5.31562	-0.21098	-0.78052	-0.80155

**Table 8.** The partitioning of the two-center H---H non-bonded energy (a.u.) into its physical components

$\angle\text{HOH}$ angle	$E_{\text{H-H}}^{\text{J}}$	$E_{\text{H-H}}^{\text{N}}$	$E_{\text{H-H}}^{\text{V}}$	$E_{\text{H-H}}^{\text{K}}$	$E_{\text{H-H}}^{\text{R}}$	$E_{\text{H-H}}$
90	0.26717	0.36155	-0.61344	-0.00076	-0.01257	0.00195
100	0.24857	0.33534	-0.57219	-0.00000	-0.00318	0.00854
104	0.24142	0.32632	-0.55695	-0.00000	-0.00044	0.01035
104.1	0.24129	0.32614	-0.55665	-0.00000	-0.00039	0.01039
105	0.23968	0.32417	-0.55325	-0.00000	0.00016	0.01076
110	0.23131	0.31456	-0.53601	-0.00006	0.00285	0.01265
115	0.22305	0.30581	-0.51947	-0.00023	0.00516	0.01432
120	0.21521	0.29810	-0.50418	-0.00048	0.00705	0.01570
125	0.20761	0.29132	-0.48984	-0.00082	0.00875	0.01702
130	0.20024	0.28539	-0.47638	-0.00125	0.01028	0.01828
135	0.19321	0.28051	-0.46410	-0.00176	0.01172	0.01958
140	0.18630	0.27606	-0.45223	-0.00235	0.01306	0.02084
145	0.17939	0.27199	-0.44061	-0.00308	0.01441	0.02210
150	0.17304	0.26935	-0.43071	-0.00389	0.01581	0.02360
155	0.16675	0.26674	-0.42082	-0.00483	0.01718	0.02502
160	0.16114	0.26522	-0.41254	-0.00580	0.01856	0.02658
165	0.15600	0.26370	-0.40478	-0.00679	0.01979	0.02792
170	0.15188	0.26271	-0.39867	-0.00768	0.02083	0.02907
175	0.14926	0.26221	-0.39485	-0.00826	0.02151	0.02987
180	0.14832	0.26196	-0.39342	-0.00848	0.02174	0.03012

### 3.3 Dipole moment

The fact that the dipole moment of water molecule is quite high and has two components at all conformations excepting the linear form only is well demonstrated by the computed results (Table 4). It is also evident from the results of dipole calculation that as the molecule evolves in shape from a close  $\angle\text{HOH}$  angles towards the TS for inversion, the dipole moment and its dissected components, the bond moment and the lone pair moment, all decrease steadily and becomes zero at the linear conformation of the molecule. The gradual decrease in the lone pair moment with structural evolution and its vanishing at the linear form may be justified from the gradual destruction of asymmetry of charge distribution of the hybrid orbital accommodating such lone pair. We have already noted above that, with the evolution of structure with gradual opening of  $\angle\text{HOH}$  angle, the contribution of s-orbital in the s-p hybrid accommodating the lone pair decreases sharply. The nature of hybrid is changing very fast with the evolution of conformations and it is becoming predominantly p-character by elimination of the contribution of s-orbital from the s-p hybrid, which is evident from the percentage of s character of the lone pair in Table 2. We have seen above that in the linear form of the molecule, the lone pairs are all accommodated in pure p type orbitals and hence the contribution of lone pair to the dipole vanishes because of symmetry. The bond moment vanishes by the geometrical symmetry of the transition state where two bond moments cancel each other. Evaluated data reveal that the bond moment component decreases as a function of the physical process of structural evolution of the molecule from close bond angle to linear transition state. Now let us attempt a rationale of variation of bond moment component with structural evolution. With the increase in valence angle above  $90^\circ$ , the

resultant of bond moments,  $\mu_R$  should decrease because the resultant of the two bond moments is given by

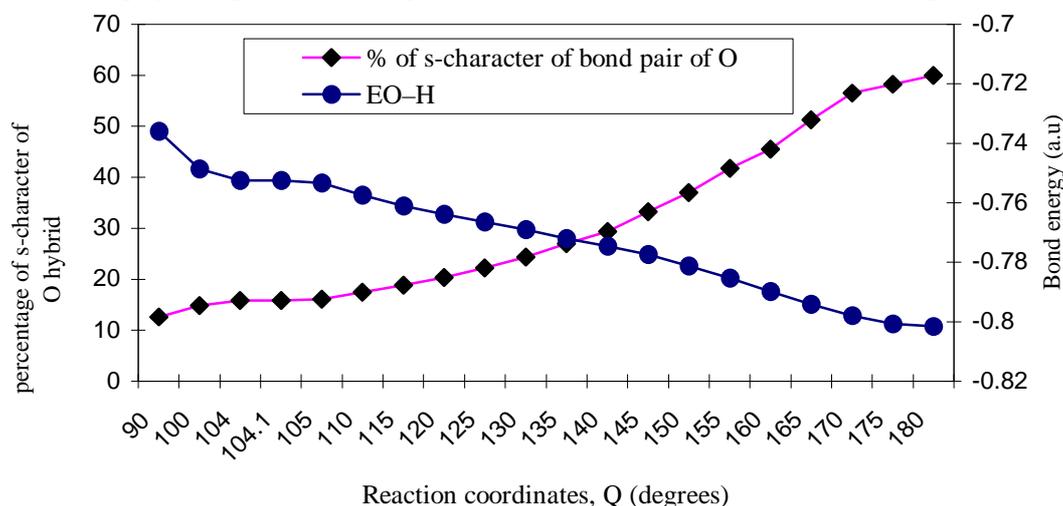
$$\mu_R = \sqrt{2} \mu_b (1 + \cos \theta) \quad (2)$$

where  $\theta$  is the valence angles and  $\mu_b$  is the bond moment.

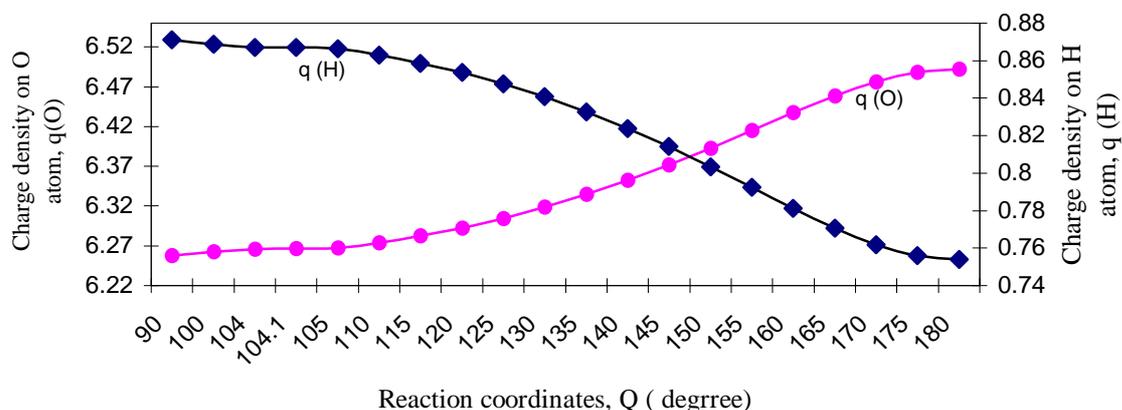
Table 4 demonstrates that, with the evolution of the geometry and shape of H<sub>2</sub>O molecule in space towards the transition state, the charge density on O atom increases and that on H-atom decreases. This pattern of charge rearrangement on the atomic sites with the physical process of structural evolution is more transparent in Figure 2. This computed pattern of charge rearrangement goes to increase the charge disbalance between O and H atoms, and hence the charge rearrangement goes to increase the bond moment. Table 3 demonstrates that the 'O–H' bond length decreases with the structural evolution. Thus the structural effect associated with the transition of the molecule from angular to the linear shape goes to decrease the bond moment component of the water dipole. It transpires that the increase in  $\angle$ HOH angles during the physical process of structural evolution from angular shape has diverse effect on the factors contributing to the bond moment. To sum up, we see that the physical process of opening of  $\angle$ HOH angles has the effect on bond moment as follows: (i) the charge imbalance on O and H atoms tends to increase, which tends to increase the bond moment; (ii) the 'O–H' bond length shortens, which tends to decrease the bond moment; (iii) the effect of increasing bond angle tends to decrease the dipole moment according to eqn.2 above. Thus the resultant effect of these three components tends to decrease bond moment with structural evolution of the molecule following the normal modes of vibrations and in the linear form, the bond moment becomes zero by cancellation because of structural symmetry. The lone pair moment also vanishes at the linear form because of the symmetry of atomic orbital functions. The Figure 3 nicely reveals the correlation of the variation of the total dipole moment and its components of the H<sub>2</sub>O molecule with the physical process of C<sub>2v</sub> to D<sub>∞h</sub> structural evolution. From Figure 3 and Table 4 it is evident that, in making the molecular dipole, the contribution of the bond moment is smaller than lone pair moments in all conformations of the molecule. This implies that the major fraction of the dipole moment of H<sub>2</sub>O molecule comes from the lone pair moment. From the Figure 3 it transpires that, with the gradual evolution of the molecular shape, the total and the lone pair component decrease at an accelerated rate but the bond moment decreases very slowly. It is further demonstrated by Figure 3 that the pace of variation of total moment and the lone pair component are very close to each other while that of bond moment is slow. The lone pair moment is controlled by its asymmetry in charge distribution. This asymmetry sharply declines with structural evolution whereas the bond moment has at least three contributing but mutually opposing components. Thus, the magnitude of dipole moment of the H<sub>2</sub>O molecule and its variation with the physical process of C<sub>2v</sub> to D<sub>∞h</sub> structural evolution cannot be justified unless we consider that at least one lone pair on O atom is housed in a hybrid orbital because, if the two lone pairs are in pure s and pure p type orbitals, the dipole due to lone pairs would vanish identically to zero [20, 21]. The variation of lone pair moment with the change in asymmetry of the orbital accommodating such lone pair is more transparent in Figure 4. An interesting result transpires from the present study. For the generation of dipole, it is absolutely necessary that the orbital accommodating electrons must have asymmetry. To induce the required asymmetry, the mixing of different orbitals is a condition

precedent. The larger the induced asymmetry, the larger is the magnitude of dipole. The variation of the magnitude of lone pair moment and the role of the percentage of s-character of hybrid accommodating this lone pair electron is distinct from Figure 4. It is also transparent from Figure 4 that the rate of reduction in magnitude of lone pair moment and the percentage of s-character of the hybrid accommodating the lone pair become accelerated as the molecular conformations reach nearer and nearer the transition state for inversion. Thus the present analysis of the dipole moment of H<sub>2</sub>O molecule in terms of computed results proves unequivocally that the two lone pairs of O atom are non-equivalent and it can not be fact that one lone pair is in a pure p type and the other is not in s type orbital at equilibrium or at conformation nearing the equilibrium conformation. It is once again transparent that the dipole moment and the hybridization status of an orbital accommodating lone pair electrons are webbed with each other. One is the descriptor of the other.

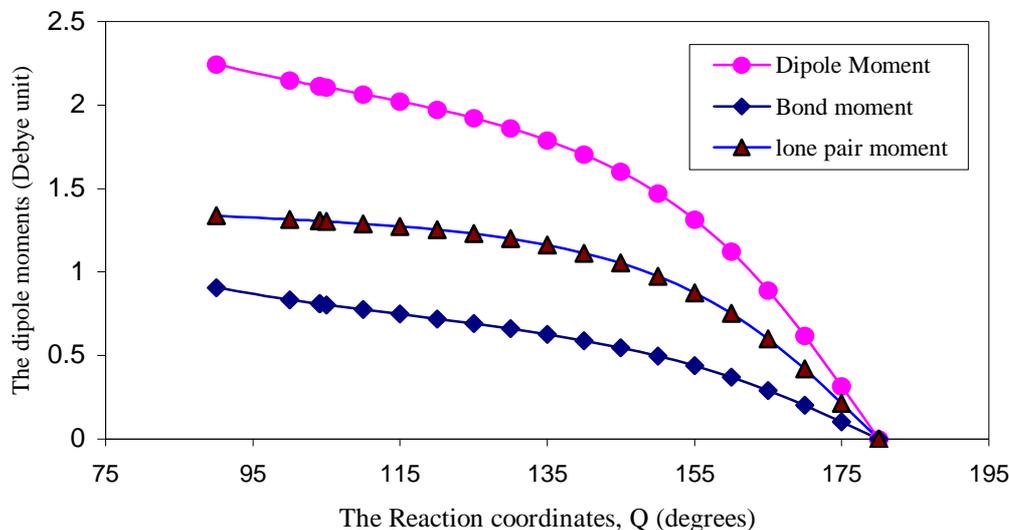
**Figure 1.** Plot of 'O-H' bond energy (a.u) and percentage of s-character of the O hybrid forming the bond as a function of bond angles during the physical process of angular to linear evolution of molecular shape.



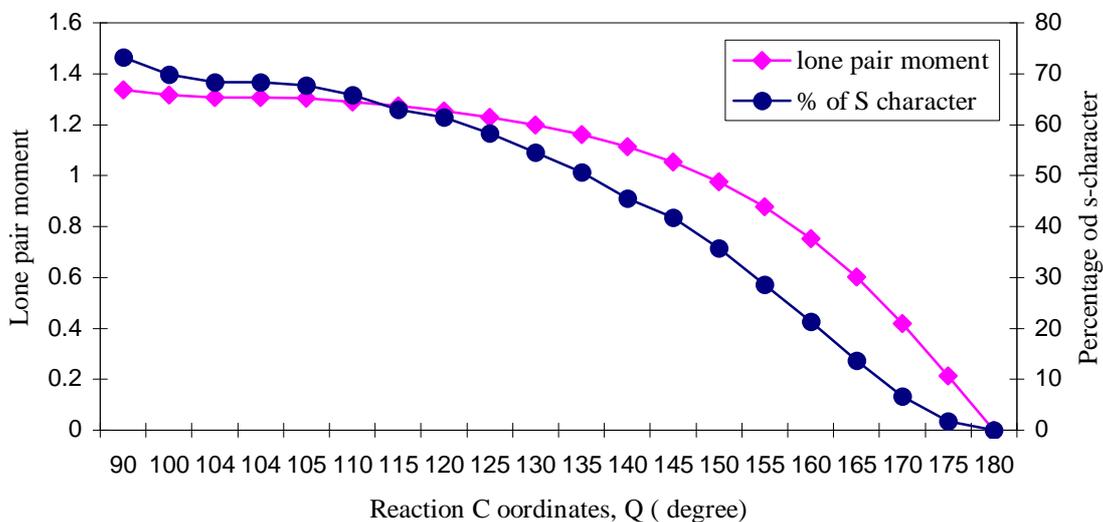
**Figure 2.** Plot of gross atomic charge densities on O,  $q(O)$  and H,  $q(H)$  atoms as a function of bond angles during the physical process of angular to linear evolution of molecular shape.



**Figure 3.** Plot of the total dipole moment and its dissected components as a function bond angles during the physical process of angular to linear evolution of molecular shape of water molecule.



**Figure 4.** Plot of lone pair moment and percentage of s-character of O-lone pair as a function of bond angles during the physical process of angular to linear evolution of molecular shape.



### 3. 4 Energy partitioning analysis and the origin of barrier

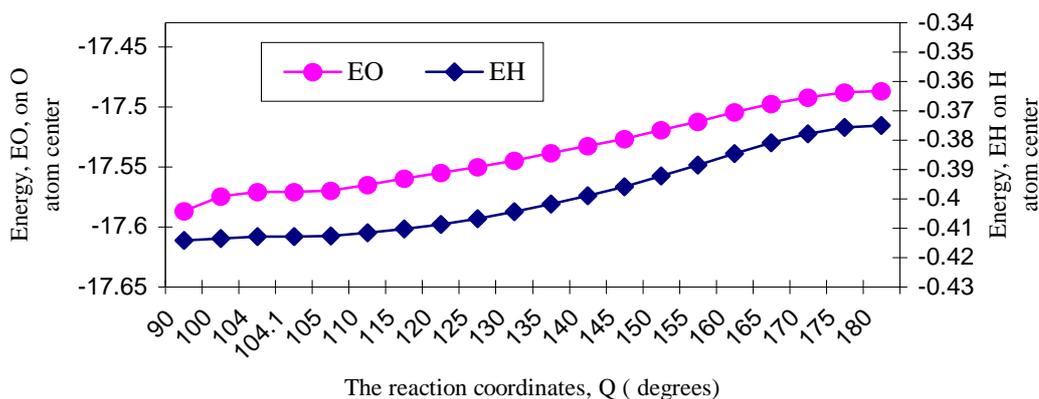
We have already pointed out that the inversion barrier of water molecule is quite high [41,42]. This implies that the major population of water structure will be at the equilibrium shape. We have studied the electronic structure and the variation of the strength of ‘O–H’ bond of the conformations of the molecule. The high magnitude of linearization barrier has a deep bearing on the shape and the magnitude of dipole moment of the molecule. Hence, glimpses of the origin of the barrier and the reason of its high magnitude are highly relevant to settle the electronic structure of water molecule. We

attempt to rationalize conformational behaviour of water molecule in terms of decomposed energy components. The type and number of one- and two-center bonded and non-bonded interactions are transparent from the shape of the molecule. There are only three one-center energetic effects on O atom and two H atoms, only two bonded 'O-H' interactions and only one 'H---H' nonbonded interaction.

#### One-center effect

It is distinct from the evaluated one-center energetic effects on 'H' and 'O' atoms that all the one-center effects act in same direction when the structure of the molecule evolves through opening the  $\angle$ HOH angles and effects strongly resist the opening of  $\angle$ HOH angle. The nature of variation of the one-center energies on 'H' and 'O' atoms are more revealing from Figure 5. Figure which demonstrates that the one-center energetic effects on H and O atoms increase sharply with increasing  $\angle$ HOH angles. A close look at the Tables 5-6 and Figure 5 reveals that the rate of rise in the magnitudes of the one-center energetic effects with the opening of  $\angle$ HOH angle is so accelerated that these energetic interactions make the inversion barrier of water molecule quite high.

**Figure 5.** Plot of one-center energies on O and H atoms (a.u) as a function of bond angles during the physical process of angular to linear evolution of molecular shape.



#### Two-center effect

From the computed data of the two center bonded ('O-H') interaction it is evident the bond energy decreases sharply with the opening of  $\angle$ HOH bond angles and strongly accelerates the

Physical process of evolution of conformations from  $C_{2v}$  to  $D_{\infty h}$  form and this bonded interaction goes to reduce the height of the barrier to inversion. The evaluated two-center 'H---H' nonbonded interaction demonstrates that is repulsive in all conformations and the interaction decreases with increasing  $\angle$ HOH angles. The two energetic effects are plotted as a function of reaction coordinates in Figure 6. The nature of variation of these two-center effects is transparent from the profiles of the respective energetic effects. The steady variation of these energetic effects with reaction coordinates shows that these effects tend to accelerate the physical process evolution of conformations following the normal modes of vibration by opening the  $\angle$ HOH angles. The two-center energetic effects, bonded and non-bonded, together reduces the height of the barrier to inversion. The energy partitioning analysis reveals that one-center effects retard the physical process of linearization of structure where as the two-center effects accelerates the process. But from Tables 5-8 it is evident that the magnitude of

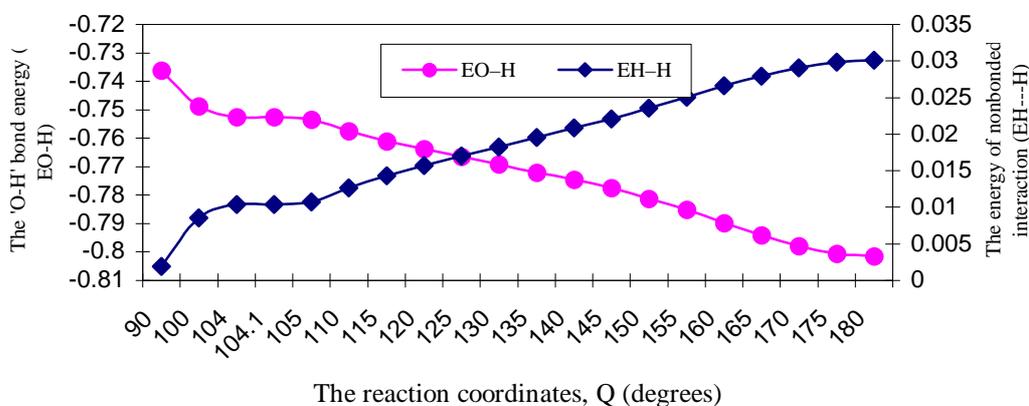
one-center energetic effect at each stage of structural evolution is considerably higher than that of two-center effects and as a result, the barrier height is quite high. It may be argued in terms of the explicit algorithm of energetic effects that the of accelerated rate of variation of the one-center energetic effects occur following the pattern of charge rearrangement as a function of evolution of molecular conformations.

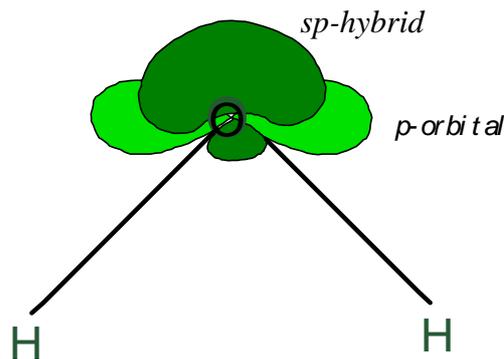
#### 4. Conclusion

A detailed quantum chemical computation of the hybridizations at O atomic center, and the dipole moments of large number of conformations between a close angular shape to linear transition state for inversion of H<sub>2</sub>O molecule have been performed. The purpose of the present study is to settle the problem of the electronic structure of the molecule with regard to the hybridization status of the two lone pairs of electrons on the O atom. Impetus of the present study comes from the fact that it is deeply implanted in the minds of chemists and physicists that the electronic structure of water molecule is such that the two lone pairs of O atom are equivalent popularly known as “squirrel ear” structure for quite a long time. Recently there is another suggestion regarding the electronic structure of water on the basis of photoelectron spectroscopy that one lone pair is in p type orbital and the other lone pair is in s type orbital [12,18]. We have recently observed [22] that dipole is a good descriptor of the status of hybridization of lone pair electrons. Our approach is two fold: Direct evaluation of quantum mechanical hybridization of all bond pairs and lone pairs and the analysis of molecular dipole in terms of its origin. The evaluated dipole is partitioned into its contributing components and then the component dipoles are correlated in terms of quantum mechanical hybridization of lone pairs and charge distribution in the molecule. We have theoretically generated a large number of molecular conformations below and above the equilibrium geometry and the method of geometry optimization, GOT, has been adopted. The electronic structures and its hybridization status of all conformations are straightforward in terms of the localized molecular orbitals, LMO's. Although the two bond pairs and lone pairs are distinct in all conformations, the molecule rehybridizes continuously as a function of evolution of shape. The computed hybridization shows that one lone pair is accommodated in a pure p orbital and another lone pair is in a hybrid orbital in almost all conformations. The asymmetry of the hybrid orbital accommodating a lone pair electrons is appreciable in conformations around the equilibrium conformations but such asymmetry fast diminishes with the physical process of attaining the transition state of inversion through the normal modes of vibration. The molecule has symmetric electronic structure at the linear form where all components of dipole vanish. In the above we have seen that the dipole moment and nature of hybrids accommodating lone pair electrons may be used as their mutual descriptor. When the hybridization status of a lone pair electron is known, the lone pair dipole can be predicted and when the lone pair component of the molecular dipole is known, the nature of hybrids accommodating lone pair electrons in molecules can be guessed. The obvious correlation comes from the fact that if lone pair electrons are accommodated in pure atomic orbitals, its dipole vanishes identically to zero because of symmetry. But if a lone pair is accommodated in a hybrid orbital, asymmetry is induced resulting in the generation of high dipole moment. Thus a dipole correlation of the electronic structure of water molecule is a quite meaningful attempt of depicting its true representative electronic structure. The results of calculation of hybridization status and lone pair

component of molecular dipole seem to demonstrate unequivocally that the two lone pairs are not equivalent. The analysis of the variation of dipole moment as a function of angular to linear structural evolution reveals that the dipole moment of H<sub>2</sub>O molecule is not due to the bond moments only but a significant contribution comes from a lone pair. Thus it is strongly established that the dipole moment of water molecule at and around the equilibrium geometry is not due to the bond moments only and the major part of the molecular dipole comes from the contribution of lone pair electrons. This necessitates the accommodation of a lone pair of electrons in a hybrid orbital. The computed data reveals that one lone pair is in a pure p-type orbital and the other lone pair is in a hybrid of s and p, and not in a pure s type orbital as suggested on the basis of photoelectron spectra. The problem of equivalence or non-equivalence of the two lone pairs of the O atom in water seems to have been finally resolved by the present quantum chemical dipole correlation of electronic structure. Present detailed quantitative study completely rules out the possibility of accommodating one of the two lone pairs in pure s orbital at equilibrium or near equilibrium shape of water molecule. We may refer to one qualitative and another quantitative suggestion regarding the electronic structure of water molecule which support the findings of the present analysis. Hall [57], and Foster and Weinhold [56] suggested that, of the two lone pairs of water molecule, one should be in a pure p-type orbital and the other in a hybrid. One more important result of the present study is that with the physical process of structural evolution from close angular shape to the linear transition state the length of the  $\sigma$  (O–H) decreases and its strength increases as a monotone function of reaction coordinates. The bond length is shortest and strength is largest at the transition state of structural inversion. We may refer to the results of a very refined calculation [42] that one physically significant feature of force field that the stretching force constants at the linear geometry are considerably larger than their equilibrium counter parts. The energy partitioning analysis has been invoked to rationalize the high barrier height of the inversion of structure of the water molecule. The electronic structure of the equilibrium geometry of the water molecule, on the basis of the present calculation, has been depicted in Figure 7.

**Figure 6.** Plot of 'O-H' bonded and 'H---H' non-bonded interaction energy (a.u) as a function of bond angles during the physical process of angular to linear evolution of molecular shape.





**Figure 7.** The electronic structure of water molecule at equilibrium geometry.

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