

Quantum Mechanical Description of H-O-H Bond Angle
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Abstract: Quantum mechanical descriptions of polyatomic molecules can be, in principle, obtained directly from solutions to a multi-electron/nuclei Schrodinger equation; however, these solutions are extremely difficult to obtain. Here we show that approximations of the electronic ground state are sufficient to describe rudimentary geometric properties of polyatomic molecules by using the water molecule as an example.

Introduction: One of the obvious strengths of Quantum Mechanics (QM) is its complete description of simple molecular systems such as H₂. In principle, the same general formalism for developing a description of H₂ can be used to describe much more complicated polyatomic molecules. If we head down this path, we arrive at the following relations:

$$\begin{aligned}
 \hat{H}_T \Psi_n &= E_n \Psi_n \\
 \hat{H}_T &= T_N + T_e + U \\
 T_N &= \frac{1}{2} \sum_{a=1}^A \sum_{b=1}^A ((P_a + \sum_{S=1}^A A_S^{(a)} p_S) \mu_{ab} \\
 &+ (P_b + \sum_{S=1}^A A_S^{(b)} p_S)) + \frac{1}{2} \sum_{S=1}^A P_S^2 - \frac{\square^2}{8} \sum_{S=1}^A \mu_{aa} \\
 1) \quad T_e &= -\frac{\hbar^2}{2m} \sum_{k=0}^N \nabla_k^2 \\
 U &= -\sum_{K=1}^A \sum_{k=1}^N \frac{Z_K e^2}{|R_K - r_k|} + \frac{1}{2} \sum_{K=1}^3 \sum_{K' \neq K}^3 \frac{Z_K Z_{K'} e^2}{|R_K - R_{K'}|} \\
 &+ \frac{1}{2} \sum_{k=1}^{10} \sum_{k' \neq k}^{10} \frac{-e^2}{|r_k - r_{k'}|}
 \end{aligned}$$

Where A is the number of nuclei and N is the number of electrons in the system, and U is the expression of the potential energy taking into account electrostatic energy contributions between both nuclei and electrons, T_N is the kinetic energy contribution taking into account vector potential correction for the motion of charged particles, and T_e is the kinetic energy contribution due to electron motion. If we follow the Born-Oppenheimer approximation, mass differences between electrons and nuclei

are of the order of 10⁴ so we can neglect kinetic energy contributions from nuclei and concern ourselves with electron motion in a constant electric potential.

Variational Approximation and Hartree-Fock Method: With the neglect of nuclear motion, we can rewrite our equation 1) as two-separated equation, once with explicit dependence on electron distances and an implicit dependence on nuclei positions and one dependent on the sum of nuclear kinetic energy and electronic energy contributions:

$$\begin{aligned}
 \hat{H}_e \phi_n(r; R) &= E'_n(R) \phi_n(r; R) \\
 \hat{H}_e &= T_e + U \\
 2) \quad [T_N + E'_n(R)] \chi_{nv}(R) &= W_{nv}(R) \chi_{nv}(R) \\
 \Psi_{nv}(r; R) &= \chi_{nv}(R) \phi_n(r; R)
 \end{aligned}$$

The trouble with this simplification is the need to obtain solutions for the electronic eigenvalue problem. To remedy this, we can make use of the Rayleigh-Ritz (RR) variational principle to obtain upper bounds for the electronic energies. A consequence of utilizing the RR variational principle is that it is necessary to obtain reasonable well-behaved trial wavefunctions. Since we are looking for wavefunctions that could describe an N electron system, we need trial functions that take into account both spatial and spin contribution. As it turns out the criteria for the trial wavefunctions are satisfied by a Slater determinant. If we now minimize the upper bound on the energy obtained by

the RR scheme¹, we arrive at the Hartree-Fock Equations:

$$\hat{F}(k)\varphi_i(k) = \varepsilon_i\varphi_i(k)$$

$$\hat{F}(k) = \hat{H}(k) + \hat{G}(k)$$

$$\hat{H}(k) = T_e - \sum_{K=1}^A \frac{Z_K e^2}{|R_K - r_k|}$$

$$G(k) = e^2 \sum_{j=1}^N \left[\int \varphi_j^*(l)\varphi_i(l) \frac{dr_l}{|r_k - r_l|} - \varphi_j(l) \int dr_l \varphi_j^*(l) \frac{\Pi_{kl}}{|r_k - r_l|} \right]$$

3) $\Pi_{kl} \Rightarrow$ Permutation Operator

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) + \frac{1}{2} \sum_{K=1}^A \sum_{K' \neq K}^A \frac{Z_K Z_{K'} e^2}{|R_K - R_{K'}|}$$

$$\varepsilon_i = H_{ii} + \sum_{j=1}^N (J_{ij} - K_{ij})$$

$$H_{ii} = \int \varphi_i^*(k) H(k) \varphi_i(k) dr_k$$

$$J_{ij} = \int \varphi_i^*(k) \varphi_i(k) \left(\frac{e^2}{|r_k - r_l|} \right) \varphi_j^*(l) \varphi_j(l) dr_k dr_l$$

$$K_{ij} = \int \varphi_i^*(k) \varphi_j(k) \left(\frac{e^2}{|r_k - r_l|} \right) \varphi_j^*(l) \varphi_i(l) dr_k dr_l$$

Where φ 's the terms in a series expansion of the test wavefunctions. If we look at the expression for ε we should note that this produces a set of N linear equations which we can put into matrix form and find eigenvalues.

Before we can find the eigenvalues of the matrix, it is necessary to evaluate the K and J matrix elements before we can diagonalize. This could potentially be very problematic; however, since we have defined the φ 's as terms in the series of the wavefunction we are free to choose their form, so long as their behavior is similar to the behavior of the test wavefunction. A common choice at this point is to assume the φ takes a Gaussian form, and as a result will provide a reduction of total integral calculations due to symmetry considerations. By choosing the form of the φ , we need to find series coefficients to get back the test wavefunction we had used to start the analysis. We can avoid this problem, to

¹ See ref (2) for a derivation of this minimization procedure

some extent, by instead guessing as to what the coefficients are then diagonalizing the ε_i matrix with them, and take the new coefficients from the diagonalization to form an updated ε_i matrix and repeat until the coefficients converge.

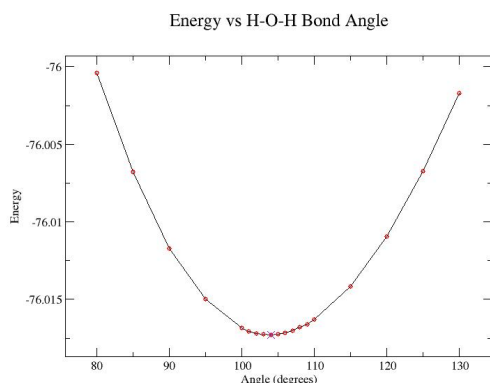
Once we have the converged ε_i matrix and associated φ 's with proper coefficients we can then use these results to find the energy surface described by the E equation of equation set 3). With the energy surface obtained, we can take the gradient and obtain the minimum energy conformation of the nuclei, and extract geometric information² for the ground state conformation of the molecule.

The Water Molecule: As an example of the method described in the previous sections, we seek to find the optimum H-O-H bond angle for the water molecule. In principle, we should select hundreds of nuclei positions and compute energies for each to construct an energy surface; however, we can avoid these massive computations in the search for the H-O-H bond angle by fixing the lengths of the H-O bond and varying the positions of the H nuclei. To do this, we note that we need at least ten test wavefunctions, one for each electron in the H₂O molecule. By using the PyQuante quantum chemistry module for python, we perform twenty Hartree-Fock calculations on the ground state of H₂O by placing nuclei at their approximate accepted equilibrium bond lengths and then varying the H-O-H bond angle

² We can also obtain the Hellmann-Feynman force, nuclear quadrupole coupling constant, electrical dipole/quadrupole moments, and diamagnetic shielding constant by using our converged expansion of the test wavefunction. See ref (1).

ranging from 80° to 130° degrees. The results of these calculations are found in figure 1.

Minimal Basis Set.” *Chem. Phys. Lett.* **3**, 257, (1969)



It is clear from the plot that the minimum occurs between 100° and 110°. A closer examination near the cusp of the energy curve permits a minimum at 104°. A comparison with other studies [3,4] shows that the accepted equilibrium H-O-H angle is found to be 104.5°.

Conclusion: In this short paper, we have demonstrated the use of the quantum mechanics in describing polyatomic molecular structure through the example of finding the accepted H-O-H bond angle.

References:

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