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Physics 517- Quantum Mechanics II

Quantum Mechanics of Hydrogen Bonding With Applications to Biophysics

Introduction

Hydrogen Bonding is a complex process that plays an important role in biophysics. Hydrogen bonds, although much weaker than many other forms of chemical bonds, have major effects on the structure and function of the proteins, polypeptide chains, and strands of DNA that are essential to biological systems.

Hydrogen bonding will only occur under very specific conditions and only between particles with very particular properties. Hydrogen bonds form between proton donor molecules that contain a hydrogen atom covalently bonded to one or more electronegative atoms and a proton acceptor molecule. The electronegative atom(s) in the proton donor molecule attracts the electron of the bonded hydrogen to such an extent that the attached hydrogen gains a net positive charge that allows it to interact with the more negatively charged proton acceptor molecule. In fact, there are several other factors that must be taken into account to fully explain the nature of hydrogen bonds (H bonds), but a simple model of a H bond is a proton being shared by two different molecules [1].

A more complicated model of hydrogen bonds involve contributions from several different interactions. The most prevalent of these interactions are: electrostatic, delocalization, dispersive, and repulsive interactions. As previously noted, the proton donor molecule consists of a hydrogen atom bonded to one or more electronegative atoms which attract the electron on the attached hydrogen, essentially reducing the negative charge distribution in the region around the hydrogen proton. This delocalization of charge produces a Coulombic attraction between the donor molecule's hydrogen atom and the electrons of the proton acceptor molecule. Furthermore, the motion of electrons in both the donor and acceptor molecules behave much like fluctuating electric dipoles resulting in additional attractive interactions. Finally, overlaps in the electron clouds of the proton -donor and -acceptor molecules add a repulsive interaction to the nature of H bonds [1]. There are several different methods which attempt to model the complex interactions that produce hydrogen bonds. Among the most successful are the molecular orbits (MO) method and the Hartree-Fock (HF) (or self-consistent field (SCF)) method which will be considered here [2][3].

Hatree-Fock (HF) Methods

Hydrogen bonding is a complicated phenomenon to study in the context of quantum mechanics because it involves several particles. Of particular interest in biophysics is the hydrogen bonding that occurs between two water molecules. A single water molecule contains two hydrogen nuclei, one oxygen nuclei, and ten electrons. Therefore, to study the properties of two hydrogen bonded water molecules (or water-dimer), the interactions between all six nuclei with all twenty electrons must be studied as well as the interactions between each electron with every other electron in the system. This becomes increasingly complicated. The Schrodinger equation for the water-dimer (or any other system containing multiple nuclei and multiple electrons) assuming the locations of the nuclei of each atom are fixed is give in equation (1).

$$H|\psi\rangle = \mathrm{E}|\psi\rangle$$

(1) where

$$H = -\frac{\hbar^2}{2m}\sum_{i}^{n}\nabla_i^2 - \sum_{i}^{n}\sum_{I}^{N}\frac{Z_I\, e^2}{4\pi\epsilon_0 r_{Ii}} + \frac{1}{2}\sum_{i,j}^{n}\frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

The first term accounts for the kinetic energy of the electrons; the second term accounts for the attraction between each electron and each nuclei of charge $Z_I e$ separated by distance r_{Ii}; and the final term accounts for the repulsion between each pair of electrons separated by a distance r_{ij}. The repulsion between each nuclei has been neglected in this formulation, but due to the shielding of the nuclei's positive charge by the surrounding electrons, equation (1) is a very good approximation of the complete Schrodinger's equation[2][3][4].

To understand the nature of hydrogen bonding, the energy states and wavefunctions of the electrons in this system of multiple electrons and nuclei must be determined. One technique for determining the wavefunctions (or atomic orbitals) was developed D.R. Hartree in association with V. Fock and J.C. Slater. This method is the appropriately named Hartree-Fock (HF) Method. The

HF method makes one major assumption: that any single electron moves in a potential which is a spherical average of the potential due to all the other electrons and nuclei. However, this requires that the wavefunctions of all the other electrons in the system be well known. As this is generally not the case, the wavefunctions of the electrons are supposed to be of a form developed by J.C. Slater as shown in equation (2).

$$\psi_{nlm_r}(r, \theta, \phi) = N r^{n_{eff} - 1} e^{-\frac{Z_{eff}\,\rho}{n_{eff}}} Y_{lm_l}(\theta, \phi) \tag{2}$$

Where n, l, and m_l are the orbital quantum numbers belonging to a nucleus of atomic number Z, Y_{ml} are spherical harmonics, ρ is the distance of the electron from the nucleus divided by the Bohr radius, and N is normalization constant. Schrodinger's equation is then solved numerically, returning a new set of wavefunctions which are improved approximations of the true wavefunctions of the electrons in a system. This procedure can be repeated several times to attain very precise wavefunctions for every electron. These wavefunctions can then be used is Schrodinger's equation to determine the energy associated with hydrogen bonds [4].

Water-Dimer

A paper written by Michael Frisch, Janet E. Del Bene, J. Stephen Binkley, and Henry F. Schaefer III and published in the Journal of Chemical Physics in 1986 studied the structure of water-dimers in extensive detail. The study used a series of basis sets, many of which are simple improvements of the wavefunctions predicted by J.C. Slater. Frisch, et al. then used the Hartree-Fock method among other methods to produce highly optimized models of the water-dimer. Depending on the initial basis set used in the HF method, slightly different values were obtained for such important features such as the distance between oxygen nuclei, O-H bond length in the individual water monomers, and the shift in O-H distance upon dimerization. Frisch, et al. used the HF method on a total of thirteen different trial basis sets and obtained hydrogen bonding energies ranging from -3.91 kCal/mol to -10.97 kCal/mol with the average being -5.44 ± 0.97 kCal/mol. Because of the considerable differences the bond energies calculate, the best model of the water-dimer could not be determined from this study [5].

Hydrogen Bonds in Biophysics

Proteins are the primary components of most biological systems and have a plethora of functions and structures. Proteins are composed of long chains of amino acids linked by peptide bonds. A section of protein containing several amino acids is called a peptide chain. Although the number and sequence of amino acids in a peptide chain or protein determine its primary structure, the secondary structure is strongly affected by hydrogen bonding. Peptide chains can have two different forms both of which involve hydrogen bonds. In one configuration, H bonds can occur between neighboring peptide chains. In the other, hydrogen bonds form between the imino group and carbonyl group of different peptides in the same chain creating a distinct helical structure. The hydrogen bonding that occurs between different peptide groups in proteins are thought be the main interactions for determining the total structure of larger proteins and how those proteins interact with each other and their biological environment.

Hydrogen bonds also play an important role in the structure of DNA molecules which contain the genetic information for life. In fact, the nucleic acid base pairs that make up the double helical structure of DNA are bonded to each other by one or more hydrogen bonds. According the Watson and Crick model of DNA, the genetic information can be determined based solely on the arrangement of the H bonds between base pairs. As mentioned previously, H bonds can be viewed as a single proton being shared by two molecules. In DNA, the degree to which the proton is shared is determined by the base pair that is sharing the proton, the neighboring base pairs, and the biological environment. In certain cases, quantum mechanics allows a proton to be completely transferred from one base to another through the process of quantum tunneling. It is thought that this tunneling can have adverse effects when DNA is copied causing a depletion or even mutation of genetic information. The contributions of hydrogen bonding to the structure of function of proteins and DNA have proven hydrogen bonding to be exceedingly important in the functioning of biological systems [1].

References

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