Effect Of External Electric Field On O-H----O, O-H----N And N-H----N Hydrogen Bonded Dimmers: A Theoretical Study

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Abstract:

Effect of external electric field on the interaction energy as well as stability of the hydrogen bonded dimer of water, ammonia and water-ammonia are analyzed in light of density functional theory (DFT) and density functional reactivity theory (DFRT). Interaction energy as well as stability of the dimers (measured in terms of global hardness, total electronic energy and HOMO energy) is observed to be sensitive towards the strength and direction of the applied electric field. Reactivity parameters like global hardness and electrophilicity are also influenced significantly by the applied electric field.

Key words: DFT, DFRT, external electric field, hydrogen bonding.

Introduction:

Hydrogen bond is one of the most prolific non-covalent bonds that finds its overwhelming presence across different strata of science *viz.* physics, chemistry and biology. Diverse application of hydrogen bonding in interpretation of various structure, function and reactivity issues has been of great interest in both chemical and biochemical sciences.[1-2] Intramolecular and intermolecular hydrogen bonds are believed to be responsible for the binding between nucleobases, formation of DNA double helices, structural arrangement of carbohydrates, as well as for the folding patterns of proteins. Hydrogen bonds also play a key role in determining the shapes, properties and functions of various biomolecules. For instance, hydrogen bonding is instrumental in course of salt bridge formation by amino acids.[3]

Extent and strength of hydrogen bonding is affected by number of factors

such as presence of electron donating or withdrawing group, polarity of solvents, steric hindrance etc. Further, the strength of hydrogen bonds might affected by the presence of external electric fields. Especially in the context of biological systems, the ions present in cellular environment impart strong local electric field and it affects the hydrogen bonding in biomolecules. Recent works shows that biological systems can experience a strong field of magnitude ranging from $\sim10^8$ to $\sim10^{10}$ Vm^{-1}.[4-5] Eventually, in a cellular environment reactivity pattern of biomolecules may be altered by the presence of such electric field. Effect of external electric field on the stability of drug-guanine adducts is documented in earlier literature.[6]

The effect of electric field on the chemical reactivity has been illustrated in several of earlier studies.[7-11] Particularly, the chemical reactivity as a function of orientation in the electric field has been investigated in depth.[7] Structural characterization of a water-micelle system in presence of an external electric field has been extensively studied by the use of MD simulations.[8] Chattaraj and his co-workers have observed the effect of electric field on the global and local reactivity indices and confirmed that electric field considerably affects all the local reactivity indices.[9] Pal and co-workers have studied the behavior of these descriptors in presence of external

electric field as well as solvent media.[10] That introduction of electric field influences both physical and chemical properties of various molecular systems are evident from these studies. Recently a number of works has been devoted to the study of application of external electric field on biological molecules.[11]

In recent years density functional theory (DFT) has proved its applicability to interpret chemical reactivity in complex phenomenon.[12] Density functional reactivity theory (DFRT) finds utility in estimating reactivity parameters. These parameters, called reactivity descriptors, defined within the framework of density functional theory are global hardness (also called chemical hardness), electrophilicity, chemical potential etc.[13] These descriptors have been tested and studied by several research groups and are reportedly very useful in rationalizing the reactivity patterns in the molecular systems[14]. Geerlings *et al.* and Chattaraj *et al.* have reviewed the theoretical basis for these descriptors and their applicability[15]. Some of the recent developments and applications of these descriptors are highly appreciable[16].

Herein we have attempted to exploit the DFT and DFRT to study the effect of external electric fields on interaction energy and stability of the H_2O-H_2O, H_2O-NH_3 and NH_3-NH_3 dimers that contains O-H××××O, O-H××××N and N-H××××N hydrogen bonds.

Theoretical and Computational details:

In DFT, chemical potential (μ) and global hardness (η) are defined as the first and second derivative of energy with respect to the number of electrons respectively[17,18]. Use of finite difference approximation and Koopmans' theorem[19] leads to the working formulae for μ and η as:

$$\eta = \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2} \quad (1)$$

and

$$\mu = \frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2} \quad (2)$$

Electrophilicity (ω) [20] is expressed as:

$$\dot{u} = \frac{\dot{\imath}^2}{2\varsigma} \quad (3)$$

The geometrical minima of the species are obtained using 6-311++G(d,p) basis set with Becke three parameter exchange and Lee, Yang and Parr correlation functional (B3LYP)[21] and is confirmed by frequency calculations. After locating the minima, single point energy calculations are carried out at different external electric field values in six directions (along positive and negative directions of x, y and z-axes, the sign + means that the field is applied along + direction of the axis and − sign means that the field is applied along the − direction of the axis). The range of the strength of the external field chosen from 0.00 a.u. to 0.01 a.u. [1 a.u. = 51.4 V/Å = 51.4 ×10¹⁰Vm⁻¹]. The global reactivity descriptors (chemical potential, global hardness and electrophilicity) are calculated using equations (1)-(3).

Strength of hydrogen bond is expressed in terms of interaction energy (ΔE_{int}) which is calculated using super molecular approach [for A + B → AB, $\Delta E_{int} = (E_{AB}) - (E_A + E_B)$, where, E is the total energy of the corresponding species]. Calculations are carried out using Gaussian09[22].

Results and discussion:

Effect of external electric field on the geometrical parameters is extensively studied in earlier literature.[23] Herein, the focus is to examine the variation of interaction energy and stability of the dimers on application of external electric fields.

Effect electric field on interaction energies:

Interaction energy is an important factor that governs the stability of a system. In view of this, the effect of the electric field on the interaction energies in the dimmers is scrutinised. Figs. 1a-1c shows the optimised geometry of the dimer along with their Cartesian axis and Figs. 1d-1f, depict the variation respective interaction energy along the three axes.
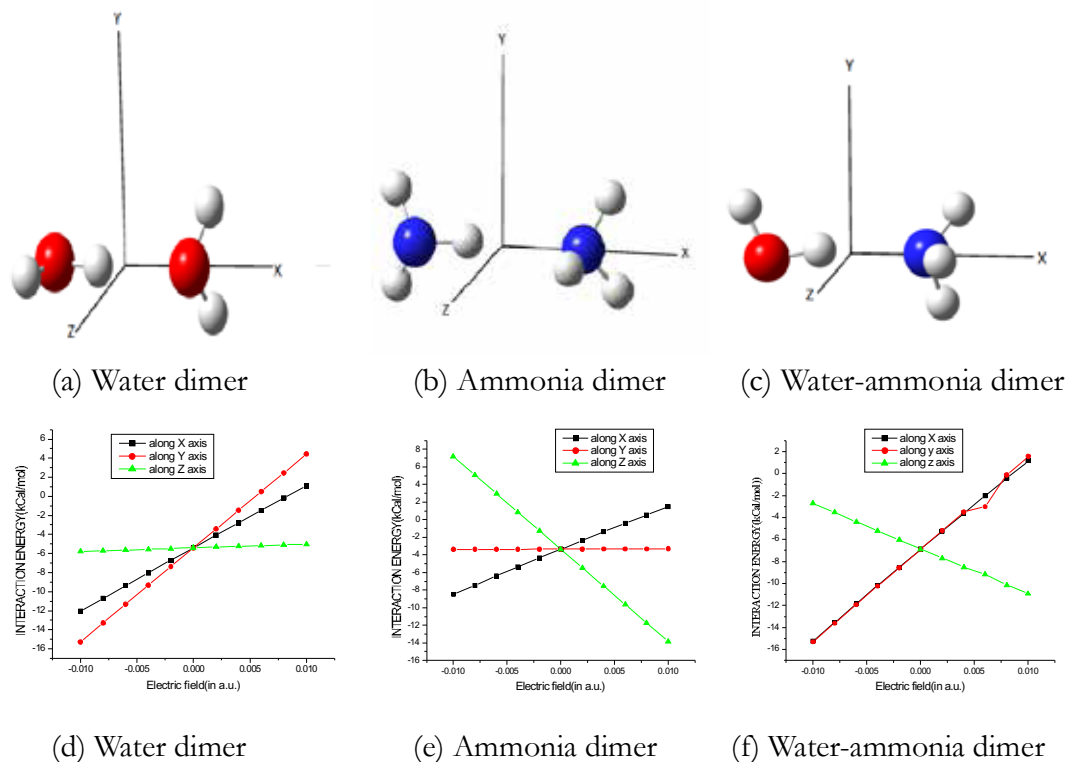
(a) Water dimer

(b) Ammonia dimer

(c) Water-ammonia dimer

(d) Water dimer

(e) Ammonia dimer

(f) Water-ammonia dimer

Fig. 1: (a)-(c) Optimized structures (obtained at B3LYP/6-31+G(d,p) level of theory) of the dimers showing the direction of the axes, (d)-(f) variation of interaction energy (in kcal/mol).

The gas phase interaction energies in the dimers are observed to be -3.35 kcal/mol, -5.40 kcal/mol, -6.87 kcal/mol for ammonia, water and ammonia-water respectively (in absence of an electric field). On applying an electric field upon the dimers, interaction energy is significantly changed and the effect produced by the field depends on the direction of the applied field. In case of water dimer, application of the field along y-axis leads to a sharp variation in interaction energies and the variation is observed to be insensitive towards applied field along z-axis and comparatively lesser variation along the x-axis, fig. 1d. Application of the field along $-y$ direction of water dimer leads to maximum interaction energy; -15.27 kcal/mol with 0.01 a.u. field; opposite results is observed along $+y$ direction.

Variation of interaction energy in case of ammonia dimer differs from that of water dimer. Maximum variation is observed along $-z$ direction; interaction energy is -13.83 kcal/mol in presence

of field of strength of 0.01 a.u., fig. 1e. Significantly, interaction energy in ammonia dimer exhibits a moderate variation, in contrast to an intense variation in water dimer, towards application of the field along y and x-axis.

Interestingly, in case of water-ammonia dimer, application of the field along $-x$ and $-y$ directions leads to increase in interaction energy (-15.23 kcal/mol and -15.30 kcal/mol respectively upon application of field of strength 0.01 a.u.) and application of the field along z-axis show a reverse trend, Fig. 1f. This study advocates that the interaction energy of the dimers respond to the direction as well as strength of the applied electric field.

Variation of total electronic energy (E_{el}) of the dimers:

Total electronic energy of a system is also a measure of the stability of a system. Therefore, the variation of total electronic energies of the chosen dimers on application of electric field is examined; results are presented in fig. 2.

It is interesting to note that in gas phase, application of external electric field on the dimers perturb the total electronic energy of the system. In case of all the three dimers, application of the field along x-axis leads to a sharp variation in E_{el}, Fig. 2. In contrast, application of fields along y and z-axis imparts almost no effect on E_{el} of water dimer, Fig. 2a. However, in case of water-ammonia and ammonia-ammonia dimers application of fields along y and z-axis (respectively) imparts significant effect on E_{el}, Fig. 2b-2c. E_{el} is observed to be indifferent to application of fields along y in case of ammonia dimer and z-axis in case of water-ammonia dimers. Moreover, it is worth mentioning that E_{el} of the dimers are sensitive toward the direction of the applied field; lowering of E_{el} results on application of the field along $-x$ direction of all the dimers, z of ammonia dimer and $-y$ direction of water-ammonia dimer. For e.g. on applying a field of strength 0.01 a.u. along $-x$ direction causes a spiky fall in E_{el} by 7.15 kcal/mol, 5.83 kcal/mol , 8.97

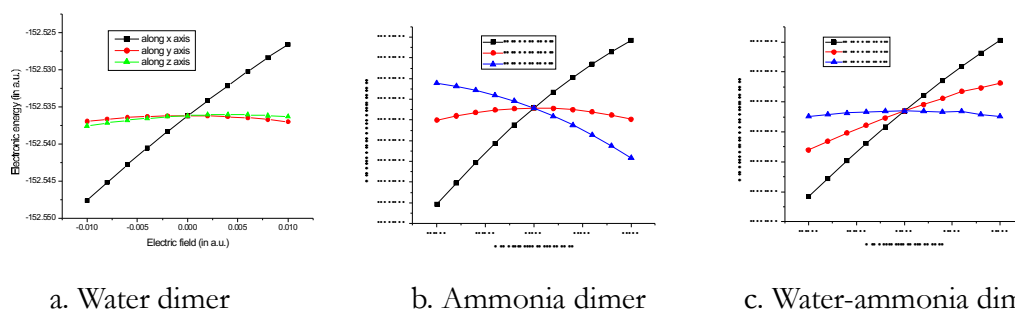a. Water dimer   b. Ammonia dimer   c. Water-ammonia dimer

Fig. 2: Variation of total electronic energy of the dimers at B3LYP/6-31+G(d,p) level of theory.

kcal/mol on water dimer, ammonia dimer and water-ammonia dimer respectively.

Variation of reactivity parameters of the dimers:

Variation of gas phase reactivity parameters, namely global hardness and electrophilicity of a system is indicative of their chemical stability in a changing environment and hence is important from chemical viewpoint. Variations of the gas phase global hardness and electrophilicity of the dimers along the three axes upon application of external electric field are presented in fig. 3.

From Fig. 3 it is evident that the gas phase global hardness of all the dimers decreases in a regular fashion on both sides of the axes imparting instability (and hence reactivity) to the systems. The implication lying herein advocates for a relatively lower chemical stability of all the three chosen dimers at higher field strength. Electrophilicity shows exactly the reverse trends; implying that both the MHP and MEP are obeyed.

Variation of HOMO of the adducts:

Water dimer along *x*-axis | Water dimer along *y*-axis | Water dimer along *z*-axis

Ammonia dimer along x-axis | Ammonia dimer along y-axis | Ammonia dimer along z-axis

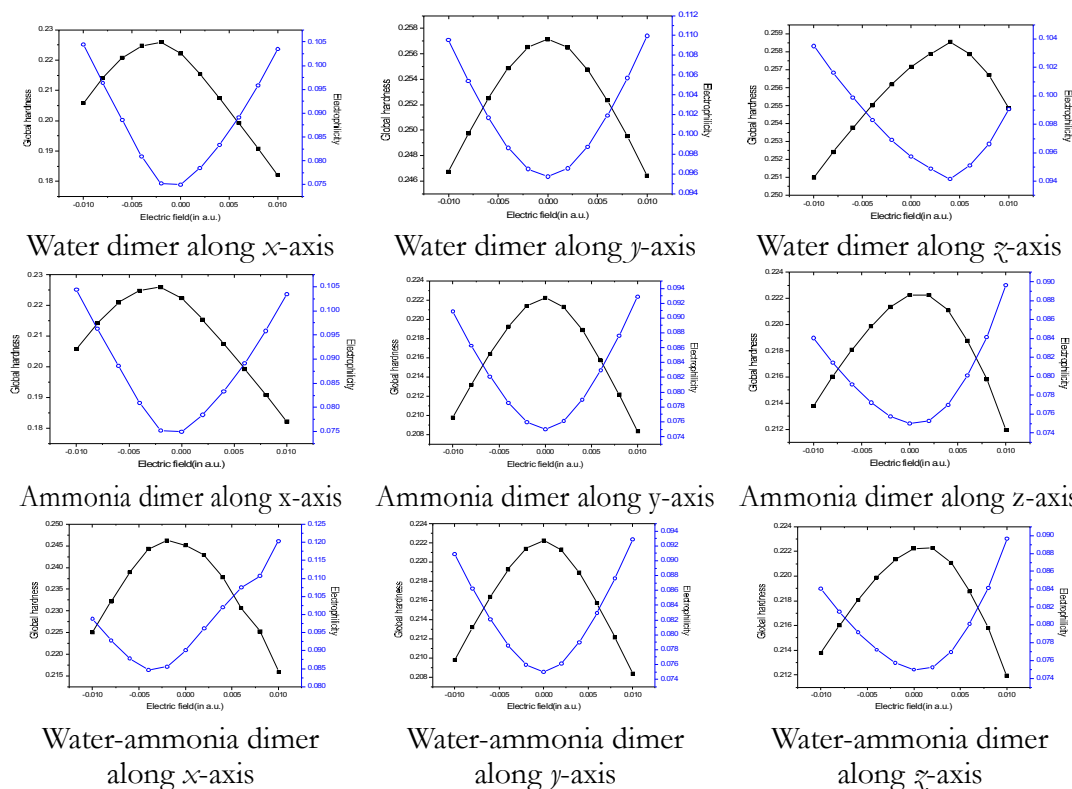Water-ammonia dimer along *x*-axis | Water-ammonia dimer along *y*-axis | Water-ammonia dimer along *z*-axis

Fig. 3: Variation of gas phase global hardness and electrophilicity of the dimers (■ represents global hardness and ○ represents electrophilicity, at B3LYP/6-31+G(d,p) level of theory).

Variation of the HOMO energy of the dimers in presence external electric fields is traced. Plots of HOMO energy of the dimers with strength of the electric fields are shown in Fig. 4.
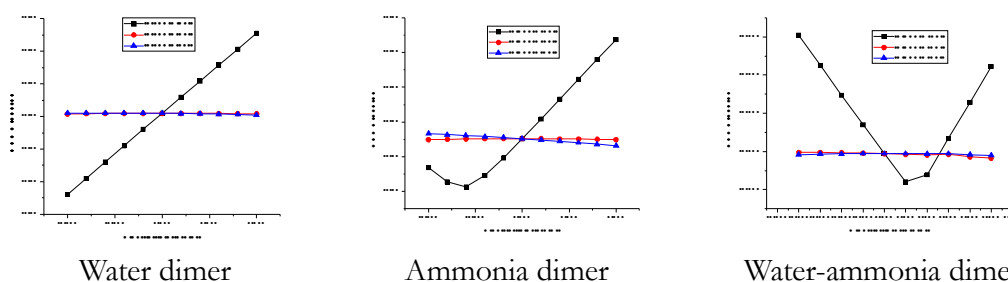
It is seen that application of the

Water dimer   Ammonia dimer   Water-ammonia dimer

Fig. 4: Variation of HOMO energy of the dimers with the applied field strength (at B3LYP/6-31G(d,p) level of theory).

electric field along y and z-axis does not lead to any change of the HOMO energy of the dimers. However, a considerable impact on HOMO energy is observed upon application of electric fields along x-axis. In case of water dimer, a sharp variation of HOMO energy is observed and HOMO energy drops by a magnitude of 15.6 kcal/mol on application of the field along $-x$ direction and a reverse trend is observed along $+x$ direction. In case of ammonia dimer, application of field of strength 0.06 a.u. along $-x$ direction drops the HOMO by 12.3 kcal/mol. In contrast, ammonia-water dimer shows an exceptional behaviour, HOMO energy increases on application of the field on either side of x-axis. Thus from the frontier orbital (HOMO) perspective, application of the field along y and z-axes does not impart any significant effect on the chemical stability of the system albeit, one can expect the dimers to be chemically stable under the influence of electric field applied along a particular direction.

Conclusion:

Hydrogen bonding has been of great interest in both chemical and biochemical sciences. The present study deals with the effect of the external electric field on hydrogen bonding in three dimers. Our findings suggest that the hydrogen bonding is significantly influenced by the presence of an external electric field and variation in interaction energy of the hydrogen-bonded systems inflicted upon by variation in the magnitude and direction of applied field vindicates this statement. Similarly, external electric field on the dimers perturbs the total electronic energy of the system. Reactivity of the dimer measured in terms reactivity parameter such as global hardness, electrophilicity and HOMO energy, shows that reactivity of the molecule can also

be modified in presence of the external electric field. Further, reactivity pattern of the dimers follow the MHP and MEP. Thus, this study will help future researchers to understand the behaviour of hydrogen bonded dimers in presence of the external applied field.

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(Endnotes)

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