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Computer Assessment Science Related to Materials and Bio-Materials

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Abstract

For biological processes to occur, noncovalent interactions are essential. Everything from molecular recognition to molecular assembly to enzyme catalysis to the dynamic behaviour of biomolecules is aided by noncovalent interactions. Applications of noncovalent interactions have been increasingly important in recent years and are on the verge of becoming much more so in issues relating to a variety of fields of chemistry, biology, and physics. Due to their prevalence and high binding energy, noncovalent interactions that are dominated by electrostatic contributions have drawn the most attention. Electrostatic interactions have a wide spectrum and are directed. However, the directional components of electrostatic dominated noncovalent interactions have been completely ignored in the literature up to this point due to the fundamentally long range impactful nature of electrostatic contributions. To fully comprehend the electrostatic contributions, this thesis focuses on the significance and directional nature of long-range electrostatic interactions. In this chapter, we have provided a quick introduction of noncovalent bonds and their function in chemistry. In order to demonstrate how understanding of the significance of long-range electrostatic interactions has changed over time, we also went over a brief history of the scientific literature.

Keywords- *Computer, Assessment, Science, Related to Materials, Bio-Materials*

INTRODUCTION

The E and Z isomerization of molecules, the designing of various receptors to recover metal ions from sea water, the designing of electrolyte in metal ions batteries, the designing of drug-like molecules for the treatment of various diseases, and other applications all rely on non-covalent interactions for their success. The importance of noncovalent interactions cannot be overstated in terms of their role in biological processes. Noncovalent interactions are involved in everything, from the initial step of molecular recognition to the final step of molecular assembly, from the catalysis of enzymes to the dynamic behaviour of biomolecules. Applications of noncovalent interactions in problems relating to several fields of chemistry, biology, and physics have gotten quite substantial in recent years and are on the cusp of increasing even further. Those noncovalent interactions that are dominated by electrostatic contributions have received the most attention and coverage due to their prevalence and bond strength. This is because electrostatic contributions play a significant role in these interactions. The nature of electrostatic interactions is such that they are long range and directed. However, the directional aspects of electrostatically dominated noncovalent interactions, which arise as a result of the intrinsic long range influential nature of electrostatic contributions, have been totally overlooked so far in the literature. This is despite the fact that these aspects have arisen due to the fact that electrostatic contributions are themselves long range influential. In order to provide a comprehensive explanation of the electrostatic contributions, this thesis focuses primarily on demonstrating the significance of long-range electrostatic interactions as well as the directed character of these interactions. In this chapter, we have discussed noncovalent bonds and their significance in the field of chemistry. We have also offered a quick introduction to these concepts. In addition, we have gone over a concise history of the dominant body of literature in order to describe the development of an increased knowledge over the course of time regarding the relevance of long range electrostatic interactions. Molecules are formed when certain circumstances are met, and atoms interact with one another. It is believed that these atomic pairs come together to form a chemical bond, which may have a polar, ionic, or covalent nature, respectively. These bonds are powerful, and they typically result in the greatest possible attraction between the atoms that they link together. On the other hand, there

are some interactions between atoms, molecules, or ions that are relatively much weaker but are nevertheless strong enough to define the physical and/or chemical properties of a wide variety of chemical substances when a large number of such bonds work in conjunction with one another. The size and frequency of weak bonds between molecules of the given material under the given conditions are what determine the condensed phase of matter, which is one of the most well-known examples of the features described here. Non-covalent bonds are the general name for several types of weak bonding. The term "noncovalent bonds" refers, quite literally, to the sorts of interactions that do not have a covalent starting point. More specifically, noncovalent bonds are the bonds that do not form as a direct result of the actual sharing of electrons between the atoms that are interacting with one another. Nonetheless, the interactions between ions in ionic crystal lattices or atoms in metallic lattices are similarly not covalent in origin; however, noncovalent bonds are not typically thought of as referring to these types of interactions. Traditionally, the term "noncovalent bonds" refers to just those interactions that are relatively weak and are of a type other than covalent. As a consequence of this quality, noncovalent bonds are sometimes sometimes referred to as simply weak bonds. Because these bonds are not as strong as the typical chemical bonds (electrovalent or covalent), they have been ignored for use in practical applications for a considerable amount of time. This is due to the fact that these bonds are weaker after it was found out about them. Far later on, it was understood that noncovalent interactions are important enough to impart selective effects or functionality into systems. This realisation came much too late. Recent years have seen the development of methodologies that aim to take advantage of these interactions in order to accomplish predetermined objectives in a variety of scientific subfields. This topic is constantly expanding, and it has recently gained attention as being both multidisciplinary and multifaceted. There are a large number of researchers working in this field from all areas of chemistry, biology, and material science, and they are located all over the world. The significant increase in the number of publications that have been published in recent times that contain the word "noncovalent interaction" is indicative of the prominence that this field has earned over the course of the past few years. It is important to keep in mind that the amount of energy required to establish a noncovalent bond is normally between between 1 and 5 kcal/mol/bond. As a result

of the fact that the average kinetic energy of molecules at room temperature is approximately 0.6 kcal/mol, many molecules gain enough energy to break these connections. As a result, these bonds are regarded to be dynamic and are frequently referred to simply as interactions. On the other hand, many noncovalent bonds are able to maintain a large molecule in a certain shape and conformation, as well as particular relationships between two or more large molecules. For instance, the three-dimensional structures of proteins, nucleic acids, and supramolecular structures rely heavily on a variety of different forms of noncovalent bonding in order to be preserved. In addition, noncovalent bonds permit one big molecule to temporarily attach in a variety of accessible conformations, which is one reason why they serve as the foundation for a huge number of dynamic biological activities. 8 Noncovalent interactions play an important role in facilitating molecular recognition, which is particularly important for the selectivity and reactivity of biomolecules.

Computational Details and Background Theory

All the DFT calculations, until unless mentioned specifically, were carried out using the Turbomole 6.4 suite of quantum-chemical programs.41 Geometry optimizations were performed using the PBE42 functional in the solvent phase with the Conductor like Screening Model (COSMO)43 employing chloroform (epsilon = 4.81) as the solvent. The electronic configuration of the atoms was described by a triple-zeta basis set augmented by apolarization function (TURBOMOLE basis set TZVP). The resolution of identity (RI),44 along with the multipole accelerated resolution of identity (marij)45 approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. The option “disp” provided in Turbomole package (DFT-D2, a general, empirical dispersion correction proposed by Stefan Grimme for density functional calculations) was used for dispersion corrected DFT calculations for all the calculations with Turbomole.46. The Energy Decomposition analysis (EDA) was carried out using Turbomole 7.0 at the same level of theory and under the same conditions of solvent and dispersion that have been used for geometry optimizations using the Turbomole version 6.4 (the EDA implementation is not available with Turbomole 6.4). The Mulliken47, NBO48 and Löwdin49 charges have been used to calculate electrostatic forces on each

fragment of every complex along a particular direction that described the intermolecular interactions most suitably (i.e. along the line of direction, see the figures 7a and 7b). To compute the magnitude of the net force of binding, i.e., the binding force, the vector sum of electrostatic forces experienced by each fragment along the above said direction has been considered. It is to be noted here that interactions involving the hydrogen bond acceptors and donors that are directly involved in hydrogen bonding with each other are referred to as primary interactions. The electrostatic interactions between any pair of atoms between two partners that are not directly involved in hydrogen bonding have been defined as long range secondary electrostatic interactions. These interactions also include the Jorgensen's type of secondary electrostatic interactions (SEIs). A recent review by Clark, Politzer, Murray and others states that even the polarization/induction and covalent (or donor-acceptor charge transfer) factors in the noncovalent bonds are essentially electrostatic in nature.19 According to the Feynman interpretation, even the dispersion interaction is electrostatic in nature.50 This indicates that the proper treatment of electrostatic interactions is adequate enough to fully describe all kinds of noncovalent interactions. The Born-Oppenheimer approximation reveals molecules to be a collection of point charge nuclei and a cloud of indistinguishable electrons described by electron density. To distinguish a molecule in the form of atoms and bonds, in a point charge analysis, the electron density is divided on the criteria of basis sets, i.e., the atomic orbitals. When a noncovalent bonding partner is kept in the electric field of another partner, the induction causes a change in the local electron density of the first, and vice versa. This is reflected in the point charge calculation as the modification in the charges of the atoms when the charges are calculated for partners in the complex in comparison to the charges when calculated with the two partners infinitely separated. The point charges that are calculated for the atoms in a complex will, therefore, also include the polarization and donor-acceptor charge transfer in an approximate way. This kind of analyses has been done by other groups as well to account for the effect of polarization and donor-acceptor contributions.51 Recently, noncovalent interactions between covalently bonded atoms of the Groups IV-VII and a negative site (e.g. a Lewis base) have been discovered, and are commonly referred to as σ-hole bonding, because of the presence

of a positive cap on the electrostatic potential surface on the opposite side of one of the covalent bonds of the atom, labeled as a σ-hole.52-54 One of the most common known cases of σ-hole bonding is halogen bonding. The σ-hole arises due to anisotropy of the atomic charge distribution, and can be visualized through an anisotropic electrostatic potential around the atom. This results in unusual behavior of atoms that have σ-holes. Such atoms can have regions of both positive and negative electrostatic potential on their surfaces, and they can thus interact attractively with both negative and positive sites respectively, in different directions.52,54 Assigning a single atomic charge to such atoms in molecular complexes will fail to describe σ-hole bonding. More recently, methods have been developed in molecular dynamics (MD) simulations to address such behavior in a more accurate way. Force fields have been developed where the positive region of halogen atoms are represented as an extra point of charge in a way so that the net formal charge and the electrostatic potential assigned to the atom remain the same.55,56 The results of this method have also been corroborated by high level quantum chemical calculations.55 Therefore, assigning one extra-point charge to every positive hole in a molecule/complex was found to give a good reasonable approximation for modulating other electrostatic properties. However, σ-hole bonding is not found to be universally manifested by all the elements of Groups IV-VII in every chemicalcomposition. In general, σ-hole bonding is not exhibited by fluorines and is insignificant in other elements of the same period, particularly when they are not covalently linked to more electronegative atoms.55,57 This can be justified by looking at the molecular electrostatic potential surface map of the corresponding compounds. Molecules that do not possess σ-holes may not require additional treatment (of assigning extra point charges for representing σ-holes) to accurately address the electrostatic properties. To further confirm whether the individual noncovalent hydrogen bonded partners, considered in this study, possess σ-holes on their electrostatic potential surfaces, we have constructed the molecular surface electrostatic potential map of a set of representative noncovalent partners containing nitrogen and fluorine atoms at their interactive sites. The obtained electrostatic potential surfaces reveal that none of the moieties that have been considered in this study possess σ-holes on their surface. It is, therefore, correct to conclude that the point charge calculations

employed in the current work provide a good approach to estimating the net electrostatic interactions, especially when determined from charge calculations at a high level of theory.

Unless otherwise specified, all DFT calculations were performed using the Turbomole 6.4 suite of quantum-chemical tools. 41 Geometry optimizations were carried out in the solvent phase utilising the PBE42 functional and the Conductor like Screening Model (COSMO)43, with chloroform (epsilon = 4.81) as the solvent. A triplezeta basis set with a polarisation function was used to explain the electrical configuration of the atoms (TURBOMOLE basis set TZVP).

For an accurate and efficient treatment of the electronic Coulomb term in density functional calculations, the resolution of identity (RI),44 and multipole accelerated resolution of identity (marij)45 approximations were used. For all Turbomole computations, the option "disp" (DFT-D2, a general, empirical dispersion correction suggested by Stefan Grimme for density functional calculations) was utilised for dispersion corrected DFT calculations. 46 The Energy Decomposition Analysis (EDA) was performed in Turbomole 7.0 at the same level of theory and under the same solvent and dispersion conditions as were utilised for geometry optimizations in Turbomole version 6.4. (the EDA implementation is not available with Turbomole 6.4). Mulliken47, NBO48, and Löwdin49 charges were utilised to calculate electrostatic forces on each component of each complex along a specific direction that best characterised the intermolecular interactions (i.e. along the line of direction, see the figures 7a and 7b).

The vector sum of electrostatic forces experienced by each fragment in the above-mentioned direction has been considered to compute the size of the net force of binding, i.e., the binding force. It should be highlighted here that primary interactions involve hydrogen bond acceptors and donors who are directly involved in hydrogen bonding with each other. Long range secondary electrostatic interactions are defined as electrostatic interactions between any pair of atoms between two partners that are not directly involved in hydrogen bonding. These interactions also include secondary electrostatic interactions of the Jorgensen type (SEIs). According to a recent assessment by Clark, Politzer, Murray, and others, the polarization/induction and covalent (or donor-acceptor charge

transfer) elements in noncovalent interactions are fundamentally electrostatic. 19 Even the dispersion interaction, according to the Feynman interpretation, is electrostatic in character. 50 This suggests that a proper study of electrostatic interactions is sufficient to completely describe all types of noncovalent interactions. According to the Born-Oppenheimer approximation, molecules are made up of point charge nuclei and a cloud of indistinguishable electrons defined by electron density. In a point charge analysis, the electron density is divided on the basis sets, i.e., the atomic orbitals, to distinguish a molecule in the form of atoms and bonds. When one noncovalent bonding partner is held in the electric field of another, the induction produces a change in the first partner's local electron density, and vice versa. This is represented in the point charge calculation as a change in the charges of the atoms when the charges are calculated for complex partnersvs charges calculated with the two partners infinitely apart. As a result, the point charges estimated for the atoms in a complex will incorporate polarisation and donor-acceptor charge transfer in an approximate manner.

The Impact of Polarisation and Donor-Acceptor Contributions

51 Noncovalent interactions have recently been discovered between covalently bonded atoms of Groups IV-VII and a negative site (e.g., a Lewis base), and are commonly referred to as -hole bonding, due to the presence of a positive cap on the electrostatic potential surface on the opposite side of one of the atom's covalent bonds, labeled as a -hole. 52-54 Halogen bonding is one of the most common types of -hole bonding.

The -hole forms as a result of anisotropy in the atomic charge distribution and can be seen as an anisotropic electrostatic potential around the atom. As a result, atoms with -holes exhibit peculiar behaviour. Such atoms can have positive and negative electrostatic potential areas on their surfaces, allowing them to engage favourably with both negative and positive sites in distinct orientations. 52,54 A single atomic charge assigned to such atoms in molecular complexes will not describe -hole bonding. More recently, strategies for addressing such behaviour in molecular dynamics (MD) simulations have been devised. The positive area of halogen atoms has been represented as an extra point of charge in such a way that the net formal charge and electrostatic potential

given to the atom stay constant. 55,56 High level quantum chemistry computations have also confirmed the conclusions of this strategy. 55 As a result, it was discovered that allocating one extra-point charge to each positive hole in a molecule/complex provided a good fair approximation for regulating other electrostatic properties. -hole bonding, on the other hand, is not observed to be uniformly expressed by all elements of Groups IV-VII in any chemical composition. Fluorines, in general, do not exhibit -hole bonding, and it is minimal in other elements of the same period, especially when they are not covalently coupled to more electronegative atoms. 55,57 This is supported by a look at the relevant compounds' molecular electrostatic potential surface maps. Molecules lacking -holes may not require additional treatment (assigning extra point charges to simulate -holes) to address the electrostatic characteristics appropriately.

We created a molecular surface electrostatic potential map of a set of representative noncovalent partners containing nitrogen and fluorine atoms at their interactive sites to confirm whether the individual noncovalent hydrogen bonded partners considered in this study have -holes on their electrostatic potential surfaces.

The electrostatic potential surfaces obtained show that none of the moieties studied in this work contain -holes on their surface. As a result, it is correct to conclude that the current work's point charge calculations give a good way to predicting net electrostatic interactions, especially when determined from charge calculations at a high level of theory. However, more care should be given with molecules that contain -holes.

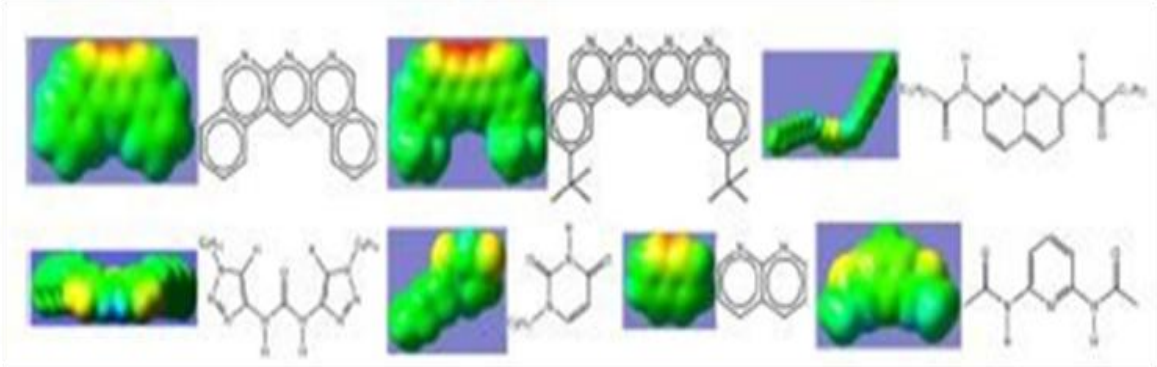

Figure 1. The molecular surface electrostatic potential

RESULTS AND DISCUSSION

In order to determine the electrostatic force of binding between two noncovalent bonded partners, the approach that has been proposed here has been to determine the Coulombic force between each pair of atoms, with the atoms being chosen from the different partners, and then taking a vector sum up all these individual contributions to obtain the net force of binding. The point charge approximation has been proposed as a practical and more general choice for this purpose, and each atom has been considered to have a charge, determined by the QM calculations, as described in the previous section. Since force has direction, the Coulombic interaction has been proposed to be considered along a certain common line to obtain the force of binding for two bonded partners: the "line of direction" for the given molecular complex. Therefore, only the component of the individual pair- wise interactions between two partners is proposed to be considered alongthat given line (Figure 1). The algorithm for the code that incorporates this approach has been provided. This method has been explained below in details considering sixteen planar hydrogen bonded complexes. The family of the planar hydrogen bonded complexes involves two partners interacting through X- H---Y hydrogen bonded interactions, with the number of such hydrogen bonds varying from two to four.

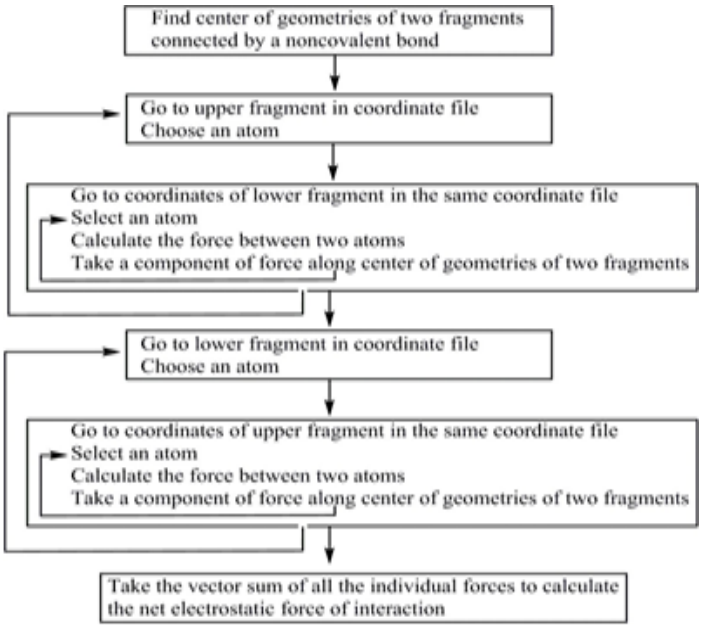

Figure 2. A flow chart of the Fortran 90 code used for calculating the net force between two partners in hydrogen bonded complexes

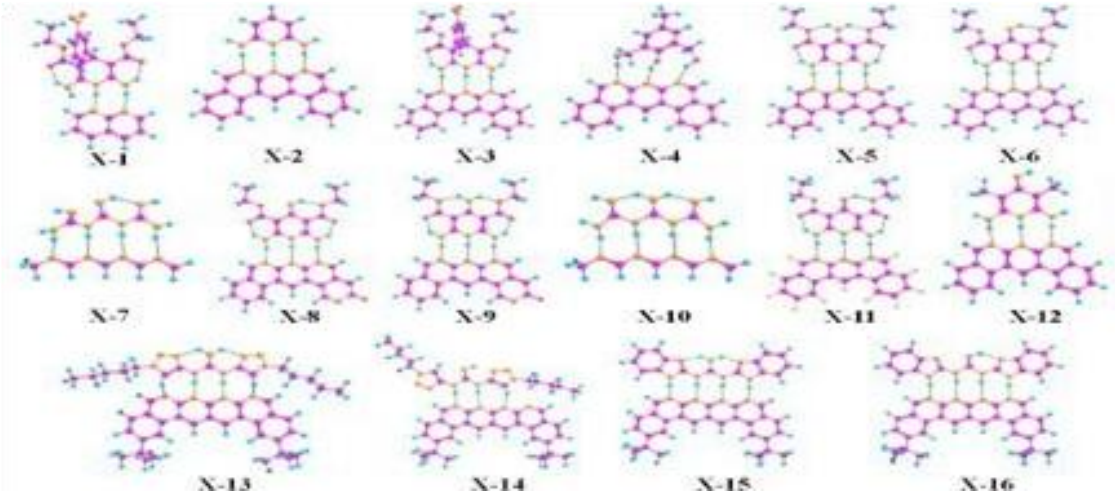

Figure 3 The optimized geometries of planar hydrogen bonded complexes at the COSMO (CHCl3)/PBE/TZVP level of theory

A flow chart of the Fortran 90 code used for calculating the net force between two partners in hydrogen bonded complexes. Bonds in these complexes exist in one plane. These complexes have been proposed to serve as useful models for investigating and understanding multipoint hydrogen bonding, which is of great importance to biological systems as well as to multifunctional materials and supramolecular polymers. This has led to publication of a large number of reports in reputed international journals in recent times that have discussed different planar hydrogen bonded structures belonging to this family. This family of planar hydrogen bonded complexes has been chosen specifically to test our approach because it has been shown that SEIs are very important for determining the stability of these complexes,23-30 which has led chemists to the design principle of having all the hydrogen bond acceptors on one partner and all the hydrogen bond donors on the other.22 We have therefore taken a sample set of sixteen different representative complexes to show the viability of our approach. The optimized structures of these complexes at the COSMO(CHCl3)/PBE/TZVP level of theory.

The optimized geometries of planar hydrogen bonded complexes at the COSMO (CHCl3)/PBE/TZVP level of theory. Pink, cyan, brown and white colors represent carbon, hydrogen, nitrogen and fluorine atoms respectively, whereas, dotted blue lines represent hydrogen bonds.

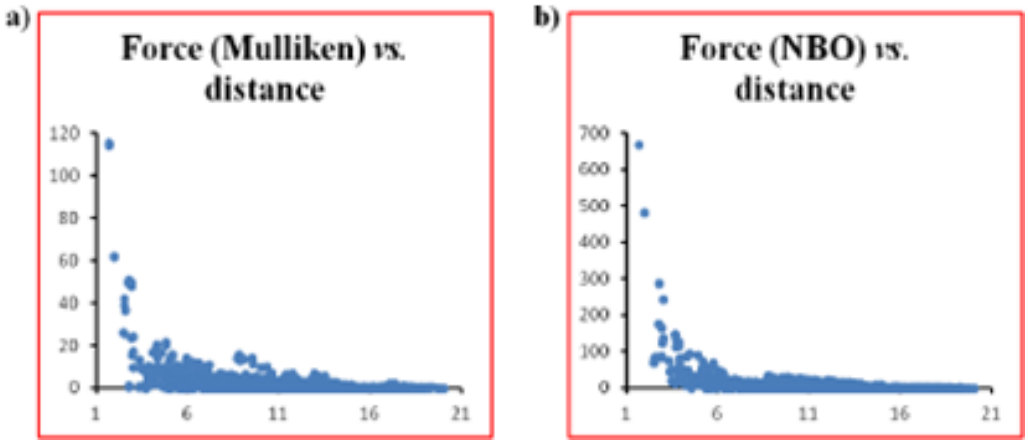

Figure 4. The pair-wise atomic electrostatic force vs. the corresponding atom-atom distance: a) with Mulliken charges, and b) with NBO charges

It has been reported that long range electrostatic interaction energies, which vary with r as r- 1, are significant in determining the net binding energy of hydrogen bonded complexes.32 The magnitudes of electrostatic forces, however, vary with r as r-2. The question that is of significant relevance in this context is this: do the electrostatic interaction forces in hydrogen bonded partners also have long range influence? To examine this, we have calculated all the pair-wise electrostatic forces between atoms on two partners in X-15 (see Figure 3.4 for the structure). The pair-wise forces in this case have been computed along the line joining the center of geometries (geometrical centers) of the frontier

In molecular complexes where noncovalent electrostatic contact is the primary element, the current study illustrates a simple method for determining hydrogen bonded atoms in two partners in X-15, as this line seems to represent binding interactions between the two partners most appropriately. A graph with the magnitude of pair-wise electrostatic force (considering Mulliken and NBO charges) on the Y axis and the corresponding atom-atom distance on the X axis is shown in Figure below. It can be deduced from that the electrostatic forces are significant even beyond 12 Å of distance between two atoms at two bonded partners. Thereby, it is concluded that the long range electrostatic forces are also significant in the hydrogen bonded systems.

CONCLUSION

the electrostatic force (EF) of interaction between two partners. More importantly, this research emphasises the significance of long-range secondary interactions

involving all of the atoms of the two binding partners. The research also highlights the significance of taking directionality into account when characterising such interactions and demonstrates how it may be used to determine the binding strength of complexes with hydrogen bonds. In multi-hydrogen bound planar complexes, it has been shown that the line linking the geometries of the border atoms of two partners best captures the molecular interactions. The forces generated by treating molecules' atoms as point charges match those found by using the finite difference method in EDA analysis linearly. The current method is very applicable because there are many areas of chemistry, material science, and biology where long-range electrostatic interactions are crucial in determining the overall strength of the contact.

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