

Hydrogen bond made visible by molecular modelling

Fer visible l'enllaç d'hidrogen mitjançant modelatge molecular

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abstract

Our understanding of hydrogen bonding is growing and becoming more precise. At the same time, the new knowledge challenges how hydrogen bonds is taught. Molecular modelling provides a modern tool on atomistic processes, and enables the researcher and student alike to study how atomic level processes happen and how the changes that occur impact the energetics of the system.

keywords

Chemical bond, hydrogen bond, computational chemistry.

resum

La nostra comprensió de l'enllaç d'hidrogen s'està tornant més profunda i precisa. Al mateix temps, el nou coneixement desafia la nostra manera d'ensenyar l'enllaç d'hidrogen. El modelatge molecular proporciona una eina moderna per abordar els processos atòmics, i permet tant a l'investigador com a l'estudiant analitzar com tenen lloc els processos en el nivell atòmic i com els canvis que es produeixen modifiquen l'energia del sistema.

paraules clau

Enllaç químic, enllaç d'hidrogen, química computacional.

Introduction

Chemical bonding is one of the key concepts in chemistry. For over a century chemists have used straight lines to describe the sharing of electrons between atoms or dotted lines describing the interaction between atoms and molecules. Learning chemistry requires understanding of the physical forces behind chemical bonds, understanding how the consequences of interactions on the microscopic level appear on the macroscopic level, and how the chemical bonds are presented.

Hydrogen bonding is a prevalent and important intermolecular interaction, which is frequently addressed in chemistry education and learning. The different models and representations used in connection with explaining and conceptualizing hydrogen bonding

yield a challenging task for the learners to understand and apply *hydrogen bonding* as a chemical concept. A wide literature has been published discussing the nature of hydrogen bond (fig. 1, taken from author's bookshelf) and the consequences of hydrogen bond in nature and in research.



Figure 1. Books about hydrogen bonding.

The current definition of the hydrogen bond

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a

molecular fragment X-H, in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. A typical hydrogen bond may be depicted as X-H...Y-Z, where the three dots denote the bond. X-H represents the hydrogen bond donor. The acceptor may be an atom or an anion Y, or a fragment or a molecule Y-Z, where Y is bonded to Z. In some cases, X and Y are the same. In more specific cases, X and Y are the same, and X-H and Y-H distances are the same as well leading to symmetric hydrogen bonds. In any event, the acceptor is an electron rich region such as, but not limited to, a lone pair of Y or π -bonded pair of Y-Z (Arunan *et al.*, 2011).

This revised definition is in line with the original definition given by

Linus Pauling already in 1939 focusing on hydrogen-mediated interaction between electronegative atoms or moieties. This thought has been translated to literature and school books in the light of biological chemistry so that hydrogen bond is something that occurs only if there is oxygen, nitrogen and fluorine present. And this is what students tend to memorise by heart. However, going deeper in the origin of the interaction becomes clear that they are many aspects of the interaction and its appearance, which are neglected in education (even at the university level). This is mainly because things tend to be presented in a simplified manner, but restrictions of the model used or the validity of the model applied is downplayed.

Criteria for a hydrogen bond

Criteria for a hydrogen bond $X-H\cdots Y-Z$ according to IUPAC (Arunan *et al.*, 2011) are the following:

1) The forces involved in the formation of a hydrogen bond include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.

2) The atoms X and H are covalently bonded to one another and the $X-H$ bond is polarized, the $H\cdots Y$ bond strength increasing with the increase in electronegativity of X.

3) The $X-H\cdots Y$ angle is usually linear (180°) and the closer the angle is to 180° , the stronger is the hydrogen bond, and the shorter is the $H\cdots Y$ distance.

4) The length of the $X-H$ bond usually increases on hydrogen bond formation leading to a red shift in the infrared $X-H$ stretching frequency and an increase in the infrared absorption cross-section for the $X-H$ stretching vibration. The greater the lengthening of the $X-H$ bond in $X-H\cdots Y$, the stronger is the $H\cdots Y$ bond. Simultaneously,

new vibrational modes associated with the formation of the $H\cdots Y$ bond are generated.

5) The $X-H\cdots Y-Z$ hydrogen bond leads to characteristic NMR signatures that typically include pronounced proton deshielding for H in $X-H$, through hydrogen bond spin-spin couplings between X and Y, and nuclear Overhauser enhancements.

6) The Gibbs energy of formation for the hydrogen bond should be greater than the thermal energy of the system for the hydrogen bond to be detected experimentally.

What follows from these distinct descriptors of the properties of a hydrogen bond is that the interaction we regard simple and straightforward have many facets that can't be classified as a standard hydrogen bond. These definitions and characteristics also challenge researchers about the nature of bonding and scholars about teaching about hydrogen bonding. In the end, what we call a *hydrogen bond* is actually an electrostatic interaction where hydrogen happens to be mediating the interaction. Consequently, hydrogen bonding is not unique but a demonstration of a general phenomenon that can be extended to lithium bonding, halogen bonding or pnictogen bonding, just to name a few. What can be done is to understand the physical origin of the interaction and use that as a starting point for teaching and learning.

Noteworthy, the IUPAC criteria for hydrogen bonding employs structural, energetic and spectroscopic observables. The common nominator for all the observables is electrostatic nature of the interactive species. What is interesting is that IUPAC uses the concept of *electronegativity*, which appears to be a source of misconceptions in many cases, especially if the bonding classification is strictly

based on electronegativity differences (Ünal *et al.*, 2006).

Molecular modelling makes interactions visible

Recent works in educational research in Israel have shown that change towards electrostatic models involving a current view of atoms and molecules with nuclei and electron clouds provide a better approach, so called *bottom-up approach*, from atoms and molecules via chemical interactions all the way to macroscopic properties (Levy Nahum *et al.*, 2007).

A simplified model based on electrostatic interactions has recently been proposed by Joki *et al.* (2015). Both of these approaches take advantage of using electrostatic interactions on the atomistic level to explain behaviour and macroscopic consequences. All what is needed are positive nuclei and negative electron clouds forming the basis of the chemical interaction, especially in the case of intermolecular interactions. Also, one needs to understand how the energy changes when the interaction takes place. This is demonstrated in fig. 2 showing the hydrogen-bonded complex of two water molecules. Both 2D and 3D models of the equilibrium structure (minimum energy structure) of the complex are shown on the left. The potential energy curve describes the change in energy when the distance between the two molecules is changed. The curve has been generated from one hundred single point quantum chemical calculations. The computed-equilibrium structure bond distances are also given in fig. 2 to demonstrate the elongation of the O-H bond upon interaction.

A more elaborate analysis of the interaction energy has revealed that the interaction results about 80 % from electrostatic interactions raised by permanent electrostatic moments like dipole

and quadrupole moments. The remaining 20 % originates from temporary fluctuations in the electron clouds, which we know as *dispersive forces* or *Van der Waals interactions*. From an educational point of view, the energy curve can be used to deduce the interaction energy from only two points of the curve as the energy difference between the energy of the equilibrium structure and the energy of the dissociated complex, i.e. when the molecules are detached from each other. This is observed as the energy curve flattening out on the right side of the graph. Using this approach it is seen that the computed interaction energy (strength of H-bond) in a water dimer is about 20 kJ/mol. This is close to what we consider to be a moderate and normal hydrogen bond prevalent in nature (Jeffrey, 1997).

Here, the current scientific approaches, especially computational methods, can be utilized to the benefit of education. A research conducted with high-school teachers revealed a distinct belief in molecular modelling to enhance and add value to chemistry learning and teaching (Aksela & Lundell, 2008). Molecular modelling provides us tools to see and understand the interactions and changes in energy upon structural changes. Molecular modelling provides us a tool to observe the changes on the atomistic level (and to visualize them). This can be done in the classroom as it is done in a research laboratory to support experimental studies. Moreover, modelling programs can be easily employed as inquiry tools to study molecular properties, chemical reactions and even dynamical processes like solubility and phase transitions. Computers are becoming very cheap compared to their performance, and many computational programs originally developed for scientific research have been downscaled

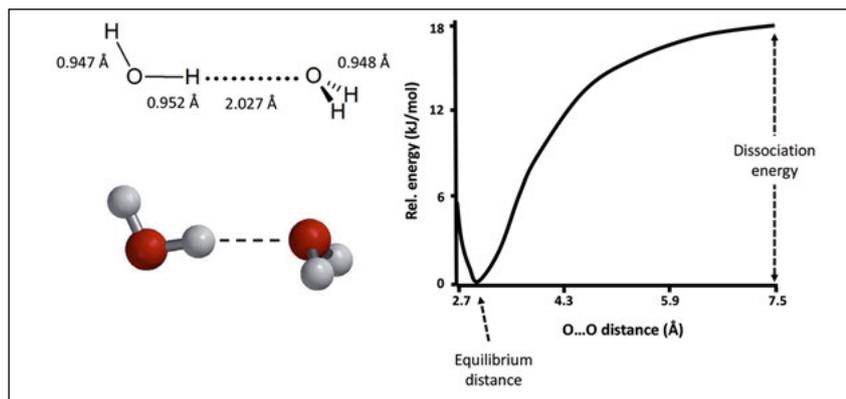


Figure 2. Models of water dimer and an energy curve describing the change of potential energy of the system when the intermolecular distance changes. The curve is drawn according to computational data presented in.

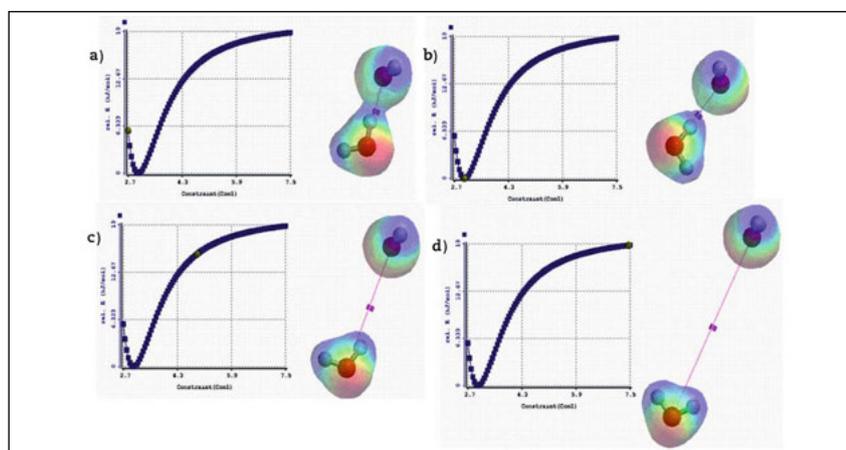


Figure 3. Snapshots of a movie of breaking the hydrogen bond in water dimer. The pink line between the molecules is denoting the reaction coordinate used in the computations. The coloured shells describe the electron density of the water molecules: red is negative, blue is positive.

for educational purposes. This puts modern molecular modelling tools to the hands of teachers and students alike.

The water dimer is used here as an example to study hydrogen bonding. Modelling can provide information about energy changes, structural changes and electrostatic changes. The interaction between electron clouds of molecules provides a first-hand understanding where the change in the interaction energy comes from. This is seen in fig. 3 showing snapshots of a movie generated from the computed structures including the electron density maps. Such interactive movies can be used to study the results of the

computed system going back and forth to look on the details presented. The use of a movie dismiss the need of doing the actual computation, but acts as a good starting point for studying the complex and the consequences of the interaction even on macroscopic scale.

The University of Jyväskylä offers chemistry teacher students a special course on models and visualization in education. One of the goals is to teach how to use molecular modelling to support chemistry education and to visualize the atomistic processes. The movie on water dimer has been used as an exercise in the course to provide pre-service teachers hands-on experience of using

modeling programs and applying them in teaching practice. It has been noted to be important that the pre-service teachers have the own experience with modelling tools and ICT during their studies. This makes it easier for them to apply the tools available in a more pedagogical way. The course focuses on three types of modelling tools: 2D/3D drawing tools (ChemSketch), animation tool (ChemSense) and molecular modelling tool (Spartan). Combining these tools together with Internet-based materials, electronic books and mind-map tools form a good basis to use ICT in a meaningful way in chemistry education. Learning these tools also prepare the students to the ever-changing ICT environment in society and education.

Some notes on chemical bonding

Many of the misconceptions on chemical bonding take place because of poor connection between microscopic and macroscopic levels of knowledge, because of insufficient models used and because of poor understanding of the concepts and phenomena (Özmen, 2004). Chemical bonding can be made much more clear and understandable if the students are introduced to electrostatic interactions and the concept of *electron density*. The latter is in fact an observable quantity whereas orbitals are not. Molecular modelling can make both of these visible on the computer screen, and deepen the learner's understanding how atoms and molecules actually interact (and at the same time provide insight on the different structural models chemists use).

Molecular modelling can demystify learning of chemical bonding by introducing tools and approaches used in research laboratories. Currently, hydrogen bond researchers are discussing topological analysis of electron

density and extensive interaction energy decomposition schemes to quantify the hydrogen bond precisely. In education positive and negative charges being attractive or repulsive towards each other is a good starting point. Inclusion of structural and energy changes in a macroscopic context makes chemical bonding understandable, comprehensive and visually interesting.

Based on quantum chemical calculations all chemical bonds are similar in origin: they all appear because of electrostatic interactions between atoms and molecules. What makes chemical bonds different is the language we use to talk about them. Chemists want to distinguish different variations of chemical bonds by giving them distinct names. From educational point of view, the continuum of electrostatic interactions of different strengths provide a solid physical basis to understand shared electrons as in covalent bonding, coulombic interactions as in ionic bonded salts, directional and undirectional long range attractions like in hydrogen bonding and Van der Waals interactions, respectively. In the long run, understanding the origin of bonding is what counts both in research and in education.

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