

DEFINITIONS OF A HYDROGEN BOND

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August 2005

(This is by no means comprehensive. These definitions are from books, papers and reports that I chanced upon. At best, they could be representative. Key word of 'hydrogen bonding' in SciFinder gave 346,465 references on 30 August 2005 and 348,410 (65928 as entered) on October 1, 2005. I could have missed many important contributions in this field and would appreciate hearing about any other contributions that could be mentioned here. These were collected mostly during the last one year. This is intended for private circulation among the IUPAC Task Group Members involved in the IUPAC project (No: 2004-026-2-100). The main objective is an attempt to help the IUPAC task group in coming out with a classification of intermolecular interactions, hydrogen bonding being the most important of all intermolecular interactions)

I. FROM SPECIALIST BOOKS/REVIEWS/PAPERS

0) Early reports

(From Huggins's article and Jeffrey's and Desiraju and Steiner's books, all referred below)

Werner (1902), Hantzsch (1910) and Pfeifer (1913) used terms such as *nebenvalenz* (near Valence) and *innere kompleksalzbildung* for inter- and intra-molecular hydrogen bonding. Moore and Winmill (1912) used the term *weak union* to describe the weaker basic properties of trimethylammonium hydroxide.

A. Werenr, *Leibig's Annalen der Chemie* **322**, 261 (1902) ; *Ber.*, **36**, 147 (1903)

A. Hantzsch, *Chemische Berichte* **43**, 3049 (1910).

T. S. Moore and T. F. Winmill, *J. Chem. Soc.* **101**, 1635 (1912)

Pfeiffer, Fischer, Kunter, Monti, and Pros, *Leibig's Annalen der Chemie* **398**, 137 (1913)

1) M. L. Huggins, *Angew. Chem. Int. Ed. Eng.* 10, 147 (1971) and *J. Org. Chem.* 1, 407 (1936); M. L. Huggins, *Phys. Rev.* 18, 333 (1921)

It seemed reasonable that a hydrogen kernel like the silver kernel in $\text{Ag}(\text{NH}_3)_2^+$, should be able to hold two sufficiently electronegative atoms in this way: X:H:X. Such hydrogen bridges were postulated, for instance, between oxygen atoms of oxyacids and between fluorine atoms in polymerized hydrogen fluoride. (1936)

The hydrogen bond or hydrogen bridge concept has proved to be one of the most useful structural concepts in modern sciences --- I therefore take pride in the fact that I was the first to introduce the hydrogen bond concept. It seemed reasonable to me that a non bonding electron pair – a “lone pair” as I called it – should have a considerable attraction for a positively charged proton, even if it is already bonded to another atom. (1971)

Both Pauling and Latimer and Rodebush refer to Huggins, but it appears that an M.S Thesis (1919) in which Huggins discussed the hydrogen bond concept could not be traced. Huggins has preferred the term hydrogen bridge in 1936 and seems to have reconciled with the term hydrogen bond in 1971. Certainly the analogy to $\text{Ag}(\text{NH}_3)_2^+$ looks out of place now, as both Ag-N bonds would be identical unlike typical hydrogen bonds, excluding the symmetric hydrogen bond in $(\text{FHF})^-$.

2) W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. 42, 1419 (1920)

In comparing NH_3 , H_2O and HCl , they state the following:

Ammonia adds a hydrogen readily but little tendency to give one up. Hydrogen chloride, on the other hand, shows just the opposite tendencies. Water occupies an intermediate position and shows tendencies to both add and give up hydrogen, which are nearly balanced. Then, in terms of the Lewis theory, a free pair of electrons from one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together ... Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak “bond”.

Widely recognized as the first to mention a hydrogen ‘bond’, Latimer and Rodebush had given “bond” within double quotes. They discuss the difference between ammonium hydroxide and ammonium chloride and suggest that the ammonium hydroxide might actually be a hydrogen bonded system and ammonium chloride ionic like sodium chloride. What is written about ammonia is quite remarkable as there are only two examples in the gas phase in which NH_3 acts as a proton donor. One is the famous ammonia dimer (Loeser et al. J. Chem. Phys. 97, 4727 (1992)) in which one ammonia has to give in and the other is benzene-ammonia dimer (Rodham et al. Nature, 362, 735 (1993)).

3) L. Pauling in J. Am. Chem. Soc. 57, 2680 (1935) and The Nature of Chemical Bond, III Edition Ch 12. p 449 (1960) I edition in 1939

It has been generally recognized since the discovery of hydrogen bond (*Latimer and Rodebush paper*) that the unusual properties of water and ice owe their existence to hydrogen bonds between water molecules. The arrangement of oxygen atoms (but not of hydrogen atoms) in crystals of ice is known from x-ray studies; it is not a close-packed arrangement (as of sulfur atoms in the high temperature form of hydrogen sulfide), but a very open one, like that of silicon atoms in high-tridymites. Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms at the distance of 2.76 Å., and it has been assumed that it is bonded to these atoms by hydrogen bonds, the number of

hydrogen atoms being just that required to place one H atom between each pair of oxygen atoms. The question now arises as to whether a given hydrogen atom is midway between the two oxygen atoms it connects or closer to one than to the other. The answer is that it is closer to one than to the other. In the gas molecule, the O-H distance is 0.95 Å, and the magnitudes of the changes in properties from steam to ice are not sufficiently great to permit us to assume that this distance is increased to 1.38 Å. In ice, each hydrogen atom is about 0.95 Å from one oxygen atom and 1.81 Å from another. (1935 paper)

My comment: Without experimental position for hydrogen, Pauling has used sound logic to give an accurate picture. Interestingly, he has used 'oxygen bonds' to describe the bonding in high-tridymite. In his words, each silicon atom is attached to four others by oxygen bonds. What happens to hydrogen sulfide at low temperatures?

It was recognized some decades ago that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond ... It is now recognized that the hydrogen bond is largely ionic in character, and that it is formed only between the most electronegative atoms. (From the book)

My comment: should ionic be interpreted as electrostatic, excluding Coulombic, to avoid confusion with the ionic bonds as in KCl? 'Most electronegative' atoms do not appear to be a requirement any more.

4) W. D. Kumlur, J. Am. Chem. Soc. 57, 600 (1935)

Prof. G. E. K. Branch has suggested that the conditions necessary for hydrogen bond formation may be formulated as follows: a lone pair of electron on an atom to act as donor; hydrogen on an atom from which it is fairly easily removed as hydrogen ion; both atoms to which the hydrogen may be attached must be small (there may be a few cases in which the last provision is not necessary.)

My comment: These criteria would have been certainly applicable for the well-established examples in 1935.

5. R. M. Badger and S. H. Bauer, J. Chem. Phys. 5, 605 (1937) and 5, 839 (1937)

It is suggested that the spectroscopic criterion for the presence of hydrogen bonds is not the disappearance but rather the shift and modification of the O-H absorption.

Earlier Hilbert, Wulf, Hendricks and Liddel, J. Am. Chem. Soc. 58, 548 (1936) had suggested that the criterion is disappearance of the O-H absorption band.

Recently, there has been considerable interest shown in a peculiar form of linkage sometimes known as the "hydrogen bond" in which as hydrogen atom, usually belonging to an hydroxyl or amino group, appears to serve as a connecting bridge between two electronegative atoms.

In order to establish such criteria (*given above*) one must of course decide what is meant by a hydrogen bond. Shall the term be reserved for certain cases in which O-O or other internuclear distance concerned and energy required to break the bond lie within rather narrow limits, or shall it be extended to include a great variety of weaker interactions such as are responsible for the low frequency of vibration of the O-H group in single molecules of the acids and in ortho-chlorophenol, and for a part of the heats of vaporization of HCN and HCl? These latter, of course, merge into the group of interactions known as van der Waals forces.

My comment: It is interesting to read the last paragraph. Today, no one would question the 'hydrogen bonds' formed by HCN and HCl, discussed above. We have arguments about SH and CH groups. It appears that, from the early days, most everyone invokes van der Waals forces, when in doubt. Do we really have a consensus on what van der Waals forces are? Look at the next brief section on van der Waals interactions.

6) G. C. Pimentel and A. L. McLellan, The Hydrogen Bond p 195 (1960) Starts by saying, there is no universally accepted definition.

“A hydrogen bond is said to exist when:

- 1) there is evidence of a bond
- 2) there is evidence that this bond involves a hydrogen atom already bonded to another atom.

My comment: Emphasis on evidence is important. Should all accepted evidences be part of a definition? Is Ar-HF hydrogen bonded? There is a clear evidence of a bond according to the definition of a bond given by Pauling. It does not have binding energy and shift in HF stretching frequency, that are typical of other 'hydrogen bonded complexes by HF' However, we do have blue-shifting hydrogen bonds today! I certainly like this definition.

7. A. S. N. Murthy and C. N. R. Rao, Appl. Spectrosc. Rev. 2, 69 (1968)

This comprehensive review covers the spectroscopic studies of the hydrogen bond. Does not discuss about what is a hydrogen bond. However, it includes examples in which CH, SH and PH are referred as weak hydrogen bond donors.

8) P. A. Kollman and L. C. Allen, Chem. Rev. 72, 283 (1972)

“The hydrogen bond is an intermediate range intermolecular interaction between an electron-deficient hydrogen and a region of high electron density”

Further, they talk about two types of hydrogen bonds. One by hydrogen covalently bonded to atoms having higher electronegativity (C, N, O, F, P, S, Cl, Se, Br and I) and the other by H bonded to atoms of lower electronegativity such as B). Also, an energy

cutoff is suggested. Complexation energy should be more than 'London dispersion force energy'.

My comment: Intramolecular should be included. The last point could be a useful criterion, but would depend on the level of theory. Really, one should define London complexes/molecules that are bound only by dispersive forces.

9. H. Umeyama and K. Morokuma, J. Am. Chem. Soc. 99, 1316 (1977)

Hydrogen bonded complexes, $(\text{H}_2\text{O})_2$, $(\text{HF})_2$ and $\text{NH}_3\text{-HF}$, can be qualitatively called "electrostatic > charge transfer" or "electrostatic" complexes.

The uniqueness of "normal" hydrogen bonding lies in the basic fact that it always involves a moderately polar, short and strong H-Y bond as the proton donor ... the "normal" hydrogen bond is always an intermediate to weak interaction with linear bonding and appropriate directionality.

While complexes of H_2O , HF and NH_3 may qualify as electrostatic complexes, hydrogen bonded complexes of second row hydrides are unlikely to be dominated by electrostatics.

10) A. D. Buckingham in Intermolecular Interactions from Diatomics to Biopolymers. Ed. B. Pullman, John Wiley, 1978

"The intermolecular or intramolecular interaction between a hydrogen atom bonded to an electronegative atom and another electronegative atom or group of atoms, known as the hydrogen bond..."

"The hydrogen bond results from interatomic forces that probably should not be divided into components, although no doubt electrostatic and overlap interactions are the principal ingredients."

"The question of what it is, if anything, that is special about a hydrogen bond has been considered by a number of Authors, it is probable that the great strength of some hydrogen bonds compared to other intermolecular energies (mainly van der Waals?) is due to the weakness of the short-range overlap repulsive forces. The proton in an X-H bond is in a region of low electron density; it has no inner shell of electrons and can therefore approach abnormally close to electronegative atoms, thereby increasing the negative energy resulting from the electrostatic and other forces of attraction.

Thus we do not often need to speak of a "lithium bond", and one explanation for this would be that the electron core of the lithium atom prevents the nucleus from approaching as closely to an electronegative atom as can the proton, in spite of stronger electrostatic forces."

My comment: Halogen bonding, especially chlorine bonding, analogous to hydrogen bonding appears to be well established both in gas phase and condensed phase. Nature of chlorine bonding could be totally different from that of hydrogen bonding.

11) P. Schuster in Intermolecular Interactions from Diatomics to Biopolymers. Ed. B. Pullman, John Wiley, 1978 p 364-365

“The term hydrogen bond or hydrogen bridge is used for two different phenomena (1) electron deficient three centre two electron bonds such as found in boranes and three centre-four-electron interactions as in X-H•••Y”

“Instead of presenting a rigorous definition, we propose a number of characteristic criteria for hydrogen bonds: 1) Distance between neighbouring atoms of the two functional groups (XH•••Y) involved in hydrogen bonds are substantially smaller than the sum of their van der Waals radii 2) XH stretching modes are shifted towards lower wave numbers on H bond formation 3) Polarity of XH bond increases and so does IR intensity and 4) NMR chemical shifts of protons in hydrogen bonds are substantially smaller than those observed in corresponding isolated molecules.

My comment: Boranes are no longer considered as hydrogen bonded systems. There are numerous reports in the literature about the failure of distance criterion based on van der Waals radii of heavy atoms, which is often used. The H---Y distance being less than the sum of van der Waals radii of H and Y may be better. Recently, we have defined a hydrogen bond radius, which could explain hydrogen bonds with much longer distances between the heavy atoms than the sum of their van der Waals radii.

12) H. Ratajczak and W. J. Orville-Thomas (Eds), Molecular Interactions, John-Wiley and Sons, (1980) page 15 Introductory chapter on “Some problems of Molecular Interactions.

“Thus finally one comes to the important conclusion that fundamentally there is no difference between ‘charge transfer’ and ‘hydrogen bond’ interactions. Further, the hydrogen bond may be considered as a specific type of electron donor-acceptor interaction which is within the medium to strong range of interactions.”

My comment: Kollman and Allen have argued against the importance of charge transfer based on the absence of charge transfer bands in hydrogen-bonded complexes

13) M. A. Benzel and C. E. Dykstra, J. Chem. Phys. 78, 4052 (1983).

At the simplest level, the concept of hydrogen bonding implies an attractive potential between two otherwise non-bonded atomic centers because of the presence of an intervening proton chemically bonded to one of the centers.

My comment: Does look appealing. Would ‘atomic centers’ include π centers as well?

14. A. C. Legon, Chem. Soc. Rev. 19, 197 (1990)

It is well known that the hydrogen bond is usually a relatively weak interaction (typically, the dissociation energy D_0 and the restoring force constant k_σ lie in the ranges of 10 – 50 kJ mol⁻¹ and 5 – 20 N m⁻¹.) ... In the context of the present article, to understand the hydrogen bond means to know experimentally the various properties of the molecules containing the bond and then to be able to predict these by means of a model.

15) R. F. W. Bader: Atoms in Molecules, Oxford 1990 pages 302-303

“The van der Waals molecules NeHF and ArHF, although, very weakly bound, can also be classified as hydrogen-bonded complexes, since the hydrogen in these molecules is bonded to the acid fragment by a shared interaction and to the base by a closed-shell interaction. The charge density at the critical point linking the hydrogen to the base atom in the van der Waals molecules exhibits the same characteristics as it does in the hydrogen-bonded molecules”.

My comment: Is frequency shift important? Of course, we do have ‘blue shifting hydrogen bonds’ in the literature now. If we can have hydrogen-bonded complexes showing both blue- and red-shifting of frequencies, it is only logical that there may be hydrogen-bonded complexes with no shift in vibrational frequency.

16) J. Isralechvili, “Intermolecular and Surface Forces” Academic Press, Second Edition (1991)

The Hydrogen bonding is no more than a particularly strong type of directional dipole-dipole interaction. Because of the small size of the H⁺ group, it is far stronger than that predicted by the point dipole approximation.

My comment: Like Buckingham, Isralechvili is pointing out the importance of the small size of H⁺. However, Buckingham has shown the importance of the complete electrostatics, rather than just dipole-dipole interactions in explaining the geometry of hydrogen bonded complexes in the gas phase.

This book could form the basis of a modern classification of intermolecular interactions based on the physical forces involved. I had suggested using the phrase London molecules to classify rare gas clusters in which the interaction is mainly due to dispersion (write-up to IUPAC). In this book, Isralechvili has used Keesom interaction for dipole-dipole and Debye interaction for dipole induced dipole interactions. Would London, Keesom and Debye cover all possible intermolecular interactions? Would Keesom and Debye be widely accepted?

17) M. M. Szczeńniak, G. Chalasiński, S. M. Cybulski and P. Cieplak, J. Chem. Phys. 98, 3078 (1993).

The lack of distinct directionality is often regarded as one of the features that distinguish the van der Waals interaction from hydrogen bonding. Although the main attractive van der Waals forces, dispersion and induction are attractive at any mutual orientation of interacting species, the potential energy surfaces of these complexes are far from isotropic.

The $\text{CH}_4\text{-H}_2\text{O}$ is related to $\text{Ar-H}_2\text{O}$ in a number of ways. The charge distribution of the CH_4 molecule is very close to spherical, as the lowest non-vanishing multipole moment is octupole.

The dispersion energy is responsible for the overall anisotropy of the potential energy surface (in $\text{CH}_4\text{-H}_2\text{O}$ complex).

My comment: This paper highlights the important point that van der Waals forces need not be isotropic as often assumed. Moreover, the global minimum is found to be different from the C-H...O bonded complex predicted by theoretical works till then. It has OH pointing towards one of the tetrahedron plane of CH_4 , which can be considered as hydrogen bonding. For CH_4 , electron density is maximum along the C_3 axis and is perpendicular the tetrahedron plane. This geometry has been experimentally observed by FTMW spectroscopy. (Suenram et al., J. Chem. Phys. 101, 7230 (1994))

18) B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. 94, 1887 (1994).

By intermolecular interactions, we will understand all interactions between molecules, which are significantly weaker than the chemical bond ... Some Authors introduce a further division into subtypes such as van der Waals interactions or the hydrogen bonding interactions.

All the intermolecular interactions contain the four fundamental physical contributions: electrostatic, induction, dispersion and exchange – and differ only by proportions of these ingredients. The strongest of these interactions involve a large negative contribution from the electrostatic forces as in hydrogen-bonded systems. If the electrostatic contribution is small, like in interaction of rare gas atoms with molecules, the minima depths are often below 1 kcal mol^{-1} . Nevertheless in all cases the basic physics of the process is the same. Thus, from this point of view, a molecule such as the water dimer is also a van der Waals complex.

My comment: I fully agree with this interpretation. Interestingly, the well-referred Buckingham and Fowler model for the hydrogen bonded complexes of HF has the title as “A model for the geometries of van der Waals complexes” Can. J. Chem. 63, 2018 (1985). More interestingly, Jeffrey in his book An Introduction to Hydrogen bonding (1997) states the following on page 19: “He (Spackman) extended an electrostatic model, which Buckingham and Fowler used for van der Waals complexes, to some hydrogen bonded dimers.” (M. A. Spackman, J. Chem. Phys. 85, 6587 (1986).)

I agree with the first sentence differentiating these interactions from the chemical bond. The term 'non-covalent interactions' is widely used in the literature. I would prefer non-chemical, as ionic bonding in KCl would be non covalent. Should one worry about partial covalency in hydrogen bonding interaction, which is not covered in the four physical forces mentioned above?

19) B. F. King and F. Weinhold, J. Chem. Phys. 103, 333 (1995)

The differences between electrostatic and partial covalent viewpoints can be most sharply contrasted with respect to H bonding involving (a) cooperativity effects and (b) low-polarity CH bonds.

Our conclusion strongly contradicts the assumptions of conventional "electrostatic" theories of H bonding (or associated pairwise additive potentials widely used to model hydrogen bonding) which makes no provision for cooperativity, nor for significant C-H...N bonding. Thus, the results of this investigations (on (HCN)_n clusters n=2-7) serve to strongly challenge current conventional wisdom concerning the nature of hydrogen bonding and the adequacy of widely used model potentials and numerical simulation techniques for describing H-bonded systems.

My comment: Introduction gives a nice summary of previous work emphasizing the significant valance type (resonance, delocalization, charge transfer, overlap-type and exchange-type) character for hydrogen bonding. However, HCN is certainly not a good example for low polarity CH bonds. Of course, King and Weinhold quote from Pauling's book (page 458 of III edition) where Pauling has mainly taken the low electronegativity difference between C and H to conclude that HCN would not show hydrogen bonding. Weinhold continues to emphasize the importance of valence forces in hydrogen bonding (J. Am. Chem. Soc. 125, 5973 (2003) and shows that both red- and blue-shifting hydrogen bonds could be explained by similar considerations.

20) U. Koch and P. L. A. Popelier J. Phys. Chem. 99, 9747 (1995)

It is shown that the total charge density is a valid source to confirm hydrogen bonding without invoking a reference charge density.

Lists down eight criteria based on the total charge density using AIM theory to confirm or rule out hydrogen bonding. While all eight criteria are necessary conditions, it has been shown that one condition (mutual penetration of hydrogen and acceptor atoms) is a sufficient condition.

21) M. A. Suhm and D. J. Nesbitt, Chem. Soc. Rev. 45 (1995)

This review summarizes the available results on Ar₃, Ar₂HF, Ar-(HF)₂ and (HF)₃. Intermolecular interactions are 'loosely' classified as hydrogen bonding,, electrostatic interactions, induction forces and dispersion interactions.

22) A. J. Stone, The Theory of Intermolecular Forces, Clarendon Press, Oxford 115 (1996)

“It has been recognized for many years that there is a significant attractive interaction between a hydrogen atom attached to an electronegative atom such as oxygen or a halogen or to a lesser extent nitrogen and another electronegative atom. Hydrogen bonds involving C-H are also now recognized, following some initial controversy.”

Goes on to list the experimental observations as criteria for hydrogen bonds.

23) R. H. Crabtree et al. Acc. Chem. Res. 29, 348 (1996)

...a new type of intermolecular interaction, the H•••H or dihydrogen bond, which operates between a conventional hydrogen bond donor such as an NH or OH bond as the weak acid component and an element-hydride bond as the weak base component, where the element in question can be a transition metal or boron...

Important paper highlighting that the electron rich region in a hydrogen bond need not be restricted to a lone pair or π pair.

24) M. C. Wahl and M. Sundaralingam, Trends Biochem. Sci. 22, 97 (1997)

“Hydrogen bonds are attractive electrostatic interactions of the type X-H•••Y, in which Y, the hydrogen bond acceptor carries a full or partial negative charge, while the hydrogen bond donor, X, is more electronegative than H”

My comment: This seems reasonable, though dihydrogen bonding would need to be considered. Electronegativity of H in MH and XH should be different. It does exclude diborane as a hydrogen bonded system

25) S. Scheiner “Hydrogen Bonding” Oxford University Press (1997)

Instead of a rigid definition, criteria for hydrogen bonding in terms of distance, strength, directionality, nature of interaction and spectroscopic observations are given in 2 pages. The discussion also points out the need to be careful in using these criteria either to rule out or conclude hydrogen bonding.

Can we do better?

26) G. A. Jeffrey “Introduction to Hydrogen Bonding” Oxford University Press (1997)

Hydrogen bonding is a donor-acceptor interaction specifically involving hydrogen atoms.

Discusses strong, moderate and weak hydrogen bonds and also uses terms as ionic hydrogen bonding and forced strong hydrogen bonds etc...

My comment: Response to No 8 above. Does Jeffrey mean electron donor-acceptor in this sentence? Many use hydrogen bond donor and hydrogen bond acceptor in the literature now.

27) G. Desiraju and T. Steiner, “The Weak Hydrogen Bond”, Oxford University Press (1997)

The weak hydrogen bond may be defined as an interaction $X-H\cdots A$, wherein a hydrogen atom forms a bond between two structural moieties X and A, of which one or even both are only of moderate or low electronegativity.

Also, classifies hydrogen bonds as very strong, strong and weak depending on the strength of the bond.

This is a comprehensive book summarizing the hydrogen bonding by weak donors. Hydrogen bonding is indeed fascinating. It appears that there was no need to define a weak covalent bond or a weak ionic bond. Covalent bonds can vary in strength significantly. Even if one considers only single bonds, HF is $135 \text{ kcal mol}^{-1}$ and HI is roughly half at 71 kcal mol^{-1} . When it comes to hydrogen bonding, a limit (either geometric, energetic, or spectroscopic) is always specified!

28) IUPAC Compendium of Chemical Terminology Gold Book)

Hydrogen bond

A form of *association* between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e. N, O or F. Hydrogen bonds may be intermolecular or intramolecular. With a few exceptions, usually involving fluorine, the associated energies are less than $20\text{--}25 \text{ kJ mol}^{-1}$ ($5\text{--}6 \text{ kcal mol}^{-1}$).

1994, 66, 1123

IUPAC Compendium of Chemical Terminology 2nd Edition (1997)

My comment: It is not exclusive like Scheiner’s book quoted above, may be rightly so. Is there any need to be exclusive?

29) CCSD Mercury On-line Documentation:

The default definition of a hydrogen bond ($D-H\cdots A$) is a contact meeting the following criteria:

- The donor (D) must be a nitrogen, oxygen or sulphur atom covalently bound to at least one hydrogen. It is not necessary for the 3D coordinates of the H atom to be

known, i.e. H-bonds will be found even if H atoms have not been located in the crystal structure.

- The acceptor (A) must be a nitrogen, oxygen, sulphur or halogen with at least one available lone pair (e.g. pyramidal trigonal nitrogen is regarded as a donor but planar trigonal nitrogen is not).
- The $D...A$ distance must be less than the sum of van der Waals Radii of the D and A atoms.
- The contact may be (a) intermolecular, or (b) intramolecular involving donor and acceptor atoms separated by at least 3 covalent bonds within the molecule.

The third criterion is certainly not appropriate any more.

30) I. Alkorta, Isabel Roza and José Ekguero Chem. Soc. Rev. 27, 163 (1998).

The hydrogen bond can be defined as an attractive interaction between two molecular moieties in which at least one of them contains a hydrogen atom that plays a pivotal role.

A reasonable definition. Does cover dihydrogen bonding and other weak hydrogen bonds (CH and SH groups), but leaves out intramolecular hydrogen bonds. This review covers non-conventional hydrogen bond donors and acceptors.

31) E. Cubero, M. Orozco, P. Hobza and F. J. Luque, J. Phys. Chem. A. 103, 6394 (1999).

Defines an anti-hydrogen bond, typically $C-H\cdots\pi$ interactions, which show a blue shift in the C-H stretching frequency following complex formation, unlike the typical red-shift that is observed in the X-H stretching frequency in normal hydrogen bonds.

32) A. C. Legon, Angew. Chem. Int. Ed. 38, 2686 (1999)

The hydrogen bond resembles the 'halogen bond' so that complexes $B\cdots HCl$ and $B\cdots ClF$ are isostructural, as when B is cyclopropane. When symmetry allows, the hydrogen bond can show a significant non-linearity, which appears to be absent in the corresponding halogen-bonded system, as when B is thiirane.

This comprehensive review on $B\cdots XY$ complexes (where X and Y are halogens) makes a strong case for a halogen bond analogous to hydrogen bonds.

33) T. H. Dunning Jr. J. Phys. Chem. A. 104, 9062 (2000)

Hydrogen bonding interactions results from the sharing of a hydrogen atom between two other atoms. The strengths of hydrogen bonds vary from a few kcal mol^{-1} to tens of kcal mol^{-1} and are typically weaker than chemical bonds by a factor of 10 or more.

While this definition looks reasonable, Dunning has listed N₂-HF as an example for electrostatic interactions, though it has a hydrogen atom shared between N and F, which are both prototypical atoms involved in hydrogen bonding.

34) K. Muller-Dethlefs and P. Hobza, Chem. Rev. 100, 143 (2000)

Comprehensive review on non-covalent interactions. A classification of non-covalent interactions is given somewhat similar to Dunning's paper. Has not 'defined' hydrogen bonds, but describes the features of normal, improper (instead of anti) and dihydrogen bonds.

35) P. Hobza and Z. Havlas, Chem. Rev. 100, 4253 (2000).

Although it is not easy to define H-bonds to include all the features ascribed to it by the different branches of science, these hydrogen bonds always describe an attractive interaction between two species (atoms, groups, molecules) in a structural arrangement where the hydrogen atom, which is covalently bound to one of the species is placed in between of these species.

The H-bond is a bond between electron deficient hydrogen and a region of high electron density.

Though, this review on Blue Shifting Hydrogen Bonds begins by saying it is not possible to define hydrogen bonds, it has given a definition, which appears quite reasonable.

36) C. E. Dykstra and J. M. Lisy J. Mol. Structure (Theochem) 500, 375 (2000).

This review on experimental and theoretical challenges in non-covalent intermolecular interaction does not worry about classifying different types of interactions. Rather, it talks about molecules as building blocks towards a new chemistry, different from the chemistry of molecules with atoms as building blocks.

37) D. L. Bergman, Chem. Phys. 253, 267 (2000).

Discusses an effective definition of hydrogen bond for use in molecular dynamics simulations.

38) J. J. Novoa and F. Mota, Chem. Phys. Lett. 318, 345 (2000)

This paper summarizes results on several C-H... π bonds and concludes that these are hydrogen bonds like C-H...O and O-H... π bonds. The presence of these bonds has been identified by observing the characteristics of bond critical points and the vibrational shifts.

39) S. J. Grabowski, J. Phys. Chem. A. 105, 10739 (2001)

Despite the great variability of systems, which are classified as hydrogen bonds, we may specify the criteria of the existence of such interactions. The most important geometrical characteristic of X-H...Y hydrogen bond is that the distance between the proton and the acceptor atom (H...Y) is shorter than the sum of their van der Waals radii...The use of energetic criteria is more problematic.

The distance criterion given here is better than the one based on heavy atom (X and Y) distances. This paper also talks about conventional and unconventional hydrogen bonds. The latter includes CH as unconventional donors, π cloud as acceptor and dihydrogen bonds. In a later paper (J. Phys. Chem. A. 108, 5823 (2004), Grabowski et al. have considered dihydrogen bonding and X-H... σ interactions and conclude that dihydrogen bonding can be classified as H bond but X-H... σ interaction is van der Waals.

40) B. J. van der Veken, W. A. Herrebout, R. Szostak, D. N. Shchepkin, Z. Havlas, and P. Hobza J. Am. Chem. Soc. 123, 12290 (2001).

A hydrogen bond is formed when the hydrogen atom of a covalent A-H bond of a proton donor molecule interacts with a lone electron pair of an atom X of a proton acceptor.

This paper discusses the improper, blue shifting hydrogen bonds and compares and contrasts them with classic hydrogen bonds. See also: S. Scheiner and T. Kar, J. Phys. Chem. A. 106, 1784 (2002) K. Hermansson, J. Phys. Chem. A. 106, 4695 (2002) and I. V. Alabugin, M. Manoharan, S. Peabody and F. Weinhold, J. Am. Chem. Soc. 125, 5973 (2003).

41) B. Mennucci, J. Am. Chem. Soc. 124, 1506 (2001)

In the original scheme (of Buckingham), H-bonding specific interactions were mentioned as a possible extreme of the "polar" effect, but in the numerous applications, which followed, they have always been treated as a separate contribution.

Discusses 'hydrogen bonds' and 'polar effects' independently.

42) I. David Brown, The Chemical Bond in Inorganic Chemistry, Oxford, p 75 (2002)

"The combination of an H⁺ cation asymmetrically bonded to its two ligands is called a hydrogen bond. The hydrogen bond is often represented by the bonding scheme X'-H...X (X, X' = O²⁻, N³⁻, C⁴⁻, F⁻, Cl⁻, Br⁻, I⁻ etc...) where the strongly bonded X' anion is called the hydrogen bond donor and the weakly bonded X anion is called the hydrogen bond acceptor."

While most definitions recognize a partial positive charge on H, Brown has chosen to make the charge on H as +1. It appears to be consistent with the bond valence model he has used for all chemical bonds.

43) J. J. Dannenberg, J. Mol. Structure 615, 219 (2002)

The precise definition of a hydrogen bond continues to be elusive. The nature of the physical interactions that contribute to hydrogen bonds has been the subject of numerous discussions in the chemical literature. At one extreme, hydrogen bonds are attributed to purely electrostatic interactions, or electrostatic plus polarization interactions; at the other, covalent interactions are held to be extremely important. The comparison between the H₂O/HF and H₂O/HCN hydrogen-bonding dimers is useful. An electrostatic dipole–dipole interaction between the water dipole and that of either H-donor would lead to a planar dimer. However, the first is predicted to be nonplanar, and the second planar. Clearly, there must be a difference in the H-bonding interactions. ---

--- From the review of the work presented, one can clearly see that cooperative interactions can play a very important role in the description of H-bonding in aggregates, crystals and biochemical materials such as proteins. Modeling these interactions with pairwise potentials provides an inadequate description of the relevant interactions.

Despite, Buckingham and Fowler's electrostatic model showing the importance of multipoles, it appears that electrostatics continue to imply dipole-dipole. This paper highlights the importance of cooperativity and failure of pair-wise potentials in several hydrogen bonded systems, especially in condensed phase.

44. M. Pecul and J. Sadlej, Chem. Phys. Lett. 360, 272 (2002).

The experimental observation of the hydrogen-bond-transmitted indirect nuclear spin–spin coupling constants in several systems, has invoked much interest in these parameters among theoretical chemists. In particular, this discovery has raised once more the question of the covalent character of hydrogen bond. Recent theoretical studies, suggest that intermolecular indirect spin–spin coupling constants may have measurable values not only in hydrogen-bonded complexes, but also in other van der Waals molecules, including dimers of rare gases.

The analysis of intermolecular coupling constants calculated for the three stationary points on the potential energy surface indicates that these couplings are determined primarily by the internuclear distances, with surprisingly little angular dependence.

NMR experiments by Dingley and Grzesiek J. Am. Chem. Soc. 120, 8293 (1998) and Compton scattering experiments by Isaacs et al. Phys. Rev. Lett. 82, 600 (1998) had indicated that there is partial covalency in hydrogen bonding. This paper argues against partial covalency in hydrogen bonding and shows that the spin-spin coupling seen in NMR could be through space. Would it explain Compton scattering results?

45) Roger Klein: J. Am. Chem. Soc. 2002, 124, 13931-13937.

A hydrogen bond can be defined as the interaction between an electron-deficient hydrogen atom and an electron rich region such as an electronegative atom e.g., N, O, F

or π electron cloud, together with the presence of two of Popelier's criteria based on AIM theory, namely a bond critical point and an atomic bond path.

My comment: OH---H₂ appears to be a hydrogen bond with a sigma acceptor. FH---CH₃ complex has C as an acceptor with one electron!

46) Li Bian, J. Phys. Chem. A. 107, 11517 (2003)

The hydrogen bond can be roughly characterized as weak bonding, usually having a bond strength below 10 kcal mol⁻¹ and forming between two neutral partners, or strong bonding, usually having a bond strength from 10 – 50 kcal mol⁻¹ and forming between a neutral molecule and a charged partner, either positive or negative.

This paper concludes that hydrogen bond donor is more important than the proton acceptor in determining the bond formation and strength.

47) W. Aquilanti, E. Cornicchi, M. M. Teixidor, N. Saendig, F. Pirani, and D. Cappelletti, Angew. Chem. Int. Ed. Engl. 44, 2356 (2005)

Among intermolecular interactions, those involving water are of paramount relevance as the archetype of polar hydrogen containing molecules. Manifestations and properties of the hydrogen bond have been intensively studied over three quarters of a century, and are currently under more scrutiny than ever, as the list of basic open questions is still impressive.

Describes Glory scattering experiments on Rg-H₂O and Rg-O₂ systems and concludes that the Rg-H₂O attains hydrogen bonding character for Rg = Kr and Xe

48). P. K. Mandal and E. Arunan, J. Chem. Phys. 114, 3880 (2001) and B. Lakshmi, A. G. Samuelson, K. V. Jovan Jose, S. R. Gadre and E. Arunan, New J. Chem. 29, 371 (2005)

A hydrogen bond radius for a donor DH, R_H(DH), is defined using the experimental H...A distance (R_{H-A}) in a D-H...A hydrogen bond and R_E(A), which is the distance from the minimum in the electrostatic potential of A to the bonding atom or center in A. R_E(A) is typically close to the van der Waals radii of A. Hydrogen bond radii for various DH groups vary between the covalent (0.3 Å) and van der Waals (1.2 Å) radii of hydrogen atom and show a strong inverse correlation with the dipole moment of DH and the electronegativity difference between D and H.

$$R_{H-A} = R_H(DH) + R_E(A)$$

This definition of hydrogen bond radius could resolve the ambiguities involved in defining hydrogen bonds using the heavy atom distances.

49) P. Munshi and T. N. Guru Row J. Phys. Chem. A. 109, 659 (2005).

Koch and Popelier's criteria for a hydrogen bond has been used to conclude that C-H...O contacts are hydrogen bonding and C-H... π contacts are van der Waals interactions in substituted coumarins. The defining characteristic is taken to be the fourth criterion that there should be mutual penetration of the hydrogen and acceptor atoms. It depends on non-bonded radii of atoms, which are taken to be the van der Waals radii of atoms.

van der Waals interactions

What is meant by van der Waals interaction? This is a very short compilation just to show the variation in perceptions. That van der Waals forces are not always isotropic is not appreciated widely.

E. R. Bernstein, *Ann. Rev. Phys. Chem.* **46**, 205 (1995)

A van der Waals complex is a collection of two or more atoms or molecules held together by **van der Waals or dispersion forces**.

G. Desiraju and T. Steiner p 17 of their book *The Weak Hydrogen Bond* (1997)

The isotropic terms are **exchange repulsion and dispersion**, the sum of which is often called 'van der Waals interaction'

V. Aquilanti et al. *Angew. Chemie. Int. Ed.* **44**, 2356 (2005)

The standard picture – **size repulsion and induction plus dispersion attraction** – is commonly referred as the van der Waals interaction.

A. J. Stone *The Theory of Intermolecular Forces*, Clarendon Press, Oxford 1996

The forces of attraction and repulsion between molecules are called van der Waals forces.

Koperski *van der Waals complexes in supersonic beams*, Wiley-VCH 2003

van der Waals binding, known also as polarization binding, is one of the four basic interactions between atoms and molecules. **It relies on the long-range weak attraction between permanent and induced electric dipole (and higher) moments as well as instantaneous asymmetric charge distributions in atoms and molecules (dispersion interaction)**. The other three heteropolar (ionic) homopolar (atomic or covalent) and metallic rely on valence forces between electrons.

E. Arunan

If one considers van der Waals equations as the origin for van der Waals interactions, it appears that all intermolecular interactions, including hydrogen bonding, should be classified as van der Waals interactions. van der Waals interactions could be further classified as hydrogen bonding, halogen bonding etc...

The views expressed in the last three do appear to be generally accepted. *Chemical Reviews* came out with three special issues on *van der Waals molecules* (1988, 1994 and 2000), all of which had several articles on hydrogen bonded complexes.

II. DEFINITION OF HYDROGEN BONDING FROM GENERAL TEXT BOOKS

(not extensive, may be representative)

1. I. N. Levine, Physical Chemistry IV Edition p 788 Tata McGraw-Hill (1995)

“Hydrogen bond is an attraction between an electronegative atom in one molecule and a hydrogen atom bound to an electronegative atom in a second molecule. The electronegative atoms involved are F, O, N, and, to a lesser extent, Cl and S.”

2. P. W. Atkins, Physical Chemistry VI Edition p 666 Oxford (1998)

“A hydrogen bond is an attractive interaction between two species that arises from a link of the form $A-H\cdots B$, where A and B are highly electronegative elements and B possess a lone pair of electrons”

3. R. S. Berry, S. A. Rice and J. Ross, Physical Chemistry

No definitions. Illustrated by comparing the boiling points for HF, H₂O, NH₃ and He with subsequent row analogs.

4. Advanced Organic Chemistry Jerry March II Edition p 75, McGraw Hill (1977)

“A hydrogen bond is a bond between a functional group A-H and an atom or group of atoms B in the same or a different molecule. With exceptions, hydrogen bonds are formed only when A and B are O, N or F.

5. Inorganic Chemistry, J. E. Huheey III Edition (1983)

Although some would contend that hydrogen bonding is merely an extreme manifestation of dipole-dipole interactions, it appears to be sufficiently different to warrant a short, separate discussion. In addition, there is no universal agreement on the best description of the nature of forces in the hydrogen bond.

We shall adapt an operational definition on the hydrogen bond: A hydrogen bond exists when a hydrogen atom is bonded to two or more other atoms. This definition implies that the hydrogen bond cannot be an ordinary covalent bond since the hydrogen atom has only one orbital (1s) at sufficiently low energy to engage in covalent bonding.

6. D. F Shriver, P. W. Atkins and C. H. Langford, Inorganic Chemistry, Second Edition (1994)

A hydrogen bond consists of an H atom between atoms of more electronegative non metallic elements. This definition includes the widely recognized $N-H\cdots N$ and $O-H\cdots O$ hydrogen bonds but excludes the B-H-B bridges in boron hydrides. It also excludes the W-H-W link present in $[(CO)_6WHW(CO)_6]$, for tungsten in a metal.

COMMUNICATION FROM TASK GROUP MEMBERS

1) Robert Crabtree (Email communication)

Hydrogen bonding is an acid-base interaction that occurs when a protonic hydrogen atom has a coordination number greater than one and the hydrogen bonded unit has an electron count greater than two. Bifluoride ion, $[\text{FHF}]^-$ and water dimer, $\text{HOH}\cdots\text{OH}_2$, fulfil this requirement, while trihydrogen cation, $[\text{H}_3]^+$, and diborane, $\text{H}_2\text{BH}_2\text{BH}_2$, do not.

The dihydrogen bond is a type of hydrogen bond that occurs when at least one of the atoms coordinated to the protonic hydrogen is a hydridic hydrogen, as in borane-ammonia dimer, $\text{H}_3\text{BH}_2\text{N-H}\cdots\text{H-BH}_2\text{NH}_3$.

2) E. Arunan (proposed classification)

van der Waals interactions: All non-chemical interactions between atoms and molecules are called van der Waals interactions. The origins of this interaction are typically the permanent and induced electric dipole (and higher) moments as well as instantaneous asymmetric charge distributions in atoms and molecules. Chemical interactions include covalent, ionic and metallic bonding.

Hydrogen bonding: An electron deficient hydrogen covalently bonded to an atom D can attractively interact with regions of electron density present either within the same chemical moiety or another, leading to intra/intermolecular hydrogen bonding, respectively. The existence of a bond should be experimentally and/or theoretically verified. In general, D has been found to be more electronegative than H and the regions of high electron density could be a lone pair of electrons in an acceptor atom, A or π electron cloud in a molecule. Hydrogen bonding may be represented as $\text{D-H}\cdots\text{A}$. Examples of hydrogen bonding with unpaired electron or sigma bond electrons as acceptor are known.

Hydrogen bonding is a special case of van der Waals bonding in which a hydrogen atom plays a significant role. Typically, electrostatic interactions, i.e. interactions between permanent or induced multipole moments, dominate hydrogen bonding leading to directionality in hydrogen bonds. However, dispersive forces and partial covalency have been seen in some hydrogen bonded systems.

3) J. Sadlej by email: Features of Hydrogen Bonds

The heart of chemistry it is the bond making and bond breaking. The intermolecular interactions are the first stage of these processes. So large part of frontier chemistry deals with the intermolecular interactions.

We understand that two atoms are joined by a chemical bond when: (i) the energy of a system is lowered as a consequence of this process (thermodynamical point of view), (ii) the nuclei are constrained at a distance which is significantly smaller than the sum of the

atomic radii (structural point of view), (iii) the electron density of both are perturbed by the approach of the partners (electronic structure point of view). These three points are valid for the intermolecular interactions.

The chemical bonds are divided into the groups, which differ by energy and their characteristics. Similar, the systems which are bound by intermolecular interactions could be differentiated by their interaction energies. And similar as the chemical bonds, there is no sharp border between the subgroups: van der Waals systems and H-bonding systems.

In my opinion, the hydrogen bond forms the subgroup of the systems bound by intermolecular interactions. Paulings description of the hydrogen bond remains valid today under the condition of changing the sentence: 'hydrogen bond exists if one hydrogen is bonded to more than one other atom' to 'hydrogen bond exists if one hydrogen is bonded to more than one electron-rich region' (the proton acceptor is either a lone pair or a sigma or pi-electron orbital or H atom).

There are many faces of the hydrogen bond. Hydrogen bond gives rise itself to its own classification on the basis of energetic criteria: (i) weak H-bond is characterized by an intermolecular energy of the order of 20 kJ/mol or less, (ii) medium H-bond, for which the complexation energy is ca 20-50 kJ/mol, and (iii) the strong H-bond with the interaction energy 80-150 kJ/mol.

The essential feature of hydrogen bond is that its attractive intermolecular potential can be described by combination of electrostatic, induction and dispersion energies. The short-range repulsive forces balances the attraction. Based on the decomposition of the interaction energy into the physically meaningful terms one can distinguish three subgroups of the systems: weak, medium and strong hydrogen bonds.

The 'atom in molecule' theory of Bader (AIM) was applied to find the critical points and to analyze them in terms of electron densities and the topological parameters. The characteristics of the bond critical points (BCP) reveal the nature of the interaction. It is observed for interactions between closed-shell systems such as ionic interactions of hydrogen bonding that Laplacian at BCP is greater than zero.

Two last suggestions: the energy decompositions and AIM analysis are however method-dependent or model-dependent (AIM). It is desirable, insofar as possible, to avoid analysis of hydrogen bonded systems by such methods.

FROM THE INTERNET

Definitions of **HYDROGEN BOND** on the Web:

<http://www.google.com/search?q=define:HYDROGEN+BOND>

A intermolecular interaction formed between a hydrogen atom covalently bonded to an electronegative atom (such as oxygen or nitrogen) and a second electronegative atom that serves as the hydrogen bond acceptor.

home.san.rr.com/dna/darryl/glossary.html

A hydrogen atom ^ocovalently bound to an electronegative atom (e.g., nitrogen, oxygen) has a significant positive charge and can form a weak bond to another electronegative atom; this is termed a hydrogen bond.

www.foresight.org/Nanosystems/glossary/glossary_h.html

A relatively weak bond formed between a hydrogen atom (which is covalently bound to a nitrogen or oxygen atom) and a nitrogen or oxygen with an unshared electron pair.

www.biotechwithitaly.com/nw_glossary_hl.html

A weak bond between hydrogen and another atom (usually oxygen, fluorine, or nitrogen). Hydrogen bonds are critical in the formation of many biological molecules, including DNA and proteins.

www.stanford.edu/group/hopes/sttools/gloss/h.html

A fairly strong dipole-dipole interaction (but still considerably weaker than the covalent or ionic bonds) between molecules containing hydrogen directly bonded to a small, highly electronegative atom, such as N, O, or F.

www.netaccess.on.ca/~dbc/cic_hamilton/dictionary/h.html

The bond formed when the positive end of one polar molecule, such as water, is attracted to the negative end of another polar molecule.

chemed.chem.purdue.edu/genchem/glossary/h.html

An interaction between an electropositive hydrogen (bonded to an electronegative atom) and an electronegative atom it is not bonded to.

www.chem.swin.edu.au/modules/mod2/gloss.html

a strong secondary interatomic bond which exists between a bound hydrogen atom (its unscreened proton) and the electrons of adjacent atoms.

www.tulane.edu/~bmitche/book/glossary.html

Chemical bond between a hydrogen atom of one molecule and two unshared electrons of another molecule.

wvlc.uwaterloo.ca/biology447/modules/intro/microbiologyglossary.htm

a weak electrostatic bond formed by linking a hydrogen atom between two electronegative atoms

www.msncucleus.org/membership/html/jh/earth/dictionary/water/definitions.htm

a special type of intermolecular interaction whereby the hydrogen of one molecule is attracted to the oxygen, nitrogen, or fluorine of another molecule (if the molecule is large enough to fold on itself, this attraction can be between the hydrogen of one molecule and an oxygen, nitrogen or fluorine of the same molecule). This interaction will increase the overall stability of the substance or molecule.

www.biologylessons.sdsu.edu/ta/classes/lab3/glossary.html

An intermolecular bond formed with hydrogen.

college.hmco.com/geology/resources/geologylink/glossary/h.html

The hydrogen atoms in water are very positive, because the oxygen atom strongly withdraws the electrons in the O-H bonds. The hydrogen atoms on adjacent molecules are attracted to the oxygen atoms forming a bond which is stronger than the usual polar attraction, but less strong than a typical covalent bond. This accounts for the very high boiling point of water compared with other similar weight molecules.

eies.njit.edu/~kebbekus/definitions-aquatic-chem%20htm.htm

The force of attraction between a hydrogen atom bonded to an electronegative species such as a N,O or F atom and another electronegative species such as a N,O or F atom.

members.lycos.co.uk/chemistry/definitions.html

A weak bond between two atoms formed when a hydrogen atom is shared between two atoms, one of which is usually oxygen; primarily of importance in the structure of nucleic acids and proteins.

whitewolf.newcastle.edu.au/techinfo/glossary.html

The bond formed when the positive end of one polar molecule is attracted to the negative end of another polar molecule.

library.thinkquest.org/C006669/data/Chem/glossary2.html

An intramolecular chemical bond between a hydrogen atom of one molecule and a highly electronegative atom (e.g. O, N) of another molecule.

www.soils.org/cgi-bin/gloss_search.cgi

the strong electrostatic attraction that occurs between molecules in which hydrogen is in a covalent bond with a highly

www.towson.edu/~sshah/glossary.htm

a chemical bond consisting of a hydrogen atom between two electronegative atoms (e.g., oxygen or nitrogen) with one side be a covalent bond and the other being an ionic bond

www.cogsci.princeton.edu/cgi-bin/webwn

9. http://mml.phy.tufts.edu/MMLCourse96/BMM4_3/BMM4X5F3-13.html

Hydrogen Bonds

It is most common to identify regular secondary elements (helix and sheet) based on the hydrogen-bonding patterns of helices and sheets. There are two problems in identifying secondary structure from hydrogen bonds. One is the definition used for a hydrogen bond, and the other is the criteria used for identifying the secondary structure element (given exact locations of all hydrogen bonds).

There is no universal definition of a hydrogen bond. From analysis of small molecule structures, an ideal hydrogen bond has a donor-acceptor distance of 2.9 Angstroms and a hydrogen-donor-acceptor angle of 0 degrees, i.e., C=O---H-N.

Once the definition of a hydrogen bond is adopted and all such hydrogen bonds in the protein under investigation are identified, the location and extent of the secondary structural segments remain to be determined. In principle, the core of alpha, 3.10, and pi helical segments should be unambiguous due to the repeating (i, i+4), (i, i+3), and (i, i+5) hydrogen bonds, respectively. However, the first and the last helical turns each contain four residues in which only one of the two potential backbone hydrogen bonds are formed in the helix. These residues are usually included in helical definitions.

Similarly, the central residues of beta strands are straightforward to align into sheets whereas the end residues of each strand can contain dihedral angles characteristic of extended conformations yet not participate in the hydrogen bonding of the sheet. To qualify as a strand of a beta sheet, most definitions require the backbone amide nitrogen and carbonyl oxygen atoms of at least one residue.

Despite potential ambiguities, regular hydrogen bond patterns remain the most widely used and reliable method of secondary structure identification.

NDI Foundation http://www.ndif.org/Terms/hydrogen_bond.html

DEFINITION:

A relatively weak, primarily electrostatic, bond between a hydrogen atom bound to a highly electronegative element (such as oxygen or nitrogen) in a given molecule, or part of a molecule, and a second highly electronegative atom in another molecule or in a different part of the same molecule. The hydrogen bond is generally represented by three dots, e.g., X—H···Y, where X and Y are electronegative atoms.

From Dictionaries

1. The American Heritage® Dictionary of the English Language: Fourth Edition. 2000

A chemical bond in which a hydrogen atom of one molecule is attracted to an electronegative atom, especially a nitrogen, oxygen, or fluorine atom, usually of another molecule.

2. The Penguin Dictionary of Science, Penguin, London (1971)

A weak electrostatic chemical bond which forms between covalently bonded hydrogen atoms and a strongly electronegative atom with a lone pair of electrons. The hydrogen bond is of enormous importance in biochemical processes, especially the N-H•••N bond which enables complex proteins to be built up. Life would be impossible without this type of bond. (Jeffrey and Saenger have added (and N-H•••O) after NH•••N in their book).

<http://www.hyperdictionary.com/dictionary/hydrogen+bond>

3. Wordnet Dictionary:

Definition: [n] a chemical bond consisting of a hydrogen atom between two electronegative atoms (e.g., oxygen or nitrogen) with one side being a covalent bond and the other being an ionic bond

4. Biology Dictionary:

Definition: A weak electrostatic link between an electronegative atom (such as oxygen) and a hydrogen atom which is linked covalently to another electronegative atom; hydrogen bonding is what makes water stick to itself.

5. Glossary

Definition: A relatively weak bond formed between a hydrogen atom (which is covalently bound to a nitrogen or oxygen atom) and a nitrogen or oxygen with an unshared electron pair.