# Crystal Engineering

## How molecules build solids

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**Jeffrey H Williams**

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*As always, for Bruce Taylor Currie*

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# Preface

There are more than 20 million chemicals in the literature, with new materials being synthesized each week. Most of these molecules are stable, and the 3-dimensional arrangement of the atoms in the molecules, in the various solids may be determined by routine x-ray crystallography. When this is done, it is found that this vast range of molecules, with varying sizes and shapes can be accommodated by only a handful of solid structures.

This limited number of architectures for the packing of molecules of all shapes and sizes, to maximize attractive intermolecular forces and minimize repulsive intermolecular forces, allows us to develop simple models of what holds the molecules together in the solid. In this volume we look at the origin of the molecular architecture of crystals; a topic that is becoming increasingly important and is often termed, crystal engineering. Such studies are a means of predicting crystal structures, and of designing crystals with particular properties by manipulating the structure and interaction of large molecules. That is, creating new crystal architectures with desired physical characteristics in which the molecules pack together in particular architectures; a subject of particular interest to the pharmaceutical industry.

# Introduction: Crystal engineering

Chemists are busy people; there are over 20 million chemicals known in the literature, with many new molecules being synthesized each and every week. Most of these molecules are stable enough to be studied as they change state from solid to liquid, or solid to gas as the temperature is varied. And this huge number of molecules come in an appropriately wide variety of shapes and sizes. However, when it comes to how this huge diversity of molecules are packed together in solids, under the influence of the attractive electromagnetic forces that exist between all molecules, it is found that there are only a limited number of ways of ordering the stable packing of these variously sized and shaped molecules. This limited number of architectures for the packing of molecules to maximize attractive intermolecular forces and, consequently, minimize repulsive intermolecular forces, is the subject of this volume. We will look at the molecular architecture of crystals.

Looking at intermolecular interactions via a consideration of the detailed 3-dimensional arrangements of the molecules that constitute the solid, is not the usual route for studying intermolecular forces. However, the stable structure of a solid is the result of all possible interactions between the molecules that constitute that solid; that is, binary-interactions plus tertiary-interactions plus… N-body interactions, and I hope that my choice of the molecules reveals something of the contribution of these various terms that make up the intermolecular potential to the observed solid structure.

As the Nobel laureate Francis Crick said, ‘If you want to understand function, study structure’, and we will therefore consider the structure or internal architecture of a number of materials as determined by x-ray and neutron crystallography. Some of the 27 materials that I discuss in this volume have interesting and unusual bulk properties; for example, high-temperature superconductivity, birefringence, or laser activity. The data required to construct these 3-dimensional structures is stored in databases such as the Cambridge Structural Database (www.ccdc.cam.ac.uk), which presently contains the structure of over 875 000 covalently-bonded crystals; with new structures being added continually. These structures represent data accumulated by studies on single-crystals and on powders over the period 1914 (when the first crystal structure was published) to the present day.

In our study, we will concentrate on the weak, non-bonding intermolecular forces that lead gases to condense into liquids, and liquids to transform into ordered solids as the temperature is lowered, or the pressure increased. It is these weak forces that cause covalently bonded organic compounds to crystallize in the manner they do, and it is the study and comparison of these crystal structures that allow us to comprehend the nature of the underlying intermolecular forces.

In one of the earlies conjectures about the architecture of solids; the Roman poet and philosopher Titus Lucretius Carus (c 99–c 55 BCE) said in his *De Rerum Natura*, ‘Those things, whose textures fall so aptly contrary to one another that hollows fit solids, each in the one and the other, make the best joining’. This qualitative observation of how macroscopic objects, or jigsaw puzzles fit together has its modern counterpart in the observations of the Russian physicist Alexander I Kitaigorodsky who wrote, ‘The projections of one molecule get into the “hollows” of adjacent molecules, so that the molecules are closely packed with the minimum [number of] voids between them’; that is, as the crystallographer Jack Dunitz has said, ‘As far as the packing energy is concerned, empty space is wasted space’. Thus, we observe that molecules pack so as to avoid empty space; but why? What forces the molecules together to minimize intervening vacuum? This is what we will explore in this volume.

At the beginning of the last century, hardly anything was known about the arrangement of molecules in crystals. Indeed, the external point group symmetries of crystals had been determined from the examination of the symmetry of their external faces. As far as the internal structure of the crystals was concerned, the concept of space lattices had been introduced in the 18th century to explain the constancy of interfacial angles in differently shaped crystals of the same compound. The geometric theory of space lattices was complete by the end of the 19th century, culminating in the almost simultaneous recognition that there are only a finite number (230) of ways of combining elements of point symmetry with translational symmetry to form space groups. The mathematical theory of crystals may have been complete, but nothing was known about the underlying structure of the repeating units within those complex shapes.

This all changed with the discovery of x-ray diffraction by crystals. The first x-ray studies were of simple ionic crystals of high symmetry, such as the alkali halides (cubic), but it was not long before complex minerals, such as mica, $KAl_3Si_3O_{10}(OH)_2$ (monoclinic) were being studied. With metals, the x-ray diffraction studies of the American physicist Albert Hull showed that the arrangement of atomic nuclei in many metallic crystals corresponds to the close-packed structures of spheres.

But for all the technical advances, questions about how organic molecules attracted or repelled one another took longer to be asked, and still longer to be answered. Such quantitative relationships as we have to explain the condensed phases came from experimental observations and ideas about the shape and size of molecules, although the nature of the molecular entities and of the forces acting among them were only approximately known. Today we still talk about van der Waals molecular volumes and van der Waals radii, and also about van der Waals forces without defining too closely what they mean.

In contrast to inorganic compounds, even simple organic compounds typically form crystals of low symmetry. Thus, crystals of anthracene examined by x-ray diffraction in 1920, were found to be monoclinic and thus intractable by the methods then in use. According to folklore, the idea for the ring structure of benzene came to German chemist Friedrich August Kekulé (1829–1896) in a daydream of 1865, in which he envisioned a snake eating its own tail. Kekulé’s daydream led him to propose that the structure contained a six-membered ring of carbon atoms with alternating single and double bonds. But questions still remained; for example, in what configuration was this ring? Was it puckered, bowed, or flat? Did the molecule have three distinct double bonds? Most chemists subscribed to the theory that benzene was flat, but it was not until British crystallographer Kathleen Lonsdale

(1903–1971) began her research in 1929 that the mystery was finally solved. Unlike benzene, hexamethylbenzene has just one molecule per unit cell, making it easier to distinguish the orientation of the molecule's central benzene ring. Lonsdale's x-ray crystallography experiments unequivocally demonstrated that the benzene ring was not only flat, but also had an evenly distributed cloud of electrons; there were no single or double carbon–carbon bonds. Because the benzene ring is the foundation of aromatic compounds, Lonsdale's discovery made it possible to advance the chemistry of aromatic molecules, and laid the basis for the modern form of organic chemistry, and for molecule and crystal design. As Lonsdale's head of department, Christopher K Ingold commented on her discovery, 'The calculations must have been dreadful… but one structure like this brings more certainty into organic chemistry than generations of activity by us [physicist] professionals'.

In quantum mechanics, there is no such thing as empty space. As far as the physics of intermolecular interactions is concerned, what matters is the nature and strength of the fields of force generated by the electrons and nuclei. In inorganic structures, the strong Coulombic fields exerted by the cations and anions were comparatively easy to understand, and atomic cohesion in such crystals seemed to present no fundamental problems. Similarly, as an obvious extension, it was soon realized that the interaction between molecules with permanent dipole moments, such as water, is subject to analogous Coulombic fields and may be attractive or repulsive, depending on the mutual orientation of the molecules. The nature of the cohesive forces among neutral non-polar molecules remained elusive for a longer time. For example, no theory based on classical mechanics and electrostatics could possibly reproduce the lattice energy of methane or the inert gases. This may be a small effect, but it is undoubtedly present, as witnessed by the condensation of these gases and the solidification of the liquid at sufficiently low temperature. The mysterious missing term, the dispersion energy, had to await the advent of quantum mechanics and Fritz London who first described dispersion interactions. Thus, explaining weak intermolecular interactions and pointing out that for these short-range forces to be effective, molecules must be in close contact; bumps into hollows, with as little empty space as possible. It was Kitaigorodsky's achievement, in the early-1960s, to put these concepts on a systematic footing beginning with a critical survey of organic crystal structures.

X-ray crystallography is not a difficult or obscure branch of science; on the contrary it is now a routine procedure, and measurements are today automated and the data analysis has become a *black-box* technology. This volume seeks to show that the beautiful and fascinating, detailed 3-dimensional pictures of closely-packed molecules tells us a great deal about molecular interactions, and the bulk behavior of solids. However, before we start exploring crystal architecture we will consider some of the basics of chemical structure, bonding and the nature of intermolecular forces. First, we will look at how atoms bond to form molecules and how electrons are distributed in those molecules. The reader will then discover that considerations of symmetry play a central role in classifying the structure of solids as well as in rationalizing the properties of crystalline materials.

Attentive readers will have noticed that it is barely a century since the very first crystal structure determination using x-ray diffraction, 1914. Not surprisingly, this anniversary generated a number of review articles. One of the most interesting is to be found at http://cen.xraycrystals.org/introduction.html, and comprises a set of highlights of crystallography over the last century as chosen by *Chemical&Engineering News*, the news magazine of the American Chemical Society.

# Acknowledgement

With this volume, *Crystal Engineering: How molecules build solids*, I should like to thank Dr Jeremy Karl Cockcroft, Chemistry Department, University College London, for all his help. I have known Jeremy Cockcroft since we both worked as experimental scientists at the Institute Laue-Langevin, Grenoble; where I was a solid and liquid-state physicist and Jeremy was a neutron crystallographer. Over the years, Jeremy has taught me a great deal about crystallography and about how a crystallographer looks at molecular interactions; and his help has been central in writing this volume. In addition, he has also got me back in the laboratory doing research. Earlier this year, I published my first technical paper in the peer-reviewed literature since 1993… back to the future.

# Author biography

## Jeffrey Huw Williams

Jeffrey Huw Williams was born in Swansea, Wales, on 13 April 1956, and gained a PhD in chemical physics from Cambridge University in 1981.

Subsequently, his career as a research scientist was in the physical sciences. First, as a research scientist in the universities of Cambridge, Oxford, Harvard and Illinois, and subsequently as an experimental physicist at the Institute Laue-Langevin, Grenoble, which still remains one of the world's leading centres for research involving neutrons; particularly, neutron scattering. During this research career, he published more than sixty technical papers and invited review articles in the peer-reviewed literature. However, after much thought he left research in 1992 and moved to the world of science publishing and the communication of science by becoming the European editor for the physical sciences for the AAAS's *Science*.

Subsequently, he was Assistant Executive Secretary of the International Union of Pure and Applied Chemistry; the agency responsible for the world-wide advancement of chemistry through international collaboration. Most recently, 2003–2008, he was the head of publications at the *Bureau international des poids et mesures* (BIPM), Sèvres. The BIPM is charged by the Metre Convention of 1875 with ensuring world-wide uniformity of measurements, and their traceability to the International System of Units (SI). It was during these years at the BIPM that he became interested in, and familiar with the origin of the Metric System, its subsequent evolution into the SI, and the coming transformation into the Quantum-SI.

Since retiring, he has devoted himself to writing; in 2014, he published *Defining and Measuring Nature: The make of all things* in the IOP Concise Physics series. This publication outlined the coming changes to the definitions of several of the base units of the SI, and the evolution of the SI into the Quantum-SI. In 2015, he published *Order from Force: A natural history of the vacuum* in the IOP Concise Physics series. This title looks at intermolecular forces, but also explores how ordered structures, whether they are galaxies or crystalline solids, arise via the application of a force. Then in 2016, he published *Quantifying Measurement: The tyranny of number*, again the IOP Concise Physics series. This title is intended to explain the concepts essential in an understanding of the origins of measurement uncertainty. No matter how well an experiment is done, there is always an uncertainty associated with the final result—something that is often forgotten.

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# Chapter 1

## Holding things together

The chemical bond is the heart of chemistry. If we can understand what holds atoms together in molecules, we may begin to understand why, under certain conditions, existing arrangements of atoms may change to become different arrangements; that is, to understand the basis of chemical transformation. And if we understand molecular structure, we may hope to identify the mechanism of chemical change. In addition, if the structure and bonding of molecules is understood, one may also attempt to model the non-bonding interactions that arise between molecules, and which are responsible for condensed phases.

All this is, of course, a tall order; so let us first simplify things. In quantum chemistry and molecular physics, the Born–Oppenheimer (BO) approximation is the assumption that the motion, or dynamics of the atomic nuclei and the electrons in a molecule can be separated. It is the means by which a meaningful approach can be made to using quantum mechanics to explain molecular phenomena. The approach is named after the German physicist and one of the originators of quantum mechanics Max Born (1882–1970) and one of his doctoral students, the American physicist and 'father of the atom bomb' J Robert Oppenheimer (1904–1967). In mathematical terms, the BO approximation allows the wavefunction of a molecule to be factorized into its electronic and nuclear (that is, vibrational, rotational and translational) components,

$$\Psi_{\text{molecule}} = \psi_{\text{electronic}} \times \psi_{\text{nuclear.}}$$

Computation of the energy and the wavefunction of an average-size molecule is simplified by this approximation; for example, the benzene molecule consists of 12 nuclei and 42 electrons. The time-independent Schrödinger equation, which must be solved to obtain the energy and wavefunction of this molecule ($\Psi_{\text{molecule}}$), is a partial differential eigenvalue equation in 162 (3 × 54) variables; the spatial coordinates of the electrons and the nuclei. The BO approximation makes it possible to compute the wavefunction in two, less complicated consecutive steps. This approximation

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was proposed in 1927, in the glory days of quantum mechanics and is still indispensable in quantum chemistry. The success of the BO approximation is due to the significant difference between nuclear and electronic masses[1].

## 1.1 Covalent bonds

A covalent bond is a chemical bond that involves the sharing of electron pairs between atoms. Where each atom contributes one electron to the intervening covalent bond. For many molecules, the sharing of electrons to form covalent bonds allows each atom to attain the equivalent of a full outer shell of electrons; this being a stable electronic configuration. The term *covalent bond* dates from the 1930s, and the prefix co-signifies shared or partnered; thus a co-valent bond means that the atoms share valence electrons; that is, electrons in the outer-most atomic orbitals.

In the simplest of all stable molecules, $H_2$, the hydrogen atoms share the two electrons via a single covalent bond. However, covalent bonding does not necessarily require that the two atoms be of the same element, only that they have a comparable capacity for pulling electrons to themselves; that is, a comparable electronegativity (a heuristic atomic quantity devised by the Swedish chemist Jöns Jacob Berzelius (1779–1848), and put on a quantitative basis in 1932 by the American chemist Linus Pauling (1901–1994).

The idea of covalent bonding can be traced back to Gilbert N Lewis (1875–1946), who in 1916 first described the sharing of electron pairs between atoms. He introduced the Lewis notation in which valence electrons are represented as dots around the atomic symbols in a chemical formula. Pairs of electrons located between atoms representing covalent bonds, and multiple pairs representing multiple bonds, such as double bonds and triple bonds. Lewis proposed that an atom forms enough covalent bonds so as to form a full (or closed) outer electron shell. In the covalent bonding seen in methane ($CH_4$), for example, the carbon atom has a valence of four and is, therefore, surrounded by eight electrons; four from the carbon atom and four from the four hydrogen atoms to which it is bonded. Each hydrogen atom has a valence of one and is surrounded by two electrons; that is, its own $1s^1$ electron plus one electron from the carbon.

Atomic orbitals (except *s*-orbitals, which are spherically symmetric) have specific directional properties leading to different types of covalent bonds when they overlap with similar orbitals on other atoms. Covalent bonding includes many kinds of orbital interactions that lead to variations of a simple covalent bond. For example, atomic *s*-orbitals can form a covalent bond, as can atoms with single electron in a *p*-orbital. But if there are three electrons in an atom's *p*-orbitals, there is the possibility of $\sigma$-bonding and $\pi$-bonding in a bonded homonuclear pair; these interactions lead to single, double or even triple covalent bonds as in: ethane (a single $\sigma$ covalent C–C bond), ethylene (a $\sigma$ covalent C–C bond and a single $\pi$ covalent C–C bond) and acetylene (a $\sigma$ covalent C–C bond and two $\pi$ covalent C–C bonds).

---

[1] A factor, of order, 1833; the ratio of the mass of the proton to the mass of the electron.

Covalent bonds are also affected by the relative electronegativities of the bonded atoms, which determines the chemical polarity of the bond. Two atoms with equal electronegativity will form a non-polar covalent bond; for example, $H_2$, $N_2$, and $O_2$. An unequal electronegativity creates a polar covalent bond such as HF and CO. Such heteropolar bonds lead to the presence of electric dipole moments in the molecule; that is, there is a difference between the centre of the distributions of positive and of negative charge within the molecule. However, a permanent molecular polarity also requires geometric asymmetry, or else the dipoles may cancel out resulting in a non-polar molecule; as in benzene, where the vector sum of the six bond dipole moments is zero.

There are an enormous range of structures that may be generated using covalent bonds, including molecules that are stable in both the gaseous and condensed phases. Yet, even if individual molecules are made up of covalently bound atoms and even when they have an asymmetry of charge, there are only weak interactions between the individual molecules. For example, a typical bond energy (the energy required to break a covalent bond, or the energy liberated when such a bond forms) for a C–H covalent bond is large at 439 $\mathrm{kJmol^{-1}}$ in methane, but a material like methane is a gas at room temperature as there are only weak interactions between the individual molecules; and benzene, which contains six strong C–C bonds (each with a strength of about 350 $\mathrm{kJ\ mol^{-1}}$) and six strong C–H bonds is a volatile liquid at room temperature. Thus, molecules made up of covalent bonds retain their individuality in the condensed phase.

## 1.2 Ionic bonds

Ionic bonding involves the electrostatic attraction between oppositely charged ions, and is the primary interaction occurring in ionic compounds. The ions are atoms that have either gained one or more electrons (anions, which are negatively charged), or atoms that have lost one or more electrons (cations, which are positively charged). This transfer of electrons is known as electrovalence in contrast to covalence. In the simplest case, the cation is a metal atom and the anion is a non-metal atom, but ions can be of a more complex nature; for example, molecular ions like $NH_4^+$ or $SO_4^{2-}$. Again, we may think of an ionic bond as the transfer of electrons from one atom to another atom so as to allow both atoms to obtain a full valence shell.

Ionic compounds reveal their ionic character by being able to conduct electricity when molten, or in aqueous solution. And because of the very powerful electrostatic forces generated over molecular dimensions by a transferred electron, ionic compounds generally have a high melting point, depending upon the charge of the ions present. The higher the electric charge ($Na^+$, $Ca^{2+}$, $Al^{3+}$) present on the constituent ions, the stronger the cohesive forces that bind the ions together, and the higher the melting point. This also makes such materials soluble in water, as the electric dipole moments of the water molecules are strongly attracted to the electrically-charged ions.

Ionic compounds in the solid-state are able to form giant lattice structures, built up of repeated subunits. The two principal factors in determining the form of the lattice are the relative charges of the ions and their relative sizes. Some structures are adopted by a number of compounds; for example, the structure of rock-salt, or sodium chloride is also adopted by many other alkali metal halides and binary oxides such as MgO. Linus Pauling formulated heuristic rules, by examining a vast number of materials, to provide guidelines for predicting and rationalizing the crystal structures of ionic crystals.

Ions in lattices of ionic compounds are spherical; however, if the positive ion is small and/or highly charged, it will distort the electron cloud of neighbouring negative ions, an effect summarised in Fajans' rules of 1923 (named for the Polish chemist Kazimierz Fajans). This polarization of the negative ion leads to a build-up of extra charge density between the two nuclei; that is, to a partial covalency. Larger negative ions are more easily polarized, but the effect is usually important only when cations with charges of 3+ are involved. However, 2+ ions and even 1+ show some polarizing power when their sizes are small; for example, $BeF_2$ is mostly covalent, and LiI is more ionic but has a significant covalency.

## 1.3 Comparison of ionic and covalent bonding

In ionic bonding, electrically-charged atoms are bound by the electrostatic attraction of oppositely-charged ions, whereas, in covalent bonding, atoms are bound together by the sharing of electrons to attain stable configurations of electrons. In covalent bonding, the molecular geometry around each atom is determined by valence shell electron pair repulsion rules (VSEPR), whereas, in ionic materials, the geometry follows maximum packing rules (the most effective way of packing pairs of charged-particles into a solid framework). One could say that covalent bonding is more directional in the sense that the energy penalty for not adhering to the optimum bond angles is large, whereas ionic bonding has no such penalty. In ionic solids there are no shared electron pairs to repel each other; the ions should simply be packed as efficiently as possible to maximize electrostatic attraction and to minimize electrostatic repulsion. This often leads to much higher coordination numbers; in NaCl, each ion has six ionic bonds and all the bond angles are 90 degrees; that is, octahedral coordination. In CsCl, because the $Cs^+$ ion is much bigger than $Na^+$, the coordination number is 8. By comparison, carbon forms a maximum of four bonds and they are disposed tetrahedrally.

Purely ionic bonding cannot exist, as the proximity of the entities involved in the bonding allows some degree of the sharing of the electron density between them. Therefore, all ionic bonding has some covalent character. The larger the difference in electronegativity between the two atoms involved in the bonding, the more ionic (polar) it is. In general, when ionic bonding occurs in the solid state, it is not possible to speak about a single ionic bond between two individual atoms, because the cohesive forces that keep the lattice together are of a more collective nature. This is quite different in the case of covalent bonding, where we can often speak of a distinct bond localized between two particular atoms, oriented in a particular direction.

## 1.4 Non-bonding interactions

Non-polar molecules (including closed-shell atoms, such as neon and argon) attract one another even though the interacting molecules do not possess permanent dipole moments, as demonstrated by the condensation of these materials. The interaction between non-polar molecules arises from the transient dipoles that all atoms and molecules possess as a consequence of fluctuations in the instantaneous positions of the electrons found in those molecules. To appreciate the origin of this purely quantum mechanical interaction, suppose that the electrons in one molecule instantly move into an arrangement that gives the molecule an instantaneous, or fluctuating dipole moment $\mu_1$. This dipole generates an electric field that polarizes a neighbouring molecule, and induces in that molecule an instantaneous dipole moment $\mu_2$. The two dipoles attract each other and the potential energy of the pair is lowered. This interaction is often termed the dispersion interaction, or the London interaction (for Fritz London).

Polar molecules also interact by a dispersion interaction. However, as such molecules possess a permanent dipole moment, it is this intermolecular interaction that will dominate over the instantaneous dispersion interaction. Consequently, the interaction between two water molecules will be dominated by the electrostatic interaction of the large permanent electric dipole moments, but the interaction of two argon atoms will consist only of the dispersion interaction (the boiling point of argon is 87 K, and that of water is 373 K).

## 1.5 Hydrogen bonding

The dispersion interaction is universal in that it is exhibited by all molecules. However, there is a type of interaction possessed by molecules that have a particular chemical constitution. A hydrogen bond is an attractive interaction between two species that arises from a link (···) of the form A–H···B, where A and B are strongly electronegative elements and B possesses a lone pair of electrons. Hydrogen bonding is conventionally regarded as being limited to N, O, and F but, if B is an anionic species (such as $Cl^-$), it may also participate in hydrogen bonding. A hydrogen atom attached to a carbon atom can also participate in hydrogen bonding when the carbon atom is bound to electronegative atoms, as is the case in chloroform, $H–CCl_3$ (this point will be considered later with regard to the interaction between C–F and C–H bonds; that is C–F···H–C).

In a hydrogen bond, the electronegative atom not covalently attached to the hydrogen is termed the proton acceptor, whereas the atom covalently bound to the hydrogen is termed the proton donor. In the donor molecule, the electronegative atom attracts the electron density from around the hydrogen nucleus of the donor group, and leaves the atom with a positive partial-charge. Because of the small size of hydrogen relative to other atoms, the resulting charge, though only partial, represents a significant charge density. A hydrogen bond results when this strong positive charge-density attracts a lone pair of electrons on another atom, which then becomes the hydrogen-bond acceptor.

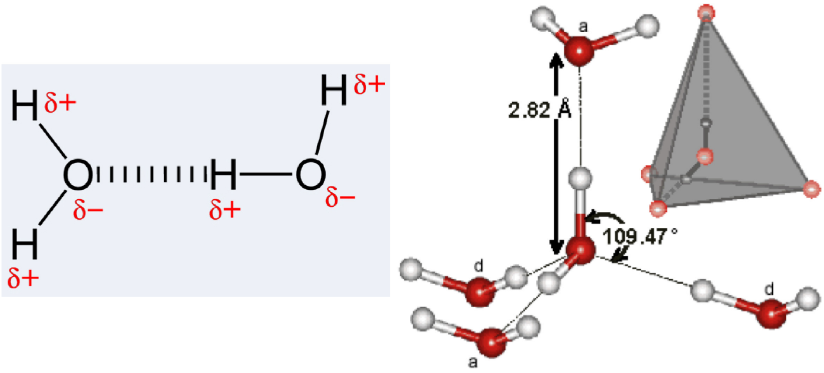

**Figure 1.1.** Some of the features of a ‘classic’ strong hydrogen bond as exemplified in liquid water and ice.

The hydrogen bond is sometimes described as an electrostatic dipole–dipole interaction; however, when we are speaking of strong hydrogen bonds it also has some features of covalent bonding; it is directional and can be strong, produces interatomic distances shorter than the sum of the van der Waals radii, and usually involves a limited number of interaction partners, which can be interpreted as a type of valence. These covalent features are more substantial when acceptors bind hydrogen atoms shared with more electronegative donors.

The partially covalent nature of a hydrogen bond raises a question as to which molecule or atom does the hydrogen nucleus belong, and which moiety should be labelled donor and which acceptor? Usually, this is clearly seen on the basis of interatomic distances in the X–H···Y system, where the dots represent the hydrogen bond: the X–H distance is typically 1.1 Å, whereas the H···Y distance is between 1.6 and 2.0 Å. Liquids that display strong hydrogen bonding, such as the archetype water, are termed associated liquids. Figure 1.1, give the classic features of hydrogen bonds, as seen in water.

Hydrogen bonds can vary greatly in strength; from weak (1–2 kJ $mol^{-1}$) to strong (161.5 kJ $mol^{-1}$ in the ion $HF_2^-$. Some typical values are: F–H···F (161.5 kJ $mol^{-1}$), O–H···N (29 kJ $mol^{-1}$), O–H···O (21 kJ $mol^{-1}$), N–H···N (13 kJ $mol^{-1}$) and N–H···O (8 kJ $mol^{-1}$).

The length of hydrogen bonds depends on bond strength, temperature, and pressure. The bond strength itself is dependent on temperature, pressure, bond angle, and environment (usually characterized by local dielectric constant). The typical length of a hydrogen bond in water is 1.97 Å. The ideal bond angle depends on the nature of the hydrogen bond donor[2].

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[2] In the gas-state, high-resolution microwave spectroscopy of molecular dimers gives a value of 2.14 Å between the oxygen atom of $CO_2$ and the hydrogen atom of HCl in the linear hydrogen-bonded dimer O–C–O···H–Cl, and a distance of 3.17 Å between the plane of the benzene molecule and the fluorine of HF in the symmetric-top dimer benzene:HF where the hydrogen of the HF is pointing towards the centre-of-mass of the benzene ring.

## 1.6 Hybrid atomic orbitals and the shape of molecules

One of the more emblematic images in the Zodiac is the Centaur; a hybrid animal having the head, arms and torso of a man on the body and legs of a horse. The application of quantum mechanics to chemistry with a view to explaining the bonding and the shape of molecules also contains such hybrids. In quantum chemistry, one mixes atomic orbitals that have been hybridized in the same way that the Ancient Greeks mixed humans and animals to create hybrid mythological species. But whereas hybridizing and mixing orbitals to explain molecular structure is a much more recent myth than that of the Centaurs, it is still only an attempt to explain reality. There is no fully functioning quantum model of chemical bonding and of chemical structure; there are only approximate, hybrid methods.

The atomic orbitals needed to explain bonding in polyatomic systems need not necessarily be pure atomic orbitals; that is purely *s*-orbitals or purely *p*-orbits. Often, the bonding atomic orbitals have a character consisting of several types of atomic orbitals. Using quantum mechanical methods to combine the wavefunctions of atomic orbitals to construct new hybrid orbitals, more suitable to describe the bonding in molecules, is termed hybridization of atomic orbitals. For example, *sp* hybrid atomic orbitals are possible states of an electron in an atom, especially when it is bonded to other atoms. These electron states have, for example, half the character of 2*s* and half of 2*p* orbitals, and there are two ways to combine the 2*s* and 2*p* atomic orbitals: $sp(1) = 2s + 2p$ or $sp(2) = 2s - 2p$.

These energy states, *sp*(1) and *sp*(2), each have a region of high electron probability, and the two atomic orbitals are located opposite to each other, centered on the atom. For example, the molecule H–Be–H is formed by the overlapping of two 1*s* orbitals from two H atoms and the two *sp* hybridized orbitals of Be. The H–Be–H molecule is linear, as is the isolated (gas-phase) F–Be–F molecule. The unhybridized electronic configuration of Be is $1s^2 2s^2$, and one may think of the electronic configuration upon hybridization (before bonding) as $1s^2 sp^2$. The two electrons in the new *sp* hybrid orbitals having the same energy as the unhybridized configuration.

In general, when two and only two atoms bond to a third atom and the third atom makes use of *sp* hybridized orbitals, the three atoms form a linear molecule; for example, *sp* hybrid orbitals are invoked to explain the shape of linear molecules such as F–Be–F, HCCH, HCN and O=C=O.

For $sp^2$ hybrid orbitals, the energy states of the valence electrons in atoms of the second period are in the 2*s* and 2*p* orbitals. If we mix two of the 2*p* orbitals with a 2*s* orbital, we generate three $sp^2$ hybrid orbitals. These three orbitals lie on a plane pointing to the vertices of an equilateral triangle; for example, $BF_3$, and the carbonate anion $CO_3^{2-}$. However, not all three $sp^2$ hybridized orbitals have to be used in bonding. One of the orbitals may be occupied by a pair of, or by a single electron. And these molecules are bent rather than linear; for example, $SO_2$.

Carbon is famously capable of generating four $sp^3$ hybrid orbitals and these are directed to the vertices of a regular tetrahedron, thus explaining a great deal of organic chemistry. Carbon atoms also makes use of the $sp^2$ hybrid orbitals in ethylene (also known as ethene), $H_2C{=}CH_2$. Here, the remaining *p*-orbital from each of the carbon overlap sideways to form an additional $\pi$-bond. As in the situation of $sp^2$ hybrid orbitals, one or two of the $sp^3$ hybrid orbitals may be occupied by non-bonding electrons; as in water and ammonia. The C, N and O atoms in $CH_4$, $NH_3$, $H_2O$ molecules use the $sp^3$ hybrid orbitals, however, a lone pair occupies one of the orbitals in $NH_3$, and two lone pairs occupy two of the $sp^3$ hybrid orbitals in $H_2O$. And there is electrostatic repulsion between these bonding and lone pairs of electrons, which is invoked to explain the shape of the molecules.

For $sp^3d$ hybrid orbitals, five hybrid orbitals formed when one 3*d*, one 3*s*, and three 3*p* atomic orbitals are mixed. When an atom makes use of five $dsp^3$ hybrid orbitals to bond to five other atoms, the geometry of the molecule is often a trigonal bipyramid; for example, the molecule $PClF_4$. In this molecule, the Cl atom takes up an axial position of the trigonal bipyramid. There are also structures in which the Cl atom may take up the equatorial position. The change in arrangement is accomplished by simply changing the bond angles. Again, some of the $dsp^3$ hybrid orbitals may be occupied by electron pairs.

The six $d^2sp^3$ hybrid orbitals result when two 3*d*, one 3*s*, and three 3*p* atomic orbitals are mixed. When an atom makes use of six $d^2sp^3$ hybrid orbitals to bond to six other atoms, the molecule takes the shape of an octahedron, as in $SF_6$. There are also cases that some of the $d^2sp^3$ hybrid orbitals are occupied by lone pair electrons.

## Further reading

For a general consideration of chemical bonding, there is no better source than the classic text by Peter W Atkins and Julio de Paula, *Physical Chemistry* (9th edition, 2010) Oxford University Press. For those readers seeking a more theoretical approach to the subject; particularly concerning the observed shapes of molecules, I recommend Peter W Atkins and Ronald Friedman, *Molecular Quantum Mechanics* (4th edition, 2005) Oxford University Press.

# Full list of references

## Chapter 1

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