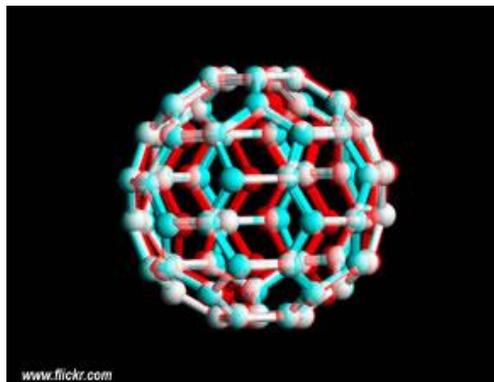


Chemistry Topics

Chemical Bond

A **chemical bond** is the PHYSICAL process responsible for the ATTRACTIVE “INTERACTIONS” between atoms and molecules, and that which confers stability to diatomic and polyatomic chemical compounds. The explanation of the attractive forces is a complex area that is described by the laws of quantum



electrodynamics. In practice, however, chemists usually rely on quantum theory or qualitative descriptions that are less rigorous but more easily explained to describe chemical bonding. In general, strong chemical bonding is associated with the sharing or transfer of electrons between the participating atoms. Molecules, crystals, and diatomic gases - indeed most of the physical environment around us - are held together by chemical bonds, which dictate the structure of matter.

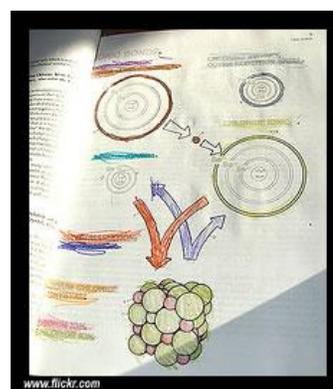
Bonds vary widely in their strength. Weak interactions between atoms and molecules can arise from induced polarity (such as London forces) between the electron clouds. Generally covalent and ionic bonds are often described as strong, whereas hydrogen bonds and van der Waals are generally considered to be weaker. Care should be taken because the strongest of the weak cases can be stronger than the weakest of the “strong” bonds.

Overview

Remembering that opposite forces attract and that the electrons orbiting the nucleus are negatively charged and protons in the nucleus are positively charged, then imagine two atoms near each other which form a covalent bond.

In the simplest view of a so-called *covalent* bond, one or more electrons - often a pair as in this example - is drawn into the space between the two atomic nuclei. Here the negatively charged electrons are attracted to the positive charges of *both* nuclei, instead of just their own. This overcomes the repulsion between the two positively charged nuclei of the two atoms and so this overwhelming attraction holds the two nuclei in a relatively fixed configuration of equilibrium, even though they will still vibrate about that equilibrium position. In summary, covalent bonding involves sharing of electrons in which the positively charged nuclei of two or more atoms simultaneously attract the negatively charged electrons that are being shared.

In a simplified view of an *ionic* bond, the positive charge of one of the nuclei overwhelms the positive charge of the other nucleus, thus effectively transferring an electron from one atom to another, causing one atom to assume a net positive charge, and the other to assume a net negative charge. The *bond* then results from electrostatic attraction between atoms, and the atoms become positive or negatively charged ions. All bonds can be explained by quantum theory, but in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic



orbitals molecular orbital method which includes ligand field theory. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

History

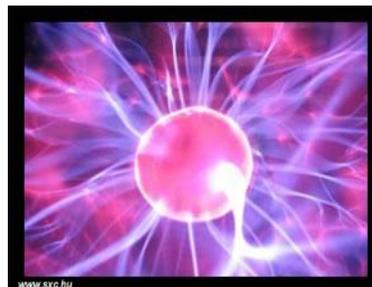
Early speculations into the nature of the **chemical bond**, from as early as the 12th century, supposed that certain types of chemical species were joined by a type of chemical affinity. In 1704, Issac Newton famously outlined his atomic bonding theory, in “Query 31” of his Opticks, whereby atoms attach to each other by some “force”. Specifically, after acknowledging the various popular theories, in vogue at the time, of how atoms were reasoned to attach to each other, i.e. “hooked atoms”, “glued together by rest”, or “stuck together by conspiring motions”, Newton states that he would rather infer from their cohesion, that:

Particles attract one another by some force, which in immediate contact is exceedingly strong, at small distances performs the chemical operations, and reaches not far from the particles with any sensible effect.

In 1819, on the heels of the invention of the voltaic pile, Berzelius developed a theory of chemical combination stressing the electronegative and electropositive character of the combining atoms. By the mid 19th century, Edward Frankland, F.A. Kekule, A.S. Couper, A.M. Butlerov, and Hermann Kolbe, building on the theory of radicals, developed the theory of valency, originally called “combining power”, in which compounds were joined owing to an attraction of positive and negative poles. In 1916, chemist Gilbert Lewis developed the concept of the electron-pair bond, in which two atoms may share one to six electrons, thus forming the single electron bond, a single bond, a double bond, or a triple bond:

In Lewis' own words:

“An electron may form a part of the shell of two different atoms and cannot be said to belong to either one exclusively”.



That same year, Walther Kossel put forward a theory similar to Lewis' only his model assumed complete transfers of electrons between atoms, and was thus a model of polar bonds. Both Lewis and Kossel structured their bonding models on that of Abegg's rule (1904).

In 1927, the first mathematically complete quantum description of a simple chemical bond, i.e. that produced by one electron in the hydrogen molecular ion, H_2^+ , was derived by the Danish physicist Oyvind Burrau. This work showed that the quantum approach to chemical bonds could be fundamentally and quantitatively correct, but the mathematical methods used could not be extended to molecules containing more than one electron. A more practical, albeit less quantitative, approach was put forward in the same year by Walter Heitler and Fritz London. The Heitler-London method forms the basis of what is now called valence bond theory. In 1929, the linear combination of atomic orbitals molecular orbital method (LCAO) approximation was introduced by Sir John Lennard-Jones, who also suggested methods to derive electronic structures of molecules of F_2 (fluorine) and O_2 (oxygen) molecules, from basic quantum principles. This molecular orbital theory represented a covalent bond as a orbitals formed by combining the quantum mechanical Schrödinger atomic orbitals which had been hypothesized for electrons in single atoms. The equations for bonding electrons in multi-electron atoms could

not be solved to mathematical perfection (i.e., *analytically*), but approximations for them still gave many good qualitative predictions and results. Most quantitative calculations in modern quantum chemistry use either valence bond or molecular orbital theory as a starting point, although a third approach, Density Functional Theory, has become increasingly popular in recent years.

In 1935, H. H. James and A. S. Coolidge carried out a calculation on the dihydrogen molecule that, unlike all previous calculation which used functions only of the distance of the electron from the atomic nucleus, used functions which also explicitly added the distance between the two electrons. With up to 13 adjustable parameters they obtained a result very close to the experimental result for the dissociation energy. Later extensions have used up to 54 parameters and give excellent agreement with experiment. This calculation convinced the scientific community that quantum theory could give agreement with experiment. However this approach has none of the physical pictures of the valence bond and molecular orbital theories and is difficult to extend to larger molecules.

Valence Bond Theory

In 1927, valence bond theory was formulated which argued essentially that a chemical bond forms when two valence electrons, in their respective atomic orbitals, work or function to hold two nuclei together, by virtue of system energy lowering effects. In 1931, building on this theory, chemist Linus Pauling published what some consider one of the most important papers in the history of chemistry: “On the Nature of the Chemical Bond”. In this paper, building on the works of Lewis, and the valence bond

Courtesy of Wikipedia



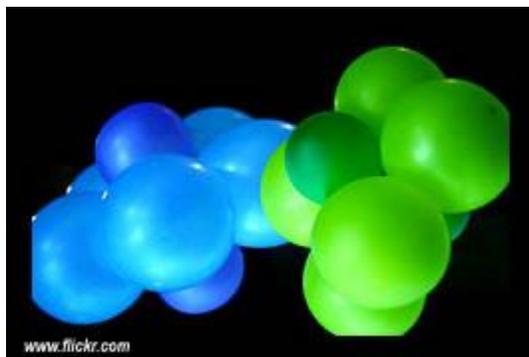
theory (VB) of Heitler and London, and his own earlier work, he presented six rules for the shared electron bond, the first three of which were already generally known:

1. The electron-pair bond forms through the interaction of an unpaired electron on each of two atoms.
2. The spins of the electrons have to be opposed.
3. Once paired, the two electrons cannot take part in additional bonds.
4. His last three rules were new:
5. The electron-exchange terms for the bond involves only one wave function from each atom.
6. The available electrons in the lowest energy level form the strongest bonds.
7. Of two orbitals in an atom, the one that can overlap the most with an orbital from another atom will form the strongest bond, and this bond will tend to lie in the direction of the concentrated orbital.

Building on this article, Pauling's 1939 textbook: *On the Nature of the Chemical Bond* would become what some have called the "bible" of modern chemistry. This book helped experimental chemists to understand the impact of quantum theory on chemistry. However, the later edition in 1959 failed to address adequately the problems that appeared to be better understood by molecular orbital theory. The impact of valence theory declined during the 1960's and 1970's as molecular orbital theory grew in popularity and was implemented in many large computer programs. Since the 1980s, the more difficult problems of implementing valence bond theory into computer programs have been largely solved and valence bond theory has seen a resurgence.

Molecular Orbital Theory

Molecular orbital theory (MO) uses a linear combination of atomic orbitals to form molecular orbitals which cover the whole molecule. These are often divided into bonding orbitals, anti-bonding orbitals, and non-bonding orbitals. A molecular orbital is merely a Schrödinger orbital



which includes several, but often only two nuclei. If this orbital is of type in which the electron(s) in the orbital have a higher probability of being *between* nuclei than elsewhere, the orbital will be a bonding orbital, and will tend to hold the nuclei together. If

the electrons tend to be present in a molecular orbital in which they spend more time elsewhere than between the nuclei, the orbital will function as an anti-bonding orbital and will actually weaken the bond. Electrons in non-bonding orbitals tend to be in deep orbitals (nearly atomic orbitals) associated almost entirely with one nucleus or the other, and thus they spend equal time between nuclei or not. These electrons neither contribute nor detract from bond strength.

Comparison of Valence Bond and Molecular Orbital Theory

In some respects valence bond theory is superior to molecular orbital theory. When applied to the simplest two-electron molecule, H_2 , valence bond theory, even at the simplest Heitler-London approach, gives a much closer approximation to the bond energy, and it provides a much more accurate representation of the behavior of the electrons as chemical bonds are formed and broken. In contrast simple molecular orbital theory predicts that the hydrogen molecule dissociates into a linear superposition of hydrogen atoms and positive and negative hydrogen

ions, a completely unphysical result. This explains in part why the curve of total energy against interatomic distance for the valence bond method lies above the curve for the molecular orbital method at all distances and most particularly so for large distances. This situation arises for all homonuclear diatomic molecules and is particularly a problem for F_2 , where the minimum energy of the curve with molecular orbital theory is still higher in energy than the energy of two F atoms.

The concepts of hybridization are so versatile, and the variability in bonding in most organic compounds is so modest, that valence bond theory remains an integral part of the vocabulary of organic chemistry. However, the work of Friedrich Hund, Robert Mulliken, and Gerhard Herzberg showed that molecular orbital theory provided a more appropriate description of the spectroscopic, ionization and magnetic properties of molecules. The deficiencies of valence bond theory became apparent when hypervalent molecules (e.g. PF_5) were explained without the use of d orbitals that were crucial to the bonding hybridisation scheme proposed for such molecules by Pauling. Metal complexes and electron deficient compounds (e.g. diborane) also appeared to be well described by molecular orbital theory, although valence bond descriptions have been made.

In the 1930s the two methods strongly competed until it was realised that they are both approximations to a better theory. If we take the simple valence bond structure and mix in all possible covalent and ionic structures arising from a particular set of atomic orbitals, we reach what is called the full configuration interaction wave function. If we take the simple molecular orbital description of the ground state and combine that function with the functions describing all

possible excited states using unoccupied orbitals arising from the same set of atomic orbitals, we also reach the full configuration interaction wavefunction. It can be then seen that the simple molecular orbital approach gives too much weight to the ionic structures, while the simple valence bond approach gives too little. This can also be described as saying that the molecular



orbital approach is too *delocalised*, while the valence bond approach is too *localised*.

The two approaches are now regarded as complementary, each providing its own insights into the problem of chemical bonding. Modern calculations in quantum chemistry usually start from (but ultimately go far beyond) a molecular orbital rather than a valence bond approach, not because of any intrinsic superiority in

the former but rather because the MO approach is more readily adapted to numerical computations. However better valence bond programs are now available.

Bonds in Chemical Formulas

The 3-dimensionality of atoms and molecules makes it difficult to use a single technique for indicating orbitals and bonds. In **molecular formulas** the chemical bonds (binding orbitals) between atoms are indicated by various different methods according to the type of discussion. Sometimes, they are completely neglected. For example, in organic chemistry chemists are sometimes concerned only with the functional groups of the molecule. Thus, the molecular formula of ethanol (a compound in alcoholic beverages) may be written in a paper in conformational, 3-dimensional, full 2-dimensional (indicating every bond with no 3-dimensional

directions), compressed 2-dimensional ($\text{CH}_3\text{-CH}_2\text{-OH}$), separating the functional group from another part of the molecule ($\text{C}_2\text{H}_5\text{OH}$), or by its atomic constituents ($\text{C}_2\text{H}_6\text{O}$), according to what is discussed. Sometimes, even the non-bonding valence shell electrons (with the 2-dimensionalized approximate directions) are marked, f.e. for elemental carbon $\cdot\text{C}\cdot$. Some chemists may also mark the respective orbitals, f.e. the hypothetical ethene⁻⁴ anion ($\langle\text{C}=\text{C}\rangle^{-4}$) indicating the possibility of bond formation.

Strong Chemical Bonds

These chemical bonds are *intramolecular* forces, which hold atoms together in molecules. In the simplistic localized view of bonding, the number of electrons participating in a bond (or located in a bonding orbital) is typically multiples of two, four, or six, respectively. Even numbers are common because electrons enjoy lower energy states, if paired. Substantially more advanced bonding theories have shown that bond strength is not always a whole number, depending on the distribution of electrons to each atom involved in a bond. For example, the carbons in benzene are connected to each other with about 1.5 bonds, and the two atoms in nitric oxide NO, are connected with about 2.5 bonds. Quadruple bonds are also well known. The type of strong bond depends on the difference in electronegativity and the distribution of the electron orbital paths available to the atoms that are bonded. The larger the difference in electronegativity, the more an electron is attracted to a particular atom involved in the bond, and the more “ionic” properties the bond is said to have (“ionic” means the bond electron(s) are unequally shared). The smaller the difference in electronegativity, the more covalent properties (full sharing) the bond has.

Covalent Bond

Covalent bonding is a common type of bonding, in which the electronegativity difference between the bonded atoms is small or non-existent. Bonds within most organic compounds are described as covalent. See sigma bonds and pi bonds for LCAO-description of such bonding.

Ionic Bond

Ionic bonding is a type of electrostatic interaction between atoms which have an electronegativity difference of over 1.6 (this limit is a convention). These form in a solution between two ions after the excess of the solvent is removed. Ionic charges are commonly between $-3e$ to $+7e$



Other Strong Bonds

Coordinate Covalent Bond

Coordinate covalent bonding, sometimes referred to as dative bonding, is a kind of covalent bonding, in which the covalent bonding electrons originate solely from one of the atoms, the electron-pair donor or Lewis base but are approximately equally shared in the formation of a covalent bond. This concept is somewhat fading as chemists increasingly embrace molecular orbital theory. Examples of coordinate covalent bonding occur in nitrones and ammonia borane. The arrangement is different from an ionic bond in that the electronegativity difference is small, resulting in covalency.

Banana Bond

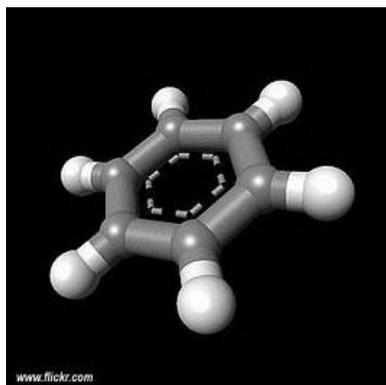
The Banana bond is a kind of bonding in which the bond bends, often due to the presence of an influencing atom in the middle of another covalent bond. These bonds are likely to be more

susceptible to reactions than ordinary bonds. An example can be found in diborane, where the bonds between boron atoms are known as “three center, two-electron bonds”. Each such bond (2 per molecule in diborane) contains a pair of electrons which connect the boron atoms to each other in a banana shape, with a proton (nucleus of a hydrogen atom) in the middle of the bond, sharing electrons with both boron atoms.

Chemical Bonds Involving More Than Two Atoms

Aromatic Bond

In most cases, the locations of electrons cannot be simplified to simple lines (place for two electrons) or dots (a single electron). In aromatic bonds which occur in rings of atoms where the $4n+2$ rule determines whether ring molecules comprised of C=C bonds would show behavior extra stability by allowing extra sharing of electrons below and above the ring plane.



In benzene, the prototypical aromatic compound, 18 bonding electrons bind 6 carbon atoms together to form a planar ring structure. The bond “order” (average number of bonds) between the different carbon atoms may be said to be $(18/6)/2=1.5$, but in this case the bonds are all identical from the chemical point of view. They may sometimes be written as single bonds alternating with double bonds, but the view of all ring bonds as being equivalently about 1.5 bonds in strength, is much closer to truth.

In the case of heterocyclic aromatics and substituted benzenes, the electronegativity differences between different parts of the ring may dominate the chemical behaviour of aromatic ring bonds, which otherwise are equivalent.

Metallic Bond

In a metallic bond, bonding electrons are delocalized over a lattice of atoms. By contrast, in ionic compounds, the locations of the binding electrons and their charges are static.



Intermolecular Bonding

There are four basic types of bonds that can be formed between two or more (otherwise non-associated) molecules, ions or atoms.

Permanent Dipole to Permanent Dipole

A large electronegativity difference between two strongly bonded atoms within a molecule causes a dipole to form (a dipole is a pair of permanent partial charges). Dipoles will attract or repel each other.

Hydrogen Bond

In some ways this is an especially strong example of a permanent dipole bond, as above. However, in the hydrogen bond, the hydrogen proton comes closer to being shared between target and donor atoms, in a three-center two-electron bond like that in diborane. Hydrogen

bonds explain the relatively high boiling points of liquids like water, ammonia, and hydrogen fluoride, compared with their heavier counterparts in the same periodic table column.

Instantaneous Dipole to Induced Dipole (van der Waals)

Instantaneous dipole to induced dipole, or van der Waals forces, are the weakest, but also the most prolific - occurring between **all** chemical substances. Imagine a helium atom: At any one point in time, the electron cloud around the - otherwise-neutral - atom can be thought to be slightly imbalanced, with momentarily more negative charge on one side. This is referred to as an instantaneous dipole. This dipole, with its slight charge imbalance, may attract or repel the electrons within a neighbouring helium atom, setting up another dipole. The two atoms will be attracted for an instant, before the charge rebalances and the atoms move on.

Additional Topics

Cation-pi Interaction

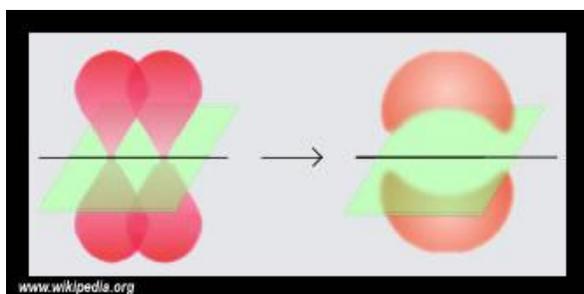
Cation-pi interactions occur between the localized negative charge of π orbital electrons, located above and below the plane of an aromatic ring, and a positive charge.

Electrons in Chemical Bonds

Many simple compounds involve covalent bonds. These molecules have structures that can be predicted using **valence bond theory**, and the properties of atoms involved can be understood using concepts such as oxidation number. Other compounds that involve ionic structures can be understood using theories from classical physics.

In the case of ionic bonding, electrons are mainly localized on the individual atoms, and electrons do not travel between the atoms very much. Each atom is assigned an overall electric charge to help conceptualize the molecular orbital's distribution. The forces between atoms (or ions) are largely characterized by isotropic continuum electrostatic potentials.

By contrast, in covalent bonding, the electron density within a bond is not assigned to individual atoms, but is instead delocalized in the MOs between atoms. The widely-accepted theory of the



linear combination of atomic orbitals (LCAO) helps describe the molecular orbital structures and energies based on the atomic orbitals of the atoms they came from. Unlike pure ionic bonds, covalent bonds may have directed anisotropic

properties. These may have their own names, too, such as Sigma and Pi bond.

Atoms can also form bonds that are intermediates between ionic and covalent. This is because these definitions are based on the extent of electron delocalization. Electrons can be partially delocalized between atoms, but spend more time around one atom than another. This type of bond is often called polar covalent. See electronegativity.

Thus, the electrons in a molecular orbital (or 'in a polar covalent, or in a covalent bond') can be said to be either *localized* on certain atom(s) or *delocalized* between two or more atoms. The type of bond between two atoms is defined by how much the electron density is localized or delocalized among the atoms of the substance.

Determination of Chemical Properties Through Chemical Bonding

Intermolecular forces cause molecules to be attracted or repulsed by each other. Often, these define some of the physical characteristics (such as the melting point) of a substance. These forces include ionic interactions, hydrogen bonds, dipole-dipole interactions, and induced dipole interactions.

States of Matter

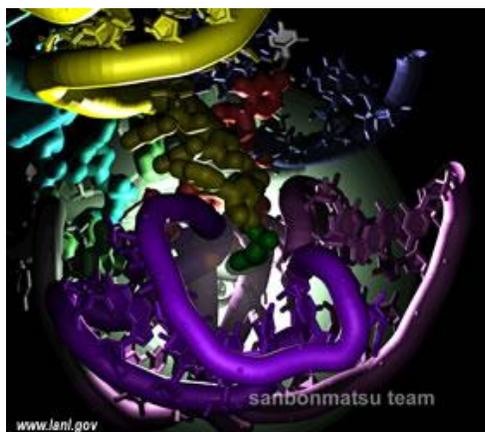
A *phase* is a set of states of a chemical system that have similar bulk structural properties, over a range of conditions, such as pressure or temperature. Physical properties, such as density and refractive index tend to fall within values characteristic of the phase. The phase of matter is defined by the *phase transition*, which is when energy put into or taken out of the system goes into rearranging the structure of the system, instead of changing the bulk conditions.

Sometimes the distinction between phases can be continuous instead of having a discrete boundary, in this case the matter is considered to be in a supercritical state. When three states meet based on the conditions, it is known as a triple point and since this is invariant, it is a convenient way to define a set of conditions.

The most familiar examples of phases are solids, liquids, and gases. Less familiar phases include plasmas, Bose-Einstein condensates and fermionic condensates and the paramagnetic and ferromagnetic phases of magnetic materials. Even the familiar ice has many different phases, depending on the pressure and temperature of the system. While most familiar phases deal with

three-dimensional systems, it is also possible to define analogs in two-dimensional systems, which has received attention for its relevance to systems in biology.

Chemical Reactions



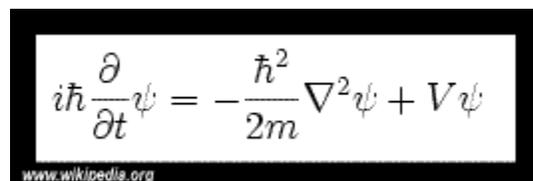
A *Chemical reaction* is a process that results in the interconversion of chemical substances. Such reactions can result in molecules combining to form larger molecules, molecules breaking apart to form two or more smaller molecules, or rearrangement of atoms within or across molecules. Chemical reactions usually involve the making or breaking of chemical bonds. For example, substances that react with oxygen to produce other substances are said to undergo oxidation; similarly a group of substances called acids or alkalis can react with one another to neutralize each other's effect, a phenomenon known as neutralization. Substances can also be dissociated or synthesized from other substances by various different chemical processes.

A stricter definition exists that states “a Chemical Reaction is a process that results in the interconversion of chemical species”. Under this definition, a chemical reaction may be an elementary reaction or a stepwise reaction. An additional caveat is made, in that this definition includes cases where the interconversion of conformers is experimentally observable. Such detectable chemical reactions normally involve sets of molecular entities as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. ‘microscopic chemical events’).

Quantum Chemistry

Quantum chemistry mathematically describes the fundamental behavior of matter at the molecular scale. It is, in principle, possible to describe all chemical systems using this theory. In practice, only the simplest chemical systems may realistically be investigated in purely quantum mechanical terms, and approximations must be made for most practical purposes (e.g., Hartree-Fock, post Hartree-Fock or Density functional theory, see computational chemistry for more details). Hence a detailed understanding of quantum mechanics is not necessary for most chemistry, as the important implications of the theory (principally the orbital approximation) can be understood and applied in simpler terms.

In quantum mechanics (several applications in computational chemistry and quantum chemistry), the Hamiltonian, or the physical state, of a particle can be expressed as the sum of two operators, one corresponding to kinetic energy and the other to potential energy. The Hamiltonian in the Schrödinger wave equation used in quantum chemistry does not contain terms for the spin of the electron.


$$i\hbar \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

www.wikipedia.org

Solutions of the Schrödinger equation for the hydrogen atom gives the form of the wave function for atomic orbitals, and the relative energy of say the

1s,2s,2p and 3s orbitals. The orbital approximation can be used to understand the other atoms e.g. helium, lithium and carbon.

Chemical Laws

The most fundamental concept in chemistry is the law of conservation of mass, which states that there is no detectable change in the quantity of matter during an ordinary chemical reaction. Modern physics shows that it is actually energy that is conserved, and that energy and mass are related; a concept which becomes important in nuclear chemistry. Conservation of energy leads to the important concepts of equilibrium, thermodynamics, and kinetics.

Further laws of chemistry elaborate on the law of conservation of mass. Joseph Proust's law of definite composition says that pure chemicals are composed of elements in a definite formulation; we now know that the structural arrangement of these elements is also important.

Dalton's law of multiple proportions says that these chemicals will present themselves in proportions that are small whole numbers (i.e. 1:2 O:H in water); although in many systems (notably biomacromolecules and minerals) the ratios tend to require large numbers, and are frequently represented as a fraction. Such compounds are known as non-stoichiometric compounds.



Etymology

The word *chemistry* comes from the earlier study of alchemy, which is basically the quest to make gold from earthen starting materials. As to the origin of the word “alchemy” the question is a debatable one; it certainly has Greek origins, and some, following E. Wallis Budge, have also asserted Egyptian origins. Alchemy, generally, derives from the old French *alkemie*; and the Arabic *al-kimia*: “the art of

transformation.” The Arabs borrowed the word “kimia” from the Greeks when they conquered Alexandria in the year 642 AD. A tentative outline is as follows:

1. Egyptian alchemy [5,000 BC – 400 BC]
2. Greek alchemy [332 BC – 642 AD], the Greek king Alexander the Great conquers Egypt and founds Alexandria where in its enormous library scholars and “wise” men from all the known world gather and study
3. Arabian alchemy [642 AD – 1200], the Arabs take over Alexandria; Jabir is the main chemist
4. European alchemy [1300 – present], Pseudo-Geber builds on Arabic chemistry
5. Chemistry [1661], Boyle writes his classic chemistry text *The Sceptical Chymist*
6. Chemistry [1787], Lavoisier writes his classic *Elements of Chemistry*
7. Chemistry [1803], Dalton publishes his *Atomic Theory*
8. Thus, an alchemist was called a ‘chemist’ in popular speech, and later the suffix “-ry” was added to this to describe the art of the chemist as “chemistry”.