Density-Functional Theory for Practitioners

Types of Bonds

Adapted from Atomistic Computer Simulations – A Practical Guide by V. Brazdova and D. R. Bowler

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Bonding

Atoms are quantum mechanical objects with both the nucleus and the electrons properly described by the laws of quantum mechanics. However, when considering the interactions between atoms in molecules and solids, the nucleus can, to a very good approximation, be treated classically: it serves as a source of electrostatic potential. The interaction of electrons, however, remains entirely quantum mechanical. In this chapter, we consider the behavior of electrons and how they are responsible both for the properties of atoms and for the interactions between atoms which make the world so interesting. The interaction between atoms is generally known as bonding.

There are many different types of bonds, and the structure of molecules and solids is linked strongly to the bonding. We have seen that some bonds are strongly directional, which are responsible for the structures of molecules such as water and methane. Other bonds are nondirectional, and the structure of materials with these bonds is determined by other factors that increase the stability of the system, for example, by maximizing the number of neighbors. The strength of bonds also varies, and goes some way towards determining the strength of materials, though other factors such as microstructure can be important.

This chapter focuses on the electrons and their role in atomic structure, and many atomistic simulations will include the electrons explicitly. However, it is perfectly possible to consider the electrons implicitly and to parameterize the interactions between atoms, replacing the bonds with numerical functions. At the simplest level, these act very much like springs. For instance, forcefields such as CHARMM, Amber and GROMACS are widely used within biochemistry, while empirical potentials have a long history within physics. However, these methods still need data for fitting the potentials, which often comes from electronic structure calculations; understanding electronic interactions is therefore extremely important.

Electronic Ground State

The starting point for all simulations must be the lowest energy or ground state: any understanding of the properties of a system must build from the most stable configuration. Any system which is not in its lowest energy state will be liable to fall into that state as it evolves. The response of a system to excitation is an important means of characterization, but we must start from a thorough understanding of the ground state.

In most circumstances, the behavior of a set of atoms, and hence of many forms of matter including molecules and solids, can be modelled by assuming that the electrons arrange themselves in their lowest energy state for a given set of atomic positions; in other words, we can place the electrons in their ground state for every set of atomic positions. This approximation is known as the Born-Oppenheimer approximation. Naturally, there are occasions when this is not applicable: to take a simple example, consider a flame, which is a complex system involving heat, chemical reactions, electronic excitations and de-excitations with emission of light, and many other processes. The question of excitations is too complex for a detailed treatment in a textbook of this nature.

As we have seen, the electronic structure of atoms is an important starting point in understanding the interactions between atoms. The structure of the periodic table of the elements reflects the distribution of electrons in atoms, and this distribution of electrons determines the bonding properties of atoms. The outermost electrons, known as valence electrons, are most strongly involved in determining how atoms interact, whatever the bonding mechanism.

The electronic ground state can be calculated using density-functional theory, for example. The interaction between atoms will disturb the atomic electronic configurations, leading to new distributions of electrons: bonds. Chemistry textbooks define a number of different types of bonds which are useful in understanding the behavior of matter; it is important to note, however, that the real world rarely fits well within any particular picture, and bonds tend to have a mixture of characters.

Types of Bonds

Different types of bonds have different strengths, and behave differently as atoms move. We present a brief overview of the types of bonds and their characteristics here. A fuller discussion can be found in standard textbooks, and you are encouraged to read several of these, to gain a fuller picture.

A simple understanding of bonding can be gained from thinking about two hydrogen atoms. When separated by a large distance, they each have their ground state orbital (the 1s orbital). As the two atoms come closer, their orbitals start to overlap; we can make symmetric and antisymmetric combinations of the orbitals which are known as bonding and antibonding orbitals. A schematic illustration of this is shown in Figure 1. This is an example of covalent bonding.



Figure 1: (a)The ground state orbitals of two widely separated hydrogen atoms plotted against the separation. (b) The resulting bonding orbital made from combining the two hydrogen orbitals in asymmetric way. (c) The resulting antibonding orbital made from combining the two hydrogen orbitals in an antisymmetric way.

If we bring together two atomic orbitals so that they overlap, they will combine to form

one bonding orbital and one antibonding orbital. Putting two electrons into the bonding orbital gives the strongest bond, while adding more electrons starts to populate the antibonding orbital, weakening the bond. Consider the difference between bringing two hydrogen atoms together and bringing two helium atoms together: in both cases, we have two 1s orbitals overlapping, thus forming a bonding and an antibonding orbital. With hydrogen, we have two electrons which fully populate the bonding orbital, giving a strong bond. With helium, however, there are four electrons, which will fill both the bonding orbital and the antibonding orbital, giving no bond. This is reflected in nature, where H₂ molecules are common (and atomic H is short-lived and can only be made by putting energy into the system) and He is found in atomic form only. The strength of the bonding can be described by the bond order. The bond order relates to the strength of bonds between atoms, and can be defined as one-half of the difference between the number of bonding electrons and the number of antibonding electrons. In H₂, the bond order is zero.

The concept of molecular orbitals is helpful, even though it is not applicable to all types of bonding. The type of the molecular orbital depends on the types of the original atomic orbitals and the way they overlap. A σ molecular orbital is created by two atomic orbitals overlapping head-on. A σ orbital has an ellipsoid shape with a circular cross-section in the direction perpendicular to the atoms (see Figure 2). Antibonding orbitals are denoted with an asterisk added to the orbital type, for example, σ^* . A σ molecular orbital can be formed from many combinations of atomic orbitals, for instance: two *s* orbitals; one *s* and one *p* orbitals; two *p* orbitals; or two *d* orbitals. The electron distribution in hydrogen, water, and methane molecules is well-described by σ orbitals. We say that electrons in a bonding σ orbital create a σ bond.

 π orbitals are a combination of two p or d orbitals, or one p and one d orbital that overlap "sideways". While a σ bonding orbital does not have a nodal plane through the ionic cores, a π bonding orbital has one nodal plane. π bonds, then, have zero electron density in the nodal plane through the ionic cores. δ orbitals are created from two d orbitals that overlap so that there are two nodal planes going through the nuclei. One bonding orbital constitutes a single bond, and a single bond therefore involves two electrons. Two bonding orbitals, with four electrons in total, can form a double bond. Double bonds are shorter and stronger than single bonds. Three orbitals can form a triple bond, involving six electrons.

Only the electrons that fill the orbitals of the outermost shell in a given atom participate in chemical bonding; they are called valence electrons. It has been observed that atoms that are not transition metals tend to form complexes such that the s and p valence shells are fully filled (closed). This empirical rule is called the octet rule because one closed s and p shell have eight electrons in total. The octet rule is a useful guideline in predicting the maximum number of bonds an element is likely to form as well as the type of complex it is likely to form: elements with an almost-filled p valence shell, for example, halides (group 17 elements), will likely accept one electron from elements with an almost-empty valence shell, such as, the alkali metals (group



Figure 2: The formation of molecular orbitals. (a) Two p_x orbitals combining along the x-axis to give σ bonding (B) and antibonding (AB) orbitals. (b) Two p_y orbitals combining along the x-axis to give π bonding and antibonding orbitals. Blue and red indicate the sign of the wavefunction.

1 elements), which will donate their valence electron so as to be left with the lower-lying closed shells. Bear in mind, though, that however elegant the octet rule looks in its simplicity, it is only a guideline and there are many compounds that violate it, most notably the *d*-block elements.

This understanding of bonding arising from molecular orbitals is most clearly seen in covalent bonding, and we start our survey of bonding with this type.

Bond breaking and making

Having reviewed the types of bonds found, we must turn to the important question of the formation and breaking of bonds. These processes are key to any dynamical process on the atomic scale, such as chemical reactions, or in determining diffusion barriers.

A typical covalent bond will have an energy of several electron volts, with ionic bonds similarly strong. Metallic bonding is weaker, but the close packed nature of most metals compensates for this, as each atom will have many neighbors, so the total bonding energy in a metal can be high. A typical hydrogen bond is a few tenths of an electron volt, while dispersion bonding is weaker.

It should be clear from these energy scales that the formation of a bond will stabilize a structure considerably. The presence of a covalent bond can compensate for significant amounts of strain: some surprising organic molecules such as cubane, which features carbon atoms with 90° bonds, are excellent examples of this. The strength of bonds provides most of the driving force behind the structures of the materials observed in the world around us.

The breaking of a bond, as is evident from the energies just mentioned, will require input of energy to the system. There are ways to reduce the energy required to break a bond, often found in active sites of enzymes or industrial catalysts. The interaction of molecules with the active site or the industrial catalyst reduces the barrier. The detailed energy profile of a reaction will determine whether more enthalpy is released by breaking a bond than is needed to break it: this is an exothermic reaction. The storage of chemical energy in bonds forms the basis for many biochemical processes, notably the storage and release of energy in adenosine triphosphate, ATP. The opposite of exothermic reactions are endothermic, and require more energy input than is released.

Bonds are formed between atoms when they move close enough for electron clouds to start interacting, or when electrostatic interactions are stronger than thermal energy. In both cases, it is important to realize that atoms are mobile, except at extremely low temperatures which are only reached in experiments or under certain astrophysical conditions: the study of small molecules in space is an important area. Bonds can be broken by stretching due to thermal motion or some larger motion of the system. Electron injection into an antibonding orbital will weaken a bond, and can also lead to bond breaking.