
Density-Functional Theory for Practitioners

Covalent Bonding

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Atomistic Computer Simulations – A Practical Guide

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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.

Covalent Bonding

Covalent bonding involves the formation of bonds by overlapping atomic orbitals in order to permit the sharing of valence electrons between atoms. The most stable structures have atoms with a full outer shell (which, as we have seen, contains eight electrons when considering just the s and p electrons). Our example of hydrogen above is the simplest example, giving two electrons shared between the two hydrogens (hence mimicking the electronic structure of helium). Classic examples are seen in organic molecules: methane, CH_4 , allows the carbon atom to share its four valence electrons – the $2s$ and $2p$ electrons – with four hydrogen atoms, each of which contribute a single $1s$ electron. The hydrogen atoms end up with two outer electrons and the carbon atom with eight outer electrons. Similarly, the structure of diamond allows each carbon atom to share an electron with each of four neighbors, giving four stable bonds. The resulting tetrahedral crystal structure reflects the electronic ground state.

Covalent bonds tend to be highly directional: they will be oriented along directions determined by symmetry and the overlap of orbitals. This means that the strength and stability of the bonding is affected by both stretching of bonds and distortion of the bond angles, whereas other forms of bonding (discussed below) are less affected by direction and more by numbers of neighbors and other factors.

Carbon is particularly notable in its ability to share differing numbers of electrons with other atoms to form bonds of different strength. Single bonds, where each atom contributes one electron, tend to be σ bonds, while double bonds, where each atom contributes two electrons, consist of a σ and a π bond. Triple bonds consist of a σ and two π bonds, and each atom contributes three electrons. It is possible to form even stronger bonds, for instance, quadruple and quintuple bonds formed by d-block elements, but these are rare. Double and triple bonds

are also seen with oxygen and nitrogen, both in the gaseous molecules and in their bonding with carbon. It is also possible to create delocalized bonds, where adjacent double and single bonds are in resonance, giving a bond midway between single and double, and a delocalized electronic structure; the classic example is the aromatic bonds in a benzene ring, though aromatic polymers are also very common and their electronic structure is used as the basis of conduction in polymers.

Figure 1 illustrates the charge density in a number of simple organic molecules: ethyne (C_2H_2); ethene (C_2H_4); ethane (C_2H_6); and benzene (C_6H_6). These illustrate single bonds (for instance, between the carbon atoms in ethane, or the hydrogen and carbon atoms in all the molecules), double bonds (between the carbon atoms in ethene), triple bonds (between the carbon atoms in ethyne), and aromatic bonds (between the carbon atoms in benzene). Note how the electron density increases with increasing bond strength, with the aromatic bonds midway between single and double bonds. The symmetry of the bond is reflected in the spatial distribution of the electrons, and the increased strength of the bond also leads to the shorter bond length.

A possible indication of the length of the bond which an atom can form is given by the covalent radius. This is defined for each element, so that the sum of the covalent radii of two bonded atoms gives the correct bond distance. There is a degree of empiricism in this definition, which dates back at least to the ideas of Pauling, who defined it in homonuclear dimers as half the bond distance, and Bragg. There have been recent efforts to put this on a firmer footing based on mining crystallographic databases or on wider data sets including theory and small molecules. Similar radii have been proposed for other types of bonding, and these are discussed in standard textbooks.

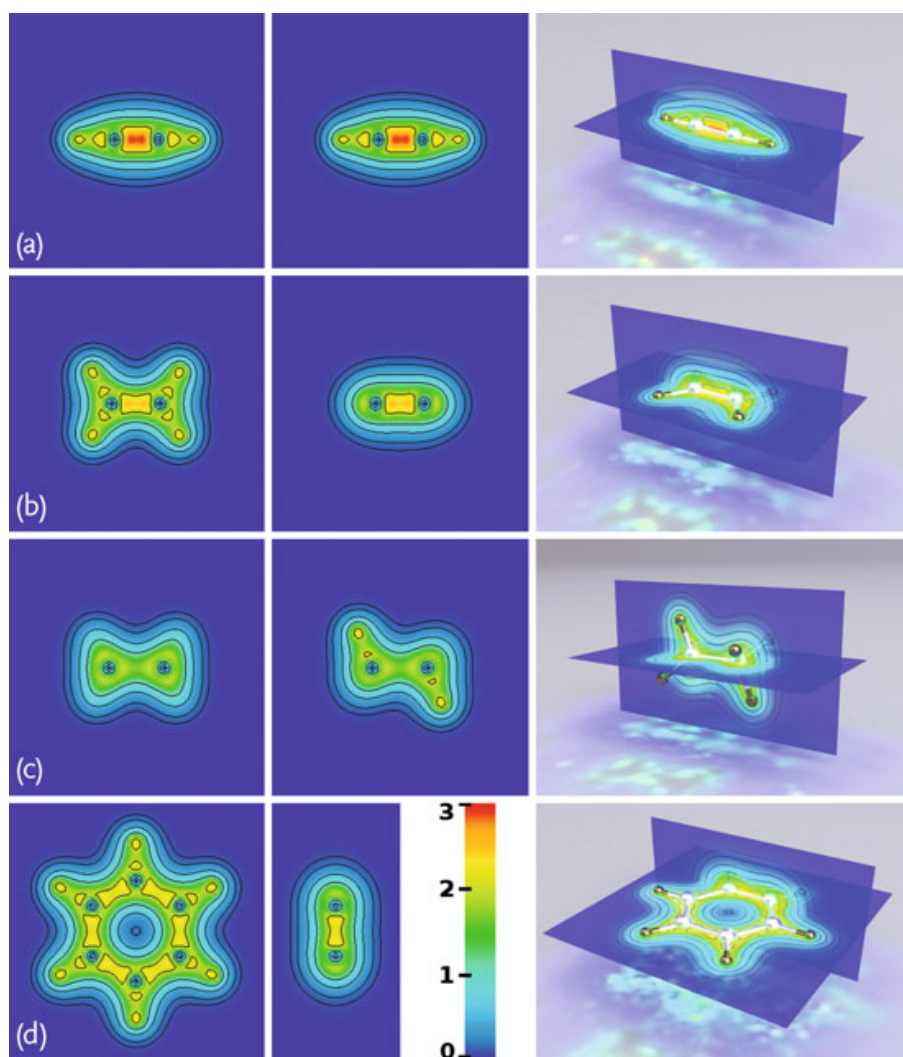


Figure 1: Charge density plotted in planes for simple organic molecules: (a) C_2H_2 , (b) C_2H_4 , (c) C_2H_6 and (d) C_6H_6 . Scale is in units of electrons/ \AA^3 .

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.