
Density-Functional Theory for Practitioners

Distortion of Bonds

Adapted from

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.

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.

Distortion of Bonds

There is a bond length associated with all types of bonding: at this point, the energy is at a minimum. Figure 1 plots an idealized energy for a bond between two atoms, and its associated force (we have defined attractive forces as positive). The bond energy consists of an attractive term and a repulsive term. The attraction comes from the overlap of electron clouds, while the repulsive term comes from core repulsion and compression of the electron clouds due to electrostatics; the repulsive term falls off faster than the attractive term. The force is zero when the energy is at a minimum, which defines the equilibrium bond length.

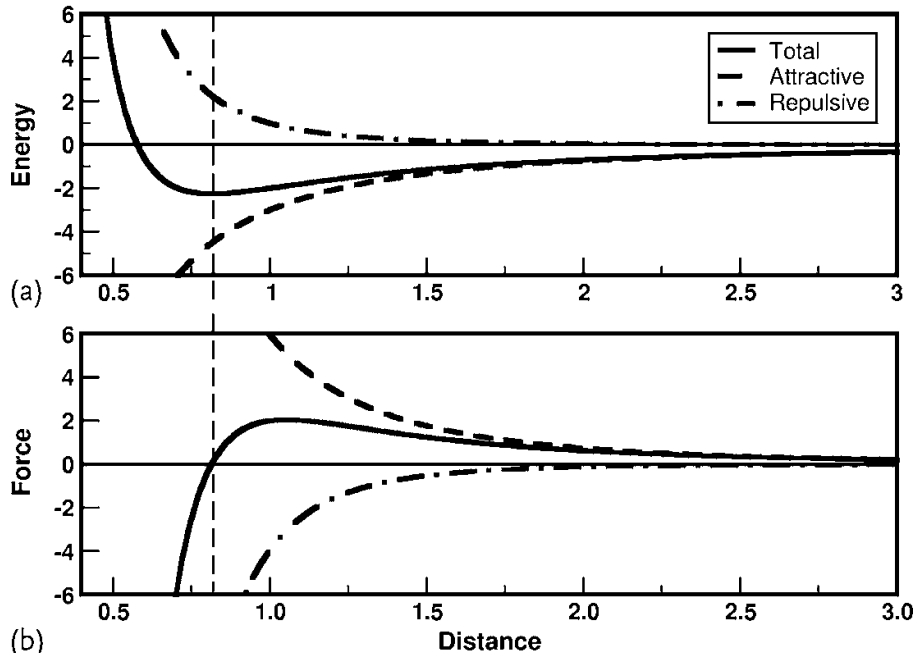


Figure 1: The energy of an idealized bond (a) and the associated force (b). In this plot, we define an attractive force as positive and a repulsive force as negative. Generally, the force is $-\frac{dE}{dx}$ for a coordinate x . The vertical dashed line indicates the energy minimum which corresponds to the force zero. Units are arbitrary.

Clearly, the bond can be stretched or compressed while still giving a negative energy. These changes in energy are seen in solids as strain. The amount of strain which can be tolerated will depend on the shape of the bonding energy: the curve we have plotted is quite shallow, which would allow relatively long bonds without a high energy cost. Other bonds have steeper energy curves, and are harder to stretch. Some reactions and structures are stabilized by stretching existing bonds to allow new bonds to be formed.

In systems with directional bonds, for example covalent bonds, the distortion of bond angles can be important as well. The hybridization of the atomic orbitals determines the ideal bond angles, and structures which distort these angles will involve an energy cost. The different hybridization states of carbon (sp^3 , sp^2 or even sp) lead to the different bonding angles (see covalent bonding). The surfaces of semiconductors are a classic example of balancing energetics: the bulk termination leaves dangling bonds which can be combined to form new bonds at the expense of bond angle distortions. The resulting reconstructions of the surface give new characteristic structures and lower energies, though the bond lengths and angles are not at their ideal values. We will mention some of these reconstructions in later chapters.