

Carbon-Carbon bonds: Hybridization

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Abstract:

Molecular binding behavior has a large influence on the structure of a material and their properties. As an exception, carbon binds itself not in form of identical molecular orbitals but in form of hybridization. I explain the term hybridization and specify the influence to the properties on the example of graphite and diamond. Furthermore, I present the change of properties by curvature effects.

1 Manifestation of Carbon

Carbon is one of the most important materials and especially essential for organic connections, because all organic structures include carbon. Carbon atoms can contribute to many different crystal structures which reveal also very different properties. In the following I will explain how the different properties of materials consisting out of carbon alone are linked up with the bonding behavior between carbon atoms.

2 Hybridization

The normal binding behavior of molecular orbitals is the binding of the same kind of orbital. Two s -orbitals or two similar p -orbitals bind together in an antibonding and bonding way depending on the sign of the orbital.

For many of the carbon atoms the binding of the same kind of molecular orbitals is not the case. In fact they form bonds by mixing different orbitals, namely s - and p -orbitals. Also a mixture of s -, p - and d -orbitals is possible, but less important for combining carbon-orbitals alone. In the following sp^3 - and sp^2 -hybridization will be explained in detail.

2.1 sp^3 -Hybridization

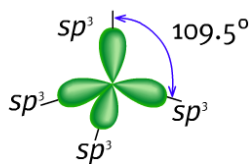


Figure 1: [1] sp^3 -hybrid orbital.

A carbon atom contains six electrons which occupy the following electron configuration: $(1s)^2(2s)^2(2p)^2$. In the ground state there are two unpaired electrons in the outer shell, so that one could assume the ability to bind only two additional molecules. In contrast, a binding ability for four electrons is detected

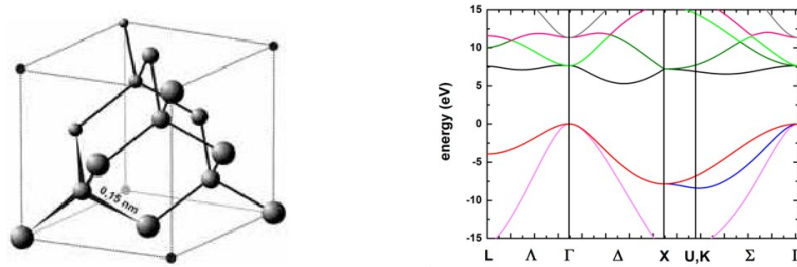


Figure 2: [2, 3] Crystal structure (left) and electronic band structure (right) of diamond.

in experiments. The reason is the small energy difference between the $2s$ - and the $2p$ -state, so that it is easily possible to excite one electron from the $2s$ -state into the $2p$ -state. In the presence of a external perturbation, such as a nearby by hydrogen, the energy difference is overcome. This result in a mixed state formed out of one s -orbital and three p -orbitals, namely p_x , p_y and p_z , is produced. Four new hybrid orbitals are formed. The direction of the orbitals and also the center of mass are determined by the specific contributions of the p -orbitals and the s -orbital. A combination of the hybrid orbitals produces a tetrahedral assembly with the center of masses in the corners (see Fig. 1). The characteristic angle between the hybrid orbitals in sp^3 -configuration is 109.5 degree.

Assembling many different sp^3 - hybridized carbon atoms to one crystal, one achieves the typical diamond structure(see Fig. 2 on the left). Due to the three dimensional sp^3 -structure the binding strength between neighboring carbon atoms is equal for each atom and very strong. Therefore, diamond is one of the hardest materials known; it is used as a cutting tool. The corresponding band structure reveals a large band gap of 5 eV, which corresponds to an insulator. The electrical conductivity is very low. Furthermore, the transparent appearance of diamond corresponds to the fact that electrons cannot be excited out of the valence band into the conduction band with a wavelength in the optical range.

2.2 sp^2 -hybridization

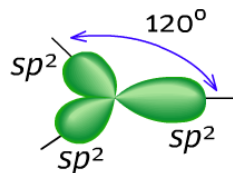


Figure 3: [1] sp^2 -hybrid orbital.

The sp^2 -hybridization is the combination of one s -orbitals with only two p -

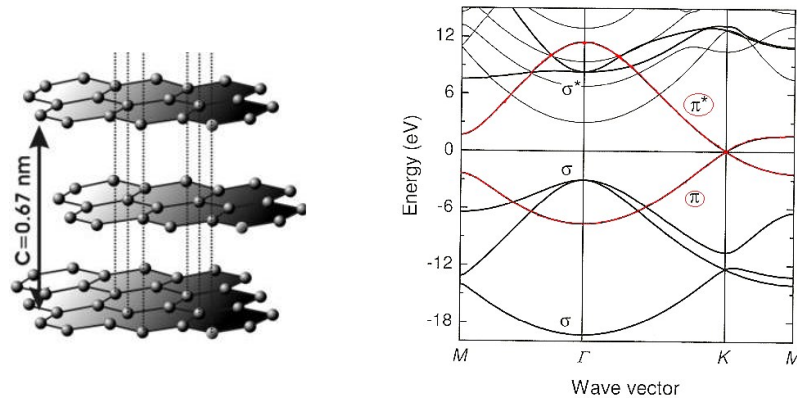


Figure 4: [4, 5] Crystal structure (left) and band structure (right) of graphite.

orbitals, namely p_x and p_y . They contribute together to a planar assembly (see Fig. 3) with a characteristic angle of 120 degree between hybrid orbitals forming a σ -bond. The additional p_z -orbital is perpendicular to the sp^2 -hybrid orbitals and forms a π -bond.

A typical example of a sp^2 -hybridized crystal structure is graphite (see Fig. 4, left). It consists of parallel carbon layers. Within a layer the planar sp^2 -hybrid orbitals align themselves to a structure with strong binding. Between the layers the π -orbitals give rise to weak Van-der-Waales-forces. As a result graphite is one of the softest materials known and is used in pencils. The band structure of graphite (see Fig. 4, right) reveals valence and conduction band, consisting of the bonding and antibonding π - and π^* -orbitals, which touch at the K -point. Due this fact graphite can be described as a semimetal. The connection of the two bands influence the possibility to easily excite electrons out of the valence into the conduction band, independent of the wavelength, so that graphite is a very good electrical conductor and opaque.

2.3 Other hybridization

For carbon the most important forms of hybridization are the sp^2 - and sp^3 -hybridization. Besides these structures there are more possibilities to mix different molecular orbitals to a hybrid orbital. An important one is the sp -hybridization, where one s - and one p -orbital are mixed together. The characteristic angle between the two hybrid orbitals is 180 degree. Furthermore, there are also hybridizations of d -orbitals together with s - and p -orbitals. Some of these possibilities are shown in Fig. 5.

3 Rolled carbon materials

In this paragraph I will introduce the influence of rolling up a graphene sheet into a carbon nanotube on their hybrid orbitals and properties.

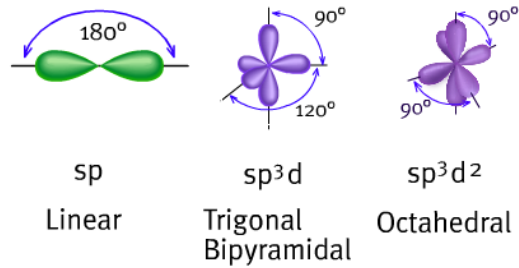


Figure 5: [1] sp -, sp^3d - and sp^3d^2 -hybridization as further possibilities for hybridization.

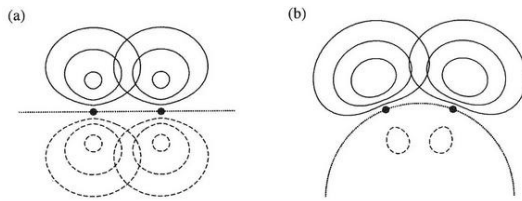


Figure 6: [6] a) π -orbitals of graphene b) Rearrangement of π -orbitals in C20.



Figure 7: [5] Rehybridization of a carbon nanotube.

3.1 Rehybridization

If a graphene sheet is theoretically rolled up into a structure like a carbon nanotube or fullerene the orbital structure of carbon is altered, because the bond length between carbon atoms decreases and the bond angle changes. σ - and π -orbitals are no longer perpendicular to each other. Overlap of the π -orbitals is introduced. As a consequence the parts of the π -orbitals inside and outside of a nanotube rearrange, in a way, that the outer contribution is much larger than the inner one (see Fig. 6). The curvature induces a mixed state of σ - and π -orbitals. In Fig. 7 one can see the wavefunctions of a carbon nanotube from the top view. The dark and bright areas indicate positive and negative sign, respectively. In the inner circle one sees a continuous ring, which is a typical σ -characteristic. In comparison, outside of the carbon nanotube one sees alternating positive and negative (bright and dark) wavefunctions, which show the already described rearrangement of π -orbitals. This is called rehybridization. The effect could also be explained by a mixture of sp^2 and sp^3 -orbitals.

An alternative way to introduce rehybridization is the following [7]:

The tilting angle contribute to the bending of π -orbitals outside the carbon nanotube, as described above. It is strongly dependent on the diameter and chirality of the curved wall. Even though carbon nanotubes of different chiralities are very different, the tilting angle could be calculated by $\delta = a/(2\sqrt{3}d)$ with a the length of the lattice unit vector and d the diameter. Rehybridized states have new wavefunctions where the π -orbital wavefunction consists out of σ - as well as s-orbitals. Moreover the degree of hybridization $sp^{2+\eta}$ could be

obtained, η being a number between 0 and 1. With this description one can specify the ratio between sp^2 - and sp^3 -orbitals.

All these characteristics are strongly dependent on the diameter and the chiral angle.

3.2 Reactivity

One of the crucial properties, which changes due to the curved form of a carbon nanotubes is the ability to react with the surroundings. While the single sp^2 - and sp^3 - orbitals are saturated, the mixed state contains unsaturated orbitals. The bonding of a tetravalent sp^3 -orbital to a trivalent sp^2 -orbitals leaves one hybrid orbital unattached and therefore free for binding. This is called π -orbital misalignment. The higher the ratio of the sp^3 - contribution the more free bonds exist and the higher the reactivity. As a index for local reactivity the pyramidalization angle θ is used (see Fig. 8). It is the angle between the σ - and π -orbitals minus 90 degree to classify an angle of $\theta = 0$ degree to the sp^2 -hybridization. The tetrahedral sp^3 -orbital has a pyramidalization angle of 19.5 degree. Dependent on the local mixture of sp^2 - and sp^3 -orbitals this angle

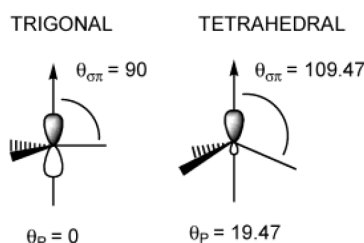


Figure 8: [8] Pyramidalization angle for sp^2 - (left) and sp^3 -hybridization (right).

changes. The comparison between different pyramidalization angles allows the comparison of reactivity, where a higher angle results in a larger reactivity. The degree of hybridization is highly curvature dependent, so that it is even possible to increase the reactivity alone by bending a carbon nanotube [9].

A further example is a fullerene, which consists out of six-membered rings, a flat graphene and additional five-membered rings. At positions where a tetravalent orbital is converted into a trivalent orbital, namely at the position of the five-membered rings, the ratio of free orbitals, and with that the reactivity, increases. In experiments these position are used for attaching molecules.[10]

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