Intermediate $sp$-hybridization for chemical bonds in nonplanar covalent molecules of carbon

Cao Ze-Xian(曹则贤)†

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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General representations for symmetrical and asymmetrical intermediate $sp$-hybridization are provided, with which the development of electronic structure in $C_{60}$-symmetrical $C_{2v}H_{6}$ and the bonding configuration in $C_{60}$ have been analyzed as an example. The spherical structure of $C_{60}$ does not necessarily require the fourth hybrid, $h_4$, to lie along the radial direction. Rather, $h_4$ runs at an angle of $3.83^\circ$ from the radius, in the plane bisecting a pentagon, to achieve maximum overlap with adjacent $h_2$-hybrids. By virtue of these representations, a number of properties of covalent molecules and solids can be conveniently calculated. This work might be particularly helpful for the study of C–C bonding in curved structures of carbon, such as fullerenes, carbon nanotubes, and buckled graphene.

Keywords: orbital hybridization, representation, buckled graphene, $C_{60}$

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In the course of studying the electronic properties of covalent molecules and solids, it is usually convenient to employ hybrids with suitable combinations of atomic orbitals, which allow significant approximations to be made. A linear combination of $p$-orbitals with the $s$-orbital (called an $sp$-hybrid) corresponds to a directional probability distribution. With given $sp$–hybrids, the bond angles and a number of other relevant quantities can be calculated by simple algebra. The best known example of $sp$–hybridization is that of a carbon atom, which has the configuration $2s^22p^2$ in its ground state. Generally, it costs some energy to promote one $s$-electron to the $p$-orbital to generate the $sp$–hybrids, but that energy is outbalanced by the enhanced strength of $\sigma$–bonds formed in these hybrids. Depending on the chemical environment, two, three or four hybrids at adjustable orientations can be formed at a carbon atom. This fact has been adopted to account for the rich variety of carbon-based materials.

The representations for linear $sp^1$-, planar-triangular $sp^2$- and the tetrahedral $sp^3$-hybridizations were worked out long ago and can be found in many textbooks devoted to bonding theory.[1,2] Here, the atomic orbitals are either $2s$- and $2p$-orbitals, as for carbon, or $3s$- and $3p$-orbitals, as for silicon. In terms of these hybrids, the electronic structures in graphite and diamond, among many others, have been well understood.[14] However, these three simple bonding-configurations are far from enough to exhaust all the possibilities for covalent structures in nature. Very often, the covalent molecules exhibit pyramidalized local geometry, which may be ascribed to an intermediate $sp$–hybridization; that is, in the hybrids, the $p$-component might be a fractional unit of the $s$-component.

Two all-carbon structures, the spheroidal icosahedral $C_{60}$ discovered by Smalley[5] and the carbon nanotubes first synthesized by Iijima,[6] have aroused the interest of researchers in a wide range of disciplines. In these macromolecules, the carbon atoms are connected at three-fold vertices to form a closed structure, where the building-blocks are pentagons, hexagons, and also minor heptagons.[7] To understand the electronic structure and the bonding in $C_{60}$, Haddron made a POAV (π-orbital axis vector) analysis of $C_{60}$, assuming that the $\pi$-orbital is situated at equal angles with respect to the three “equivalent” $\sigma$-bonds in non-planar geometry, albeit the three $\sigma$-bonds of two distinct bond lengths actually subtend different angles.[8–10] In this case, Haddron introduced the concept of a pyramidalization angle to quantify the non-planarity. More surprisingly, he gave a quite reasonable plot of the pyramidalization angle as a function of the $s$-component in the $\pi$-bonded hybrid without referring to any explicit relation between these two quantities. In recent years, graphene has attracted much interest due to its vast range of unique properties.[11] C-atoms in a graphene layer are connected via the perfect $sp^2$-bond, but in multi-layered or buckled single-layered graphene structures[11,12] the C–C bond always deviates to a variable content from the $sp^2$-hybridization. A precise presentation of the actual orbital hybridization can significantly improve the calculation and understanding of the properties of these intriguing structures.

We recognized that any covalent bonding configuration of an atom, in particular those of carbon atoms, can be well described from the point of view of suitable $sp$–hybridization. From the viewpoint of mathematics, the four hybrids are all linear transformations of one $s$-orbital and three $p$-orbitals realized through a $4 \times 4$ matrix. The orthonormality requirement upon the resulting hybrids in conjunction with the possible symmetry of the bonds they form may considerably reduce the...
number of independent variables in the transformation. The principle of orthogonality is not a physical requirement, but it is imposed in order to ensure a physically transparent breakdown of the total valence electronic charge of a molecule into separate contributions, one from each hybrid. Taking the C$_{60}$ molecule as an example, the two distinct angles subtended by three σ-bonds can uniquely determine the composition of the hybrids, hence the orientation of the fourth hybrid. Therefore, it is absolutely unnecessary and, furthermore, improper to adopt the unjustified assumption that the “π-orbital” leans along the radial direction with a nodal at the cage surface of C$_{60}$.[13] In this article we give an explicit, general representation of the intermediate $sp$-hybrids for two cases: (i) three equivalent σ-bonded hybrids, with the fourth hybrid $h_4$ forming either a π-like bond or a σ-bond with other $h_4$ hybrids at adjacent atoms. This is the case when the bonds exhibit C$_3v$ symmetry. Here we use the phrase “π-like bond” since the bonding between two $h_4$-hybrids is no longer of a pure π-nature. (ii) Only two among the three σ-bonded hybrids are equivalent, as in C$_{60}$. In the latter case, the local geometry is characterized by four bond angles. A few properties of the carbon macromolecules can be discussed by virtue of these representations.

We first consider the simpler case where three of the four intermediate $sp$-hybrids, denoted as $sp^{2+δ}$-hybrids, are equivalent. To start with, let us write down a representation for the $sp^2$-hybridization in the form

$$
\begin{align*}
    h_1 &= (3)^{-1/2}(s + \sqrt{1/2}p_x + \sqrt{3/2}p_y), \\
    h_2 &= (3)^{-1/2}(s + \sqrt{1/2}p_x - \sqrt{3/2}p_y), \\
    h_3 &= (3)^{-1/2}(s - \sqrt{2}p_z), \\
    h_4 &= p_z.
\end{align*}
$$

One can verify with a pencil that the hybrids in Eqs. (1) are indeed orthonormal and the $sp$-ratio in the first three hybrids is 1:2. In order to construct the symmetrical $sp^{2+δ}$-hybrids, an equal part of $p_z$ should be admixed into the first three hybrids in Eqs. (1) to elevate the $p$-component. Correspondingly, some $s$-component will be incorporated into $h_4$ to make it an $sp^{3/3}p$-hybrid, as required by the orthogonality condition. After a proper adjustment of other coefficients, a proper representation for the $sp^{2+δ}$-hybridization is immediately obtained:

$$
\begin{align*}
    h_1 &= (3 + \delta)^{-1/2}(s + \sqrt{3 + \delta}/6p_x + \sqrt{3 + \delta}/6p_z), \\
    h_2 &= (3 + \delta)^{-1/2}(s + \sqrt{3 + \delta}/6p_x - \sqrt{3 + \delta}/6p_z), \\
    h_3 &= (3 + \delta)^{-1/2}(s - \sqrt{3 + \delta}/3p_x - \sqrt{3 + \delta}/3p_y - \sqrt{6 + 2\delta}/3p_z), \\
    h_4 &= (3 + \delta)^{-1/2}(\sqrt{3 + \delta}/2p_x + \sqrt{3 + \delta}/2p_z).
\end{align*}
$$

This degenerates into the customary representation for $sp^2$-hybridization in Eqs. (1) at $δ = 0$, and at $δ = 1$ it turns into

$$
\begin{align*}
    h_1 &= 1/2(s + \sqrt{2/3}p_x + \sqrt{2/3}p_y - p_z/\sqrt{3}), \\
    h_2 &= 1/2(s + \sqrt{2/3}p_x - \sqrt{2/3}p_y - p_z/\sqrt{3}), \\
    h_3 &= 1/2(s - \sqrt{2/3}p_x - p_z/\sqrt{3}), \\
    h_4 &= 1/2(s + \sqrt{3}p_z),
\end{align*}
$$

which is the representation for the $sp^3$-hybridization other than the conventional form

$$
\begin{align*}
    h_1 &= 1/2(s + p_x + p_y + p_z), \\
    h_2 &= 1/2(s + p_x - p_y - p_z), \\
    h_3 &= 1/2(s - p_x + p_y - p_z), \\
    h_4 &= 1/2(s - p_x - p_y + p_z).
\end{align*}
$$

The transformation (2) contains a unique parameter $δ$. The orientation of the four hybrids can be characterized with two bond angles, that is, $φ$ subtended by any pair of $h_1$, $h_2$, and $h_3$, with $θ$ that $h_4$ spans with regard to any of the other three hybrids (Fig. 1(a)). They are simple functions of the parameter $δ$,

$$
\begin{align*}
    \cos(φ) &= −\sqrt{δ/(6 + 3δ)} \quad (5a) \\
    \cos(θ) &= −1/(2 + δ) \quad (5b)
\end{align*}
$$

Clearly, either $θ$ or $φ$ suffices to define the local geometry of the symmetrical $sp^{2+δ}$-bonded structures. When $δ$ increases from zero to unity, both angles, starting from 120° and 90°, respectively, simultaneously approach a value of 109.47° (Fig. 1(b)), referring to the bonding configuration found in the tetrahedral structure.

Fig. 1. (color online) (a) Illustrative diagram of the hybrids for the construction of C$_3$ symmetrical bonds. (b) Variation of the angles $θ$ and $φ$ characterizing a C$_3$ local bonding with the parameter $δ$. Cross: $sp^2$-hybridization in diamond; circle: the hybridization in C$_3$H$_6$. The experimental value of the angle ΩCCH is 111.17°,[14] therefore, from the knowledge of solid geometry,
an angle $\angle \text{HCH} = 107.72^\circ$ is expected. We anticipate that the four $\sigma$-bonding hybrids of the carbon atom in $C_3H_6$ be given by representation (2). To prove this, substituting $\phi = 111.17^\circ$ into Eq. (5a) and solving for $\delta$, one obtains $\delta = 1.2845$. Thus, one finds that the atomic orbitals on the carbon atom are $sp^3$-hybridized to form C–H bonds in $C_2H_6$. This value of $\delta$, from Eq. (5b), gives rise to an angle of exactly $107.72^\circ$ between two neighboring C–H bonds. That is to say, both the homopolar and heteropolar bonds formed by hybrids at carbon atoms have a maximum probability along the intra-atomic connections.

As confirmed by the analysis above, the hybrids $h_1$, $h_2$, and $h_3$ for the C–H bonds have the composition of $sp^3$-hybrids. With these given hybrids, the development of the electronic structure in $C_2H_6$ can be traced following the scheme in Harrison [3,4] (Fig. 2). The covalent energy of the C–C bond in $C_2H_6$ is

$$E_{CC}^{cove} = -\left(3V_{pp} + 2\sqrt{3}V_{sp} + \delta V_{ss}\right)/(3 + \delta).$$

(6)

The values of the hopping integrals $V_{pp}$, $V_{sp}$, and $V_{ss}$ can be derived from the universal formula (1-21) in Harrison. For a C–C bond of length 0.1535 nm, $E_{CC}^{cove}$ $= -10.60$ eV. Consequently, the covalent energy of the C–H bond $E_{CH}^{cove}$ is $-11.97$ eV. We then proceed to write the molecular state as a combination of the resulting bonding or antibonding orbitals:

$$|\text{MO}\rangle = u_0 |\psi_{C-C}\rangle + \sum_{i=1}^{6} u_i |\psi_{C-H_i}\rangle.$$  

(7)

The energy levels of the molecular state can be determined by minimizing the energy of this molecular state with respect to the coefficients and diagonalizing the resulting $7 \times 7$ Hamiltonian matrix. [4] The coupling between the bonds can be reasonably approximated by that between the hybrids at carbon atoms. By denoting the coupling between $h_1$ and $h_2$ as $\alpha$, and that between $h_4$ and $h_1$ as $\beta$, the eigenvalues of the Hamiltonian are given by

$$\lambda_{1,2} = \varepsilon_2 + (\varepsilon_1 - \varepsilon_2 + 2\alpha)/2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2 - 2\alpha)^2/4 + 6\beta^2},$$

$$\lambda_{3,4,5,6} = \varepsilon_2 - \alpha,$$

$$\lambda_7 = \varepsilon_2 + 2\alpha,$$

(8)

The role of the parameters $a$ and $\gamma$ is to be understood in the following manner. While $a$ denotes the proportion of $p_z$-component in the $h_4$-hybrid, $\gamma$ signifies the apportioning of the remaining $p_z$-component among the other three hybrids. As expected, this representation reproduces the $sp^3$-hybridization at $a = 3/4$, $\gamma = 1/3$ (another linear transformation of repre-
sentation (4)) and the $sp^2$-hybridization at $a = 1$, $\gamma = 1/3$. The geometry that these hybrids make is characterized by four angles, $\theta_{34}$, $\theta_{42}$, $\phi_{23}$, and $\phi_{12} = \phi_{13}$, but only two of them are independent. Those two are explicit functions of the parameters $a$ and $\gamma$:

$$\cos \theta_{34} = -\sqrt{(1-a)(1-2\gamma)\gamma(1-a+2\gamma a)},$$  
$$\cos \theta_{42} = -\sqrt{\gamma(1-a)/(1-\gamma a)},$$  
$$\cos \phi_{12} = -\sqrt{\gamma a(1-2\gamma)(1-a+2\gamma a)},$$  
$$\cos \phi_{23} = -\sqrt{\gamma a/(1-\gamma a)}.$$

Representation (9) and the relations (10a)–(10b) can be applied to analyze the macromolecule $C_{60}$. At any carbon atom in the $C_{60}$ molecule, $\phi_{12} = \phi_{13} = 120^\circ$ and $\phi_{23} = 108^\circ$ (Fig. 3). If, as experimentally determined, $h_{bh} = 0.141$ nm and $b_{np} = 0.145$ nm, then the spherical shell enclosing the $C_{60}$ molecule should have a diameter of 0.691 nm, rather than 0.7 nm\(^{[13]}\) or 0.71 nm\(^{[15]}\). Consequently, the radial through a vortex runs at an angle of 101.67° to the bonds separating two hexagons and an angle of 101.62° to the bonds separating the hexagon from a pentagon. These two angles differ only negligibly, confirming the nearly spherical conformation of this macromolecule. Many questions can be raised about the bonding configuration in this structure: what $sp$-leads to such a geometry for an $sp$-hybridization? Does the fourth orbital, as it has been treated, lie along the radial direction, making equal angles with the three $\sigma$-bonded hybrids? And so on.

To answer such questions, let us first find the hybrids that give the correct bond orientations. Since $\phi_{12} = \phi_{13} = 120^\circ$ and $\phi_{23} = 108^\circ$, by solving Eqs. (10c) and (10d), the parameters $a$ and $\gamma$ are determined, $a = 0.91934$, $\gamma = 0.25677$. Thus, the angles $\theta_{34}$ and $\theta_{42}$, from Eqs. (10a) and (10b), are accurately 105.45° and 91.55°, respectively. We see that, in order to adopt the cage geometry, the three $\sigma$-bonded hybrids at a carbon atom in $C_{60}$ might contain a small portion of $p_\pi$, namely 3.92% in $h_1$ and 2.07% in $h_2$ and $h_3$. Therefore, the $sp$-mixing in $h_1$ is $1:1.236$, and in both $h_2$ and $h_3$ it is $1:3.236$. The fourth hybrid is nearly a pure $p$-orbit, yet mixed with about 8.1% $s$-component. From the relations (10a)–(10d) one sees that $h_4$ does not point along the radial direction; rather it makes an angle of $\sim 3.83^\circ$ to the radial direction in the plane bisecting the pentagon attached to that carbon atom. This indeed leads to an enhanced overlap between $h_4$-hybrids at adjacent carbon atoms, as confirmed by the following simple calculation. The covalent energy of two coplanar $h_4$-hybrids at angle of $2\theta$ is given by

$$-E_c = (1-a)V_{s\sigma} + 2\sqrt{a(1-a)}\sin \theta V_{sp\sigma} + a(\cos^2 \theta V_{pp\pi} - \sin^2 \theta V_{pp\sigma}).$$

In comparison to the situation where $h_4$ lies along the radial direction, the covalent energy of the actual “$p$-like” bond of a length given by $b_{hh}$ is 0.08 eV larger, and that at a distance of $b_{np}$ increases by 0.13 eV.

In summary, explicit representations for the symmetrical and asymmetrical intermediate $sp^{2+\delta}$ hybridization are given. They were also applied to the quantitative discussion of the electronic structure evolution in $C_2H_6$ and the bonding configuration in $C_{60}$. It was shown that the $C_{60}$ molecule strives for a cage geometry by bending the $\sigma$-bonds, yet this does not necessarily require the fourth hybrid, of only 8.1% $s$-character, to align along the radius of the spherical cage. With the given representation, the calculation of valence configuration and of many other quantities referring to a specific geometry is significantly facilitated. It also enables us to make very elementary but reasonably quantitative discussion of a number of other properties. Remarkably, the continuous variation of the parameter $a$ and $\gamma$ across the critical points $a = 3/4$, $\gamma = 1/3$ and $a = 1$, $\gamma = 1/3$ may describe the situation when the symmetry is broken. This is especially useful for the process of rehybridization, as by evaluating the shear constants relating to the reduction of local symmetry; for instance, $C_{44}$ in a zinc-blende structure.

References