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

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(Received 20 February 2014; revised manuscript received 17 March 2014; published online 20 April 2014)

General representations for symmetrical and asymmetrical intermediate sp-hybridization are provided, with which the development of electronic structure in C_{3v}-symmetrical C_2H_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° from the radius, in the plane bisecting a pentagon, to achieve maximum overlap with adjacent h_4-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}

PACS: 31.10.+z, 31.15.v–, 81.05.ue, 81.05.ub **DOI:** 10.1088/1674-1056/23/6/063102

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 $2s^2 2p^2$ 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 σ-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.[4] 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 Ijima,[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 π-orbital is situated at equal angles with respect to the three "equivalent" σ-bonds in non-planar geometry, albeit the three σ-bonds of two distinct bond lengths actually subtend two different angles.[8–10] In this case, Haddron introduced the concept of a pyramidalization angle to quantify the nonplanarity. More surprisingly, he gave a quite reasonable plot of the pyramidalization angle as a function of the s-component in the π-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 4×4 matrix. The orthonormality requirement upon the resulting hybrids in conjunction with the possible symmetry of the bonds they form may considerably reduce the

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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 $sp^{2+\delta}$-hybrids, are equivalent. To start with, let us write down a representation for the sp^2-hybridization in the form

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

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 $sp^{2+\delta}$-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 $s^{\delta/3}p$-hybrid, as required by the orthogonality condition. After a proper adjustment of other coefficients, a proper representation for the $sp^{2+\delta}$-hybridization is immediately obtained:

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

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

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

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

$$\begin{aligned} h_1 &= 1/2(s+p_x+p_y+p_z),\\ h_2 &= 1/2(s+p_x-p_y-p_z),\\ h_3 &= 1/2(s-p_x+p_y-p_z),\\ h_4 &= 1/2(s-p_x-p_y+p_z). \end{aligned} \tag{4}$$

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,

$$\cos(\phi)=-\sqrt{\delta/(6+3\delta)} \tag{5a}$$

and

$$\cos(\theta)=-1/(2+\delta). \tag{5b}$$

Clearly, either θ or ϕ suffices to define the local geometry of the symmetrical $sp^{2+\delta}$-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.

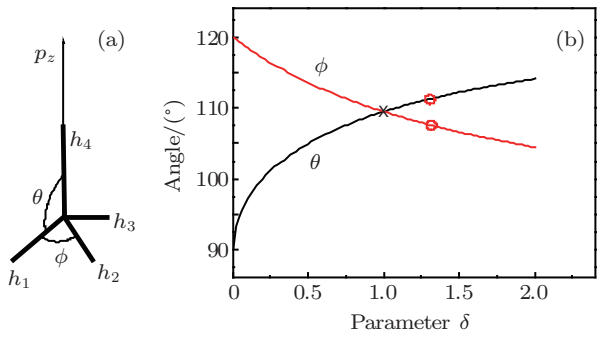


Fig. 1. (color online) (a) Illustrative diagram of the hybrids for the construction of C_{3v} symmetrical bonds; (b) Variation of the angles θ and ϕ characterizing a C_{3v} local bonding with the parameter δ. Cross: sp^3-hybridization in diamond; circle: the hybridization in C_2H_6.

Notice that the parameter δ is not limited to unity as is widely believed. Let us analyze, for instance, the hybrids at a carbon atom in the ethane molecule C_2H_6, which displays a C_{3v} symmetry. The experimental value of the angle $\angle$CCH is 111.17°,[14] therefore, from the knowledge of solid geometry,

an angle ∠HCH = 107.72° is expected. We anticipate that the four σ-bonding hybrids of the carbon atom in C_2H_6 be given by representation (2). To prove this, substituting $\phi = 111.17°$ into Eq. (5a) and solving for δ, one obtains $\delta = 1.2845$. Thus, one finds that the atomic orbitals on the carbon atom are $sp^{3.28}$-hybridized to form C–H bonds in C_2H_6. This value of δ, from Eq. (5b), gives rise to an angle of exactly 107.72° 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 $sp^{3.28}$, and the h_4-orbit for the C–C bond is an $s^{0.428}p$-hybrid. 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

$$E_{CC}^{cov} = -(-3V_{pp\sigma} + 2\sqrt{3\delta}V_{sp\sigma} + \delta V_{ss\sigma})/(3+\delta). \quad (6)$$

The values of the hopping integrals $V_{pp\sigma}$, $V_{sp\sigma}$, and $V_{ss\sigma}$ can be derived from the universal formula (1-21) in Harrison.[4] For a C–C bond of length 0.1535 nm, $E_{CC}^{cov} = -10.60$ eV. Correspondingly, the covalent energy of the C–H bond E_{CH}^{cov} is -11.97 eV. We then proceed to write the molecular state as a combination of the resulting bonding or antibonding orbitals:

$$|\mathrm{MO}\rangle = u_0\,|\psi_{\mathrm{C-C}}\rangle + \sum_{i=1}^{6} u_i\,|\psi_{\mathrm{C-H},i}\rangle. \quad (7)$$

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 7×7 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 α, and that between h_4 and h_1 as β, the eigenvalues of the Hamiltonian are given by

$$\begin{aligned}
&\lambda_{1,2} = \varepsilon_2 + (\varepsilon_1 - u_2 + 2\alpha)/2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2 - 2\alpha)^2/4 + 6\beta^2},\\
&\lambda_{3,4,5,6} = \varepsilon_2 - \alpha,\\
&\lambda_7 = \varepsilon_2 + 2\alpha,
\end{aligned} \quad (8)$$

where ε_1 and ε_2 are the term values of the C–C bond and the C–H bond, respectively. The coupling constants α and β can be directly calculated from Eqs. (2), resulting in $\alpha = -1.94$ eV, and $\beta = -2.17$ eV. The C_2H_6 molecule has just 14 electrons to occupy the 7 bonding molecular orbitals (Fig. 2).

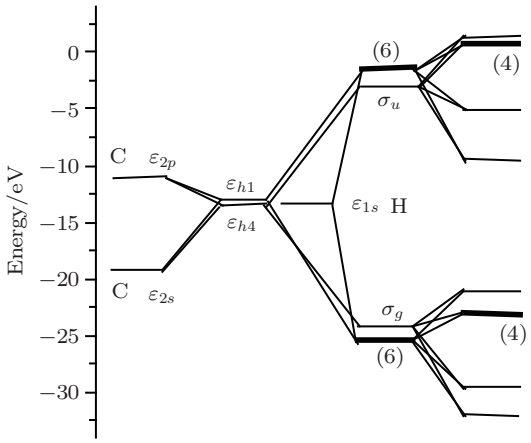


Fig. 2. Development of the electronic structure of C_2H_6. The C $2s$- and $2p$-states are transformed into four hybridized states. The h_4-hybrid is combined with h_4 on the other carbon atom to form the C–C bond while the h_1 through h_3-hybrids are combined with H $1s$-state. The coupling between the bonds has split the two bonding and two anti-bonding orbitals each into four. Numbers in brackets denote the degeneracy of the energy levels drawn in bold line.

Now we turn to the case in which only two of the hybrids form equivalent σ-bonds, as found in some fullerene molecules and carbon nanotubes. We study the particular case, denoted as b_{hp}, in which two σ-bonds of a carbon atom in the C_{60} molecule, one connecting to a pentagon and one to a hexagon. The two b_{hp} are equivalent, while the third one, denoted as b_{hh}, which separates two hexagons, differs both in orientation and bond length. To signify this asymmetry, an additional parameter must be introduced into the representation (2). In constructing the proper asymmetrical hybrids, the following considerations might be conducive: i) without any loss of generality, the hybrid h_4 is supposed to contain only contributions from s- and p_z-orbitals; ii) h_2 and h_3 are made equivalent, that is, subtending identical angles to the other two hybrids. Bearing these in mind, the following presentation can be readily obtained:

$$\begin{pmatrix} h_1\\ h_2\\ h_3\\ h_4 \end{pmatrix} = \begin{pmatrix} \sqrt{a-2\gamma a} & \sqrt{\gamma} & -\sqrt{\gamma} & -\sqrt{(1-a)(1-2\gamma)}\\ \sqrt{\gamma a} & (1-\sqrt{1-2\gamma})/2 & (1+\sqrt{1-2\gamma})/2 & -\sqrt{\gamma(1-a)}\\ \sqrt{\gamma a} & -(1+\sqrt{1-2\gamma})/2 & (-1+\sqrt{1-2\gamma})/2 & -\sqrt{\gamma(1-a)}\\ \sqrt{1-a} & 0 & 0 & \sqrt{a} \end{pmatrix} \begin{pmatrix} s\\ p_x\\ p_y\\ p_z \end{pmatrix}. \quad (9)$$

The role of the parameters a and γ is to be understood in the following manner. While a denotes the proportion of p_z-component in the h_4-hybrid, γ 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, θ_{41}, $\theta_{42} = \theta_{43}$, ϕ_{23}, and $\phi_{12} = \phi_{13}$, but only two of them are independent. Those two are explicit functions of the parameters a and γ:

$$\cos\theta_{41} = -\sqrt{(1-a)(1-2\gamma)/(1-a+2\gamma a)}, \quad (10a)$$

$$\cos\theta_{42} = -\sqrt{\gamma(1-a)/(1-\gamma a)}, \quad (10b)$$

$$\cos\phi_{12} = -\sqrt{\gamma a^2(1-2\gamma)/(1-\gamma a)(1-a+2\gamma a)}, \quad (10c)$$

$$\cos\phi_{23} = -\gamma a/(1-\gamma a). \quad (10d)$$

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, $b_{\rm hh} = 0.141$ nm and $b_{\rm hp} = 0.145$ 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 σ-bonded hybrids? And so on.

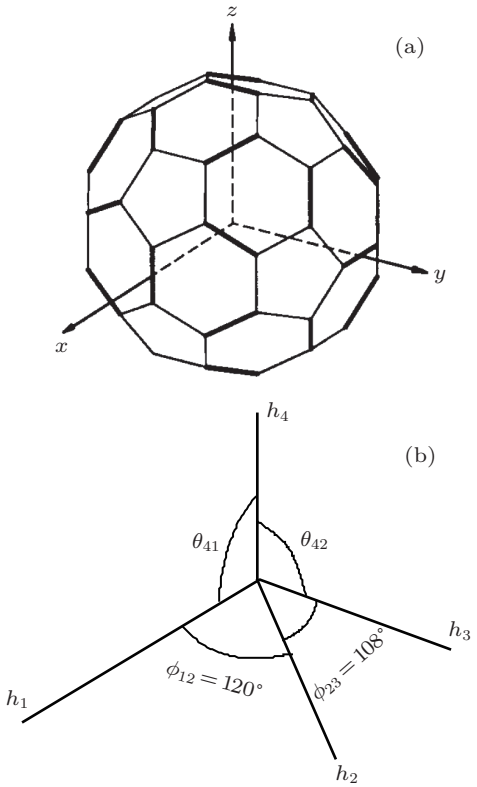


Fig. 3. (a) The structure of the C_{60} molecule and (b) the orientation of hybrids at a carbon atom.

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 γ are determined, $a = 0.91934$, $\gamma = 0.25677$. Thus, the angles θ_{41} and θ_{42}, from Eqs. (10a) and (10b), are accordingly 105.45° and 91.55°, respectively. We see that, in order to adopt the cage geometry, the three σ-bonded hybrids at a carbon atom in C_{60} might contain a small portion of p_z, 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 2θ is given by

$$\begin{aligned} -E_{\rm c} &= (1-a)V_{ss\sigma} + 2\sqrt{a(1-a)}\sin\theta V_{sp\sigma} \\ &\quad + a(\cos^2\theta V_{pp\pi} - \sin^2\theta V_{pp\sigma}). \end{aligned} \quad (11)$$

In comparison to the situation where h_4 lies along the radial direction, the covalent energy of the actual "π-like" bond of a length given by $b_{\rm hh}$ is 0.08 eV larger, and that at a distance of $b_{\rm hp}$ 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 σ-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 γ 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.

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