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HYBRID ORBITALS OF CARBON ATOMS IN THE $D_{6h}C_{36}$ MOLECULE UNDER THE ROTATING ELLIPSOID MODEL

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The hybrid orbitals of carbon atoms in the D_{6h} C_{36} molecule are studied using two rotating ellipsoid models. The model 1 is $1.66R$ for the short semi-axis and $2.34R$ for the long semi-axis, and the model 2 is $1.78R$ and $2.26R$ respectively, where R is the C-C bond length. By comparison,we think the model 2 to be more proper in revealing the electronic properties of the D_{6h} C_{36} molecule. The component of s orbitals in the π states hybridized for each of the atoms is much larger than C_{60}, in which the s-orbit component is 0.0380 and the p-orbit is 0.9620. The most component is 0.2098 and the least is 0.0482 for model 1; the most is 0.1764 and the least is 0.0656 for model 2.

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PACC: 3110, 3120, 3640

The discovery of high superconducting transition temperatures in the alkali-doped C_{60} solids has contributed to the intense research effort to study this class of materials. Theoretical studies indicate that electron-phonon interactions are responsible for superconductivity in these materials.[1−3] Simple models based on the curvature of the fullerenes have been proposed to explain their high T_c compared to intercalated graphite.[1,4] Smaller C_{36} fullerenes have been observed experimentally[5] and the solid C_{36} has been synthesized by the arc-discharge method.[6] Solid-state nuclear magnetic resonance (NMR) measurements suggest that the C_{36} molecule has D_{6h} symmetry. The solid C_{36} suggests the possibility of enhancing T_c and further enriching this class of materials.The results of *ab initio* calculations for molecular and solid C_{36} show that the C_{36} can form a periodic structure and this crystal is likely to form covalent bonds between the molecules.[7]

The C_{36} molecule consists of 8 hexagons and 12 pentagons and resembles C_{70} since both possess a stretched c axis, as shown in Fig.1. In the curved structure of C_{60}, an extra small component from $2s$, $2p_x$, and $2p_y$ is induced along the radial direction due to the surface curvature,[8,9] which is called the unequal sp^3 hybrid. Nevertheless, the structure of C_{36}, which is similar to a rotating ellipsoid with a long semi-axis c and a short semi-axis a, is different from that of C_{60}. Since C_{36} is even more curved than C_{60}, we can infer that an extra larger component from $2s$, $2p_x$, and $2p_y$ is induced along the normal direction of the ellipsoid due to the surface curvature. It cannot be questioned, but σ electrons play a more important role in the band structure, as compared with C_{60} . However,the electronic and structural properties of the C_{36} molecule have been evaluated using an *ab initio* pseudopotential plane wave method within the local density approximation.[10] But the problem of the hybrid orbitals for carbon atoms in C_{36} still remain unsolved. Therefore, it is worth while discussing this problem. In this letter,the hybrid orbitals of carbon atoms in the D_{6h} C_{36} molecule for the two kinds of models are given and compared with that of carbon atoms in C_{60}.

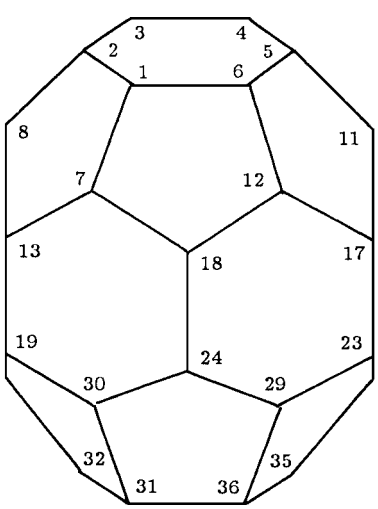


Fig.1. A C_{36} molecule with D_{6h} symmetry. The carbon sites are numbered from 1 to 36 in clockwise.

For the convenience of discussion we label the carbon sites with code number, as shown in Fig.1. It may be verified that the 36 sites do not lie in the same ellipsoidal surface. If the sites 1 to 12 and 25 to 36 are regarded as in the same surface, the rest of the sites is outside the surface and very close on the surface, which is called "model 1". On the other hand, if the sites 1 to 6, 13 to 24, and 31 to 36 are considered to be in the same surface, then the rest is within the surface and very close to the surface, which is called "model 2". In order to make certain of the electronic properties of C_{36} we assume that the 36 carbon atoms lie in the same ellipsoidal surface. According to the surface curvature the carbon sites can be divided into three classes. The first class of sites is numbered from 1 to 6 and 31 to 36. The second is numbered from 7 to 12 and 25 to 30. The third is numbered from 13 to 24. If we choose the z-axis along the long semi-axis of the ellipsoid, the ellipsoid equation can be written as

$$\frac{r^2}{a^2} + \frac{z^2}{c^2} = 1, \tag{1}$$

where

$$r^2 = x^2 + y^2.$$

Here a and c denote the short and long semi-axis of the ellipsoid, respectively. For model 1, using Eq.(1) and the geometric structure of C_{36},we get $a = 1.66R$ and $c = 2.34R$, where R is the C-C bond length. From a and c we can easily obtain $e = 0.705$, where e denotes the eccentricity of the ellipsoid. For model 2, we have $a = 1.78R$, $c = 2.26R$, and $e = 0.617$. According to the above hypothesis the π orbitals are normal to the ellipsoidal surface. From Fig.2, it is easy to show that the normal equation of the surface through the ith carbon site is

$$c^2 r_i z - a^2 z_i r = (c^2 - a^2) r_i z_i, \tag{2}$$

where $r_i = \sqrt{x_i^2 + y_i^2}$, and x_i, y_i, z_i are the coordinates of the ith carbon site. When $r = 0$ in Eq.(2), we have

$$z = \frac{(c^2 - a^2)}{c^2} z_i = e^2 z_i. \tag{3}$$

The angle between the z-axis and the normal corresponding to the ith site can be written as

$$\tan\delta_i = \frac{r_i}{(z_i - z)} = \frac{r_i}{(1 - e^2) z_i}. \tag{4}$$

The 36 $2p_z$ orbitals, each pointing along the outward normal direction,are hybridized to form π states. From a physical point of view,the 36 outer π orbitals are relevant to the conducting properties of the molecules and the 108 σ orbitals are mainly responsible for the elastic properties.

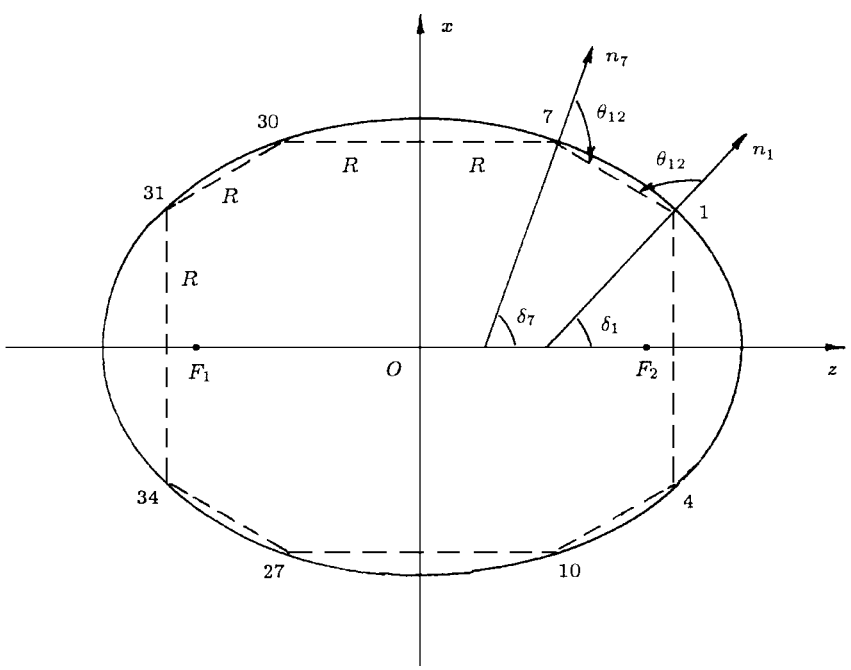


Fig.2. A sectional drawing of the rotating ellipsoid model with a short semi-axis $1.66R$ and a long semi-axis $2.34R$,where R denotes the C-C bond length.

To state in brief, we use 1 for π bonds and 2,3,4 for σ bonds, such as the sites 1 and 7, some bonds connected with pentagons are labeled with 2 and others with 3 and 4. Similarly, for the site 13 the bond linked with hexagons is labeled with 2. For example, the coordinates of the site 1 in the model 1 are $x_1 = R$, $y_1 = 0$, and $z_1 = (1 + \sqrt{3}/2)R$, from Eq.(4) we get

$$\tan\delta_1 = \frac{(6 + 8\sqrt{3})}{(10 + 5\sqrt{3})} = 1.0641.$$

From Fig.2, we have then

$$\theta_{12} = \pi - \frac{\pi}{6} - \delta_1.$$

In general,the angle θ_{ij} between the ith and jth bond is given by

$$\cos\theta_{ij} = \cos\theta_i\cos\theta_j + \sin\theta_i\sin\theta_j\cos(\varphi_i - \varphi_j), \quad (5)$$

where θ_i is the angle between the ith bond and the z-axis and φ_i is the angle between the projection of the ith bond in xy-plane and the x-axis. From Eqs.(4) and (5) we can obtain the angles between bonds for the different sites 1,7, and 13 for two models, which are listed in Table 1. For the sake of contrast,Table 1 also shows the corresponding angles of C_{60},where the short bond linked with hexagons is labeled with 2. From Table 1 we can infer that the hybrid orbitals of carbon atoms are not identical for the components of s orbitals because each of the three angles is not equal to 109.5°, which implies that this hybrid belongs to the unequal sp^3 hybrid. Besides, from Table 1 we see that model 2 is more reasonable than model 1 because the three angles between the π and σ bond for each of the sites are roughly close to one another.

Table 1. A comparison of the D_{6h} C_{36} molecule with C_{60} for the angles (degree) between π and σ bonds.

Molecules	Sites	θ_{12}	θ_{13}	θ_{14}
C_{36} (Mod.1)	1	103.2212	111.3681	111.3681
	7	101.4409	99.1573	99.1573
	13	98.2717	103.5292	103.5292
C_{36} (Mod.2)	1	109.1069	109.1064	109.1064
	7	97.9842	100.8029	100.8029
	13	100.1280	102.4948	102.4948
C_{60}	i	101.3017	101.8245	101.8245

Let k_i be the component of s orbitals in the ith hybrid orbital ψ_i. The corresponding wave function can be written as

$$\psi_i = \sqrt{k_i}\varphi_s + \sqrt{1 - k_i}\varphi_{p_i}, (i = 1, 2, 3, 4), \quad (6)$$

where φ_{p_i} is the linear combination of atomic orbitals φ_{p_x}, φ_{p_y}, and φ_{p_z}. The s-orbital component k_i can be determined from the following relations

$$\cos\theta_{ij} = -\sqrt{\frac{k_i k_j}{(1 - k_i)(1 - k_j)}}, \quad (7)$$

and

$$\sum_{i=1}^{4} k_i = 1. \quad (8)$$

Substituting the values in Table 1 into Eq.(7) and taking the angles between σ bonds into consideration we can easily give the components k_i of s orbitals for different sites for the two models, which are listed in Table 2. It may be seen from Table 2 that whatever the model is, the components of s orbitals in the hybridized π states are the most for the site 1 and the least for the site 7. But in the case of each of the sites, the components are much larger than that in C_{60}. This is why the conducting properties of the C_{36} molecule are superior to C_{60}. As to the proportions of $2p_x$,$2p_y$, and $2p_z$ orbitals in hybrid orbital ψ_i, they can be easily calculated by virtue of the above results and by choosing an appropriate coordinate system for a site. The hybrid orbitals of each carbon atom are given by

$$\psi_i = \sum_j b_{ij}\varphi_j, \quad (9)$$

Table 2. The components of s and p orbitals for the sp^3 hybrid in the D_{6h} C_{36} molecule.

Molecules	Sites	ψ_i	s	p
C_{36}(Mod.1)	1	ψ_1	0.2098	0.7902
		ψ_2	0.1236	0.8764
		$\psi_3(\psi_4)$	0.3333	0.6667
	7	ψ_1	0.0482	0.9518
		ψ_2	0.2852	0.7148
		$\psi_3(\psi_4)$	0.3333	0.6667
	13	ψ_1	0.1505	0.8495
		ψ_2	0.3774	0.6226
		$\psi_3(\psi_4)$	0.2361	0.7639
C_{36}(Mod.2)	1	ψ_1	0.1764	0.8235
		ψ_2	0.1569	0.8431
		$\psi_3(\psi_4)$	0.3333	0.6667
	7	ψ_1	0.0656	0.9344
		ψ_2	0.2677	0.7323
		$\psi_3(\psi_4)$	0.3333	0.6667
	13	ψ_1	0.1316	0.8684
		ψ_2	0.3963	0.6037
		$\psi_3(\psi_4)$	0.2361	0.7639
C_{60}	i	ψ_1	0.0380	0.9620
		ψ_2	0.4898	0.5102
		$\psi_3(\psi_4)$	0.2361	0.7639

where $i = 1$ represnts the π orbitals, and $i = 2, 3, 4$ denote three σ orbitals, respectively, and $j = 1, 2, 3, 4$ correspond to s,p_x,p_y,p_z. We choose the z-axis along the hybridized π orbital, which is the normal direction of the ellipsoidal surface, and then let the σ bond labeled with 2 lie in xz-plane. For the site 1 in model 1,Eq.(9) can be expressed as

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.4580 & 0.0000 & 0.0000 & 0.8889 \\ 0.3515 & 0.9185 & 0.0000 & -0.1811 \\ 0.5774 & -0.2796 & 0.7071 & -0.2975 \\ 0.5774 & -0.2796 & -0.7071 & -0.2975 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{10}$$

For site 7, we have

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.2196 & 0.0000 & 0.0000 & 0.9756 \\ 0.5340 & 0.8369 & 0.0000 & -0.1202 \\ 0.5774 & -0.3870 & 0.7071 & -0.1299 \\ 0.5774 & -0.3870 & -0.7071 & -0.1299 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{11}$$

Similarly, for site 13, Eq.(9) becomes

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.3879 & 0.0000 & 0.0000 & 0.9217 \\ 0.6143 & 0.7455 & 0.0000 & -0.2585 \\ 0.4859 & -0.4713 & 0.7071 & -0.2045 \\ 0.4859 & -0.4713 & -0.7071 & -0.2045 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{12}$$

Here we have made use of the orthogonality between the hybrid orbitals and their normalization. For model 2,

in the case of site 1, Eq.(9) becomes

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.4201 & 0.0000 & 0.0000 & 0.9075 \\ 0.3961 & 0.8997 & 0.0000 & -0.1833 \\ 0.5774 & -0.3086 & 0.7071 & -0.2673 \\ 0.5774 & -0.3086 & -0.7071 & -0.2673 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{13}$$

For site 7, we have

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.2562 & 0.0000 & 0.0000 & 0.9666 \\ 0.5174 & 0.8447 & 0.0000 & -0.1371 \\ 0.5774 & -0.3785 & 0.7071 & -0.1530 \\ 0.5774 & -0.3785 & -0.7071 & -0.1530 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{14}$$

Similarly, for site 13, Eq.(9) becomes

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.3627 & 0.0000 & 0.0000 & 0.9319 \\ 0.6295 & 0.7373 & 0.0000 & -0.2450 \\ 0.4859 & -0.4777 & 0.7071 & -0.1891 \\ 0.4859 & -0.4777 & -0.7071 & -0.1891 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{15}$$

For C_{60}, we have

$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{bmatrix} = \begin{bmatrix} 0.1949 & 0.0000 & 0.0000 & 0.9808 \\ 0.6999 & 0.7007 & 0.0000 & -0.1391 \\ 0.4859 & -0.5046 & 0.7071 & -0.0966 \\ 0.4859 & -0.5046 & -0.7071 & -0.0966 \end{bmatrix} \begin{bmatrix} \varphi_s \\ \varphi_{p_x} \\ \varphi_{p_y} \\ \varphi_{p_z} \end{bmatrix}. \tag{16}$$

Here the z-axis has been chosen along the π orbitals of C_{60} and let the short bond lie in xz-plane. As compared with C_{60}, the component of s orbitals is much larger for the π orbitals. This means that the σ electrons in C_{36} are responsible for the energy band structure. It goes without saying that the electronic hopping integrals between the nearest neighbor sites are not identical. The electronic hopping energies will be given in another paper.

In conclusion,we have discussed the hybrid orbitals of carbon atoms in the D_{6h} C_{36} molecule for two kinds of rotating ellipsoid models with different short and long semi-axes. The component of s orbitals for each carbon atom in the D_{6h} C_{36} molecule is larger than that in C_{60}. We think it proper to calculate the electronic energy band using model 2, in which the short semi-axis is $1.78R$ and the long semi-axis is $2.26R$. This work can serve as the starting point in calculating some electronic properties of C_{36} fullerenes.

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