

Note on the Electronic Structure of C₆₀ Molecule

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A molecular orbital approach to the electronic structure of C₆₀ molecule is formulated on the basis of optimized bond orbital model and the stability of the truncated icosahedron structure is examined.

I. Introduction

Since Kroto et al. reported experimental evidence¹⁾ of the existence of C₆₀ molecule (cluster) in 1985, a lot of works have been done on crystallographic and electronic properties of C₆₀ including the possibility of superconductivity. The trend has been enhanced especially after the invention of a simple way to produce C₆₀ in 1990 by Krätschmer²⁾, and many interesting properties of C₆₀ molecule and C₆₀ solid have been revealed.

We here try to examine the stability of C₆₀ cluster on the basis of the optimized bond orbital model (OBOM)³⁾ which is an extension of original bond orbital model due to Harrison⁴⁾. In the OBOM we can determine the functional form of each *sp* hybrid orbital on each carbon atom so as to minimize the evaluated electronic energy of a carbon atom with respect to the parameters included in the hybrid functions and thereby discuss the stability of various structure of carbon atoms.

The optimized *sp* hybrid orbitals are defined and the OBOM is formulated in Chap. II. In Chaps. III and IV, numerical calculations and results are given for diamond, graphite and C₆₀.

II. Formulation

Some carbon atoms in C₆₀ cluster are illustrated in Fig.1. We denote an unbonding orbital and three bonding orbitals by Ψ_0 and $\Psi_1 \sim \Psi_3$, respectively. Carbon atoms of C₆₀ are on a sphere and Ψ_0 is nearly perpendicular to the surface of the sphere while $\Psi_1 \sim \Psi_3$ are along the surface. We take the coordinate axes on each carbon atom such that Ψ_0 is parallel to *z*-axis

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and Ψ_1 is in the x - z plane. We also assume that orbitals Ψ_2 and Ψ_3 are symmetric with respect to the x - z plane as expected from the structure of C_{60} molecule.

Wave functions of four orbitals for each carbon atom may be expressed by orthonormal atomic orbitals $|s\rangle$, $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$ as

$$|\Psi_0\rangle = \sqrt{1 - a_1^2}|s\rangle + a_1|p_z\rangle, \quad (1)$$

$$|\Psi_1\rangle = \sqrt{1 - a_2^2 - a_3^2}|s\rangle + a_2|p_x\rangle - a_3|p_z\rangle, \quad (2)$$

$$|\Psi_2\rangle = a_4|s\rangle - a_5|p_x\rangle + \frac{1}{\sqrt{2}}|p_y\rangle - a_6|p_z\rangle, \quad (3)$$

$$|\Psi_3\rangle = a_4|s\rangle - a_5|p_x\rangle - \frac{1}{\sqrt{2}}|p_y\rangle - a_6|p_z\rangle. \quad (4)$$

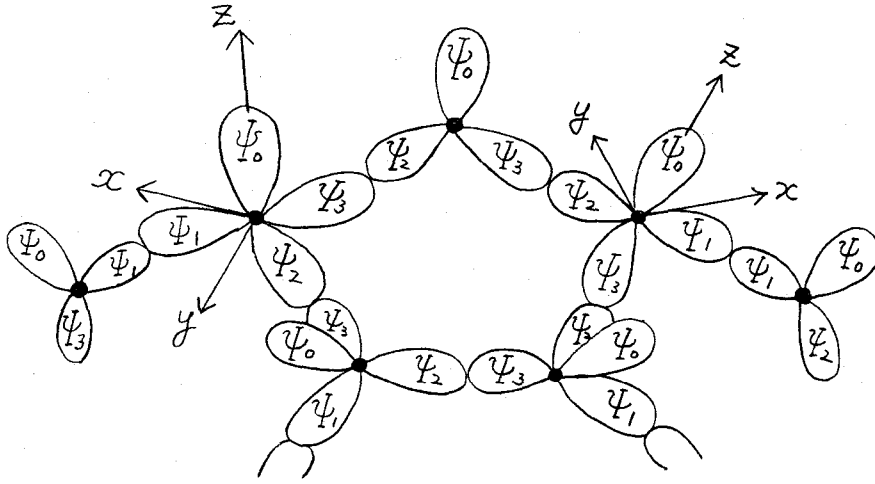


Fig. 1. Atomic orbitals of carbon atoms in C_{60} molecule.

The above orbitals include two well-known orbitals, sp^2 and sp^3 hybrid orbitals, as special cases. When we take

$$a_1 = 1, \quad a_2 = \frac{\sqrt{6}}{3}, \quad a_3 = 0, \quad a_4 = \frac{1}{\sqrt{3}}, \quad a_5 = \frac{1}{\sqrt{6}}, \quad \text{and} \quad a_6 = 0, \quad (5)$$

they reduce to sp^2 state, and when

$$a_1 = \frac{\sqrt{3}}{2}, \quad a_2 = \frac{\sqrt{6}}{3}, \quad a_4 = \frac{1}{2\sqrt{3}}, \quad a_5 = \frac{1}{2}, \quad a_6 = \frac{1}{\sqrt{6}}, \quad \text{and} \quad a_7 = \frac{1}{2\sqrt{3}}, \quad (6)$$

sp^3 state is obtained.

To obtain the orbitals of C_{60} molecule, we impose four assumptions on six coefficients included in Eqs.(1)-(4). The first two assumptions are the orthogonality conditions;

$$\langle \Psi_0 | \Psi_1 \rangle = \langle \Psi_0 | \Psi_2 \rangle = \langle \Psi_0 | \Psi_3 \rangle = 0.$$

These conditions require two relations among coefficients as

$$\sqrt{1 - a_1^2} \sqrt{1 - a_2^2 - a_3^2} - a_1 a_3 = 0, \quad (7)$$

and

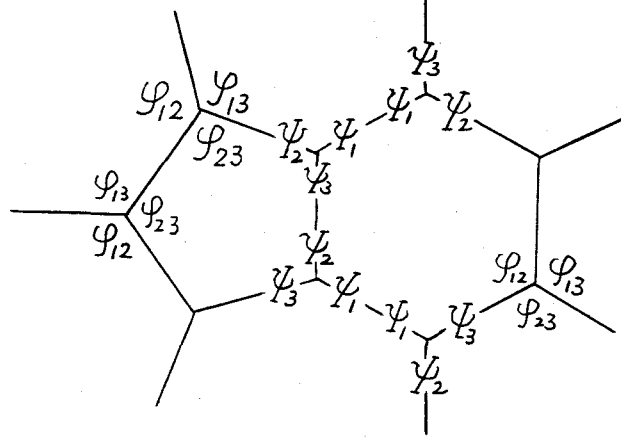


Fig.2 Relation between orbitals $\Psi_1 \sim \Psi_3$ belonging to neighbouring carbon atoms. Orbitals Ψ_0 (not shown) are almost perpendicular to these orbitals.

$$a_4\sqrt{1 - a_1^2} - a_1a_6 = 0. \quad (8)$$

We also assume the orthogonality

$$\langle \Psi_1 | \Psi_2 \rangle = \langle \Psi_1 | \Psi_3 \rangle = 0$$

which requires the condition

$$a_4\sqrt{1 - a_2^2 - a_3^2} - a_2a_5 + a_3a_6 = 0. \quad (9)$$

Another condition is the normalization of orbitals Ψ_2 and Ψ_3 :

$$\langle \Psi_2 | \Psi_2 \rangle = \langle \Psi_3 | \Psi_3 \rangle = 1$$

or

$$a_4^2 + a_5^2 + \frac{1}{2} + a_6^2 = 1. \quad (10)$$

As a result, we are left with two free parameters. These remaining parameter can be used to determine the bond angles $\varphi_{12} = \varphi_{13}$ and φ_{23} ; φ_{ij} is the angle between Ψ_i and Ψ_j .

Since the purpose of this paper is to investigate the stability of the truncated icosahedron structure, we survey the parameters so that the two bond angles φ_{12} and φ_{13} along the surface of the sphere are fixed at 120° . These angles are at apexes of a hexagon and these bonds construct six-membered ring of carbon atoms. We then expect that the remaining angle φ_{23} corresponding to the energy minimum is the angle at an apex of a pentagon and the five-membered ring of carbon atoms is obtained.

III. Calculation of Electronic Energy

The electronic energy of a carbon atom in C₆₀ molecule in the OBOM is expressed as

$$E_{\text{total}} = E_0 + E_1 + 2E_2. \quad (11)$$

The first term is the energy of a dangling bond $|\Psi_0\rangle$ and E_1 is that of the bond orbital $|\Psi_1\rangle$. The last term corresponds to the energies of the equivalent bond orbitals $|\Psi_2\rangle$ and $|\Psi_3\rangle$.

The energy of the dangling bond is given by

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = (1 - a_1^2) \langle s | \mathcal{H} | s \rangle + a_1^2 \langle p_z | \mathcal{H} | p_z \rangle.$$

Here \mathcal{H} is the Hamiltonian operator representing a carbon atom. For the energy of s and p orbitals of a carbon atom, we adopt⁵⁾

$$\langle s | \mathcal{H} | s \rangle = \varepsilon_s = -17.52 \text{ eV},$$

and

$$\langle p_x | \mathcal{H} | p_x \rangle = \langle p_y | \mathcal{H} | p_y \rangle = \langle p_z | \mathcal{H} | p_z \rangle = \varepsilon_p = -8.97 \text{ eV}.$$

When we denote the wave function on the neighboring atom by primes, the energy of the bond orbital composed of Ψ_1 and Ψ_1' is given by

$$E_1 = \varepsilon_1 - V_2^1, \tag{12}$$

$$\varepsilon_1 = \langle \Psi_1 | \mathcal{H} | \Psi_1 \rangle, \quad V_2^1 = -\langle \Psi_1 | \mathcal{H} | \Psi_1' \rangle.$$

Similarly the energy of other two bond orbitals composed of Ψ_2 and Ψ_3'' , and Ψ_3 and Ψ_2''' are written as

$$E_2 = \varepsilon_2 - V_2^2, \tag{13}$$

$$\varepsilon_2 = \langle \Psi_2 | \mathcal{H} | \Psi_2 \rangle = \langle \Psi_3 | \mathcal{H} | \Psi_3 \rangle,$$

$$V_2^2 = -\langle \Psi_2 | \mathcal{H} | \Psi_3'' \rangle = -\langle \Psi_3 | \mathcal{H} | \Psi_2''' \rangle.$$

While the intraatomic matrix elements ε_1 and ε_2 can be easily obtained from Eqs.(1) to (4) in the same manner as E_0 described above, some calculations are needed for the interatomic matrix elements V_2^1 and V_2^2 because of geometry of carbon atoms on the sphere of C_{60} molecule. Detailed processes and final expressions are given in Appendix.

IV. Numerical Analysis and Results

a) Reproduction of Graphite and Diamond Structure

Let us first examine our model by calculating the electronic energy of the graphite structure. In this case, three of four bond orbitals are placed on the same layer and the remaining orbital is taken to be perpendicular to this layer. When a_1 in Eq.(1) is fixed at $a_1 = 1$, there is no hybridization between orbital Ψ_0 and orbitals $\Psi_1 \sim \Psi_3$. We change the angles between three bond orbitals in the layer keeping the equivalence of two of them. In Fig.3, the resultant total electronic energy is plotted as a function of the angle between two equivalent orbitals (φ_{23}). The minimum of electronic energy is obtained at $\varphi_{23} = 120^\circ$, corresponding to the graphite structure as expected. From experiments, it is known that the interatomic distance within the layer is 1.428\AA and the intralayer distance is 3.55\AA . With 1.428\AA , we

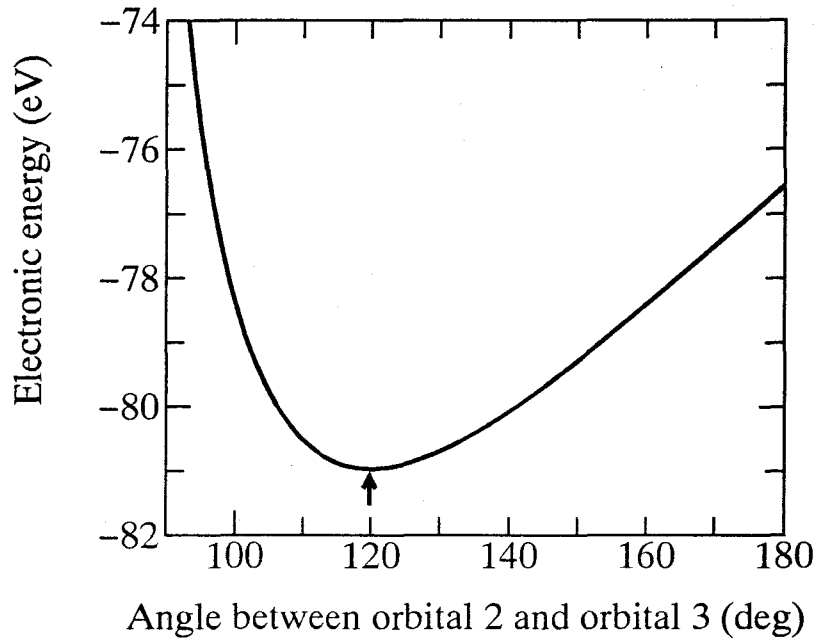


Fig. 3. Electronic energy of graphite structure.

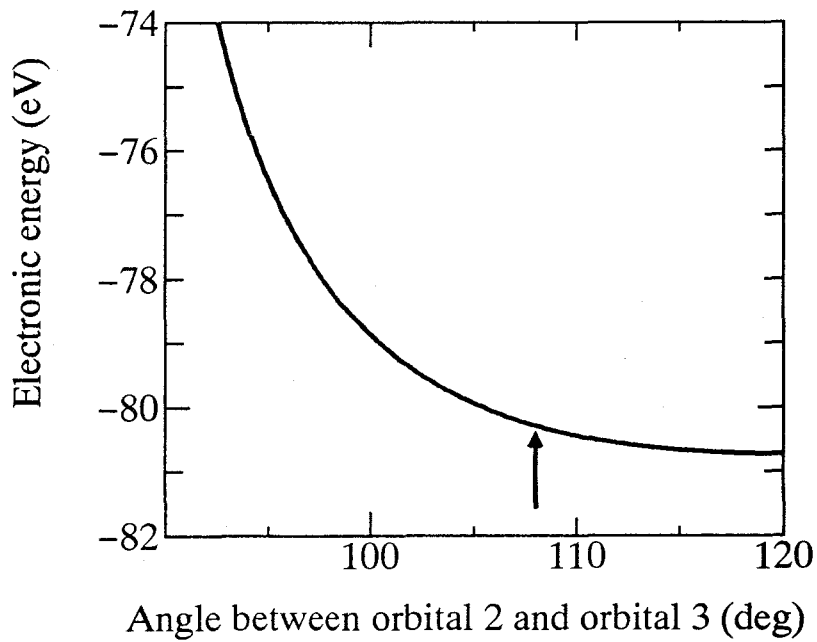


Fig. 4. Electronic energy for C_{60} structure.

obtain -80.96 eV at the minimum of the electronic energy. We here take into account of the intralayer bonding only.

To calculate the electronic energy of the diamond structure with this model, we take parameters given by (6) for sp^3 hybridized orbitals and the experimental interatomic distance $d = 1.54$ Å. The obtained energy value is -85.88 eV per carbon atom. The above results indicate that our bond orbital model works as a good approximation in these special cases.

b) Electronic energy and Stability of C_{60}

We now apply our model calculation of electronic energy to investigate the stable structure for C_{60} . As described in Chap.II, we use six parameters with four conditions. One of the remaining parameters is used to fix the two equivalent bond angles φ_{12} and φ_{13} to 120° , and the electronic energy can be determined as the function of the last parameter. The results are shown in Fig.4 where the last free parameter is expressed as the angle between two equivalent bonds (φ_{23}).

Table I. Electronic energy per carbon atom.

structure	energy
isolated atom	-44.43 eV
C_{60} molecule	-80.28 eV
graphite	-80.96 eV
diamond	-85.88 eV

Table II. Energy per electron in carbon atom.

	$\varphi_{23} = 120^\circ$	$\varphi_{23} = 108^\circ$
E_0	-8.97 eV	-9.64 eV
E_1	-24.7 eV	-25.5 eV
E_2	-23.5 eV	-22.5 eV

The electronic energy increases monotonously when the angle φ_{23} decreases. Three bonds are not planer anymore because the sum of three bond angles becomes less than 360° . The angle φ_{23} for the truncated icosahedron structure should be 108° . In Fig.4 we observe that the total electronic energy for $\varphi_{23} = 108^\circ$ is slightly higher than that for $\varphi_{23} = 120^\circ$ but this energy difference is much smaller than the difference between the energy of graphite structure and that of diamond structure as shown in Table I. The values of E_0 , E_1 , and E_2 at $\varphi_{23} = 120^\circ$ and $\varphi_{23} = 108^\circ$ are given in Table II.

Since the magnitudes of energies of bonding electrons (E_1 and E_2) are larger than that of a unbonded electron (E_0), the truncated icosahedron structure is stabilized with respect to opening of bonds constructing C_{60} . To obtain these results the experimental bond lengths for C_{60} are used; the bond length making five-membered ring is 1.455 Å and the one which is held by two neighbouring six-membered ring is 1.391 Å.

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Appendix. Calculation of Interatomic Matrix Elements

The atomic orbitals described in Chap.II are based on the individual coordinate axis where every $|\Psi_0\rangle$ is directed to z -axis. To calculate $\langle\Psi_1|\mathcal{H}|\Psi'_1\rangle$, $\langle\Psi_2|\mathcal{H}|\Psi''_2\rangle$, and $\langle\Psi_3|\mathcal{H}|\Psi'''_3\rangle$, we rewrite these wave functions so that the direction of the x -axes on the neighbouring two atoms are in common. We write $|\Psi_1\rangle$ and $|\Psi'_1\rangle$ here again (Fig.A1);

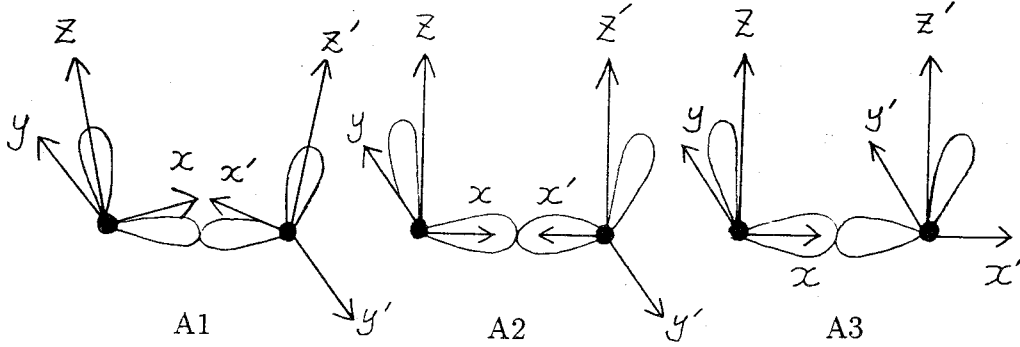


Fig. A. Rotation of coordinate axes for matrix element calculation.

$$|\Psi_1\rangle = \sqrt{1 - a_2^2 - a_3^2}|s\rangle + a_2|p_x\rangle - a_3|p_z\rangle,$$

$$|\Psi'_1\rangle = \sqrt{1 - a_2^2 - a_3^2}|s\rangle + a_2|p'_x\rangle - a_3|p'_z\rangle.$$

First both of two coordinate systems are rotated with respect to z -axis till the directions of $|\Psi_1\rangle$ and $|\Psi'_1\rangle$ coincide to x -axis and x' -axis, respectively (Fig.A2). The coordinate of $|\Psi'_1\rangle$ is then turned by π around z -axis (Fig.A3) and we obtain two wave functions expressed in the common coordinate system as

$$|\Psi_1\rangle = \sqrt{1 - a_2^2 - a_3^2}|s\rangle + \sqrt{a_2^2 + a_3^2}|p_x\rangle,$$

$$|\Psi'_1\rangle = \sqrt{1 - a_2^2 - a_3^2}|s\rangle - \sqrt{a_2^2 + a_3^2}|p_x\rangle.$$

Each matrix element is expressed by universal functional forms as

$$\langle s|\mathcal{H}|s'\rangle = V_{ss\sigma}, \quad \langle s|\mathcal{H}|p'_x\rangle = -\langle p_x|\mathcal{H}|s'\rangle = V_{sp\sigma}, \quad \text{and} \quad \langle p_x|\mathcal{H}|p'_x\rangle = V_{pp\sigma}.$$

As the universal functional forms for interatomic matrix elements, the Harrison's proposal⁶⁾ is adopted:

$$V_{ss\sigma} = -1.32(\hbar^2/m_e d^2), \quad V_{sp\sigma} = 1.42(\hbar^2/m_e d^2), \quad V_{pp\sigma} = 2.22(\hbar^2/m_e d^2),$$

where m_e is the electronic mass and d is the interatomic distance.

The energy of the bond orbital $\langle \Psi_1 | \mathcal{H} | \Psi_1' \rangle$ can be evaluated as

$$\begin{aligned} \langle \Psi_1 | \mathcal{H} | \Psi_1' \rangle &= \langle s | \mathcal{H} | s \rangle (1 - a_2^2 - a_3^2) - \langle s | \mathcal{H} | p_x \rangle \sqrt{1 - a_2^2 - a_3^2} \sqrt{a_2^2 + a_3^2} \\ &\quad + \langle p_x | \mathcal{H} | s \rangle \sqrt{1 - a_2^2 - a_3^2} \sqrt{a_2^2 + a_3^2} - \langle p_x | \mathcal{H} | p_x \rangle (a_2^2 + a_3^2). \end{aligned}$$

In case of the calculation of $\langle \Psi_2 | \mathcal{H} | \Psi_3'' \rangle$, we first convert the x -axis to the direction of the bond orbital Ψ_2 or Ψ_3'' . We then obtain

$$|\Psi_2\rangle = a_4|s\rangle + |p_x\rangle \left(-a_5 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta \right) - a_6|p_z\rangle,$$

$$|\Psi_3''\rangle = a_4|s\rangle + |p'_x\rangle \left(-a_5 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta \right) - a_6|p'_z\rangle.$$

Here, θ is determined by

$$a_5 \sin \theta + \frac{1}{\sqrt{2}} \cos \theta = 0.$$

The remaining process is the same as described above for $\langle \Psi_1 | \mathcal{H} | \Psi_1' \rangle$. The final expression is

$$\begin{aligned} \langle \Psi_2 | \mathcal{H} | \Psi_3'' \rangle &= \langle \Psi_3 | \mathcal{H} | \Psi_2''' \rangle \\ &= \langle s | \mathcal{H} | s \rangle a_4^2 - 2 \langle s | \mathcal{H} | p_x \rangle a_4 \sqrt{\left(-a_5 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta \right)^2 + a_6^2} \\ &\quad - \langle p_x | \mathcal{H} | p_x \rangle \left\{ \left(-a_5 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta \right)^2 + a_6^2 \right\}. \end{aligned}$$

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