

The Electronic Structure of C₆₀ Molecule — Structure of π -electron Band—

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The π -electron band of C₆₀ molecule has been obtained by the tight binding approximation. Application of molecular orbital wave functions derived on the basis of the optimized bond orbital model gives, with simpler calculations, the results in satisfactory agreement with those of previous theoretical analyses.

I. Introduction

Many interesting properties of C₆₀ molecule and C₆₀ solid have been investigated by numerous approaches both experimentally and theoretically. We have examined¹⁾ the stability of C₆₀ molecule on the basis of the optimized bond orbital model (OBOM)²⁾ which is an extension of original bond orbital model due to Harrison³⁾. 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 parameters included in hybrid functions and thereby discuss the stability of various structures of carbon atoms.

It has been shown that the bonding energy per carbon atom in C₆₀ molecule is slightly higher than that of a carbon atom in the graphite structure. We here show that the π -electron band energy stabilizes C₆₀ on the basis of a simple tight binding approximation. The energy gap obtained here is 1.83 eV, and this is in good agreement with previous works^{4),5)}.

The formulation of the OBOM and the bonding energy calculation in this model are outlined in Chap.II. In Chap III, the electronic band structure of C₆₀ is obtained by the tight binding approximation based on the results of OBOM calculation.

II. Formulation and Calculation of Bonding Energy

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 so

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that Ψ_0 is parallel to z -axis 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

$$|\Psi_0\rangle = a_1|s\rangle + a_2|p_z\rangle, \quad (1)$$

$$|\Psi_1\rangle = a_3|s\rangle + a_4|p_x\rangle - a_5|p_z\rangle, \quad (2)$$

$$|\Psi_2\rangle = a_6|s\rangle - a_7|p_x\rangle + \frac{1}{\sqrt{2}}|p_y\rangle - a_8|p_z\rangle, \quad (3)$$

and

$$|\Psi_3\rangle = a_6|s\rangle - a_7|p_x\rangle - \frac{1}{\sqrt{2}}|p_y\rangle - a_8|p_z\rangle. \quad (4)$$

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

$$\begin{aligned} a_1 = 0, \quad a_2 = 1, \quad a_3 = \frac{1}{\sqrt{3}}, \quad a_4 = \frac{\sqrt{6}}{3}, \quad a_5 = 0, \quad a_6 = \frac{1}{\sqrt{3}}, \\ a_7 = \frac{1}{\sqrt{6}}, \quad \text{and} \quad a_8 = 0, \end{aligned} \quad (5)$$

they reduce to sp^2 state, and when

$$\begin{aligned} a_1 = \frac{1}{2}, \quad a_2 = \frac{\sqrt{3}}{2}, \quad a_3 = \frac{1}{2}, \quad a_4 = \frac{\sqrt{6}}{3}, \quad a_5 = \frac{\sqrt{3}}{6}, \quad a_6 = \frac{1}{2}, \\ a_7 = \frac{1}{\sqrt{6}}, \quad \text{and} \quad a_8 = \frac{\sqrt{3}}{6}, \end{aligned} \quad (6)$$

sp^3 state is obtained.

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

$$\langle\Psi_0|\Psi_1\rangle = \langle\Psi_0|\Psi_2\rangle = \langle\Psi_0|\Psi_3\rangle = \langle\Psi_1|\Psi_2\rangle = \langle\Psi_1|\Psi_3\rangle = 0. \quad (7)$$

Other conditions are the normalization of each orbital which leads three relations:

$$\langle\Psi_0|\Psi_0\rangle = \langle\Psi_1|\Psi_1\rangle = \langle\Psi_2|\Psi_2\rangle = \langle\Psi_3|\Psi_3\rangle = 1. \quad (8)$$

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 .

We survey the parameter space with two bond angles φ_{12} and φ_{13} along the surface of the sphere 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.

The electronic bonding energy of a carbon atom in C_{60} molecule in the OBOM is expressed as

$$E_{\text{total}} = E_1 + 2E_2. \quad (9)$$

Here E_1 is energy of the bond orbital $|\Psi_1\rangle$ and the second term corresponds to the energies of the equivalent bond orbitals $|\Psi_2\rangle$ and $|\Psi_3\rangle$. We exclude the dangling bond which is considered later as π -electron band.

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

$$E_1 = \varepsilon_1 - V_2^1, \quad (10)$$

$$\varepsilon_1 = \langle \Psi_1 | \mathcal{H} | \Psi_1 \rangle, \quad V_2^1 = -\langle \Psi_1 | \mathcal{H} | \Psi'_1 \rangle.$$

Here \mathcal{H} is the Hamiltonian operator representing a carbon atom. For the energy of s and p orbitals of a carbon atom, we adopt⁶⁾

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

and

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

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

$$E_2 = \varepsilon_2 - V_2^2, \quad (11)$$

$$\varepsilon_2 = \langle \Psi_2 | \mathcal{H} | \Psi_2 \rangle = \langle \Psi_3 | \mathcal{H} | \Psi_3 \rangle, \quad V_2^2 = -\langle \Psi_2 | \mathcal{H} | \Psi_3'' \rangle = -\langle \Psi_3 | \mathcal{H} | \Psi_2''' \rangle.$$

While the intraatomic matrix elements ε_1 and ε_2 can be easily obtained from Eqs.(1) to (4), 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 C₆₀ molecule. The details of the bond energy calculations are explained in reference 1.

We have eight parameters with six conditions. One of the remaining parameters is used to fix the two equivalent bond angles φ_{12} and φ_{13} at 120° , and the electronic energy is determined as the function of the last parameter. The results are shown in Fig.1 where the free parameter is expressed as the angle between two equivalent bonds (φ_{23}). To obtain these results the experimental bond lengths for C₆₀ are used; the bond length making five-membered ring is 1.455\AA and the one which is shared by two neighboring six-membered ring is 1.391\AA .

The bonding 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.1 we observe that the total bonding 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. We have employed 1.54\AA as the bond length for diamond structure and 1.428\AA for graphite structure which are known experimentally, and obtained these bonding energy using our OBOM.

When φ_{23} is fixed at 108° , eight coefficients of the wave functions are determined uniquely to be $\varphi_{02} = \varphi_{03} = 99.5^\circ$ and $\varphi_{01} = 105.4^\circ$. The wave function of π -electron is now written as

$$|\Psi_0\rangle = 0.2834|s\rangle + 0.9590|p_z\rangle. \quad (12)$$

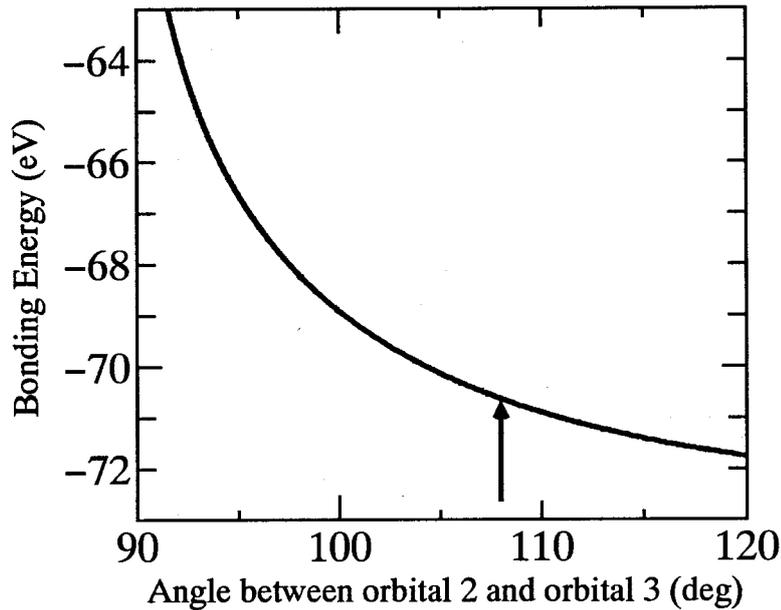


Fig. 1. Bonding energy vs. angle φ_{23} . $\varphi_{23} = 120^\circ$ corresponds to graphite structure and $\varphi_{23} = 108^\circ$, to truncated icosahedron structure.

Table I. Bonding energy per carbon atom.

structure	energy
C_{60} molecule	-70.63 eV
graphite	-71.75 eV
diamond	-85.88 eV

III. Calculation of π -electron Band

To calculate the π -electron band for C_{60} , the wave functions of π -electrons, Eq.(12), of sixty carbon atoms constructing C_{60} molecule are substituted to the tight binding Hamiltonian. Each π -electron of a carbon atom has three nearest neighbors, and we get 60×60 secular equation from tight binding Hamiltonian. We adopt Harisson's parameters³⁾ for numerical calculations of nearest neighbor interactions. The details of calculation including this large Hamiltonian matrix are displayed in Appendix.

In Fig. 2, π -electron band is illustrated for graphite structure. We only have considered intralayer overlap interactions and neglected interlayer interactions. The lowest band is filled and the middle band is half-filled. Energy gap is then zero in graphite. The π -electron band obtained here for C_{60} is shown in Fig. 3.

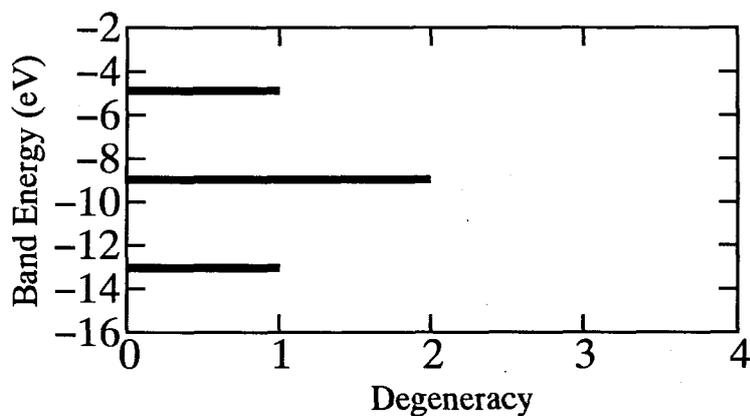
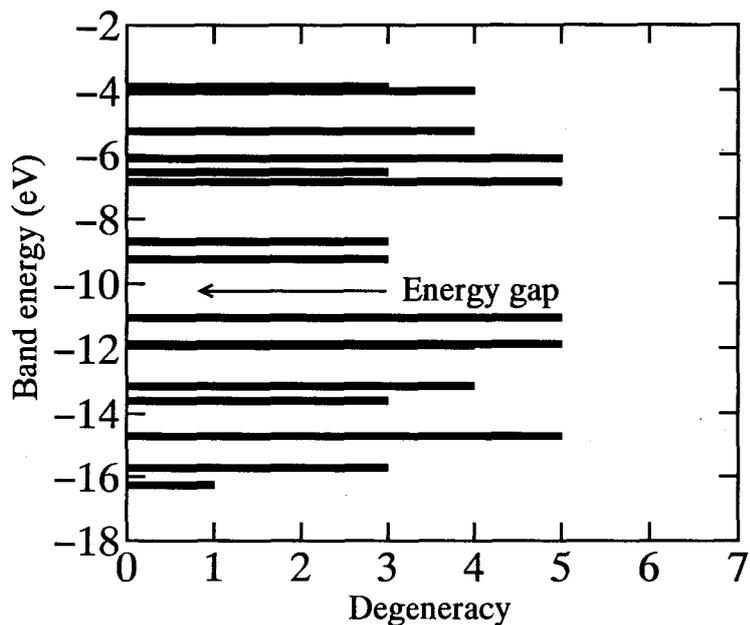
The band energies which are the average values of these filled band energy are listed in Table II, and total energies of bond and band in Table III.

Table II. π -electron band energy.

structure	energy
C_{60} molecule	-13.08 eV
graphite	-11.06 eV

Table III. Total electronic energy per atom.

structure	energy
C_{60} molecule	-83.71 eV
graphite	-82.81 eV
diamond	-85.88 eV

Fig. 2. π -electron band energy for graphite structure.Fig. 3. π -electron band energy for C_{60} structure.

IV. Discussion and Conclusion

It follows from the results of these simple calculation that the C_{60} structure is sufficiently stabilized by π -electrons. The π -electron band structure completely agrees with the results of other works^{7),8)}. The energy gap obtained is 1.83eV and this also agrees well with previous values obtained by various methods; 1.9eV by Saito et al.⁴⁾ and 2.1eV by Yorikawa et al.⁵⁾ Our OBOM has thus been shown to describe the properties of C_{60} structure appropriately.

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Appendix. Tight Binding Calculation.

The tight binding Hamiltonian \mathcal{H}_π can be written as

$$\mathcal{H}_\pi = \sum_i |\Psi_0(i)\rangle \varepsilon_\pi \langle \Psi_0(i)| + \sum_{\langle i,j \rangle} |\Psi_0(i)\rangle t_\pi \langle \Psi_0(j)|,$$

where i and j denote the individual carbon atom and $\langle i, j \rangle$ means the summation over nearest neighbors. ε_π is the site energy of π -electron and t_π the overlap integral between neighboring π -electrons: There are two types of overlap integrals; we denote by α the nearest neighbor overlap on π -bond on the edge of pentagons, and by β that on π -bond shared by two hexagons. Three kinds of elements of Hamiltonian matrix are then expressed as

$$\varepsilon = \langle \Psi_0 | \mathcal{H}_\pi | \Psi_0 \rangle = a_1^2 \varepsilon_s + a_2^2 \varepsilon_p,$$

$$\begin{aligned} \alpha &= \langle \Psi_0 | \mathcal{H}_\pi | \Psi'_0 \rangle \\ &= \langle \Psi_0 | \mathcal{H}_\pi | \Psi''_0 \rangle \\ &= a_1^2 V_{ss\sigma} + 2a_1 a_2 \sin \chi V_{sp\sigma} - a_1^2 \sin^2 \chi V_{pp\sigma} + a_2^2 \cos^2 \chi V_{pp\pi}, \end{aligned}$$

and

$$\begin{aligned} \beta &= \langle \Psi_0 | \mathcal{H}_\pi | \Psi'''_0 \rangle \\ &= a_1^2 V_{ss\sigma} + 2a_1 a_2 \sin \phi V_{sp\sigma} - a_1^2 \sin^2 \phi V_{pp\sigma} + a_2^2 \cos^2 \phi V_{pp\pi}. \end{aligned}$$

Here,

$$\sin \chi = \frac{-a_7 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta}{\sqrt{\left(-a_7 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta\right)^2 + a_8^2}},$$

$$\cos \chi = \frac{-a_8}{\sqrt{(-a_7 \cos \theta + \frac{1}{\sqrt{2}} \sin \theta)^2 + a_8^2}},$$

$$a_7 \cos \theta + \frac{1}{\sqrt{2}} \cos \theta = 0,$$

and

$$\cos \phi = \frac{a_4}{\sqrt{a_4^2 + a_5^2}}, \quad \sin \phi = \frac{a_5}{\sqrt{a_4^2 + a_5^2}}.$$

As the universal functional forms for interatomic matrix elements, the Harrison's proposal⁹⁾ is adopted:

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

$$V_{pp\sigma} = 2.22(\hbar^2/m_e d^2), \quad V_{pp\pi} = -0.63(\hbar^2/m_e d^2),$$

where m_e is the electronic mass and d is the interatomic distance. The configurations of carbon atoms on the sphere are displayed in Fig.A1, and the tight binding Hamiltonian matrix is obtained as shown in Table A.

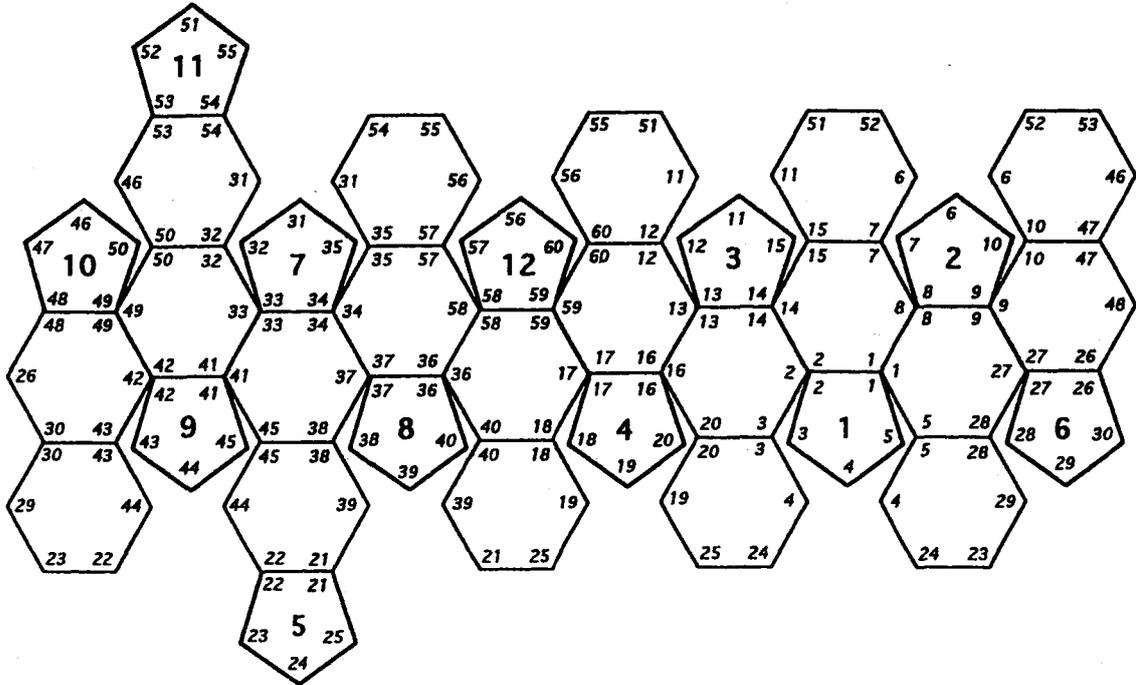


Fig. A1. Configuration of carbon atoms of C₆₀.

References

- 1) C. Totsuji, T. Matsubara and M. Obuchi, Mem. Fac. Eng. Okayama Univ., **29**, 15 (1994).
- 2) A. Nakanishi and T. Matsubara, J. Phys. Soc. Jpn., **51**, 3129 (1982).
- 3) W. A. Harrison, *Electronic Structure and the Properties of Solid*, (W. H. Freeman, San Francisco, 1980).
- 4) S. Saito and A. Oshiyama, Phys. Rev. Lett., **66**, 2637 (1991).
- 5) H. Yorikawa, M. Itenishi, and S. Muramatsu, J. Phys. Soc. Jpn., **62** 3762 (1993).
- 6) F. Harman and S. Skillman, *Atomic Structure Calculations*, (Prentice Hall, Englewood Cliffs, N.J. 1963).
- 7) A. D. J. Haymet, Chem. Phys. Lett., **122**, 421 (1985).
- 8) M. Ozaki and A. Takahashi, Chem. Phys. Lett., **127**, 242 (1986).
- 9) W. A. Harrison, Phys. Rev., **B24**, 5835 (1981).