Analytic treatment of next-nearest-neighbor hopping in C₆₀ molecules

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We extend the analytic solution of C₆₀ molecular orbitals to include nonzero next-nearest-neighbor hopping. This next-nearest-neighbor hopping term does not destroy the icosahedral symmetry in the ground state as was claimed, and plays a role in alternating electronic structures.

It is essential to understand structural and electronic properties of a single C₆₀ molecule before one can correctly investigate the bulk properties and the mechanism of superconductivity of solid C₆₀ and its alloy compounds.^{1,2} Many authors have used a tight-binding model to describe structural and electronic properties in neutral and charged C₆₀ molecules.³⁻⁶ The theory used there is similar to that used in conjugated polymers,⁷ which only includes nearest-neighbor π -electron and phonon (e -ph) interactions. But as it was pointed out,⁸ in the context of C₆₀, it is perhaps to be expected that non-nearest-neighbor interactions play a great role in C₆₀ than that in conjugated polymers because of the closed periodic five- and six-membered rings in the former. In C₆₀, each carbon has three nearest-neighbor interactions but *six* next-nearest-neighbor (NNN) interactions, compared with conjugated polymers, where each carbon only has two nearest-neighbor interactions and also two NNN interactions. In a previous paper,⁹ we analytically solved the electronic structure of neutral C₆₀ molecular orbitals with inclusion of the effects of nearest e -ph interactions. In this paper, we use a similar method to extend our analytic solutions to further consider the effect of NNN interactions. We found, unlike as it was claimed, the inclusion of NNN interactions does not destroy the icosahedral symmetry as well as the degeneracies of molecular orbitals in the ground state of neutral C₆₀. The inclusion of NNN interactions in general enlarges the gap width and the spacings between two successive energy levels in the valence band, but it reduces the spacings between two successive energy levels in the conduction band at small dimensionless hopping integral η of NNN interactions. Moreover, at large η , the sequence orders of energy levels in the conduction band are changed, and the lowest unoccupied molecular orbitals (LUMO) T_{1u} states are replaced by T_{3g} states.

Within the tight-binding approximation, the Su-Schrieffer-Heeger (SSH)-like Hamiltonian¹⁰ including NNN term is written as

$$H = - \sum_{\langle i,j \rangle s} [t_0 - \alpha(l_{i,j} - l_1)](c_{i s}^\dagger c_{j s} + c_{j s}^\dagger c_{i s}) - t_2 \sum_{[i,j]} (c_{i s}^\dagger c_{j s} + c_{j s}^\dagger c_{i s}) + \frac{K}{2} \sum_{\langle i,j \rangle} (l_{i,j} - l_1)^2, \quad (1)$$

where $c_{i s}^\dagger (c_{i s})$ are electron creation (annihilation) operators at site i of the C atom with spin s . The first term represents the electronic hopping term, where $\langle i,j \rangle$ means summation over the nearest-neighboring C atoms. The hopping integral is expanded up to the linear term proportional to the length deviation from l_1 , where $l_{i,j}$ is the distance between i and j atoms, l_1 is the length at which all springs are relaxed, and α describes the strength of intersite electron-phonon coupling. The second term represents the NNN interaction, where $[i,j]$ implies summation over the NNN C atoms. The rest term describes elastic potential energies. K is the stiffness constant of bond-stretching spring. In C₆₀, each carbon atom connects with three bonds, one short bond and two long bonds, and has six NNN carbon atoms, of which four atoms connecting through one short bond and one long bond, whereas the other two through two long bonds. Here we make an approximation which assumes all the distances between two NNN carbon atoms are same. This is a proper approximation since the difference of the distances are relative small compared with the relative long distance between NNN atoms. The angle between a long bond and a short bond is bigger than the angle between two long bonds which reduces the difference. It is convenient to introduce dimensionless parameters

$$\lambda = \frac{4\alpha^2}{\pi K t_0}, \quad \delta_{i,j} = \frac{2\alpha l_{i,j}}{t_0}, \quad \delta_1 = \frac{2\alpha l_1}{t_0}, \quad (2)$$

and to measure energy in units of t_0 , i.e., $H/t_0 \rightarrow H$. Let

$$\tau = 1 - \frac{1}{2}(\delta_S - \delta_1), \quad \sigma = \frac{1 - \frac{1}{2}(\delta_L - \delta_1)}{1 - \frac{1}{2}(\delta_S - \delta_1)},$$

$$\eta = \frac{t_2}{t_0\tau}. \quad (3)$$

Then the electronic part of Hamiltonian Eq. (1) can be expressed as

$$H = \tau(H_1 - \eta H_2), \quad (4)$$

where H_1 and H_2 represent the nearest-neighbor term and NNN term, respectively.

The icosahedral group has sixty elements which has one to one correspondence to sixty carbon sites in C_{60} , so we can use its element g to label site i of the C atom. H_1 can be reexpressed as

$$H_1 = \sum_{gg'} t_{gg'} (c_g^\dagger c_{g'} + c_{g'}^\dagger c_g) \quad (5)$$

and

$$t_{gg'} = \langle g | H_1 | g' \rangle$$

$$= \begin{cases} -\sigma & \text{for a long bond, } g' = gf_b, (b = 1, 2) \\ -1 & \text{for a short bond, } g' = gf_a \\ 0 & \text{otherwise,} \end{cases} \quad (6)$$

where $g' = gf_{a(b)}$, $f_{a(b)}$ is the proper rotation a or b to rotate g to its nearest neighbors through long or short bonds, respectively. In the right canonical representation, H_1 can be expressed in terms of three representation matrices,

$$H_1 = -D(f_a) - \sigma \sum_{b=1,2} D(f_b). \quad (7)$$

The right canonical representation of the icosahedral group is described in a 60-dimensional space, whose base vector g_i , ($i = 1, \dots, 60$), has 60 components with all the components being equal to zero except the i th component which is equal to one. This representation is reducible and contains all the irreducible representations (IR) of the I group, A , T_1 , T_3 , G , and H , with the occurrence of each IR being equal to the dimensionality of the IR. Therefore, we can simultaneously block-diagonalize $D(f_a)$ and $D(f_b)$, ($b = 1, 2$), as well as H_1 . Thus, the eigenvalue problems can be solved analytically by diagonalizing no more than 3×3 matrices. The detailed method and results of the H_1 matrix can be found in Ref. 9.

Next, we consider a simplified case where we set $\alpha = 0$, i.e., $\sigma = 1$ and $\tau = 1$. This case represents a Hamiltonian which does not include the electron-phonon interaction.⁸ H_1 becomes H_{10} , which can be explicitly expressed in matrix form as

$$H_{10} = \begin{pmatrix} 0 & -1 & 0 & 0 & -1 & -1 & 0 & 0 & \dots & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & -1 & 0 & \dots & 0 \\ & & & & & & & & \dots & \\ & & & & & & & & \dots & \\ & & & & & & & & \dots & \\ & & & & & & & & \dots & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 \end{pmatrix}. \quad (8)$$

In the fullerene, each carbon atom has three nearest-neighbor carbon atoms and six NNN carbon atoms. The matrix H_{10} maps a base vector g_i into a sum of three base vectors representing its three neighbor carbon atoms, i.e., $H_{10}g_i = -g_{i_1} - g_{i_2} - g_{i_3}$, where i_1, i_2, i_3 label the neighbor atom sites of site i . If we let the matrix H_{10} act on the base vector g_i second time, it results in mapping g_{i_1} , g_{i_2} , and g_{i_3} into their nearest-neighbor carbon atoms, respectively, which gives nine base vectors. Among these nine base vectors, three are g_i itself, since, for example, g_{i_1} has three neighbor atoms, one is g_i , the other two are the next-nearest-neighbor atoms of g_i . Thus, $H_{10}^2 g_i = g_{i_1} + g_{i_2} + g_{i_3} + g_{i_4} + g_{i_5} + g_{i_6} + 3g_i$, where indices $i_1, \dots, i_6$, indicate the NNN atoms of atom i . Apparently, the function $H_{10}^2 - 3I$ is equivalent to the function H_2 , which maps g_i into its six next neighbor base vectors. Here I is a unit matrix. Then, Eq. (4) with $\sigma = 1$ and $\tau = 1$ becomes

$$H = H_{10} - \eta(H_{10}^2 - 3I). \quad (9)$$

From the above expression, we conclude the transformation matrix which diagonalize the matrix H_{10} also diagonalize H . If ϵ_0 is eigenvalue of H_{10} , then

FIG. 1. The energy levels of Hamiltonian H against dimensionless NNN hopping integral η .

TABLE I. The analytic solution of the molecular orbitals of C_{60} , where $\theta = \frac{1}{3}\arccos(-\frac{q}{2r})$, $r = \{\frac{1}{9}[4 - 4\sigma + 10\sigma^2 + (4 + 13\sigma)\eta + 16\eta^2]\}^{3/2}$, and $q = \frac{1}{27}[16 - 24\sigma + 12\sigma^2 + 25\sigma^3 + (24 - 96\sigma - 12\sigma^2)\eta - (60 + 222\sigma)\eta^2 - 115\eta^3]$.

Representation	Eigenvalue ϵ	ϵ_0 at $\sigma = 1$ and $\eta = 0$
T_{3g}	$1 + \frac{1}{2}(1 + \sqrt{5})\sigma - \frac{1}{2}(1 + 3\sqrt{5})\eta$	$\frac{1}{2}(3 + \sqrt{5})$
G_u	$\frac{1}{2}[\sigma - 3\eta + \sqrt{4 + 8\sigma + 5\sigma^2 - (16 + 18\sigma)\eta + 17\eta^2}]$	$\frac{1}{2}(1 + \sqrt{17})$
G_g	$\frac{1}{2}[\sigma + \eta + \sqrt{4 + 5\sigma^2 - (8 + 10\sigma)\eta + 9\eta^2}]$	2
H_u	$\frac{1}{2}[\sigma + 3\eta + \sqrt{4 - 4\sigma + 5\sigma^2 - (4 + 6\sigma)\eta + 5\eta^2}]$	$\frac{1}{2}(1 + \sqrt{5})$
T_{3u}	$\frac{1}{4}\{-3\sigma + \sqrt{5}\sigma - \eta + \sqrt{5}\eta + \sqrt{2}[8 - 4\sigma - 4\sqrt{5}\sigma + 15\sigma^2 + 5\sqrt{5}\sigma^2 + (28 - 12\sqrt{5} + 24\sigma - 4\sqrt{5}\sigma)\eta + (59 - 25\sqrt{5})\eta^2]^{1/2}\}$	$\frac{1}{2}\left(-\frac{3-\sqrt{5}}{2} + \sqrt{\frac{19+\sqrt{5}}{2}}\right)$
H_g	$-\frac{1}{3}(1 + \sigma - \eta) - 2\sqrt[3]{r}\cos(\theta + \frac{2\pi}{3})$	$\frac{1}{2}(-1 + \sqrt{13})$
T_{1g}	$1 - \frac{1}{2}(\sqrt{5} - 1)\sigma - \frac{1}{2}(1 - 3\sqrt{5})\eta$	$\frac{1}{2}(3 - \sqrt{5})$
T_{1u}	$\frac{1}{4}\{-3\sigma - \sqrt{5}\sigma - \eta - \sqrt{5}\eta + \sqrt{2}[8 - 4\sigma + 4\sqrt{5}\sigma + 15\sigma^2 - 5\sqrt{5}\sigma^2 + (28 + 12\sqrt{5} + 24\sigma + 4\sqrt{5}\sigma)\eta + (59 + 25\sqrt{5})\eta^2]^{1/2}\}$	$\frac{1}{2}\left(-\frac{3+\sqrt{5}}{2} + \sqrt{\frac{19-\sqrt{5}}{2}}\right)$
H_u	$\frac{1}{2}[\sigma + 3\eta - \sqrt{4 - 4\sigma + 5\sigma^2 - (4 + 6\sigma)\eta + 5\eta^2}]$	$\frac{1}{2}(1 - \sqrt{5})$
H_g	$-\frac{1}{3}(1 + \sigma - \eta) - 2\sqrt[3]{r}\cos(\theta + \frac{4\pi}{3})$	-1
G_g	$\frac{1}{2}[\sigma + \eta - \sqrt{4 + 5\sigma^2 - (10\sigma + 8)\eta + 9\eta^2}]$	-1
G_u	$\frac{1}{2}[\sigma - 3\eta - \sqrt{4 + 8\sigma + 5\sigma^2 - (16 + 18\sigma)\eta + 17\eta^2}]$	$\frac{1}{2}(1 - \sqrt{17})$
T_{3u}	$\frac{1}{4}\{-3\sigma + \sqrt{5}\sigma - \eta + \sqrt{5}\eta - \sqrt{2}[8 - 4\sigma - 4\sqrt{5}\sigma + 15\sigma^2 + 5\sqrt{5}\sigma^2 + (28 - 12\sqrt{5} + 24\sigma - 4\sqrt{5}\sigma)\eta + (59 - 25\sqrt{5})\eta^2]^{1/2}\}$	$\frac{1}{2}\left(-\frac{3-\sqrt{5}}{2} - \sqrt{\frac{19+\sqrt{5}}{2}}\right)$
H_g	$-\frac{1}{3}(1 + \sigma - \eta) - 2\sqrt[3]{r}\cos\theta$	$\frac{1}{2}(-1 - \sqrt{13})$
T_{1u}	$\frac{1}{4}\{-3\sigma - \sqrt{5}\sigma - \eta - \sqrt{5}\eta - \sqrt{2}[8 - 4\sigma + 4\sqrt{5}\sigma + 15\sigma^2 - 5\sqrt{5}\sigma^2 + (28 + 12\sqrt{5} + 24\sigma + 4\sqrt{5}\sigma)\eta + (59 + 25\sqrt{5})\eta^2]^{1/2}\}$	$\frac{1}{2}\left(-\frac{3+\sqrt{5}}{2} - \sqrt{\frac{19-\sqrt{5}}{2}}\right)$
A_g	$-1 - 2\sigma - 6\eta$	-3

$$\epsilon = \epsilon_0 - \eta(\epsilon_0^2 - 3), \quad (10)$$

and H has the same eigenvectors as that of H_{10} . The values for ϵ_0 are listed in Table I.

Now we return to the general case of Eq. (4). Since we have proved $H_2 = H_{10}^2 - 3I$, Eq. (4) can be rewritten as

$$H = \tau[H_1 - \eta(H_{10}^2 - 3I)]. \quad (11)$$

Again, this matrix is an algebraic expression of $D(f_a)$ and $D(f_b)$, and should be invariant under any operation of the icosahedral group. It turns out that the inclusion of NNN interactions will not destroy the icosahedral symmetry and the degeneracies in the ground state as well. Because

of that, the matrix can be simultaneously block diagonalized by using the same transformation matrix to block-diagonalize H_1 matrix. Each block matrix can be diagonalized analytically for we only need to solve no more than 3×3 matrix problems. The explicit block matrix forms are constructed by using the block-diagonalized H_1 matrices which were listed in Ref. 9. For the A_g mode, we immediately obtain its eigenvalue, $\epsilon = \tau(-1 - 2\sigma - 6\eta)$.

For the rest modes, we need to diagonalize block matrix H explicitly, for we can no longer use a simple expression like Eq. (10). Taking the T_1 modes as examples, we get three eigenvalues for these modes, of which two are T_{1u} modes, the other one is T_{1g} ,

$$\epsilon = \frac{1}{4}[-3\sigma - \sqrt{5}\sigma - \eta - \sqrt{5}\eta \pm \sqrt{2}\{8 - 4\sigma + 4\sqrt{5}\sigma + 15\sigma^2 - 5\sqrt{5}\sigma^2 + (28 + 12\sqrt{5} + 24\sigma + 4\sqrt{5}\sigma)\eta + (59 + 25\sqrt{5})\eta^2\}^{1/2}],$$

$$\epsilon = 1 - \frac{\sigma}{2}(\sqrt{5} - 1) - \eta \frac{1 - 3\sqrt{5}}{2}.$$

Table I has a complete list of eigenvalues of all the modes, where all the eigenenergies should be multiplied by $t_0\tau$ in order to restore the units of eV. The analytical results in Table I have been checked by direct numerical calculation and no discrepancy has been found. Given a set of parameters, t_0 , α , K , t_2 , and l_1 , the long bond length l_L and the short bond length l_S can be determined by Bogoliubov-de Gennes equations, i.e., through $\frac{\partial}{\partial\sigma}\langle\Psi_x|H|\Psi_x\rangle = 0$ and $\frac{\partial}{\partial\tau}\langle\Psi_x|H|\Psi_x\rangle = 0$, where $|\Psi_x\rangle$ is a multielectron wave function for the ground state. The eigenvectors can be also obtained analytically in the same way as in Ref. 9.

In Fig. 1, we plot curves for all the electronic levels in terms of the dimensionless NNN hopping integral η , where we set $\sigma = 0.9236$ and $\tau = 1.3935$, which corresponding to $t_0 = 1.91$ eV, $\alpha = 5.0$ eV/Å, and $K = 42$ eV/Å². We can see from the figure that the gap width and the spacings between two successive energy levels in the valence band is, in general, enlarged as η is increased, whereas the spacings between two successive energy levels in the conduction band is reduced at small η . Moreover, at large η , the sequence orders of energy levels in the conduction band are changed (a large η maybe is unphysical, but we discuss this region for completeness), and the LUMO T_{1u} states are replaced by T_{3g} states. The above description can be easily understood qualitatively from expression (10), which is valid only at $\sigma = 1$ and $\tau = 1$, but whose behavior is similar to that at $\sigma \neq 1$ and $\tau \neq 1$. At $\epsilon_0 = 1/2\eta$, expression (10) reaches its

maximum value, so the state whose ϵ_0 value is closest to $1/2\eta$ becomes highest unoccupied state. From expression (10) we also get $\Delta\epsilon = (1 - 2\eta\epsilon_0)\Delta\epsilon_0$. In the valence band where $\epsilon_0 < 0$, and consequently, $1 - 2\eta\epsilon_0 > 1$, $\Delta\epsilon$ is enlarged (with exception for the spacing between G_g and H_g states, whose energies ϵ_0 at $\sigma = 1$, $\tau = 1$ and $\eta = 0$ are degenerate), whereas in the conduction band at small η where ϵ_0 and $0 < 1 - 2\eta\epsilon_0 < 1$, $\Delta\epsilon$ is reduced. At large η when $\epsilon_0 > 1/2\eta$ in the conduction band, and consequently $1 - 2\eta\epsilon_0 < 0$, $\Delta\epsilon$ becomes negative, thus, the sequence orders of the energy levels are alternated.

In conclusion, we have analytically solved electronic structures for the ground state of neutral C₆₀ molecule within a SSH-like tight-binding model with the inclusion of next-nearest-neighbor hopping. The key point is to block diagonalize the Hamiltonian matrix by expressing it in terms of the right canonical representation matrices of the icosahedral group, which can be block diagonalized by a matrix constructed from all the irreducible representation matrices.^{3,9} This method is only valid for the ground state which has the icosahedral symmetry. When doping or photoexcitation is taken into account, the method cannot be applied to such cases, since a polaron or an exciton will break the icosahedral symmetry.^{4,11}

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