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An analytic solution of C_{60} molecular orbitals

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Abstract. The electronic structure of C_{60} molecular orbitals is calculated analytically, with the effects of electron–phonon interaction, and, consequently, two kinds of bond length, taken into account.

1. Introduction

The success in synthesizing macroscopic quantities of solid C_{60} [1] and the discovery of the superconductivity of its alloy compounds [2] have spurred great interest in the structural and electronic properties of the C_{60} molecule. Recently, Friedberg and co-workers [3] proposed an analytic approach to the calculation of the electronic structure of the π electrons in neutral C_{60} , using the well known SO(3) group to represent the symmetry group of C_{60} , I_h , and to diagonalize the TBA molecular Hamiltonian.

However, within their calculation, one unique bond length of C_{60} was assumed, which is inconsistent with the experimental observation showing two different bond lengths in the neutral C_{60} molecule [4]. The appearance of two kinds of bond length can be explained naturally within the theory of the electron–phonon (e–ph) interaction, as in the literature of conducting polymers [5]. In this paper, using the approach of Friedberg and co-workers, we have investigated analytically the effects of the e–ph interaction and, consequently, two kinds of bond lengths on the electronic structure.

2. Icosahedral symmetry

The structure of the molecule C_{60} has been determined explicitly through well known experiments [6]. There are 12 pentagons and 20 hexagons in C_{60} , which correspond to the 12 vertices and 20 faces of an icosahedron representing the proper icosahedral symmetry, I . The 120-element icosahedral point group of C_{60} , I_h , is the cross product of the 60-element icosahedral rotation group I and the inversion group C_I , i.e. $I_h = I \otimes C_I$. The inversion group C_I contains only the unit operator and the inversion operator, both of which commute with the 60 proper rotations in I . Thus the elements of the full I_h are generated by first operating on all the rotations of I with the unit operator of C_I , replicating the class structure of I . Then all the proper rotations of I are multiplied with the inversion of C_I , creating 60 new improper rotations. There are 15, 10 and six twofold, threefold and fivefold symmetry axes, respectively, in the icosahedron. The proper rotation of I is divided into five classes, i.e. E, $12C_5$, $12C_5^2$, $20C_3$ and $15C_2$. Therefore, there are five irreducible representations

(IRs) in I . The multiplication table and character table have been given by Harter and Week [7].

According to [3] the proper icosahedral group I is a subgroup of $SO(3)$, therefore our knowledge of $SO(3)$ can be used to represent I , and then to reduce the representations of $SO(3)$ according to I . The correspondence relation of the spherical harmonics $Y_{lm}(\theta, \phi)$ of $SO(3)$ and the IR of I has been given in [3]. Then the IR and its basis of A , T_1 and H subspaces can be readily identified with the usual results of $SO(3)$ for $l = 0, 1, 2$. But the $l = 3$ IR of $SO(3)$ needs further decomposition into a quartet G and another triplet T_3 . On the other hand, the one-to-one correspondence between the 60 elements of the I group and the 60 carbon atoms of the C_{60} molecule can be proposed to define a regular representation (RR) of I ; meanwhile, the reduction coefficients of the RR according to the IR of I_h can be obtained [3].

3. Molecular orbitals of C_{60}

Within the molecular orbital theory, the SSH-like Hamiltonian of C_{60} can be written as [8]

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

where $c_{i,s}^\dagger$ ($c_{i,s}$) are electron creation (annihilation) operators at site i of a C atom with spin s . The first term represents the electronic hopping term, where $\langle i, j \rangle$ means summation over the nearest-neighbour C atoms. The hopping integral is expanded up to a linear term proportional to the length deviation from l_1 , where $l_{i,j}$ is the distance between i and j atoms, and α describes the strength of inter-site electron-phonon coupling. The other terms describe elastic potential energies; K is the stiffness constant of the bond-stretching spring; l_1 is the length at which all springs are relaxed. 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. $H/t_0 \rightarrow H$. To keep basic icosahedral symmetry in the ground state, we assume all the bond lengths $\delta_{i,j}$ between a pentagon and a hexagon are equal, $\delta_{i,j} = \delta_L$, and the bond lengths $\delta_{i,j}$ between two hexagons are equal as well, $\delta_{i,j} = \delta_s$. In the undoped case, the bond length δ_L is greater than δ_s , as will be seen below; we call δ_L the long bond and δ_s the short bond. Thus, the Hamiltonian can be rewritten as

$$H = - \sum_{\{5,6\}} [1 - \frac{1}{2}(\delta_L - \delta_1)](c_i^\dagger c_j + c_j^\dagger c_i) - \sum_{\{6,6\}} [1 - \frac{1}{2}(\delta_s - \delta_1)](c_i^\dagger c_j + c_j^\dagger c_i) + \frac{60}{2\pi\lambda} (\delta_L - \delta_1)^2 + \frac{30}{2\pi\lambda} (\delta_s - \delta_1)^2. \quad (3)$$

The symbol $\{5, 6\}$ means the summation is taken over all the bonds separating a hexagon from a pentagon and the symbol $\{6, 6\}$ means the summation is taken over all the bonds separating two hexagons. There are in total 60 $\{5, 6\}$ bonds and 30 $\{6, 6\}$ bonds. Letting

$$\tau = 1 - \frac{1}{2}(\delta_s - \delta_1) \quad \sigma = \frac{1 - \frac{1}{2}(\delta_L - \delta_1)}{1 - \frac{1}{2}(\delta_s - \delta_1)} \quad (4)$$

and using icosahedral group element g to label the site i of the C atom, we get the electronic part of the Hamiltonian as

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

and

$$t_{gg'} = \langle g | H' | g' \rangle = \begin{cases} -\sigma & \text{for a bond } (g, g') \text{ between a hexagon and a pentagon} \\ -1 & \text{for a bond } (g, g') \text{ between two hexagons} \\ 0 & \text{otherwise.} \end{cases} \quad (6)$$

Following [3], define a new basis $|d, m\lambda\rangle$ in terms of the IR of I as

$$\langle g | d, m\lambda \rangle \equiv \sqrt{\frac{d}{G}} T_{m\lambda}^d(\alpha, \beta, \gamma) \quad (7)$$

where $d = 1, 3, \bar{3}, 4$ and 5 is the dimension of the IR and $G = 60$ is the dimensionality of the RR. The unitary condition of the above transformation is

$$\begin{aligned} \sum_g \langle d, m\lambda | g \rangle \langle g | d', m'\lambda' \rangle &= \delta_{dd'} \delta_{mm'} \delta_{\lambda\lambda'} \\ \sum_{d, m\lambda} \langle g | d, m\lambda \rangle \langle d, m\lambda | g' \rangle &= \delta_{gg'}. \end{aligned} \quad (8)$$

For $d = 1, 3$ and 5 , the matrices $T_{m\lambda}^d(\alpha, \beta, \gamma)$ are simply the standard transformation matrices in a rigid body, i.e. the IR matrices of $SO(3)$, $T_{m\lambda}^d(\alpha, \beta, \gamma) = D_{m\lambda}^J(\alpha, \beta, \gamma)$ with $J = \frac{1}{2}(d-1)$. For $d = \bar{3}$ and 4 , the matrices $T_{m\lambda}^d$ result from the block diagonalization of $D_{m\lambda}^J$ with $J = 3$ according to the I group. Therefore, with the new basis $|d, m\lambda\rangle$, we have the matrix element of the Hamiltonian transformed to

$$\begin{aligned} \langle d, m\lambda | H' | d', m'\lambda' \rangle &= \sum_{gg'} \langle d, m\lambda | g \rangle \langle g | H' | g' \rangle \langle g' | d', m'\lambda' \rangle \\ &= - \sum_g \langle d, m\lambda | g \rangle \langle g f_a | d', m'\lambda' \rangle - \sigma \sum_{b, g} \langle d, m\lambda | g \rangle \langle g f_b | d', m'\lambda' \rangle \\ &= - \delta_{dd'} \delta_{mm'} T_{\lambda\lambda'}^d(f_a) - \sigma \delta_{dd'} \delta_{mm'} \sum_b T_{\lambda\lambda'}^d(f_b). \end{aligned} \quad (9)$$

Here $g' = g f_{a(b)}$, where $f_{a(b)}$ is the proper rotation a or b to rotate g to its nearest neighbours through $\{6, 6\}$ and $\{5, 6\}$ bonds, respectively. We have used the relation in (7) and (8). Letting

$$M^d = -T^d(f_a) - \sigma \sum_{b=1,2} T^d(f_b) \quad (10)$$

the eigenvalue problem of the model Hamiltonian can be solved through the diagonalization of the low-dimensional matrices M^d of the above equation. For the A_g representation, we can immediately obtain its eigenvalue $\epsilon = -1 - 2\sigma$ from (10). In practice, it turns out that we need only to diagonalize no more than 3×3 matrices after further block diagonalization through the $SU(2)$ representation, which can readily be done analytically.

Here we take the decomposition for the $l = 3$ representation of $SO(3)$ according to I . The basic functions for the $l = 3$ representation of $SO(3)$ can be redefined so that the representation will be decomposed into $G \oplus T_3$, according to icosahedral symmetry I mentioned in section 2:

$$\begin{aligned}
 G_{-2} &= \sqrt{\frac{2}{5}}Y_{3,-2} + \sqrt{\frac{3}{5}}Y_{3,3} & G_{-1} &= Y_{3,-1} & G_1 &= Y_{3,1} & G_2 &= -\sqrt{\frac{3}{5}}Y_{3,-3} + \sqrt{\frac{2}{5}}Y_{3,2} \\
 T_{-1} &= \sqrt{\frac{3}{5}}Y_{3,-2} - \sqrt{\frac{2}{5}}Y_{3,3} & T_0 &= Y_{3,0} & T_1 &= \sqrt{\frac{2}{5}}Y_{3,-3} + \sqrt{\frac{3}{5}}Y_{3,2}.
 \end{aligned}
 \tag{11}$$

The above basic functions can be further redefined in terms of real variables:

$$\begin{aligned}
 G_1 &= \frac{1}{\sqrt{2}}(G_{-2} + G_2) & G_2 &= -\frac{1}{\sqrt{2}}(G_{-1} - G_1) \\
 G_3 &= \frac{i}{\sqrt{2}}(G_{-1} + G_1) & G_4 &= -\frac{i}{\sqrt{2}}(G_{-2} - G_2) \\
 T_1 &= \frac{1}{\sqrt{2}}(T_{-1} + T_1) & T_1 &= T_0 & T_3 &= -\frac{i}{\sqrt{2}}(T_{-1} - T_1).
 \end{aligned}
 \tag{12}$$

The M matrix in the G representation then becomes

$$M = \begin{pmatrix} \frac{2}{\sqrt{5}} - 2\sigma \cos 2\zeta & \frac{1}{\sqrt{5}} & 0 & 0 \\ \frac{1}{\sqrt{5}} & -\frac{2}{\sqrt{5}} - 2\sigma \cos \zeta & 0 & 0 \\ 0 & 0 & -2\sigma \cos \zeta & -1 \\ 0 & 0 & -1 & -2\sigma \cos 2\zeta \end{pmatrix}
 \tag{13}$$

and the M matrix in the T_3 representation is

$$M = \begin{pmatrix} -\frac{i}{\sqrt{5}} - 2\sigma \cos 2\zeta & -\frac{2}{\sqrt{5}} & 0 \\ -\frac{2}{\sqrt{5}} & \frac{1}{\sqrt{5}} - 2\sigma & 0 \\ 0 & 0 & 1 - 2\sigma \cos 2\zeta \end{pmatrix}
 \tag{14}$$

where $\zeta = 2\pi/5$. We also notice that $\cos \zeta = \frac{1}{4}(\sqrt{5} - 1)$ and $\cos 2\zeta = -\frac{1}{4}(\sqrt{5} + 1)$.

Similarly, the M matrices in the T_1 representation and the H representation are easily obtained; respectively, they are

$$M = \begin{pmatrix} \frac{1}{\sqrt{5}} - 2\sigma \cos \zeta & -\frac{2}{\sqrt{5}} & 0 \\ -\frac{2}{\sqrt{5}} & -\frac{1}{\sqrt{5}} - 2\sigma & 0 \\ 0 & 0 & 1 - 2\sigma \cos \zeta \end{pmatrix}
 \tag{15}$$

$$M = \begin{pmatrix} -\frac{3}{5} - 2\sigma \cos 2\zeta & -\frac{2}{5} & -\frac{2\sqrt{3}}{5} & 0 & 0 \\ -\frac{2}{5} & -\frac{3}{5} - 2\sigma \cos \zeta & \frac{2\sqrt{3}}{5} & 0 & 0 \\ -\frac{2\sqrt{3}}{5} & \frac{2\sqrt{3}}{5} & \frac{1}{5} - 2\sigma & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{\sqrt{5}} - 2\sigma \cos \zeta & -\frac{2}{\sqrt{5}} \\ 0 & 0 & 0 & -\frac{2}{\sqrt{5}} & -\frac{1}{\sqrt{5}} - 2\sigma \cos 2\zeta \end{pmatrix}.
 \tag{16}$$

Table 1. The analytic solution of the molecular orbitals of C_{60} . $\theta = \frac{1}{3} \arccos(-\frac{2}{\sqrt{3}})$, $r = (\frac{10}{9}\sigma^2 - \frac{4}{9}\sigma + \frac{4}{9})^{3/2}$, $q = \frac{25}{27}\sigma^3 + \frac{4}{9}\sigma^2 - \frac{8}{9}\sigma + \frac{16}{27}$, ϵ is the corresponding eigenvalue; N is the normal factor belong to each eigenvector.

Rep.	Eigenvalue ϵ at $\sigma \neq 1$	Eigenvalue ϵ at $\sigma = 1$	Eigenvector ψ_0
T_{3g}	$1 + \frac{\sigma}{2}(1 + \sqrt{5})$	$\frac{1}{2}(3 + \sqrt{5})$	$(0, 0, 1)$
G_u	$\frac{1}{2}(\sigma + \sqrt{5\sigma^2 + 8\sigma + 4})$	$\frac{1}{2}(1 + \sqrt{17})$	$\frac{1}{N}(\frac{1}{\sqrt{3}}, -\frac{2}{\sqrt{3}} - \sigma \frac{1+\sqrt{5}}{2} + \epsilon, 0, 0)$
G_g	$\frac{1}{2}(\sigma + \sqrt{5\sigma^2 + 4})$	2	$\frac{1}{N}(0, 0, -1, \frac{\sqrt{5}-1}{2}\sigma + \epsilon)$
H_u	$\frac{1}{2}(\sigma + \sqrt{5\sigma^2 - 4\sigma + 4})$	$\frac{1}{2}(1 + \sqrt{5})$	$\frac{1}{N}(0, 0, 0, \frac{2}{\sqrt{3}}, \frac{1}{\sqrt{3}} - \sigma \frac{\sqrt{5}-1}{2} - \epsilon)$
T_{3u}	$\frac{1}{2}[-\frac{3+\sqrt{5}}{2}\sigma + \sqrt{\frac{1}{2}(15 + 5\sqrt{5})\sigma^2 - 2(\sqrt{5} + 1)\sigma + 4}]$	$\frac{1}{2}(-\frac{3-\sqrt{5}}{2} + \sqrt{\frac{19+\sqrt{5}}{2}})$	$\frac{1}{N}(-\frac{2}{\sqrt{3}}, \frac{1}{\sqrt{3}} - \sigma \frac{1+\sqrt{5}}{2} + \epsilon, 0)$
H_g	$-\{\frac{1+\sigma}{2} + 2\sqrt[3]{F} \cos(\theta + \frac{2\pi}{3})\}$	$\frac{1}{2}(-1 + \sqrt{13})$	$\frac{1}{N}(\epsilon^2 + \epsilon(\frac{2}{3} + \sigma \frac{\sqrt{5}+3}{2}) + \sigma^2(\sqrt{5} - 1) + \sigma \frac{13-\sqrt{5}}{10} - \frac{3}{2}, -\frac{2}{3}\epsilon - \frac{4}{3}\sigma - \frac{2}{3}, -\frac{2\sqrt{3}}{3}(1 + \frac{\sqrt{5}-1}{2}\sigma + \epsilon), 0, 0)$
T_{1g}	$1 - \frac{\sigma}{2}(\sqrt{5} - 1)$	$\frac{1}{2}(3 - \sqrt{5})$	$(0, 0, 1)$
T_{1u}	$\frac{1}{2}[-\frac{3+\sqrt{5}}{2}\sigma + \sqrt{\frac{1}{2}(15 - 5\sqrt{5})\sigma^2 + 2(\sqrt{5} - 1)\sigma + 4}]$	$\frac{1}{2}(-\frac{3+\sqrt{5}}{2} + \sqrt{\frac{19-\sqrt{5}}{2}})$	$\frac{1}{N}(-\frac{1}{\sqrt{3}} - 2\sigma - \epsilon, \frac{2}{\sqrt{3}}, 0)$
H_u	$\frac{1}{2}(\sigma - \sqrt{5\sigma^2 - 4\sigma + 4})$	$\frac{1}{2}(1 - \sqrt{5})$	$\frac{1}{N}(0, 0, 0, \frac{2}{\sqrt{3}}, \frac{1}{\sqrt{3}} - \sigma \frac{\sqrt{5}-1}{2} - \epsilon)$
H_g	$-\{\frac{1+\sigma}{2} + 2\sqrt[3]{F} \cos(\theta + \frac{4\pi}{3})\}$	-1	$\frac{1}{N}(\epsilon^2 + \epsilon(\frac{2}{3} + \sigma \frac{\sqrt{5}+3}{2}) + \sigma^2(\sqrt{5} - 1) + \sigma \frac{13-\sqrt{5}}{10} - \frac{3}{2}, -\frac{2}{3}\epsilon - \frac{4}{3}\sigma - \frac{2}{3}, -\frac{2\sqrt{3}}{3}(1 + \frac{\sqrt{5}-1}{2}\sigma + \epsilon), 0, 0)$
G_g	$\frac{1}{2}(\sigma - \sqrt{5\sigma^2 + 4})$	-1	$\frac{1}{N}(0, 0, -1, \frac{\sqrt{5}-1}{2}\sigma + \epsilon)$
G_u	$\frac{1}{2}(\sigma - \sqrt{5\sigma^2 + 8\sigma + 4})$	$\frac{1}{2}(1 - \sqrt{17})$	$\frac{1}{N}(\frac{1}{\sqrt{3}}, -\frac{2}{\sqrt{3}} - \sigma \frac{1+\sqrt{5}}{2} + \epsilon, 0, 0)$
T_{3u}	$\frac{1}{2}[-\frac{3+\sqrt{5}}{2}\sigma - \sqrt{\frac{1}{2}(15 + 5\sqrt{5})\sigma^2 - 2(\sqrt{5} + 1)\sigma + 4}]$	$\frac{1}{2}(-\frac{3-\sqrt{5}}{2} - \sqrt{\frac{19+\sqrt{5}}{2}})$	$\frac{1}{N}(-\frac{2}{\sqrt{3}}, \frac{1}{\sqrt{3}} - \sigma \frac{1+\sqrt{5}}{2} + \epsilon, 0)$
H_g	$-\{\frac{1+\sigma}{2} + 2\sqrt[3]{F} \cos\theta\}$	$\frac{1}{2}(-1 - \sqrt{13})$	$\frac{1}{N}(\epsilon^2 + \epsilon(\frac{2}{3} + \sigma \frac{\sqrt{5}+3}{2}) + \sigma^2(\sqrt{5} - 1) + \sigma \frac{13-\sqrt{5}}{10} - \frac{3}{2}, -\frac{2}{3}\epsilon - \frac{4}{3}\sigma - \frac{2}{3}, -\frac{2\sqrt{3}}{3}(1 + \frac{\sqrt{5}-1}{2}\sigma + \epsilon), 0, 0)$
T_{1u}	$\frac{1}{2}[-\frac{3+\sqrt{5}}{2}\sigma - \sqrt{\frac{1}{2}(15 - 5\sqrt{5})\sigma^2 + 2(\sqrt{5} - 1)\sigma + 4}]$	$\frac{1}{2}(-\frac{3+\sqrt{5}}{2} - \sqrt{\frac{19-\sqrt{5}}{2}})$	$\frac{1}{N}(-\frac{1}{\sqrt{3}} - 2\sigma - \epsilon, \frac{2}{\sqrt{3}}, 0)$
A_g	-1 - 2 σ	-3	1

The solutions of the eigenvalue problems for (13)–(16) are given in table 1. In table 1, we list eigenvalues ϵ of the M matrix at $\sigma \neq 1$ as well as $\sigma = 1$. The M matrices are block matrices of the electronic part of the Hamiltonian H' , so the eigenvalues for the original Hamiltonian H should be $t_0\tau\epsilon$. Eigenvectors ψ_0 of the M matrices are also listed in table 1. For clarity, we take the second row as an illustrative example. The eigenvalue for the G_u representation is $\epsilon = \frac{1}{2}(\sigma + \sqrt{5\sigma^2 + 8\sigma + 4})$; when $\sigma = 1$ it reduces to $\sigma = \frac{1}{2}(1 + \sqrt{17})$. The eigenvector ψ_0 of G_u has four components

$$\frac{1}{N} \left(\frac{1}{\sqrt{5}}, -\frac{2}{\sqrt{5}} - \sigma \frac{1 + \sqrt{5}}{2} + \epsilon, 0, 0 \right)$$

where

$$N^2 = \frac{1}{5} + \left(-\frac{2}{\sqrt{5}} - \sigma \frac{1 + \sqrt{5}}{2} + \epsilon \right)^2.$$

The wavefunction of H can be obtained through the formula

$$\Psi_\lambda^d(g) = \sqrt{\frac{d}{G}} \sum_{\lambda'} \psi_{0\lambda'}^d T_{\lambda'\lambda}^d(g^{-1}) \quad (17)$$

which can be easily verified to satisfy the orthogonal relations

$$\sum_g \Psi_\lambda^{d*}(g) \Psi_{\lambda'}^d(g) = \delta_{\lambda\lambda'} \delta_{dd'}. \quad (18)$$

For the G_u representation, as an example, we can obtain four degenerate wavefunctions corresponding to the eigenvalue $\epsilon = \frac{1}{2}(\sigma + \sqrt{5\sigma^2 + 8\sigma + 4})$ through (17).

4. Self-consistent solutions

In section 3, we have solved the eigenvalue problems of the M matrices in terms of the parameters σ and τ . The values of these parameters can be determined by a Bogoliubov–de Gennes (BdG) equation [5] for a given dimensionless e–ph coupling constant λ :

$$\frac{\delta \langle \Psi_x | H' | \Psi_x \rangle}{\delta \delta_{i,j}} = 0 \quad (19)$$

where Ψ_x is a multi-electron state of the system. Since we only have two kinds of bond length, δ_s and δ_L in our case, we can only get two equations from (19):

$$\begin{aligned} (1 - \sigma\tau) - \frac{\pi\lambda}{120} \sum_{\lambda'\lambda\{d\}} \psi_{0\lambda}^d \left(\frac{\partial M^d}{\partial \sigma} \right)_{\lambda\lambda'} \psi_{0\lambda'}^d &= 0 \\ (1 - \tau) + 2\sigma(1 - \tau\sigma) - \frac{\pi\lambda}{60} \sum_{\{d\}} \epsilon^d d &= 0 \end{aligned} \quad (20)$$

where the summation over $\{d\}$ is taken over the occupied representation. In the undoped case, 30 energy levels from the lowest A_g state to the HOMO H_u states are occupied. The

factor of two for spin is already taken out from the summations. The expressions for ϵ^d , $\psi_{0\lambda}^d$ and M^d can be found in table 1 and (13)–(16). Equation (20) is a system of non-linear equations of two variables, which cannot be solved analytically. A numerical calculation is carried out to show the relation between λ and τ and σ . In figure 1, we plot the τ against λ curve as well as the σ against λ curve. From the curves we can see τ is a monotonically increasing function of λ , while σ is a decreasing function which is always less than one. From the definition of σ , (equation (4)), $\sigma < 1$ implies that $\delta_L > \delta_s$, i.e. the {5, 6} bonds are greater than {6, 6} bonds. This is a natural result from our calculation, which is well identified by experiments. In figure 2, we plot curves for all the electronic levels in terms of the dimensionless e–ph coupling constant λ . The energy levels are expressed in units of t_0 , which are equal to $\tau\epsilon$ in our notation. We can see that the energy bandwidth becomes large when λ increases. All the negative levels are decreasing functions of λ , while all the positive levels are increasing ones. There is a crossover of the T_{3u} level and the G_u level near $\lambda = 1.3$.

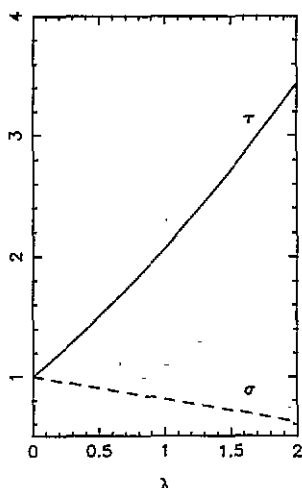


Figure 1. The dimensionless parameters τ (full curve) and σ (broken curve) against λ .

The above procedure also can be applied to calculate energy levels for the C_{60} molecule with six extra electrons doped in, C_{60}^{-6} . The only thing we should notice in this procedure is that the summation in (20) should be taken over the T_{1u} state. Since an additional six electrons will fully occupy the LUMO state T_{1u} , they will not destroy icosahedral symmetry. We did the calculation and found $\sigma > 1$ in this case, which implies $\delta_L < \delta_s$, i.e. the short bonds become longer than the long bonds.

In summary, we have improved the analytical approach of [3] to include the effect of the electron–phonon interaction, which results in two kinds of bond length and the variation of the electronic structure. The difference of two kinds of bond length and the electronic HOMO–LUMO gap are proved to increase with the dimensionless electron–phonon coupling parameter. This conclusion is consistent with the results from a directly numerical solution by Harigaya [9] and You and co-workers [10]. It is worthwhile to note that this analytical approach cannot be adopted to deal with the non-linear excitations, such as the polaron and self-trapped exciton of C_{60} , since the effect of the electron–phonon interaction will result in dynamical symmetry breaking of I_h as the molecule is excited or doped, which can only be resolved numerically through the BdG formalism [10, 11].

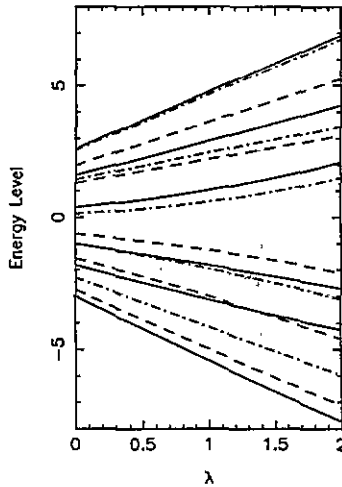


Figure 2. The energy level of Hamiltonian H' in units of t_0 against λ .

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