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Empirical tight-binding parameters for solid C_{60}

Nacir Tit and Vijay Kumar†

International Centre for Theoretical Physics, PO Box 586, 34100 Trieste, Italy

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Abstract. We present a tight-binding model for the electronic structure of solid C_{60} using four (one 2s and three 2p) orbitals per carbon atom. The model has been developed by fitting the tight-binding parameters to the *ab initio* pseudopotential calculation of Troullier and Martins in the face-centred cubic ($Fm\bar{3}$) phase. Following this, calculations of the energy bands and the density of electronic states have been carried out as a function of the lattice constant. Good agreement has been obtained with the observed lattice-constant dependence of T_c using McMillan's formula. Furthermore, calculations of the electronic structure are presented in the simple cubic ($Pa\bar{3}$) phase.

1. Introduction

The discovery of the C_{60} molecule [1] and a new form of carbon, the solid C_{60} hereafter also referred to as fullerite [2], and subsequent observation of superconductivity in alkali-doped fullerites [3] (A_3C_{60} where A is an alkali atom) with a moderately high T_c have generated an enormous interest in these systems. Despite the extensive experimental and theoretical studies, many fascinating questions, such as the mechanism of superconductivity, remain still open. On the experimental side, the electronic spectra for undoped and doped fullerites have been obtained using photoemission [4] and inverse photoemission [5]. Other experimental techniques such as infrared absorption [6] and Raman [7] spectroscopies and neutron scattering [8] have been applied to investigate the dynamical properties of the fullerites. The characterization of solid C_{60} has been carried out at various temperatures using ^{13}C nuclear magnetic resonance (NMR) [9] and neutron [10] and x-ray [11] diffractions. At room temperature solid C_{60} forms a face-centred cubic (FCC) structure. In this phase, the C_{60} molecules reorient rapidly and isotropically and the structure is believed to belong to the $Fm\bar{3}$ space group. However, below 260 K, neutron [10] and x-ray [11] diffraction experiments have shown that an orientational order develops and ultimately at low temperatures the structure becomes simple cubic (SC) belonging to the space group $Pa\bar{3}$ with four C_{60} molecules occupying the FCC lattice sites but having different orientations. Evidence has also been reported [12] for a superstructure at low temperatures with a lattice constant that is twice the value of the case of the $Pa\bar{3}$ structure. Upon doping with alkali metals (such as K, Rb and/or Cs), the sample becomes superconducting and the highest T_c (33 K) has been obtained [13] for $RbCs_2C_{60}$. While at low temperatures the C_{60} molecules do not rotate in these doped systems, some orientational disorder of C_{60} molecules is believed to exist [14].

On the theoretical side, the structural, dynamical and electronic properties have been calculated extensively by various techniques. Among these techniques, the Car–Parrinello

† Permanent address: Material Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India.

(CP) method [15] has been used to calculate the ground-state [16] and finite temperature [17, 18] properties of solid C_{60} . However, due to the heavy computational cost of the CP simulations for such systems, a need for simpler approaches is obvious. In fact, recently, a tight-binding molecular-dynamics (TBMD) method [19, 20] has been developed to study the dynamical properties of fullerenes [20–22]. This method is about one hundred times faster [21] than the *ab initio* MD (CP) simulations, and the results obtained for several fullerenes are in good agreement with both the experiments and the state-of-the-art methods wherever available. Also because of other developments of graphite tubes [23] etc, TB models are attractive to understand the general physics of these and related large systems.

Several attempts have been made recently to study the electronic properties of solid C_{60} using TB models. Gelfand and Lu [24] have reported a three-band TB model to study orientational disorder in the low-temperature C_{60} structure. However, their hopping amplitudes were only a few millielectronvolts and, as a consequence, the resulting bandwidths were smaller by a factor of 15 (10) for pure (doped) C_{60} solid as compared to *ab initio* calculations [25]. Satpathy and co-workers [25, 26] developed a TB model with a basis consisting of only 60 radial atomic orbitals per molecule. This one-orbital model was used to study the conduction band structure versus doping. Another model, reported by Xu *et al* [22], contains four orbitals per carbon atom. Their model, however, was used to investigate the ground-state structure of carbon microclusters C_n (where $n \leq 10$) [22] and small fullerenes [21]. Tománek and Schlüter [27] also used a TB model containing four orbitals (s, p_x, p_y, p_z) per carbon atom. Using an adaptive simulated annealing method, these authors studied the relative stabilities of carbon clusters with up to 60 atoms. Their TB parameters were obtained from a fit to LDA (local-density approximation) calculations for the electronic structure of C_2 , a graphite monolayer and bulk diamond. In this paper we report a TB model containing four orbitals per carbon atom for solid C_{60} . In contrast to other models discussed above, our model was developed by a fit to a well converged *ab initio* pseudopotential calculation of the FCC ($Fm\bar{3}$) phase of solid C_{60} due to Troullier and Martins [28]. The hopping matrix elements obtained from our work (see the next section) are different from those of [27], and rather substantially larger. We have applied our model to study the dependence of the electronic structure on lattice constant [29] and used the results to calculate the lattice-constant dependence of T_c in alkali-doped fullerites (A_3C_{60}). Our results are in good agreement with experimental values [30].

In the next section, we introduce our TB model and show in detail its results for the free C_{60} molecule and for both the hypothetical unidirectional ($Fm\bar{3}$) and the quadridirectional low-temperature ($Pa\bar{3}$) structures of solid C_{60} . In section 3, we show briefly our estimations of T_c for alkali-doped fullerites using McMillan's formula. The last section summarizes our results.

2. Electronic structure

The TB Hamiltonian used in our work can be written as

$$H = \sum_{i,\mu} E_{i,\mu} c_{i,\mu}^\dagger c_{i,\mu} + \sum_{(i,\mu;j,\nu)} V_{\mu,\nu}(r_{ij}) (c_{i,\mu}^\dagger c_{j,\nu} + \text{HC}) \quad (1)$$

where i and j label atomic sites; μ and ν label atomic orbitals (s, p_x, p_y, p_z) and $\langle \rangle$ indicates that the sum on (ij) is over neighbours, which we shall give more explicitly later. $c_{i,\mu}^\dagger$ is a creation operator for an electron in the orbital μ at site i . $E_{i,\mu}$ is the on-site energy and $V_{\mu,\nu}(r_{ij})$ are the hopping integrals, which decay rapidly with the interatomic distance r_{ij} . The latter are expressed [31] in terms of the two-centre integrals $V_{ss\sigma}(r_{ij})$, $V_{sp\sigma}(r_{ij})$,

$V_{pp\sigma}(r_{ij})$ and $V_{pp\pi}(r_{ij})$. In developing such parameters for solid C₆₀, we started with the TB model reported by Wang *et al* [32] for the tetrahedrally sp³-bonded carbon material (namely diamond), whose nearest-neighbour distance is d_0 . In the diamond structure the parameters are: $d_0 = 1.54 \text{ \AA}$, $E_s = -2.99 \text{ eV}$, $E_p = 3.71 \text{ eV}$, $V_{ss\sigma} = -5.55 \text{ eV}$, $V_{sp\sigma} = 5.91 \text{ eV}$, $V_{pp\sigma} = 7.78 \text{ eV}$ and $V_{pp\pi} = -2.50 \text{ eV}$.

As a first step, we modified these parameters to obtain a best fit for the free C₆₀ molecular spectrum in the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) region to the *ab initio* results of Saito and Oshiyama [33]. Further refinement to these parameters has been performed while fitting our energy bands for the FCC phase of solid C₆₀ to the well converged first-principle calculations of Troullier and Martins [28]. For the C₆₀ molecule, we have considered the hopping integrals only between the nearest neighbours and used a distance dependence of $1/r^2$ as proposed by Harrison [34]. However in the solid phase, the hopping integrals between carbon atoms on neighbouring molecules are truncated [35] after $d_c = 4.4 \text{ \AA}$ and their distance dependence is taken as an exponential decay [26]. The form of this interaction is given by

$$V(d) = (d/d_0)V_0 \exp[-(d - d_0)/L] \quad (2)$$

where V_0 denotes the two-centre integrals.

Following this procedure the best fit of both the band dispersions and widths has been achieved with the following parameters: $d_0 = 1.54 \text{ \AA}$, $E_s = -6.7 \text{ eV}$, $E_p = 0 \text{ eV}$, $V_{ss\sigma} = -5.55 \text{ eV}$, $V_{sp\sigma} = 5.31 \text{ eV}$, $V_{pp\sigma} = 6.20 \text{ eV}$ and $V_{pp\pi} = -2.30 \text{ eV}$. These parameters are not very different from the case of the diamond structure. In our work we took $L = 0.45 \text{ \AA}$. This value of L gives the highest group of valence bands and the two lowest groups of conduction bands in good agreement with those reported by Troullier and Martins for the unidirectional solid C₆₀ structure. Provided that all the other parameters are unchanged, an increase in the value of L results in larger bandwidths as would be expected from (2) and a reduction of the density of states at the Fermi level.

As expected by Kroto *et al* [1] several years ago, it has been shown that the C₆₀ molecule has a truncated icosahedral structure. The 60 carbon atoms of the molecule occupy equivalent sites and span 20 hexagons and 12 isolated pentagons. These atoms are connected via two kinds of bond: a double bond of length 1.4 \AA shared by two hexagons, and two single bonds of length 1.45 \AA shared by a hexagon and a pentagon. The molecule has a diameter of about 7.0 \AA . In the solid (fullerites), the molecules occupy the sites of the FCC structure where the centres of neighbouring molecules are separated by about 10 \AA . *Ab initio* calculations in the unidirectional FCC phase [16] using the CP method indicate that due to this change in symmetry in the solid phase, the long bond acquires three slightly different values (1.449 , 1.454 and 1.462 \AA) while the short bond is 1.404 \AA . Our TB calculations on C₆₀ molecule show that the effect of this small change in bond lengths on the energy spectrum is negligible. We have used these bond lengths in our calculations. Also as the interactions between the molecules are weak and believed to be predominantly of Van der Waals type, we expect only a minor change in bond lengths as a function of the lattice constant and also in going from the FCC to the SC phase. This is neglected in our calculations. In alkali-doped C₆₀ solid, though the intraball C–C bond lengths will be slightly modified, the main effect on the superconducting transition temperature has been shown to be due to the variation in the lattice constant [36]. This we hope to be able to see in our calculations from changes in the electronic structure as alkali atoms act predominantly as electron donors.

In figure 1, we show the spectra of the C₆₀ molecule. The HOMO is taken to be the zero of energy. Because the molecule has a high-symmetry structure belonging to the

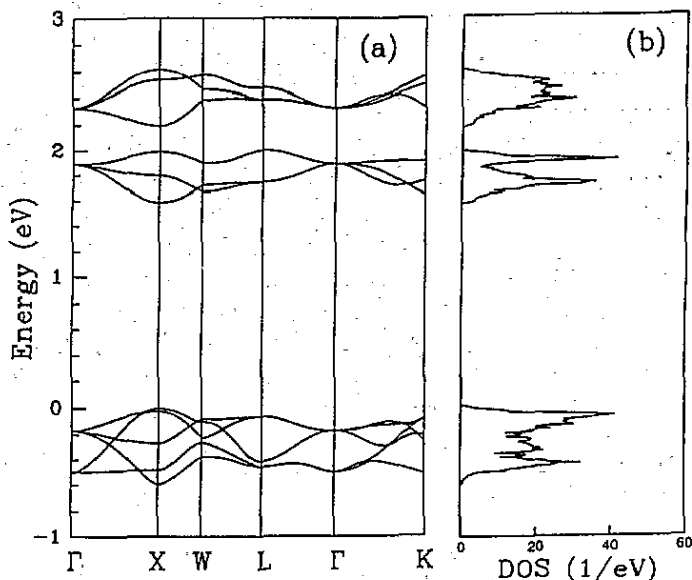


Figure 2. (a) The band structure of the FCC ($Fm\bar{3}$) phase with a lattice constant $a_0 = 13.879 \text{ \AA}$ for comparison with [28]. (b) DOS per molecule for combined spins, calculated using the tetrahedron method with 505 k vectors from the irreducible wedge of the Brillouin zone. The zero of energy is at the top of the valence band for both (a) and (b).

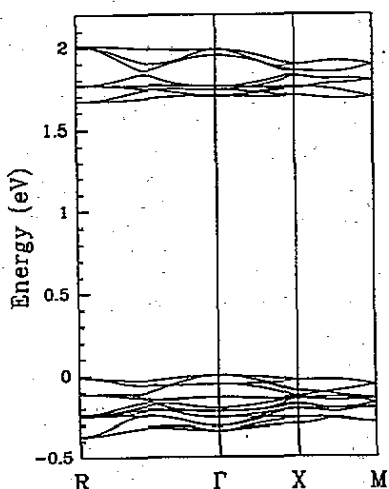


Figure 3. The band structure of the SC ($Pa\bar{3}$) phase with a lattice constant $a_0 = 14.11 \text{ \AA}$. The zero of energy is at the top of the valence band.

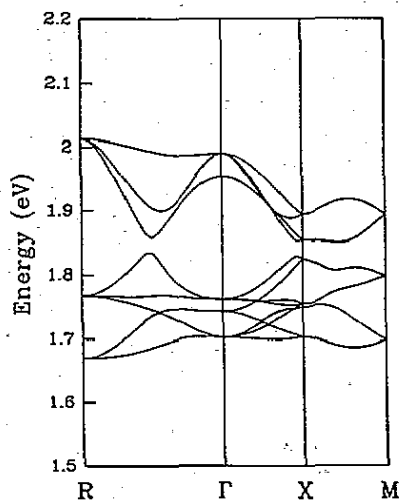


Figure 4. As figure 3, but only the conduction band is displayed.

and 0.53 eV respectively), which represents a good fit for the valence and conduction bands.

The low-temperature structure of pure C_{60} was solved by David *et al.* [10]. The molecules are centered on an FCC lattice as in the unidirectional case but they are rotated by an angle of -22.38° along the four different (111) axes [10] such that the space group symmetry is $Pa\bar{3}$. The lattice constant we used for this structure is 14.11 \AA , which is

the same as observed in experiments [10]. We calculated the energy bands along three symmetry lines (ΓR , ΓX and XM). In figure 3, we show the 20 highest valence bands as well as the 12 lowest conduction bands. In general agreement with the results obtained by Gelfand and Lu [24], the gap is indirect from Γ to R . However, our bandwidths are more realistic. The band gap is 1.669 eV and the valence and conduction bands have widths of 0.372 eV and 0.344 eV respectively. In order to facilitate the comparison with the results of Satpathy *et al* [25], we also show in figure 4 the conduction band only for this quadririrectional structure. Their conduction band [25] is a little wider (0.43 eV) as one should expect from a larger value of L , but overall, there is a good agreement in the band dispersions. Our band dispersions are also in good agreement with those obtained by Oshiyama and co-workers [41], but their valence and conduction band widths are about 0.21 eV and 0.28 eV respectively which are a little smaller than ours. In this low-temperature phase our model can also be used to study the orientational disorder effects, which are likely to be important in understanding the physical properties of solid C_{60} .

3. Superconductivity in fullerides

It has been suggested [30] that changes in T_c could be accounted for by changes in the DOS $N(E_F)$, at the Fermi level, which scales monotonically with lattice constant. Alkali-doped fullerites (A_3C_{60}) have an FCC structure with the alkali atoms occupying the interstitial tetrahedral and octahedral sites [42]. Theoretical calculations [25,43] of valence charge densities as well as Raman spectra [44] have shown that the valence electrons of the alkali atoms are almost completely transferred to the lowest unoccupied bands of the C_{60} molecular solid. Therefore for the doped systems, we used this fact in our TB calculation by treating the dopants simply as sources of electrons for the C_{60} conduction band. Also the isotope-effect measurements [45–47] indicate a phonon-mediated mechanism for superconductivity. Assuming the intramolecular vibrational modes to be playing the dominant role in the electron-phonon pairing mechanism in fullerides, then the variation in T_c should arise due to changes in the lattice constant, which affects $N(E_F)$. Thus for a comparative study of the isostructural A_3C_{60} compounds, we studied [29] the behaviour of the conduction bands of solid C_{60} as a function of the lattice constant. Here, we summarize these results in table 1 to show some trends of our model.

Table 1. The superconducting transition temperatures and structural data for A_3C_{60} .

A_3	a_0^a (Å)	T_c^a (K)	N_F^b (eV)	T_c^b (K)
K_3	14.253	19.28	17.17	20.65
K_2Rb	14.299	21.80	18.02	21.85
Rb_2K	14.364	26.40	18.42	23.82
Rb_3	14.436	29.40	18.93	26.42
Rb_2Cs	14.493	31.30	19.33	28.50

^a Experimental data [30].

^b Our theoretical results [29].

In our previous work [29], we evaluated $N(E_F)$ for different lattice constants corresponding to several fullerides (A_3C_{60}) [30] and estimated T_c using McMillan's formula [48]

$$T_c = \frac{\hbar\omega}{1.2k_B} \exp \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right]. \quad (3)$$

We assume that the averaged phonon frequency ω and the screened Coulomb interaction parameter μ^* are independent of the intermolecular separation R . Then T_c is calculated using equation (3) with $\lambda = N(E_F)V_{e-ph}$. The electron-phonon interaction V_{e-ph} is taken to be independent of R while the R dependence of the density of states at the Fermi level is obtained from our TB calculations [29]. We took [49] $V_{e-ph} = 40$ meV, $\mu^* = 0.19$ and $\hbar\omega/k_B = 1450$ K, and estimated T_c for several lattice constants as shown in table 1. The values of $N(E_F)$ are in the range of 17–20 states eV⁻¹/molecule/spin. This lies in between the values reported from susceptibility measurements (10–15) [50] and NMR data (≥ 20) [51]. The resulting T_c (table 1) is in good agreement with the experimental data [30]. Our choice of ω lies near the high-frequency [52] $H_g(7)$ and $H_g(8)$ tangential modes, and is consistent with the results of [53], which reported about 80% of the contributions to V_{e-ph} as originating from the $H_g(7)$ and $H_g(8)$ modes, and also with the calculation of Onida and Benedek [54] based on the bond charge model. On the other hand, Schlüter *et al* [49] calculated V_{e-ph} and the obtained contributions to it from both the low-frequency and the high-frequency intramolecular modes. However, due to uncertainties in the values of the parameters in equation (3), they also found [55] $\hbar\omega/k_B = 1400$ K and $\mu^* = 0.2$ to give a reasonable agreement with the experimental values of T_c for different systems. These results, therefore, are in close agreement with the values we have used to calculate T_c from our calculations of the density of states.

At this stage, we would also like to comment about the validity of McMillan's formula, equation (3), in the case of fullerides. This formula was derived [48] for weak to intermediate coupling strengths ($\lambda \leq 1$) of low-frequency phonons ($\hbar\omega \ll E_F$). However, this is not the case for fullerides as the bandwidth is quite small. In this respect it is to be noted that Oshiyama and Saito [36] reported a linear dependence of T_c on $N(E_F)$ for a wide range of T_c . This behaviour was obtained using the experimental data of T_c and the theoretical estimates of bulk moduli and $N(E_F)$ and is not quite consistent with McMillan's formula. These authors concluded that the conventional BCS theory is irrelevant for describing the superconductivity in fullerides. Conversely to this, Huang *et al* [56] found a linear dependence of $\ln T_c$ on $1/N(E_F)$ using McMillan's formula and their calculated $N(E_F)$ using the first-principles orthogonalized linear combination of atomic orbitals method. This behaviour, however, was suggesting that the BCS model could be adequate to explain the variations of T_c in fullerides. However, the intramolecular phonons that are likely to be responsible for the coupling have high frequencies (~ 0.1 – 0.2 eV), which are comparable to the Fermi energy (which is about half of the conduction bandwidth ~ 0.2 eV). The latter argument in addition to the large superconducting gap Δ measured using scanning tunnelling microscopy [57] put the validity of McMillan's formula into question in the case of doped fullerites. Though the agreement between our calculated T_c and the experiments is satisfactory, due to the uncertainties of the value of parameters used in equation (3), the question of the the superconductivity mechanisms in the fullerides remains open.

In a related work, Satpathy and co-workers [25] calculated ω for different values of μ^* using experimental data [30] for the intermolecular separation R and T_c , and assumed ω , μ^* and V_{e-ph} to be R independent. Taking the R dependence of the DOS at the Fermi level from their LDA calculations, they obtained an average phonon temperature $\hbar\omega/k_B \simeq 600$ K, which corresponds to the intramolecular low-lying $H_g(2)$ radial phonon modes. Following the same procedure as described in [25], but with $L = 0.45$ Å and using our calculated values of $N(E_F)$ [29] we also calculated ω and the results are given in table 2. We obtained an average phonon temperature $\hbar\omega/k_B \simeq 400$ K. Though it is consistent with the assumption that the phonons involved in the superconductivity mechanism are intramolecular, this value is much lower than we have taken in our calculation of T_c . If the assumptions about the R independence

Table 2. Electron-phonon coupling constant λ and the averaged phonon frequency ω as functions of the screened Coulomb interaction parameter μ^* . We used the experimental values of T_c [30] and our calculated values of $N(E_F)$ for different lattice constants (table 1) and followed the same procedure as in [25].

μ^*	λ^a	λ^b	$d \ln V_{e-ph}/d \ln N(E_F)$	$\hbar\omega/k_B^a$ (°K)	$\hbar\omega/k_B^b$ (°K)	$d \ln \omega/d \ln T_c$
0.15	0.98	1.14	3.76	403	379	-0.29
0.25	1.33	1.52	3.28	395	381	-0.16
0.35	1.75	1.99	3.00	407	400	-0.08
0.45	2.25	2.55	2.83	438	434	-0.04

^a $T_c = 20.50$ K, $s = 3.146$ Å.

^b $T_c = 25.32$ K, $s = 3.211$ Å, where s is the nearest-neighbour distance for contact between two C_{60} molecules.

of μ^* , ω and V_{e-ph} were true, one would expect [25] $|d \ln V_{e-ph}/d \ln N(E_F)| \ll 1$ and $|d \ln \omega/d \ln T_c| \ll 1$. Our results for $d \ln \omega/d \ln T_c$ are smaller than those given in [25] and are consistent with the assumption of R -independent phonon frequency, but the value of $d \ln V_{e-ph}/d \ln N(E_F)$ is too high, indicating that the assumption of R -independent ω , μ^* or V_{e-ph} in equation (3) may not be correct as was also pointed out in [25]. This suggests that at least one of the interactions, the electron-electron or the electron-phonon one, must be in part intermolecular. Our results (table 2) seem to be more in favour of the candidate V_{e-ph} . However, more work would clearly be required to obtain a clear understanding of the electron-phonon coupling and the mechanism of superconductivity in these materials.

4. Conclusions

We have developed a full TB model for C_{60} solid by fitting to the well converged *ab initio* pseudopotential calculation of Troullier and Martins [28] in the FCC phase. Using this model, we calculated the electronic structures of solid C_{60} in both the hypothetical unidirectional and the quadridirectional low-temperature phases. Our estimation of the variation of T_c with lattice constant using McMillan's formula is in good agreement with experimental data. Our model can be used to study the orientational disorder effects in the low-temperature phase as well as the dynamical properties of solid C_{60} using the TBMD simulation. From the generally good description of the highest valence band and the lowest conduction band in the two structures we hope that our TB model will also be useful in the study of higher fullerenes as well as graphite tubes. Due to the narrow bandwidths, it is expected that correlations in solid C_{60} may play an important role and our model can be extended to incorporate these effects.

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Appendix

Let us assume that the eigenvalue E_n is g_n -fold degenerate (excluding any accidental degeneracies). Then we may choose a set of g_n orthonormal eigenfunctions $\Psi_n^{(j)}$, $j = 1, \dots, g_n$, belonging to E_n to form a basis for a g_n -dimensional space. This space

is a subspace of the entire Hilbert space of eigenfunctions of the Hamiltonian H ; a subspace invariant under all the operations $\mathcal{P}_{\mathcal{R}}$ of the group of Schrödinger equation: $\mathcal{P}_{\mathcal{R}}H\Psi_n^{(j)} = H\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)} = E_n\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)}$. (Here $\mathcal{P}_{\mathcal{R}}$ is a symmetry operation corresponding to the rotation \mathcal{R} .) Thus $\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)}$ is also an eigenfunction with an eigenvalue E_n and can be expressed as a linear combination of the g_n degenerate eigenfunctions

$$\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)} = \sum_{i=1}^{g_n} \Psi_n^{(i)} \Gamma^n(\mathcal{R})_{ij} \quad (\text{A1})$$

where $\Gamma^n(\mathcal{R})$ is the irreducible representation corresponding to the point group operation \mathcal{R} . Expressing the eigenfunction $\Psi_n^{(j)}$ in the TB basis, we have

$$\Psi_n^{(j)}(\mathbf{r}) = \sum_{\alpha=1}^N C_{\alpha}^{n,j} \Phi_{\alpha}(\mathbf{r}) \quad (\text{A2})$$

where α denotes an (s, p_x, p_y or p_z) orbital centred at one of the 60 carbon atoms and $N = 240$. Then equation (A1) becomes

$$\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)} = \sum_{\alpha=1}^N \Phi_{\alpha}(\mathbf{r}) \left(\sum_{i=1}^{g_n} C_{\alpha}^{n,i} \Gamma^n(\mathcal{R})_{ij} \right). \quad (\text{A3})$$

We consider now the operation

$$\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)}(\mathbf{r}) = \Psi_n^{(j)}(\mathcal{R}^{-1}\mathbf{r}) \quad (\text{A4})$$

and using equation (A2) we find that

$$\mathcal{P}_{\mathcal{R}}\Psi_n^{(j)}(\mathbf{r}) = \sum_{\alpha=1}^N C_{\mathcal{R}^{-1}\alpha}^{n,j} \Phi_{\alpha}(\mathbf{r}). \quad (\text{A5})$$

Comparing equations (A3) and (A5), one can extract the relation governing the transformation of the g_n -degenerate eigenfunctions' components

$$C_{\mathcal{R}^{-1}\alpha}^{n,j} = \sum_{i=1}^{g_n} C_{\alpha}^{n,i} \Gamma^n(\mathcal{R})_{ij}. \quad (\text{A6})$$

We have used this relation practically to study the symmetry of the eigenstates of the C₆₀ spectrum shown in figure 1, and specifically to discriminate between t_{1g} and t_{2g} (similarly t_{1u} and t_{2u}) symmetries using the C_5 rotation.

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