Tight-binding parametrization of first-principles electronic
dispersion in orientationally disordered $A_3C_{60}$

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Abstract

We derive numerical tight-binding hopping parameters to describe conduction-band dispersion in arbitrary orientational phases of $A_3C_{60}$. The parameters are obtained by direct Fourier inversion of the spectra from self-consistent electronic-structure calculations for $K_3C_{60}$ using the local-density approximation, including the effects of orientational dependence. Using the new parameters, we revisit several earlier investigations of the orientational ordering in $A_3C_{60}$; some of the earlier results are substantiated, while others are slightly modified.
The electronic structure of the fullerene and fulleride solids has been treated at var-
ious levels of theoretical sophistication, including simple Hückel calculations for the isolated
molecule, fully self-consistent density-functional methods using the local-density approxi-
mation (LDA) for the intercalated solids, and most recently, quasiparticle-corrected GW
methods for solid C_{60} [1–3]. For the A_xC_{60} family (x=0,3,4,6, A=heavy alkali), a single
common picture emerges: C_{60} molecular states are broadened into band states in the solid,
with bandwidths on the order of ∼1 eV or less, and the alkali s-electrons populate the
C_{60}-derived band states. The small dispersion, together with the one-to-one correspondence
between molecular levels and bands, implies a nearly negligible redistribution of electronic
charge density on forming the condensed phase (the alkali ionization aside). This suggests
that a tight-binding (TB) Hamiltonian might provide an accurate description of dispersion
in this family, that TB parameters should be transferable among similar structures, and
that interactions may be limited to nearest neighbors.

We focus on the superconducting A_3C_{60} phase because the nature of fullerene molecular
orientational order in this phase is not well understood, having been variously described as
merohedrally disordered with Fm\overline{3}m symmetry [4]; orientationally disordered with lower
symmetry [5]; and partially ordered on short length scales [6]. Important theoretical work
by Gelfand and Lu [4] and by Satpathy et al. [8] demonstrated that complete merohedral
disorder has a profound effect on the conduction-band spectral density and on ac conduc-
tivity, effectively washing out the sharp structure that normally results from a well-defined
band structure. Deshpande et al. [9] subsequently developed an effective-medium theory
to describe the effects of disorder in a Green’s function formalism, essentially confirming
the results obtained numerically by Gelfand and Lu. Recently, Mele and Erwin [10] used
both formal and numerical methods to show that although disorder strongly scatters electron
states and substantially redistributes spectral density, states near the Fermi energy are char-
acterized by an effective Bloch wave vector and a mean free path of order 2–3 near-neighbor
spacings. Consequently, a relatively well-defined “Fermi surface” may be considered for
these states even in the presence of random (merohedral) disorder. In all of these studies,
the Hamiltonian of Ref. [7] was used, for which hopping parameters were calculated from $C_{60}$ interactions at the level of Hückel theory. In this Report, we provide an explicit parametrized Hamiltonian for $A_3C_{60}$, with TB parameters derived directly from first-principles LDA calculations of dispersion in $A_3C_{60}$, with the effects of orientational disorder fully accounted for.

The structure and symmetry of the nearest-neighbor hopping Hamiltonian have been discussed in detail by Yildirim et al. [11], and we will adopt their notation for the discussion here. The Hamiltonian describing conduction-band dispersion is

$$\mathcal{H} = \sum_{\mathbf{R}} \sum_{\alpha \beta} t_{\alpha \beta}(\tau; \sigma_{\mathbf{R}}, \sigma_{\mathbf{R} + \tau}) \xi_{\mathbf{R}, \alpha} \xi^{\dagger}_{\mathbf{R} + \tau, \beta},$$

where $\alpha, \beta = x, y, z$ is the orbital polarization, $\sigma_{\mathbf{R}} = \pm 1$ is an Ising variable giving the orientation of the molecule at $\mathbf{R}$, and $\tau = (a/2)(110)$, etc., gives the direction of the hop. The hopping matrix has four possible values, and can be conveniently decomposed as:

$$t_{\alpha \beta}(\tau; \sigma_{\mathbf{R}}, \sigma_{\mathbf{R} + \tau}) = t^{(0)}_{\alpha \beta}(\tau) + t^{(1)}_{\alpha \beta}(\tau) \sigma_{\mathbf{R}} + t^{(2)}_{\alpha \beta}(\tau) \sigma_{\mathbf{R} + \tau} + t^{(3)}_{\alpha \beta}(\tau) \sigma_{\mathbf{R}} \sigma_{\mathbf{R} + \tau}.$$  

For the hopping direction $\tau_0 \equiv (a/2)(110)$, Yildirim et al. showed from symmetry considerations that the $t^{(i)}$ take the form

$$t^{(0)}(\tau_0) = t \begin{bmatrix} A & B & 0 \\ B & A & 0 \\ 0 & 0 & C \end{bmatrix}, \quad t^{(1)}(\tau_0) = t \begin{bmatrix} X & Y & 0 \\ -Y & -X & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$t^{(2)}(\tau_0) = t \begin{bmatrix} X & -Y & 0 \\ Y & -X & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad t^{(3)}(\tau_0) = t \begin{bmatrix} D & E & 0 \\ E & D & 0 \\ 0 & 0 & F \end{bmatrix}. \quad (3)$$

A different, equivalent linear combination of these eight constants was used by Gelfand and Lu, who defined hopping matrices between “parallel” (like orientation) and “perpendicular”
(unlike orientation) molecules, within a basis that rotates with the molecules. These two matrices have the form

\[ t(\tau_0)_{\|} = t \begin{bmatrix} a & b & 0 \\ b & c & 0 \\ 0 & 0 & d \end{bmatrix}, \quad t(\tau_0)_{\perp} = t \begin{bmatrix} e & f & 0 \\ -f & g & 0 \\ 0 & 0 & h \end{bmatrix}. \]  

(4)

To fit the constants in Eqs. (3) and (4) to self-consistent LDA spectra, we first consider a supercell of the A$_2$C$_{60}$ fcc Bravais lattice, with a basis of C$_{60}$ molecules with orientations $\sigma_{R_i}$ ($i = 1, N$). If the orientations are not all identical, then all four terms from Eq. (2) will contribute to $\mathcal{H}$. By calculating the LDA eigenvalues, $E_{n\mathbf{k}}^{LDA}$, throughout the zone, optimal values (in the least-squares sense) for all of the constants in Tables I and II can be determined. We start by assuming we know the eigenvalues, $E_{n\mathbf{k}}^{TB}$, and eigenvectors, $|n\mathbf{k}\rangle$, of $\mathcal{H}$ in the TB basis for a particular set of hopping constants. Then $\mathcal{H}(\mathbf{k})$ can be written as

\[ \mathcal{H}(\mathbf{k}) = \sum_n E_{n\mathbf{k}}^{TB} |n\mathbf{k}\rangle\langle n\mathbf{k}|. \]  

(5)

From Eq. (4), the matrix elements of $\mathcal{H}(\mathbf{k})$ in the TB basis are also given explicitly in terms of the hopping parameters:

\[ \langle R, \alpha | \mathcal{H}(\mathbf{k}) | R + \tau, \beta \rangle = \sum_{\tau} t_{\alpha\beta}(\tau; \sigma_{R}, \sigma_{R+\tau}) \exp(i\mathbf{k} \cdot \tau). \]  

(6)

Eqs. (3) and (4) are equivalent formulations. We exploit this by first constructing $\mathcal{H}(\mathbf{k})$ according to Eq. (3) but with the substitution $E_{n\mathbf{k}}^{TB} \rightarrow E_{n\mathbf{k}}^{LDA}$. The resulting Hamiltonian matrix is Fourier inverted according to Eq. (4) to yield optimal hopping parameters in the least-squares sense. In practice, the solution is found iteratively, with the hopping constants from Ref. [7] providing the seed eigenvectors.

The supercell we choose is the smallest possible, containing two C$_{60}$ molecules (with different orientations) and six K ions. The resulting crystal structure has $D_{4h}$ symmetry, and can be described as sheets of C$_{60}$ molecules alternating along the (001) direction between the “A” and “B” orientations; this corresponds to the $A_2B_2$ structure of Yildirim et al. [11].
The computational methods for solving the Kohn-Sham equations are identical to those used in previous studies of $K_6C_{60}$, $K_3C_{60}$, and $K_4C_{60}$ [12]. The charge density and potential are completely general and without shape approximation, and were iterated to self-consistency using the $\Gamma$ point. Bloch basis functions are linear combinations of occupied and unoccupied atomic orbitals for potassium and carbon; these are in turn expanded on a set of gaussian functions. This provides a compact basis, and allows us to perform accurate all-electron calculations—without the need for pseudopotentials—in which core, valence, and conduction states are treated on equal footing. The Ceperly-Alder exchange-correlation functional was used. For the inversion of Eq. (6), we used a mesh of 40 equally spaced $k$-points in the irreducible wedge of the folded zone.

The hopping constants obtained by fitting to the LDA spectrum (denoted TB/LDA) are listed in the first row of Tables I and II; the constants obtained by Gelfand and Lu [7] (denoted TB/GL) are listed in the second row of Tables I and II. The TB/LDA values follow the qualitative trends in the TB/GL values, but substantial differences are apparent. To clarify the significance of these differences, we have used the Hamiltonian of Eq. (1) to compute spectra for three different structures: the orientationally ordered crystal (Fig. 1); the $A_2B_2$ supercell used to extract the hopping parameters (Fig. 2); and an ensemble of 27-molecule supercells with quenched disorder, which simulates the merohedrally disordered structure originally proposed by Stephens [4] (Fig. 3). For the first two structures, we also compare the TB spectra to the full self-consistent LDA spectra. We only show densities-of-states (DOS), since differences are still evident in these $k$-integrated spectra.

Not surprisingly, for the orientationally ordered crystal, the TB/LDA parameter set reproduces the full LDA calculation more faithfully than the TB/GL set. More interesting is the DOS (Fig. 1, middle panel, light curve) using the hopping constants fit to the LDA spectrum from the single-orientation fcc crystal. The close resemblance to the spectrum obtained by fitting to the LDA spectrum of the $A_2B_2$ structure illustrates the transferability of a particular hopping Hamiltonian from one crystal structure to another. This is the numerical justification for using hopping constants obtained from the $A_2B_2$ structure to
compute spectra for supercells simulating merohedral disorder. Interestingly, the ensemble average of these supercell spectra (Fig. 3) shows only small differences arising from the two parameter sets. The small dip at 0.22 eV in the TB/GL data is absent in the TB/LDA spectrum, and the band edges of the latter show more gradual tailing than the former; otherwise the spectra are very similar.

Deshpande et al. [9] have discussed the fact that the magnitudes and signs of the constants in Tables I and II depend on the choice of local basis sets for two neighboring molecules. They defined a simple gauge-invariant quantity by considering the spectrum of the Hamiltonian for hopping around the smallest possible closed path, i.e. forward and backward hopping across a single “bond”. There are two possibilities—hopping between like (AA) and unlike (AB) orientations—which the authors showed lead to numerically similar spectra, as shown in the second row of Table III. If it were true that hopping proceeded via nearest-neighbor atomic sites only, then the structure of the C_{60} molecule and the crystallographic alignment of the two C_{60} orientations would lead to exactly degenerate single-bond spectra. The deviation of the values in Table III from this equality is a direct measure of the importance of hopping between second-neighbor (and higher) atomic sites. In the first row of Table III, we have recomputed the single-bond spectra based on the new hopping constants. Again, changes are evident (especially for the smallest eigenvalue), but the approximate degeneracy is still observed. In particular, the largest AA and AB eigenvalues—which dominate the spectral features for all such retraceable paths—are nearly equal for both sets of constants. This justifies numerically the treatment of Ref. [9], in which all sites belonging to retraceable paths in the effective medium were assigned the same orientation.

Finally, we reconsider the results of Yildirim et al., who have made a systematic analysis of the ground-state energetics of various orientational phases of A_3C_{60} [11]. The authors considered the Ising-like nature of the orientational ordering problem, and showed that while the direct Coulomb interaction between molecules favors a “ferromagnetic” ordering, the indirect kinetic energy contribution from the conduction electrons favors an antiferromagnetic alignment of nearest neighbors. The orientational dependence of the Coulomb interaction
was analyzed in detail in Ref. [13]; this analysis was based directly on a multipole expansion of the electronic charge density calculated within LDA, and so remains unaffected by the present work. The kinetic energy contribution was analyzed in Ref. [11] by calculating the energy of the filled Fermi sea, \( E_{KE} = 2 \sum_{nk} E_{T B}^{nk} f_{nk} \), for three different orientational phases: the orientationally ordered fcc crystal, denoted by \( A_4 \); the \( A_2B_2 \) structure discussed above; and a cubic \((Pm\overline{3})\) structure denoted \( A_3B \). In Table IV, we have recomputed \( E_{KE} \) for these three structures, using our TB/LDA hopping constants, as well the TB/GL constants originally used in Ref. [11].

Several aspects of the results in Table IV deserve comment: (1) Both sets of hopping parameters favor the non-ferromagnetic \( A_3B \) and \( A_2B_2 \) configurations; (2) the TB/LDA set predicts the non-ferromagnetic configurations to be considerably more favored than does the TB/GL set; (3) the TB/LDA set predicts the energy ordering of the \( A_3B \) and \( A_2B_2 \) structures to be opposite to the prediction of the TB/GL set; (4) the ratio of relative energies, \( \Delta(A_2B_2)/\Delta(A_3B) \), has the value 1.06 for the TB/LDA set, considerably closer to the ideal nearest-neighbor Ising value of 4/3 than is the TB/GL value of 0.81. This last point suggests that the TB/LDA kinetic energy contribution to the orientational potential is also well modeled by a nearest-neighbor Ising model. When both Coulomb and kinetic energies are considered, the new parameter set implies that: (5) Non-ferromagnetic configurations are still favored so long as the kinetic energy scale, \( t \), and the Ising interaction strength, \( J_D \), satisfy the inequality \( t > -1.86J_D \). This condition is easily satisfied for all values of \( J_D \) considered in Ref. [11] (note that the ferromagnetic Coulomb interaction implies \( J_D < 0 \)). (6) Finally, the \( A_3B \) and \( A_2B_2 \) structures may in principle be degenerate if \( t = -8.00J_D \); the LDA value for \( t \) is smaller than this, but not unreasonably so. In summary, the new TB/LDA results suggest that the total orientational interactions is in fact reasonably well described by a nearest-neighbor antiferromagnetic Ising model, provided that current estimates of direct and indirect energy scales are meaningful.

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TABLES

TABLE I. Values for the hopping constants appearing in Eq. (3). To allow comparison between the two sets of parameters, we set $t=0.0146$ eV, which equates the bandwidth of the Gelfand/Lu spectrum with the LDA bandwidth.

|        | A   | B   | C   | D   | E   | F   | X   | Y   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|
| LDA fit| -0.20 | 0.10 | -2.77 | 1.25 | -2.74 | 1.12 | -0.66 | -0.32 |
| Gelfand/Lu | 0.01 | 0.38 | -2.29 | 2.09 | -2.36 | 0.38 | -0.63 | -0.49 |

TABLE II. Values for the hopping constants appearing in Eq. (4).

|        | a   | b   | c   | d   | e   | f   | g   | h   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|
| LDA fit| -0.27 | -2.64 | 2.36 | -1.65 | 2.20 | 1.45 | -3.46 | -3.89 |
| Gelfand/Lu | 0.83 | -1.98 | 3.36 | -1.91 | 1.75 | 2.08 | -3.71 | -2.67 |

TABLE III. The three positive eigenvalues of the Hamiltonian for hopping back and forth across a single bond, for like ($AA$) and unlike ($AB$) orientations.

|        | $AA$   | $AB$   |
|--------|--------|--------|
| LDA fit| 3.99   | 4.42   |
|        | 1.91   | 3.89   |
|        | 1.66   | 1.25   |
| Gelfand/Lu | 4.44 | 5.03   |
|        | 1.91   | 2.67   |
|        | 0.25   | 0.43   |
TABLE IV. Kinetic energy of the conduction electron states in three different orientational phases, in units of $t$. In the bottom panel the energies are given relative to the ordered $A_4$ phase. Note the overall increase in magnitude of both relative energies in the LDA results, as well as the reversal of the ordering between the LDA and Gelfand/Lu results.

| Structure       | Kinetic energy/molecule (t) |
|-----------------|-----------------------------|
|                 | LDA fit | Gelfand/Lu |
| $A_4$           | -25.12  | -24.13     |
| $A_3B$          | -28.18  | -28.08     |
| $A_2B_2$        | -28.43  | -27.53     |
| $A_3B - A_4$    | -4.05   | -2.94      |
| $A_2B_2 - A_4$  | -4.30   | -2.39      |
FIGURES

FIG. 1. Spectra for orientationally ordered fcc $A_3C_{60}$, as calculated by self-consistent local-density methods (top), the tight-binding parameters fit to LDA spectra (middle), and the parameter set introduced by Gelfand and Lu (bottom). In the middle panel, spectra are shown for TB parameters fitted to LDA spectra of two different orientational phases, illustrating the transferability of these parameters. The dotted line is the Fermi energy.

FIG. 2. Spectra for orientationally modulated $A_2B_2$ structure described in the text. Panels are labeled as in Fig. 1.

FIG. 3. Spectra for an ensemble average of 27-molecule supercells with quenched disorder, using two different hopping-parameter sets.