

## Effective Medium Theory for the Normal State in Orientationally Disordered Fullerides

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An effective medium theory for studying the electronic structure of the orientationally disordered  $M_3C_{60}$  fullerides is developed and applied to study various normal state properties. The theory is based on a cluster-Bethe-lattice method in which the disordered medium is modeled by a three-band Bethe lattice, into which we embed a molecular cluster whose scattering properties are treated exactly. Various single-particle properties and the frequency-dependent conductivity are calculated in this model, and comparison is made with numerical calculations for disordered lattices, and with experiment.

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In the metallic fullerides  $M_3C_{60}$  doped with the large alkali metals, the fullerene molecules are quenched into an orientationally disordered state [1]. In this state, each of the  $C_{60}$  molecules is centered on the sites of an fcc Bravais lattice and adopts a high symmetry setting, with the twofold symmetry axes aligned along [001] crystal directions. There are two inequivalent ways of achieving this orientation on each lattice site, and the intensities of x-ray reflections measured for these solids are well described by a merohedrally disordered structural model in which the choice of setting varies randomly from site to site in the solid [1]. It is now widely accepted that merohedral disorder is either a dominant or a contributing factor to a number of the observed electronic properties of these doped systems [2]. In this paper we apply an effective medium theory to study the conduction-electron states in these disordered solids.

The amplitude for electronic hopping across bond  $\tau$  between neighboring fullerene sites in these systems can be represented by a real  $3 \times 3$  matrix,  $T_{\mu\nu}(\tau)$ , in which each of the matrix elements corresponds to a possible choice of orbital polarization  $\mu(\nu) = x, y, z$  in the  $t_{1u}$  manifold on the initial and final sites [3-6]. Orientational disorder on the fullerene sites leads to a model with off-diagonal disorder in a Hamiltonian for an electron which carries with it an internal "orbital" degree of freedom, represented by a three component field. Gelfand and Lu [3] made the interesting observation that the sizes and signs of the various matrix elements in  $T$  can be changed by changing the relative molecular orientations on the terminal sites. This is a representation-dependent statement, since the signs and sizes of the various elements in  $T$  are also changed by any local rotation of the internal  $t_{1u}$  orbital bases on either of the terminal sites. Of course, physically measurable quantities in this problem can always be expressed in a representation-independent (gauge invariant) manner that does not refer to a specific convention for defining the orbital polarizations on the various molecular sites. For example, the total density of states is obtained from a trace over the single-

particle Green's function,  $N(E) = -(1/\pi)\text{Im tr } G_+(E)$ , where the trace requires a sum over both sites and over the orbital degrees of freedom on a single site. If one considers a moment expansion of the Green's function,

$$G(E) = \left(\frac{1}{E}\right) + \left(\frac{1}{E}\right)^2 H + \left(\frac{1}{E}\right)^3 HH + \left(\frac{1}{E}\right)^4 HHH + \dots, \quad (1)$$

the product  $H^n$  at  $n$ th order in this expansion describes a possible closed path of an electron containing  $n$  steps in configuration space. The required  $\text{tr } H^n$  may depend on the molecular orientations encountered, but it is independent of any particular orientation of the orbital basis on each site.

To study the product  $H^n$ , we examine a composite operator which describes the forward and backward propagation of a particle along a single bond  $\tau$  in the manner

$$H_{\text{bond}}(\tau) = \begin{pmatrix} 0 & T_{M,N} \\ T_{M,N}^T & 0 \end{pmatrix}, \quad (2)$$

where  $M$  and  $N$  can each adopt the values "A" or "B," denoting the two possible orientational settings on the initial and final sites. Diagonalizing this hopping operator, one sees that for any hopping matrix  $T$ , the eigenvalues of the composite operator  $H_{\text{bond}}$  must be ordered in pairs  $\pm |t_n|$ , for which their eigenvectors,  $R_n^\pm$ , are related by symmetry. An eigenvector describing a hop from site  $i$  to site  $f$  can be constructed from two normalized three-component vectors  $u_\alpha$  ( $\alpha = 1, 3$ ), so that  $R_n = (1/\sqrt{2})(u_{n,i}, u_{n,f})$ . For each of these normalized vectors  $u$ , the three components can be interpreted as three direction cosines, which locate a point on the surface of a reference sphere in three dimensions and define a set of principal axes (orbital polarizations) for the action of the bond-hopping operator.

The elementary hop from  $i$  to  $j$  can therefore be represented by the  $3 \times 3$  matrix operation  $H_{ji} = U_j^T h U_i$  where

$h$  is a diagonal matrix containing (by convention) only the three *positive* eigenvalues of  $H_{\text{bond}}$ , and  $U_i$  is a matrix whose rows are the three components of the eigenvectors of  $H_{\text{bond}}$  projected onto the site  $i$ . Here the action of the internal hopping operator  $h$  is positive definite, and all sign conventions are then in the  $U$  matrices, which rotate a state vector on the surface of the reference sphere. Interestingly, one finds that the diagonal elements of  $h$  in this problem depend only weakly on the molecular orientation. As an example, in Table I we list the diagonal elements of  $h$  obtained from the hopping matrices of [3]. For the most important (largest) of these terms, the fractional variation of the amplitude is only of order 10%, so it is apparent that the dominant effects of disorder in this problem are introduced through the polarizations of the molecular orbitals, and not through the amplitude fluctuations. We will therefore ignore this amplitude variation between the two configurations and focus solely on the variation of the  $U$  matrices as we pass from bond to bond in the structure. The  $n$ th order terms in Eq. (1) then describe a process in which the internal orbital polarization for a test particle rotates as it propagates on its closed  $n$ -step trajectory on the lattice.

For propagation in a disordered medium in which the  $U$ 's are varying randomly from bond to bond in the structure, for large loops one expects a single reference orbital polarization to propagate symmetrically over the reference sphere and not to contribute spectral weight in the one-particle Green's function. This cancellation rule fails for an orientationally ordered crystal, since the large  $n$ -fold loops remain highly correlated. Finally, even for the orientationally disordered system, at large order  $n$  the special class of "Brinkman-Rice" [7] retraceable paths, which propagate randomly from some reference site and exactly retrace their steps back to the origin, always makes a positive-definite contribution to the trace (even in this vector model) and determines the behavior of the Green's function.

In view of this we now construct an effective medium for which *only* the retracing paths are included in the single-particle Green's function. This network has the topology of a tree, or Bethe lattice, with one "ingoing" bond and eleven "outgoing" bonds at every node of the network. This network should be distinguished from the usual simple Bethe lattice in that the electron field on each site is now described by a three-component vector,

TABLE I. The three positive eigenvalues of the bond hopping operator  $H_{\text{bond}}$  for transitions between molecules with like ( $AA$ ) and unlike ( $AB$ ) settings. The eigenvalues of  $H_{\text{bond}}$  are ordered in pairs  $\pm |h|$ .

$AA$	$AB$
4.445	5.029
1.910	2.670
0.255	0.431

and the hopping amplitudes along each of the bonds are then given by the  $3 \times 3$  matrices discussed above, which explicitly depend on the fcc bond orientations. In the approximation that we ignore the weak amplitude fluctuations which are listed in Table I, the intermolecular hopping matrices between like ( $AA, BB$ ) and unlike ( $AB, BA$ ) molecular orientations can be transformed into each other by suitable local rotations of the orbital coordinate system on each lattice site. This local gauge freedom is ultimately eliminated on a physical lattice by the closure of rings of bonds in the network. On the tree which contains no closed rings we need consider only the dynamics in the fully orientationally ordered configuration.

The construction of the single-particle Green's function for the fulleride tree is now straightforward. The Dyson expansion for the Green's function  $EG(E) = I + HG$  can be closed by introducing an effective field  $\Phi(\tau_{ij}; E)$  such that  $G_{j,k}(E) = \Phi(\tau_{ij}; E)G_{i,k}(E)$ . These  $\Phi$ 's are complex energy-dependent  $3 \times 3$  matrices which satisfy the self-consistency condition  $E\Phi(\tau) = H(\tau) + \sum_{\tau' \neq \tau} H(\tau')\Phi(\tau')\Phi(\tau)$ . Once the  $\Phi$ 's are obtained, the

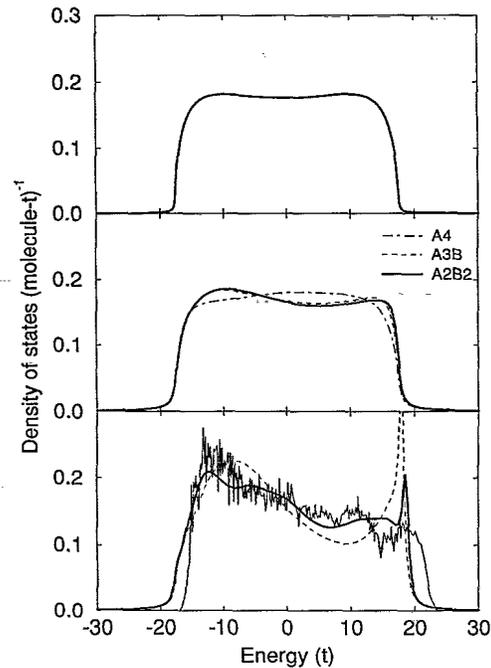


FIG. 1. Densities of states calculated for the fulleride tree and for molecular clusters embedded in the tree. Here and elsewhere in the paper the energy axis is in units of  $t \approx 10$  meV, which sets the energy scale for electronic hopping between neighboring sites. Top panel: Density of states for the tree. Middle panel: Densities of states for three embedded tetrahedral clusters with various molecular settings. Bottom panel: Densities of states at the core of embedded 19-site (dashed) and 43-site (heavy solid) clusters. The noisy curve gives the results of a quenched average on an orientationally disordered lattice.

diagonal block of the one-particle Green's function is  $G_{0,0} = [E - \sum H(\tau)\Phi(\tau, E)]^{-1}$ .

The density of states for the fcc fulleride tree is shown in Fig. 1. The symmetry about  $E = 0$  follows from the fact that closed paths on the tree require an even number of steps. The bandwidth obtained here is very nearly the bandwidth obtained from simulations on lattices with quenched orientational disorder, a feature which reflects the fact that the retracing paths control analytic structure in the Green's function for the disordered medium.

Interestingly, single-particle spectra obtained from numerical simulations on lattice models with orientational disorder exhibit a relatively large *asymmetry* with spectral weight enhanced at negative energy in the conduction band. This is a result of the phase coherent propagation of an electron through the closed rings of bonds on the fcc lattice, and the effect can be used to extract a refined estimate of the elastic mean free path in the disordered system. To illustrate this we construct a series of clusters containing the smallest closed threefold rings on the fcc lattice, and embed these clusters within an effective medium treated in the tree approximation developed above. In the middle panel of Fig. 1 we show results obtained for a tetrahedral prism in the fcc structure (four sites which are mutually nearest neighbors), with the external bonds tethered to limbs of the Bethe lattice. Here, because of the presence of closed rings of bonds, the orientational settings of the four sites inside the cluster must be specified, and the figure shows results for the three possible choices:  $A_4$ ,  $A_3B$ , and  $A_2B_2$ . For the two embedded tetrahedral clusters containing bonds between unlike orientations, the spectra are asymmetric with spectral weight enhanced at negative energies.

Similar calculations in which the size and symmetry of the embedded cluster are varied show that the dephasing of the orbital polarization introduced by the effective medium is a very strong effect in this problem, due essentially to the large coordination number on the fcc lattice. Consequently, even for fully orientationally disordered clusters, the effects of the short-range ring resonances through several coordination shells must be retained before the data converge suitably to those obtained from lattice simulations on completely disordered fullerenes. In the bottom panel of Fig. 1, for example, we display results obtained from embedded clusters containing randomly chosen  $A_{10}B_9$  and  $A_{22}B_{21}$  molecular configurations. These models just close the second (002) and third (112) coordination shells, respectively, around a reference molecule at the origin. After closing the third coordination shell on the lattice, the spectra provide a relatively good description of numerical data (also shown) obtained from a quenched average over an ensemble of orientationally disordered 27-site lattices. Apparently, in the orientationally disordered solid the effective elastic mean free path is somewhat larger than expected, and extends through several (typically 2–3) coordination shells on the fcc lattice. The physical point is that one requires phase-

coherent propagation of the electron over this distance before the constructive interference from the short range threefold ring resonances can begin to compete with the very strong dephasing of the electron orbital polarization introduced by its coupling to the external medium.

The above discussion can now be extended to study the frequency dependence of the conductivity at  $T = 0$ ,

$$\sigma(\omega) = \frac{e^2}{2\pi\omega} \int dE \operatorname{tr} [\hat{j}^\dagger G(E) \hat{j} G^\dagger(E + \omega)], \quad (3)$$

where  $G(E) = \operatorname{Re} G_+(E) \pm i \operatorname{sgn}(E - \mu) \operatorname{Im} G_+(E)$ ,  $\mu$  is the fermion chemical potential, and  $\hat{j}_{ij} = (i/\hbar) H_{ij} \tau_{ij}$  is the current operator in the  $ij$ th bond. The integrand in Eq. (3) describes a loop correlation function obtained from a trace over products of Green's functions and vertex operators [8]. The conductivity calculated in this effective medium is most naturally formulated in terms of a nonlocal bond-bond response function  $\sigma(r, r')$  so that  $j(r) = (1/\Omega_c) \int dr' \sigma(r, r') E(r')$ . Integration over all  $r$  and  $r'$  yields the  $q = 0$  limit of the correlation function which is measured with optical probes. Here, the behavior of  $\sigma(r, r')$  for large  $|r - r'|$  can be calculated exactly by introducing a vertex function,  $\Gamma(\tau; E, E')$ , which describes the contributions to the current density from processes in which an electron and hole, created inside a reference bond, propagate outward *along the same path* in the effective medium, and ultimately recombine in an external bond of the network. This vertex function plays an important role in this problem and can be calculated from the self-consistency condition [9]

$$\Gamma(\tau; E, E') = \Gamma^{(1)}(\tau; E, E') + \sum_{\tau'} \Phi(\tau, E) \Gamma(\tau'; E, E') \Phi(\tau, E'), \quad (4)$$

where  $\Gamma^{(1)}(\tau; E, E') = \hat{j}(\tau) \Phi(\tau, E') + \Phi(\tau, E) \hat{j}(-\tau)$ . The full current operator entering our discussion then takes the form  $\hat{j}_{ij} = \hat{j}_{ij}^{(0)} + \delta_{ij} \Gamma_i(E, E')$ , where the first term is the bare current-density operator acting inside a reference bond of our cluster, and the second term is a (site-diagonal) boundary term which sums all the external contributions to the current density due to excitations which leave the cluster through that boundary site.

Our results for the zero-temperature conductivity as a function of frequency on the fulleride tree are shown in Fig. 2. The top panel shows the separate contributions from the intrabond diagonal part of the conductivity  $\sigma(r, r)$  (solid), and the  $q = 0$  contribution from the interbond off-diagonal elements  $(1 - \delta_{r, r'}) \sigma(r, r')$  summed over  $r'$  (dashed). We find that the intrabond contribution has a low-frequency value near 1750 S/cm. By contrast, the nonlocal piece provides a contribution of  $\approx 650$  S/cm at zero frequency, and decreases monotonically with increasing frequency. This interbond term carries roughly one-fourth of the total spectral weight in the system, and is the remnant in the disordered model of the damped Drude response expected of a normal metal. The total

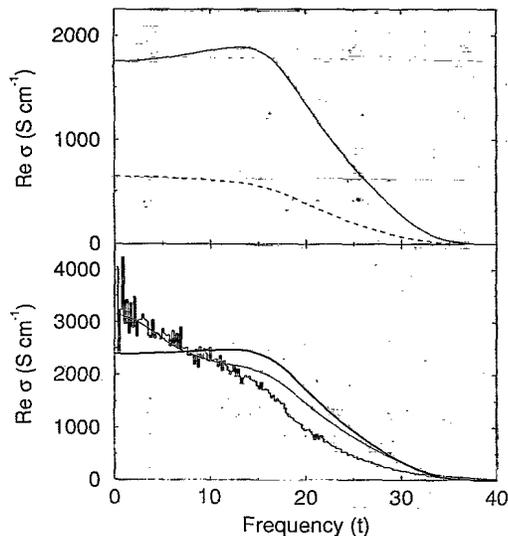


FIG. 2. Frequency-dependent conductivity on the Bethe lattice. Top: The intrabond (solid) and interbond (dashed) contributions to the nonlocal conductivity. Bottom: The total conductivity (heavy curve) is compared with results obtained from a disordered lattice model containing 32 molecular sites (histogram). In the light curve the spectral weight in the interbond contribution is collapsed to a lifetime-broadened Drude peak with a phenomenological width  $\gamma = 6t$ .

conductivity obtained by summing these contributions is shown in the lower panel; it is very weakly frequency dependent in the range  $0 < \omega < 15t$ , and has a limiting value  $\approx 2400$  S/cm at low frequency.

The separation of diagonal and off-diagonal components of the nonlocal conductivity provides a very natural method for distinguishing the interband and intraband contributions to the response function for this highly disordered medium. However, the two are more difficult to separate solely on the basis of their frequency dependence. In fact, this is true of the experimental data as well [10,11], and has led to some uncertainty as to the appropriate separation of the conductivity into contributions from the “bound” charge and that from the diffusive low-frequency dynamics of the “free” conduction charge in the disordered medium.

The data presented in Fig. 2 describe the conductivity calculated numerically for orientationally disordered superlattices [4] reasonably well. We observe that the residual resistivity calculated for the tree is 25% larger than that reported from previous theoretical work, due to the fact that the Bethe lattice yields a systematic underestimate of the effective elastic mean free path in this system. From our discussion above, the effective mean free path is  $\ell \approx 18$  Å, while for the bare tree this correlation length is clearly smaller, of order the intermolecular spacing. As a test of this conjecture, we have replotted these data collapsing *only* the interbond (dashed) contribution into a low-frequency Drude peak with a natural

width of  $\gamma \approx 6t$ , giving a good description of the superlattice data out to  $\omega \approx 15t$ , while slightly overestimating it for higher frequencies.

Experimentally, the conductivity shows a broad mid-infrared peak [10,11] near  $1200$   $\text{cm}^{-1}$ , and comparison with the data of Fig. 2 then provides an experimental estimate of the energy scale parameter,  $t \approx 10$  meV. This value is reassuringly close to the value of  $t = 14$  meV obtained from a comparison with the band calculations on the fully ordered phase, using local-density theory [12]. Extrapolations of the conductivity obtained from an analysis of the measured reflectivity spectra on  $\text{K}_3\text{C}_{60}$  at 25 K yield  $\sigma(0) \approx 1400$  S/cm [11]. An independent low-temperature extrapolation by the Berkeley group [13] yields a slightly larger value of  $\sigma(0) \approx 2000$  S/cm, in closer correspondence with the theory presented here.

We should mention that elastic scattering from the residual “amplitude” fluctuations in the electronic Hamiltonian, neglected in our model, will provide an additional elastic scattering mechanism for orientationally disordered solids, although we expect these to be quite weak. More importantly, the residual effects of electron-electron interactions, which are generally regarded as significant in the solids, and which are completely neglected in this treatment, can be expected to systematically suppress the low-frequency conductivity. A quantitative theory for treating these effects in this class of disordered conductors has yet to be developed.

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