## Effective Medium Hamiltonian for Electrons in a Topologically Disordered Model of Amorphous Graphite

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An effective medium Hamiltonian is used to describe the electronic excitations in a continuous random network model of amorphous graphite. The effective medium is obtained from an operator which describes the structural relationships of the model. This operator commutes with a Hamiltonian which differs from the network Hamiltonian by a perturbing potential which is shown to be exponentially localized on odd-membered rings. The localization of this potential transforms the extended odd-membered ring defects into pointlike impurity defects, which may be treated in an effective Hamiltonian theory.

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One of the central problems in the understanding of electrons in glassy materials is finding an effective medium for describing their excitations [1]. By comparison, excitations in crystals are well understood due to the use of the irreducible representations of their symmetry groups to provide quantum numbers. These quantum numbers are essential for understanding the transport properties of crystals, and for interpreting experimental results such as those from angle-resolved photoemission. The physical properties of substitutionally disordered materials, such as random alloys, where different species of atoms are randomly positioned on a crystal lattice in such a way as to destroy the symmetries of the Hamiltonian, are often derived from the crystal theory. For such systems it is possible to define an effective medium which possesses the same symmetry as the underlying Bravais lattice. The effect of disorder is then taken into account in an average or effective sense by simulating the properties of the disordered material by those of some ordered system. Theories based on this effective medium, such as the coherent potential approximation [2], have been successful at describing the electronic and transport properties of these materials. An effective medium Hamiltonian for a continuous random network (CRN) model of amorphous graphite, where odd-membered rings have destroyed all remnants of an ordered lattice, is presented in this Letter. This effective medium Hamiltonian is constructed using an operator which is based upon the structural relationships of the CRN model, and is analogous to an effective medium Hamiltonian in a substitutionally disordered solid which is constructed using the symmetry operators which describe the structural relationships of the underlying lattice. The uses of such an effective medium Hamiltonian are not restricted to describing the excitations of electrons in topologically disordered media, but may also prove to be of value in the study of phonons, magnons, plasmons, and so on.

In this work amorphous graphite is modeled with a CRN which contains only five-, six-, and seven-membered rings of connected and three-coordinated atoms [3]. The basis of this approach is an operator, referred to as the

network momentum operator, and its representations which are generalizations of symmetries and their representations, in that the operator preserves the glass structure everywhere except at isolated singularities [4]. The operator elucidates the properties of glasses in the same way that the translation symmetries do for the crystal. The physical basis of the operator is the tendency for each chemical species to find sites with similar local environments: neighboring species, bond lengths, and bond angles [5]. Even in the absence of long-range order these chemical forces produce structures with local order, and it is this property which suggests the existence of the structural operator under general circumstances.

A network containing a single disclination, such as a five- or seven-membered ring, may not be treated as a perturbation of the crystalline honeycomb lattice since the Hamiltonians for these systems differ from one another over a very large region of space. For example, a fivemembered-ring disclination network is constructed by removing a  $\pi/6$  sector, centered at a point of sixfold rotational symmetry from the honeycomb lattice, and then identifying the sets of points on the two edges to form a conical structure. While it is also possible to introduce sets of odd-membered rings into crystalline graphite in such a way as to not affect the honeycomb lattice away from the defective region, these special cases are not considered in this work. Such defects could be considered as substitutional defects, which may be treated in an effective medium based upon crystalline graphite.

Figure 1 shows a projection of an amorphous graphitic CRN containing five-, six-, and seven-membered rings. Triangular atomic cells are indicated with a dashed line for some of the atoms. The network momentum operator proposed for such a network, which contains N atoms, is a linear superposition of the local translations from atomic cells to all six possible second-nearest-neighbor cells, and is defined by

$$S = \sum_{j=1}^{6} \sum_{i=1}^{N} T_{ij}^{local}, \qquad (1)$$

where S is the network momentum operator and  $T_{ij}^{local}$  is

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FIG. 1. A continuous random network with five-, six-, and seven-membered rings.

the local translation operator.  $T_{ii}^{local}$  translates the set of points in an atomic cell, with label *i*, to a set of points in one of its six second-nearest-neighbor atomic cells. The network momentum operator consists of a sum of the local translation operations, such that every cell in the network is mapped into a linear superposition of each of its six second-nearest neighbors. The local translation operator  $T_{ii}^{local}$  should not be confused with a general translation operator which maps all points in space to a new set of points. The network momentum operator S is well defined in this model of the glass, since every atom always has three distinct nearest neighbors, and six distinct second-nearest neighbors. This is not true when four-membered rings are present in the structure, but these are specifically excluded from the model. In the glass structure, atomic cells are not equivalent triangles, and the translation operations must contain small geometric distortions.

The operation of S on the set of points in a triangular atomic cell is demonstrated for the cell labeled A in Fig. 1. These points are mapped into a linear combination of corresponding sets of points in cells B, C, D, E, F, and G. The vertices of these atomic cells are indicated with reference to this mapping, and labeled from 1 to 3 in the figure. In this scheme a vertex is mapped by S into the six other vertices with the same label. The mapping is unique, because the local translation  $T_{ii}^{local}$  is a unique mapping. Away from odd-membered rings, S is the sum of the six smallest Bravais lattice translations of the crystalline honeycomb structure, which independently preserve the local structure of the network. Structural relationships are preserved by a mapping when, for example, the image of two bonded atoms remains bonded under the mapping.

In atomic cells associated with odd-membered rings the

network momentum operator does not preserve structural relationships. This is illustrated by considering the bond between atoms A and H in Fig. 1. These two atomic cells share a common edge described by the vertices with labels 1 and 2 in cell A. When S maps atom A to atom C, H would have to be mapped to atom D in order to share the same common edge with the image of A. Since atom D is not a second-nearest neighbor of H, these two atomic cells are not connected by S. Consequently S breaks the structural relationship at the five-membered ring. A similar analysis leads to the same result at seven-membered rings.

In addition to acting on points in the space of the network, the operator S may also be used to act on any function of the space,  $\Phi(\mathbf{r})$ , such that

$$\mathbf{S}\boldsymbol{\Phi}(\mathbf{r}) = \sum_{j=1}^{6} \sum_{i=1}^{N} \mathsf{T}_{ij}^{\text{local}} \boldsymbol{\Phi}(\mathbf{r}) \,. \tag{2}$$

For example, in the case of the honeycomb lattice, a plane wave,  $\exp(i\mathbf{k}\cdot\mathbf{r})$ , is an eigenfunction of S with an eigenvalue spectrum  $s(\mathbf{k})$ . The network momentum operator is a Hermitian operator, and so it possesses a complete set of eigenfunctions with a corresponding eigenvalue spectrum.

The Hamiltonian for a topologically disordered solid may be decomposed such that

$$H = H_0 + V, \qquad (3)$$

where  $H_0$  is defined to only mix within irreducible representations of S, while V mixes only between different irreducible representations. An analogous approach is useful for studying impurity disorder in crystals, where Bloch states are eigenfunctions of the translation operator and of the crystalline Hamiltonian, but the localized potential of an impurity site mixes between the irreducible representations of the translation operator. For an isolated substitutional impurity, the strength of the perturbation, V, is inversely proportional to the volume of the solid, because the change in the Hamiltonian is spatially localized to the site of the impurity atom. For example, the change in the electronic structure when crystalline silicon is doped with phosphorus has been calculated in an effective Hamiltonian theory, where the wave function for the impurity disordered system is expressed as a linear superposition of the crystalline Bloch functions [6]. In this example the mixing potential V is not sufficiently strong to cause interband transitions. The usefulness of  $H_0$  and the associated eigenfunctions of S in the case of topological disorder are similarly determined by the strength of V relative to  $H_0$ . If V is strongly localized at odd-membered rings, it can be treated as a perturbation of a Hamiltonian, H<sub>0</sub>, which commutes with the network momentum operator. It is in this sense that an effective medium has been found for the CRN model of amorphous graphite, and the problem of topological disorder has been mapped to the problem of impurity disorder in solids, since the network momentum eigenfunctions of  $H_0$  are eigenfunctions of the full Hamiltonian everywhere except close to the odd-membered rings.

The spatial localization of V for a particular choice of the full Hamiltonian H has been computed for a single five-member-ring disclination network. The potential V for the topologically disordered network has been defined to be the part of the Hamiltonian which only mixes different irreducible representations of S, and may be expressed mathematically as

$$\mathsf{V} = \sum_{i,k,s_i \neq s_k} \langle \phi_i | \mathsf{H} | \phi_k \rangle | \phi_i \rangle \langle \phi_k | , \qquad (4)$$

and obeys the commutation relations

$$[S,H] = [S,V] = C$$
, (5)

where  $\{\phi_k\}$  is a complete orthonormal set of eigenstates of S, and  $s_k$  is the eigenvalue of  $\phi_k$ . V is Hermitian from its definition in Eq. (4). For a particular choice of the full Hamiltonian H, the perturbing potential V may be constructed in a computationally efficient way using both Eqs. (4) and (5) [7].

Electronic structure calculations on disordered materials are most easily performed using a basis of localized orbitals. Robertson [8] produced a set of tight-binding parameters for carbon which were found to be common to both  $sp^2$ - and  $sp^3$ -bonded structures. A simple Hamiltonian for disordered networks is the locally crystalline Hamiltonian in which the matrix elements between orbitals on near-neighbor atoms take the same values as they do in the crystal. Since bond angles and lengths for atoms on odd-membered rings do not differ significantly from their values in the crystal, the values of these Hamiltonian matrix elements cannot differ significantly from their values in the crystal. In this nearest-neighbor tight-binding model the matrix elements of the commutator C in Eq. (5) are nonzero only for some orbitals associated with atoms on the odd-membered ring, because S preserves the structure, and therefore commutes with the Hamiltonian, everywhere except along the atomic cell boundaries which are on and meet at the center of the five-membered ring.

The perturbing potential V is zero for the  $\pi$  band of amorphous graphite in the tight-binding approximation. This is because the tight-binding Hamiltonian commutes with the network momentum operator. The nearestneighbor Hamiltonian for these states is proportional to the adjacency or connectivity matrix, A, which has a unity matrix element when two atoms are nearest neighbors, and is zero otherwise. The network momentum operator for these states may be expressed as  $A^2 - 3I$ , where I is the identity operator, and so the network momentum operator commutes with the Hamiltonian for the *pi*-bonded states. A similar example of a structural map which commutes precisely with a more complicated Hamiltonian for tetrahedrally bonded semiconductors was pointed



FIG. 2. Localization of the potential V for nearest-, secondnearest, and third-nearest-neighbor distances from atoms on the five-membered ring. The magnitude of the matrix elements of the potential have been normalized using matrix elements of the potential  $V_0$  for interactions on the five-membered ring. The localization is characterized in three ways: (1) the mean magnitude of the matrix elements, (2) the mean magnitude of the matrix elements between orbitals on a given shell of neighbor atoms, and (3) the magnitude of the maximum matrix element.

out by Montgomery and Straley [9,10].

The range of the potential V on  $\sigma$ -band states in amorphous graphite is a computational issue, because it is determined by the particular choice of H. For the locally crystalline Hamiltonian, the matrix elements of V have been calculated [7], and are found to decay exponentially in the distance from the odd-membered ring in the network containing a single five-membered ring disclination. The exponential behavior for this case is demonstrated by three different characterizations of the matrix elements of V in Fig. 2. The accuracy of the computation of V has been verified by comparing the matrix elements of the commutator C when constructed according to its definitions in Eq. (5). Any deviations in bond angle and lengths in the glass structure enter the tight-binding model as deviations in the values of the matrix-element parameters which describe the interactions between neighbor atoms. No qualitative changes in the localization properties of V were exhibited when the tight-binding matrix element parameters at the five-membered ring differed from those of the locally crystalline Hamiltonian, hence the usefulness of the network momentum operator is not necessarily restricted to the approximation in which deviations in bond angles and lengths are neglected.

The local density of states (LDOS) for an atom at the



FIG. 3. The  $\sigma$ -band LDOS for an atom on the fivemembered ring computed using the locally crystalline Hamiltonian (solid line), and the effective medium Hamiltonian (dashed line).

odd-membered ring has been computed with the recursion method [11] using both the effective medium Hamiltonian,  $H_0$ , and the locally crystalline Hamiltonian,  $H_0$ +V, from which it was derived. The valence  $\sigma$ -band LDOS is presented in Fig. 3, where the solid and dashed lines correspond to the locally crystalline and effective medium Hamiltonian LDOS, respectively. This figure describes the energy dependence of the perturbing potential V on the energy eigenstates of the system. The perturbing potential is not sufficiently strong to mix valence and conduction band states, since the bounds and integrated weights of the two LDOS in Fig. 3 are found to be identical to within the accuracy of our calculations. The most significant difference between the computed LDOS is the presence of sharply peaked, defectlike, contributions at the top of the band for the case of the effective-medium Hamiltonian. Therefore the scattering potential V, which is the difference between the effective medium and locally crystalline Hamiltonians, has its largest effect on states at this energy. Electronic states at the top of the  $\sigma$ -valence band of graphite are best described as a bonding configuration of antibonding orbitals, and this state is frustrated at an odd-membered ring. The band edges are identical for both Hamiltonians, and in both cases no states are moved into the gap. The significance of this result is that the network momentum eigenfunctions (which commute with  $H_0$ ) are the eigenfunctions of H away from the odd rings where  $H = H_0$ . V is not sufficiently strong to cause interband mixing, or to shift the bounds on the density of states, and hence  $H_0$  is also good approximate Hamiltonian. A better effective medium theory would account for V. Perhaps the coherent potential approximation [2] could be applied to this problem, now that topological disorder has been separated into  $H_0 + V$ .

To summarize, an operator, referred to as the network momentum operator, is constructed from a consideration of the local bond order in a CRN model of amorphous graphite. The network is restricted to contain only fivesix-, and seven-membered rings of connected atoms. The network momentum operator is found to commute with a Hamiltonian which differs from a locally crystalline Hamiltonian only in regions which are exponentially localized at odd-membered rings. The eigenvalues of the network momentum operator are the quantum numbers for this conservative Hamiltonian. In a network with a sufficiently low density of odd-membered rings, the problem of topological disorder is mapped to the problem of isolated substitutional impurities which weakly perturb the solutions to the Hamiltonian which commutes with the network momentum operator. This principle has been demonstrated for the network which contains a single five-membered-ring disclination.

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