

## Bond-angle disorder effects on the magnetic susceptibility of amorphous semiconductors

T. Sahu and N. C. Das

*Department of Physics, Berhampur University, Berhampur-760007 Orissa, India*

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We develop a theory for the diamagnetic susceptibility ( $\chi$ ) of amorphous Si and Ge by analyzing  $\chi$  of a tetrahedrally bonded model amorphous semiconductor. We adopt a linear combination of hybrids method, recently developed by us, and derive an expression for  $\chi$  of tetrahedral semiconductors in terms of matrix elements between hybrids of the same site and hybrids of the same bond. We introduce distortions in the bond angles and construct an orthonormal set for each site for the disordered network to obtain an expression for  $\chi(\Delta)$  in terms of the bond-angle distortion parameter  $\Delta$ . Our expression for  $\chi(\Delta)$  contains three terms: (i) a core diamagnetic term,  $\chi_c$ ; (ii) a Langevin-like diamagnetic term due to valence electrons,  $\chi_v(\Delta)$ ; and (iii) a Van Vleck-like paramagnetic term,  $\chi_p(\Delta)$ . We calculate  $\chi(\Delta)$ , using various  $\Delta$  parameters, and compare our results with the corresponding crystalline values.  $\chi_c$  is found to be independent of  $\Delta$  and there is also almost no change in  $\chi_v(\Delta)$  with a change in  $\Delta$ . However, we find that  $\chi_p$  is proportional to  $S^2/(1-S^2)$ , where  $S$  is the overlap integral between two hybrids forming a bond. Since  $S$  decreases with increasing disorder,  $\chi_p(\Delta)$  is appreciably reduced with increasing  $\Delta$ . Since  $\chi_v(o)$  and  $\chi_p(o)$  are individually large and nearly cancel each other for covalent semiconductors such as Si and Ge, this reduction of  $\chi_p(\Delta)$  in the amorphous phase gives rise to a large diamagnetic enhancement. We expect our results to improve with further inclusion of effects of dihedral-angle disorder and bond-length disorder in our formulation.

### I. INTRODUCTION

Experiments on amorphous semiconductors reveal many intriguing yet interesting features associated with their physical properties.<sup>1</sup> There is an unusual enhancement in the values of the diamagnetic susceptibility ( $\chi$ ) of tetrahedral and quasitetrahedral materials like Si, Ge, and CdGeAs<sub>2</sub> in the amorphous (*a*) phase relative to their crystalline (*c*) phase. The enhancement is 450% for Si,<sup>2</sup> 270% for Ge,<sup>3</sup> and about 150% for CdGeAs<sub>2</sub> (Ref. 4) whereas, in lone-pair semiconductors, such as S,<sup>5</sup> Se,<sup>3,6</sup> As<sub>2</sub>S<sub>3</sub>,<sup>7</sup> and As<sub>2</sub>Se<sub>3</sub>,<sup>7</sup> there is no change in the *a* phase relative to the *c* phase. Measurements of dielectric constant ( $\epsilon_0$ ), i.e., refractive index (*n*) in these semiconductors, show, on the other hand, contradicting results. For Si and Ge,<sup>8</sup> there is a small change in *n*, whereas in Se (Ref. 8) there is significant decrease in *n* in the amorphous phase compared to the crystalline phase. Tetrahedral semiconductors show large changes in  $\chi$  without any change in  $\epsilon_0$ , whereas in chalcogenide semiconductors there is no change or very little change in  $\chi$  but appreciable reduction in  $\epsilon_0$  is observed while going from *c* to *a* phase. This contradicting nature of the change between the crystalline and amorphous phases, as well as different types of semiconductors, implies that these properties are related to the nature of chemical bonding and presence or absence of long-range order.

White and Anderson<sup>9</sup> have suggested two possible mechanisms as sources of diamagnetic enhancement of amorphous semiconductors relative to the corresponding crystals. One of these is the increase in the Langevin-type diamagnetic contribution ( $\chi_{loc}$ ) due to the presence of large orbits associated with localized states close to the

mobility edge. The second mechanism is the reduction in the paramagnetic Van Vleck-type interband contribution ( $\chi_{VV}$ ) arising from the loss of long-range order which leads to a breakdown of **k** conservation in the amorphous phase. Assuming the matrix elements of the angular momentum operator in  $\chi_{VV}$  are unchanged in both *c* and *a* phases, they have argued that if the minimum of the energy gap occurs in a restricted region of **k** space, the amorphous average will give a smaller value than the crystalline one. This leads to a reduction in paramagnetic contribution  $\chi_{VV}$ . One may similarly argue that since the dielectric constant ( $\epsilon_0$ ) can be written in the form of a sum of matrix elements of the electric dipole operator over the same energy-difference denominator, the above mechanism should also result in a reduction of the refractive index *n*. However, experimental results contradict this argument. Therefore, it may be concluded that a change in the effective band gap is not a major source to explain the magnetic anomalies in amorphous semiconductors.

Recently, we have developed a theory for the magnetic susceptibility of tetrahedral semiconductors,<sup>10,11</sup> by introducing a model using a linear combination of hybrids. We have constructed a basis set for the valence bands which is a linear combination of *sp*<sup>3</sup> hybrids forming a bond in which their relative phase factors, previously neglected, have been properly included. We have also constructed a basis set for the conduction bands which are orthogonal to the valence-band functions. We have constructed localized Wannier functions<sup>12</sup> from our Bloch functions and have shown that the bond orbitals used in the earlier theories<sup>13,14</sup> are not a proper choice for the Wannier functions of the valence band. We have shown that the basic assumption in the bond-orbital mod-

els, i.e., that the localized Wannier functions have the character of the chemical bonds, is equivalent to ignoring the relative Bloch phase factor  $e^{i\mathbf{k}\cdot\mathbf{d}_j}$  (where  $\mathbf{d}_j$  is a bond length) between the hybrids forming a bond. However, since  $\mathbf{d}_j - \mathbf{d}_{j'}$  ( $j \neq j'$ ) is a lattice vector, the relative phase factor plays an important role in solids, unlike in molecules where it could be neglected. We have derived a general expression for  $\chi$  of intrinsic semiconductors by using a finite-temperature Green's-function formalism. We have used our basis states in our general expression for  $\chi$  and have obtained an expression for  $\chi$  of tetrahedral semiconductors.<sup>10,11</sup> Our results have agreed well with the experiment.<sup>15</sup> We note that our expression for  $\chi$  is origin independent and free from any scaling parameter, unlike the earlier theories. The significant feature to note is that our expression for the Van Vleck-type susceptibility ( $\chi_p$ ) for elemental tetrahedral semiconductors such as Si and Ge is proportional to  $S^2/(1-S^2)$  (where  $S$  is the overlap integral), unlike the earlier theories.<sup>13,14</sup> Since  $S$  and, hence,  $\chi_p$ , decreases with increase of disorder, we note that our theory for crystalline phase with suitable modifications can explain the large diamagnetic enhancement in amorphous Si and Ge. This view is supported by our calculations<sup>16</sup> for a two-dimensional model semiconductor which shows large diamagnetic enhancement in the  $a$  phase compared to the  $c$  phase.

In the present paper we formulate a theory in an attempt to analyze and explain the experimental results for the magnetic susceptibility ( $\chi$ ) of amorphous tetrahedral semiconductors such as Si and Ge. In view of the difficulties associated with the analysis of White and Anderson, as mentioned earlier, we attempt to tackle the problem of diamagnetism in amorphous systems from a different angle. We assume that in the amorphous phase these semiconductors can be adequately described by the random-network model of Polk.<sup>17</sup> In this model the nearest-neighbor coordination is maintained both in the  $c$ , as well as in  $a$  phases. Noncrystallinity is assumed to be mainly due to deviations in tetrahedral bond angles.

We have constructed an orthonormal set of orbitals for the disorder network by introducing distortion in the angle between different hybrids at a site. We have used these orbitals and adopted a suitable averaging technique to obtain an expression for the magnetic susceptibility  $\chi(\Delta)$  of the model amorphous semiconductor in terms of the bond-angle distortion parameter  $\Delta$ . We note that there is very little change in the Langevin-type diamagnetic term  $\chi_v(\Delta)$  and an appreciable reduction in the Van Vleck-type paramagnetic term  $\chi_p(\Delta)$  due to the proportionality factor  $S^2/(1-S^2)$ . Since  $\chi_v(o)$  and  $\chi_p(o)$  nearly cancel each other for elemental semiconductors such as Si and Ge, the change in  $\chi_p(\Delta)$  drastically changes the total values of  $\chi(\Delta)$ , leading to a large diamagnetic enhancement.

The remainder of the paper is organized as follows. In Sec. II we construct the basis sets for the valence and conduction bands using a linear combination of hybrids formalism. We also derive an expression for  $\chi$  of tetrahedral semiconductors. In Sec. III, we introduce

distortion in the bond angles and construct an orthonormal set of hybrids for each site for the disorder network. We obtain an expression for  $\chi(\Delta)$  of the model amorphous semiconductor in terms of the bond-angle distortion parameter  $\Delta$ . In Sec. IV we present our numerical calculations and analyze our results. In Sec. V we summarize our results and discuss the salient points of our theory.

## II. TETRAHEDRAL SEMICONDUCTOR IN THE CRYSTALLINE PHASE

### A. Linear combination of hybrids formalism

We develop a method using a linear combination of hybrids for the tetrahedral semiconductor in the crystalline phase. We consider a diamond lattice where each atom is surrounded tetrahedrally by four nearest-neighbor atoms and vice versa. The primitive cell contains two basic atoms I and II. At each site  $i$ , we construct four  $sp^3$  hybrids  $h_j^1(\mathbf{r}-\mathbf{R}_i)$  pointing from atom I to the nearest-neighbor atom II along the direction  $j$  ( $j=0,1,2,3$ ) and four other  $sp^3$  hybrids  $h_j^2(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)$  pointing from these nearest neighbors to atom I. We choose one of I atomic sites as the origin.  $\mathbf{R}_i$  is a lattice vector for site  $i$  and  $\mathbf{d}_j$  is a nearest-neighbor vector. We construct the Bloch-like tight-binding sums for the valence-band basis functions by taking a linear combination of  $sp^3$  hybrids forming a bond

$$|v_j\rangle = \frac{1}{\sqrt{N}} \sum_i f_j^V(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}_i} \times [h_j^1(\mathbf{r}-\mathbf{R}_i) + h_j^2(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j) e^{i\mathbf{k}\cdot\mathbf{d}_j}], \quad (2.1)$$

where

$$f_j^V(\mathbf{k}) = \{2[1+S \cos(\mathbf{k}\cdot\mathbf{d}_j)]\}^{-1/2}. \quad (2.2)$$

$S$  is the overlap integral between the two hybrids forming a bond. The basis functions for the conduction bands are obtained by constructing functions orthogonal to  $|v_j\rangle$ :

$$|c_j\rangle = \frac{1}{\sqrt{N}} \sum_i f_j^c(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}_i} [(1+S e^{i\mathbf{k}\cdot\mathbf{d}_j}) h_j^1(\mathbf{r}-\mathbf{R}_i) - (S + e^{i\mathbf{k}\cdot\mathbf{d}_j}) \times h_j^2(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_j)], \quad (2.3)$$

where

$$f_j^c(\mathbf{k}) = \left[ \frac{(1+S e^{-i\mathbf{k}\cdot\mathbf{d}_j})}{2(1-S^2)[1+S \cos(\mathbf{k}\cdot\mathbf{d}_j)](1+S e^{i\mathbf{k}\cdot\mathbf{d}_j})} \right]^{1/2}. \quad (2.4)$$

The eigenfunctions corresponding to valence ( $n$ ) and conduction ( $m$ ) bands are

$$\psi_n(\mathbf{k}, \mathbf{r}) = \sum_j \alpha_{jn}^v(\mathbf{k}) |v_j\rangle \quad (2.5)$$

and

$$\psi_m(\mathbf{k}, \mathbf{r}) = \sum_j \alpha_{jm}^c(\mathbf{k}) |c_j\rangle. \quad (2.6)$$

Here the  $\alpha$ 's are elements of  $4 \times 4$  unitary matrices satisfying the relation

$$\begin{aligned} \sum_n \alpha_{jn}^v(\mathbf{k}) \alpha_{nj'}^{\dagger}(\mathbf{k}) &= \delta_{jj'}, \\ \sum_m \alpha_{jm}^c(\mathbf{k}) \alpha_{mj'}^{\dagger}(\mathbf{k}) &= \delta_{jj'}. \end{aligned} \quad (2.7)$$

### B. Diamagnetic susceptibility of crystalline semiconductors

We obtain an expression for the magnetic susceptibility of crystalline tetrahedral semiconductors by using our basis states [Eqs. (2.5) and (2.6)] in the expression for  $\chi$  of the intrinsic semiconductors recently derived by us<sup>11</sup> and which can be written as

$$\begin{aligned} \chi = \frac{2h_{\alpha\beta} h_{\gamma\delta}}{B^2} \sum_{n, \mathbf{k}} \left[ -\frac{\hbar^2}{m} Q_{nm}^{\dagger\alpha} Q_{mn}^{\gamma} \delta_{\delta\beta} + Q_{nm}^{\dagger\alpha} Q_{mn}^{\gamma} P_{n'm'}^{\delta} Q_{m'n}^{\beta} + P_{nm}^{\alpha} Q_{mn}^{\gamma} Q_{n'm'}^{\dagger\beta} Q_{m'n}^{\delta} \right. \\ \left. - Q_{nm}^{\dagger\alpha} P_{mn}^{\gamma} Q_{n'm'}^{\dagger\beta} Q_{m'n}^{\delta} + 2Q_{nm}^{\dagger\alpha} Q_{mn}^{\beta} P_{nm}^{\gamma} Q_{m'n}^{\delta} - \frac{Q_{nm}^{\dagger\alpha} P_{mm'}^{\beta} P_{m'm''}^{\gamma} Q_{m''n}^{\delta}}{E_{m'n}} \right. \\ \left. + \frac{2P_{nn'}^{\alpha} Q_{n'm}^{\dagger\beta} P_{mm'}^{\gamma} Q_{m'n}^{\delta}}{E_{m'n'}} + \frac{P_{nn'}^{\alpha} Q_{n'm}^{\dagger\beta} P_{mm'}^{\gamma} Q_{m'n}^{\delta}}{E_{mn}} \right]. \end{aligned} \quad (2.8)$$

Here  $Q_{mn}^{\alpha} = -\int U_m^* \nabla_{\mathbf{k}}^{\alpha} U_n d\mathbf{r}$ ,  $h_{\alpha\beta} = \epsilon_{\alpha\beta\gamma} h^{\gamma}$ ,  $\mathbf{h} = e\mathbf{B}/2\hbar c$ ,  $E_{mn} = E_{m\mathbf{k}} - E_{n\mathbf{k}}$ , and  $P_{nm}/\hbar$  are the matrix elements of the velocity operator between  $\psi_n$  and  $\psi_m$ ,  $U_n$  and  $U_m$  are the periodic part of the Bloch function, ( $n, n'$ , etc.) and ( $m, m'$ , etc.) denote the valence and conduction bands, and repeated indices imply summation. In order to evaluate the matrix elements between different hybrids occurring in the expression for  $\chi$  [Eq. (2.8)], we have adopted a Hall-Weaire-Thorpe approximation,<sup>18</sup> i.e., we have calculated only matrix elements between hybrids of the same site and between hybrids of the same bond. Since the Hall-Weaire-Thorpe model yields a poor description of the conduction band, we have assumed the completeness relation

$$\sum_m |m\rangle \langle m| = 1 - \sum_n |n\rangle \langle n| \quad (2.9)$$

(thereby neglecting the core states) to express the conduction-band states. We have also made an average-energy-gap ansatz ( $E_g$ ) for the energy-gap denominator and obtained an expression for  $\chi$  as

$$\chi = \chi_c + \chi_v + \chi_p, \quad (2.10)$$

where  $\chi_c$  and  $\chi_v$  are Langevin-like diamagnetic terms due to core and valence electrons and  $\chi_p$  is the Van Vleck-like paramagnetic term

$$\begin{aligned} \chi_v = -\frac{e^2 N}{2mc^2} \sum_j \{ A_j \langle h_j^1 | (x^2 + y^2) | h_j^1 \rangle \\ + B_j \langle h_j^1 | [x(x - d_j^x) \\ + y(y - d_j^y)] | h_j^2 \rangle \}, \end{aligned} \quad (2.11)$$

$$\chi_p = \frac{e^2 N S^2}{m^2 c^2 E_g (1 - S^2)} \sum_{j, j'} C_{jj'} |\langle h_j^1 | L_z | h_{j'}^1 \rangle|^2. \quad (2.12)$$

Here

$$A_j = \frac{1}{N} \sum_{\mathbf{k}} [1 + S \cos(\mathbf{k} \cdot \mathbf{d}_j)]^{-1},$$

$$B_j = \frac{1}{N} \sum_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{d}_j) [1 + S \cos(\mathbf{k} \cdot \mathbf{d}_j)]^{-1},$$

and

$$C_{jj'} = \frac{1}{N} \sum_{\mathbf{k}} \frac{\sin^2(\mathbf{k} \cdot \mathbf{d}_{j'})}{[1 + S \cos(\mathbf{k} \cdot \mathbf{d}_j)][1 + S \cos(\mathbf{k} \cdot \mathbf{d}_{j'})]}. \quad (2.13)$$

It may be noted that we have essentially obtained the valence-electron contribution to the magnetic susceptibility as a sum of contributions due to localized orbitals. In Eq. (2.11) the first term is the contribution due to matrix elements between intrasite hybrids while the second term is the contribution due to the matrix elements between two hybrids of adjacent sites forming a bond. In Eq. (2.12) the contribution is due to matrix elements between intrasite hybrids only. We are interested in analyzing the variation of  $\chi$  with disorder by introducing distortion in bond angles. Therefore, we have obtained a simple expression for  $\chi$  of the crystalline semiconductor by neglecting the terms of less physical importance and of one order less in magnitude<sup>10</sup> in the general expression for  $\chi$  in deriving Eqs. (2.11) and (2.12). However, the effect of all the terms in Eq. (2.8) has essentially been incorporated by matching Eqs. (2.11) and (2.12) with the experimentally separated values<sup>15</sup> of  $\chi_v$  and  $\chi_p$  in the final estimation of the enhancement factor.

### III. TETRAHEDRAL SEMICONDUCTOR IN THE AMORPHOUS PHASE

#### A. Orthonormal sets for the disordered network

The orthonormal set of orbitals that take part in the tetrahedral bonding are  $sp^3$  hybrids. In order to achieve

amorphous phase,<sup>17</sup> we introduce disorder in the atomic positions which, in turn, introduces disorder in the bond angles and bond lengths but still preserves the nearest-neighbor coordination. Since the bond lengths do not change appreciably<sup>19</sup> on energetic grounds, in the present calculation, we consider disorder in the bond angles only.<sup>17</sup> We construct modified  $sp^3$  orbitals<sup>20</sup> for two nearest-neighboring sites for arbitrary bond angles  $\theta$  and dihedral angles  $\phi$ . First we assume one of the bond orientations (say  $j=0$ ) along the  $z$  axis and write the pair of orbitals forming the bond as

$$a_0^1(\mathbf{r}) = \frac{1}{2}s(\mathbf{r}) + \frac{\sqrt{3}}{2}p_z(\mathbf{r})$$

and

$$a_0^2(\mathbf{r}-\mathbf{d}_0) = \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}p_z(\mathbf{r}-\mathbf{d}_0), \quad (3.1)$$

where site I is at the origin and  $\mathbf{d}_0$  is the bond length along the  $j=0$  direction.  $s$  and  $p$  are the atomic orbitals. The other three hybrids at each site are generated from the corresponding hybrids [Eq. (3.1)] by making appropriate rotations. For example, the hybrids at site I,  $a_1^1(\mathbf{r})$ ,  $a_2^1(\mathbf{r})$ , and  $a_3^1(\mathbf{r})$  (for  $j=1, 2$ , and  $3$ ) are generated from  $a_0^1(\mathbf{r})$  by giving arbitrary rotations of  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  about the  $y$  axis, followed by subsequent rotations  $\psi_1$ ,  $(\frac{2}{3}\pi + \psi_2)$ , and  $(\frac{4}{3}\pi + \psi_3)$  about the  $z$  axis, respectively. Similarly the hybrids  $a_1^2(\mathbf{r}-\mathbf{d}_0)$ ,  $a_2^2(\mathbf{r}-\mathbf{d}_0)$ , and  $a_3^2(\mathbf{r}-\mathbf{d}_0)$  are obtained from  $a_0^2(\mathbf{r}-\mathbf{d}_0)$  by giving rotations  $-\beta_1$ ,  $-\beta_2$ , and  $-\beta_3$  about an axis passing through atom II and parallel to the  $y$  axis, followed by rotations  $\pi + \phi_1$ ,  $\frac{5}{3}\pi + \phi_2$ , and  $\frac{7}{3}\pi + \phi_3$  about the  $z$  axis, respectively. Since the  $p$  functions transform as the  $D^{(1)}$  representation of the full rotation group we have

$$\begin{aligned} a_1^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) - \frac{\sqrt{3}}{2}\sin\alpha_1\cos\psi_1 p_x(\mathbf{r}) + \frac{\sqrt{3}}{2}\sin\alpha_1\sin\psi_1 p_y(\mathbf{r}) + \frac{\sqrt{3}}{2}\cos\alpha_1 p_z(\mathbf{r}), \\ a_2^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) + \frac{\sqrt{3}}{4}(\cos\psi_2 + \sqrt{3}\sin\psi_2)\sin\alpha_2 p_x(\mathbf{r}) + \frac{\sqrt{3}}{4}(\sqrt{3}\cos\psi_2 - \sin\psi_2)\sin\alpha_2 p_y(\mathbf{r}) + \frac{\sqrt{3}}{2}\cos\alpha_2 p_z(\mathbf{r}), \\ a_3^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) + \frac{\sqrt{3}}{4}(\cos\psi_3 - \sqrt{3}\sin\psi_3)\sin\alpha_3 p_x(\mathbf{r}) - \frac{\sqrt{3}}{4}(\sqrt{3}\cos\psi_3 + \sin\psi_3)\sin\alpha_3 p_y(\mathbf{r}) + \frac{\sqrt{3}}{2}\cos\alpha_3 p_z(\mathbf{r}) \end{aligned} \quad (3.2)$$

and

$$\begin{aligned} a_1^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) + \frac{\sqrt{3}}{2}\sin\beta_1\cos\phi_1 p_x(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}\sin\beta_1\sin\phi_1 p_y(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}\cos\beta_1 p_z(\mathbf{r}-\mathbf{d}_0), \\ a_2^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{4}(\cos\phi_2 + \sqrt{3}\sin\phi_2)\sin\beta_2 p_x(\mathbf{r}-\mathbf{d}_0) \\ &\quad - \frac{\sqrt{3}}{4}(\sqrt{3}\cos\phi_2 - \sin\phi_2)\sin\beta_2 p_y(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}\cos\beta_2 p_z(\mathbf{r}-\mathbf{d}_0), \\ a_3^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{4}(\cos\phi_3 - \sqrt{3}\sin\phi_3)\sin\beta_3 p_x(\mathbf{r}-\mathbf{d}_0) \\ &\quad + \frac{\sqrt{3}}{4}(\sin\phi_3 + \sqrt{3}\cos\phi_3)\sin\beta_3 p_y(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}\cos\beta_3 p_z(\mathbf{r}-\mathbf{d}_0). \end{aligned} \quad (3.3)$$

We note that the bond angle is the angle subtended by two bonds at a common site. Whereas, the dihedral angle ( $\phi$ ) is the angle between the second-neighbor bonds when projected onto a plane perpendicular to the common bond (as shown in Fig. 1). From our construction, we note that the dihedral angle  $\phi$  between the hybrids, for example,  $a_j^1(\mathbf{r})$  and  $a_j^2(\mathbf{r}-\mathbf{d}_0)$ , for  $j=1, 2$ , and  $3$ , is  $(\pi + \phi_j - \psi_j)$ , where  $(\phi_j - \psi_j)$  is the distortion in the dihedral angle from the corresponding crystalline value  $\pi$ . We note that if we set the bond angles  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  and  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  equal to the tetrahedral angle  $\alpha_T = \cos^{-1}(-\frac{1}{3})$  and the dihedral angles equal to  $\pi$ , then the hybrids of sites I and II occupy the staggered configuration of tetrahedral symmetry which corresponds to the crystalline phase. In this phase, the hybrids at each site also become orthogonal to each other. However, in the present case [Eqs. (3.1)–(3.3)], because of arbitrary

bond angles and dihedral angles, the orbitals at each site are no longer orthogonal to each other. We therefore adopt a symmetric orthogonalization procedure<sup>21</sup> to obtain orthonormal sets of hybrids for each site. The orthonormal set of orbitals for site I can be expressed as

$$O_j^1(\mathbf{r}) = a_j^1(\mathbf{r}) - \frac{1}{2} \sum_{j'} a_{j'}^1(\mathbf{r}) S_{jj'}^1 + \frac{3}{8} \sum_{j', j''} a_{j''}^1(\mathbf{r}) S_{j'j''}^1 S_{jj'}^1, \quad (3.4)$$

where

$$S_{jj'}^1 = \begin{cases} \int a_j^{1*}(\mathbf{r}) a_{j'}^1(\mathbf{r}) d\mathbf{r} & \text{for } j \neq j' \\ 0 & \text{for } j = j' \end{cases} \quad (3.5)$$

Similarly the orthonormal set of four orbitals for site II (with nearest-neighbor vector  $\mathbf{d}_0$ ) can be expressed as

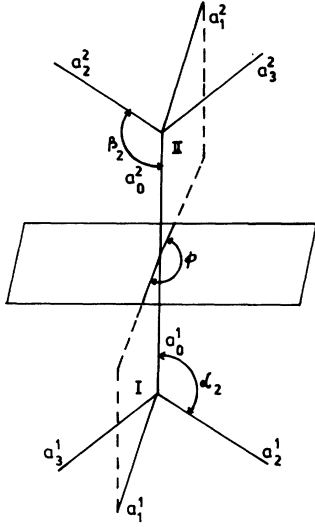


FIG. 1. Schematic representation of the  $sp^3$  orbitals: the bond angles ( $\alpha_j, \beta_j$ ) and the dihedral angles  $\phi$  for two of the four orbitals on each of the neighboring atoms [here we show, for example, the angle  $\phi$  between  $a_1^1(\mathbf{r})$  and  $a_1^2(\mathbf{r}-\mathbf{d}_0)$ ,  $\phi = \pi + \phi_1 - \psi_1$ ].

$$O_j^2(\mathbf{r}-\mathbf{d}_0) = a_j^2(\mathbf{r}-\mathbf{d}_0) - \frac{1}{2} \sum_j a_j^2(\mathbf{r}-\mathbf{d}_0) S_{jj}^2 + \frac{3}{8} \sum_{j', j''} a_{j''}^2(\mathbf{r}-\mathbf{d}_0) S_{j''j'}^2 S_{j'j}^2, \quad (3.6)$$

where

$$S_{jj'}^2 = \begin{cases} \int a_j^{2*}(\mathbf{r}-\mathbf{d}_0) a_{j'}^2(\mathbf{r}-\mathbf{d}_0) d\mathbf{r}, & j \neq j' \\ 0, & j = j'. \end{cases} \quad (3.7)$$

It may be noted that we have assumed that  $S_{jj'}^1$  and  $S_{jj'}^2$ , the overlap integrals between two intrasite hybrids, are small and, therefore, kept up to second order in  $S_{jj'}$  in Eqs. (3.4) and (3.6). Further, since the deviations of the bond angles from the tetrahedral angles ( $\alpha_T$ ) are small<sup>17</sup> (about 10%) we write  $\alpha_j = \alpha_T + \gamma_j$  and  $\beta_j = \alpha_T + \delta_j$  and expand the orthonormal orbitals in terms of these deviations. Keeping up to second order in  $\gamma_j$  ( $\gamma_j^2, \gamma_j \gamma_{j'}$ ) and  $\delta_j$  ( $\delta_j^2, \delta_j \delta_{j'}$ ) we obtain the orthonormal set of hybrids for each site for the disordered network (see Appendix).

### B. $\chi$ of the model amorphous semiconductor

We obtain an expression for  $\chi$  of the model amorphous semiconductor in the amorphous phase by using our disorder basis states [Eqs. (3.4) and (3.6)] in the expression for  $\chi_v$  and  $\chi_p$  [Eqs. (2.11) and (2.12)]. We assume that the average energy gap  $E_g$  is unchanged in the  $a$  phase, since the leading term in  $E_g$  in the Weaire-Thorpe model is  $2|V_2|$  and is not likely to change if the bond length remains the same. We note that our orthonormal set of orbitals is constructed by taking arbitrary bond angles and dihedral angles. However, in the present work we wish to study the effect of bond-angle disorder on the magnetic susceptibility of tetrahedral amorphous semi-

conductors. Therefore, in the calculation of  $\chi$  we have taken the dihedral-angle distortion ( $\phi_j, \psi_j$ ) equal to zero. We carry out a configuration averaging over the distribution of the bond-angle distortion ( $\gamma_j, \delta_j$ , etc.). In the averaging process we have used

$$\langle \gamma_j \gamma_{j'} \rangle = \langle \delta_j \delta_{j'} \rangle = \Delta \delta_{jj'},$$

where  $\delta_{jj'}$  is the Kronecker delta. The expression for the magnetic susceptibility of the model semiconductor in the amorphous is obtained as

$$\chi(\Delta) = \chi_c + \chi_v(\Delta) + \chi_p(\Delta), \quad (3.8)$$

where

$$\begin{aligned} \chi_v(\Delta) = & -\frac{e^2 N}{2mc^2} \sum_j \{ A_j(\Delta) \langle O_j^1 | (x^2 + y^2) | O_j^1 \rangle \\ & + B_j(\Delta) \langle O_j^1(\mathbf{r}) | \\ & \times [x(x-d_j^x) + y(y-d_j^y)] \\ & \times | O_j^2(\mathbf{r}-\mathbf{d}_j) \rangle \} \end{aligned} \quad (3.9)$$

and

$$\chi_p(\Delta) = \frac{e^2 N}{m^2 c^2 E_g} \sum_{\substack{j, j' \\ (j' \neq j)}} \frac{C_{jj'}(\Delta) S_{jj'}^2(\Delta)}{[1 - S_{jj'}^2(\Delta)]} |\langle O_j^1 | L_z | O_{j'}^1 \rangle|^2. \quad (3.10)$$

Here  $S_j(\Delta)$  is the overlap integral, which can be expressed as

$$S(\Delta) = S(0) \left(1 - \frac{3}{8} \Delta\right). \quad (3.11)$$

$S(0)$  is the overlap integral between two hybrids forming a bond for  $\Delta=0$  (crystalline case).  $A_j(\Delta)$ ,  $B_j(\Delta)$ , and  $C_{jj'}(\Delta)$  are coefficients dependent on the disorder parameter  $\Delta$  through  $S_j$ . Summation over  $j$  refers to summation over four nearest-neighbor bonding coordination in the disordered phase where  $\mathbf{d}_j$  is a bond length along that direction. In Eq. (3.9) the first term is the contribution due to intrasite hybrids while the second term is the contribution due to the hybrids between adjacent sites forming a bond. We note that for tetrahedral semiconductors<sup>10</sup> (Si, Ge) the magnitude of the second term is about 1% that of the first term and is within 5% of the total magnetic susceptibility. Therefore, for simplicity we neglect the second term in  $\chi_v$  in our analysis.

TABLE I. Variation of  $\chi(\Delta)$  with disorder parameter  $\Delta$  (all  $\chi$ 's in units of  $10^{-6}$  cm<sup>3</sup>/mol).

Solid	$\Delta$	$\chi_c$	$\chi_v(\Delta)$	$\chi_p(\Delta)$	$\chi(\Delta)$	$\chi(\Delta)/\chi(O)$ (%)
Si	0.0	-4.6	-39.3	37.5	-6.4	100
	0.03	-4.6	-39.31	36.3	-7.61	119
	0.12	-4.6	-39.4	32.6	-11.4	178
	0.2	-4.6	-39.46	31.3	-12.76	200
Ge	0.0	-16.6	-50.3	51.2	-15.7	100
	0.03	-16.6	-50.31	49.68	-17.23	110
	0.12	-16.6	-50.37	46.01	-20.96	134
	0.2	-16.6	-50.52	43.23	-23.89	152

#### IV. RESULTS AND DISCUSSION

We have analyzed the magnetic susceptibility of the tetrahedrally coordinated model amorphous semiconductor using Eqs. (3.8)–(3.10). The numerical value of the parameters  $d$ ,  $E_g$ , and  $\chi_c$  for Si and Ge are obtained from Refs. 14 and 15. We have used Hartree-Fock atomic orbitals from Clementi's table.<sup>22</sup> The two-center integrals are evaluated by using spheroidal transformation technique.<sup>23</sup> Our goal is to obtain the relative changes in  $\chi(\Delta)$  with increase in  $\Delta$ . We match the results of  $\chi^v(o)$  and  $\chi_p(o)$  ( $\Delta=0.0$ ) with the experimentally separated values<sup>15</sup> of  $\chi$  of crystalline Si and Ge and then study the variation of  $\chi(\Delta)$  with increase in  $\Delta$ . We note that the estimated value of the disorder parameter  $\Delta$  is not available. The root-mean-square deviation of the bond angles is reported to be about 10%. In our analyses we took  $\Delta=0.03, 0.12$ , and  $0.2$  to study the trend. Our results of  $\chi(\Delta)$  for Si and Ge are presented in Table I. We note that there is very little change, virtually no change, in the value of  $\chi_v$  as  $\Delta$  increases from  $0.0$  to  $0.03, 0.12$ , and  $0.2$ . However, the value of  $\chi_p(\Delta)$  reduces by 4%, 13%, and 17% for Si and by 3%, 11%, and 16% for Ge as the disorder parameter  $\Delta$  increases from  $0.0$  to  $0.03, 0.12$ , and  $0.2$ , respectively. As a result, we note that the net change in the total susceptibility turns out to be large and is 119%, 178%, and 200%, respectively, for Si and 110%, 134%, and 152%, respectively, for Ge corresponding to the  $\Delta$  value  $0.03, 0.12$ , and  $0.2$ .

In order to analyze our results, we note that in  $\chi_v(\Delta)$  [Eq. (3.9)] the value of the coefficient  $A_j(\Delta)$  is the same for all bond orientations ( $j$ ) and changes very little with the change in  $\Delta$ . Further, we note that although the value of the matrix elements  $\langle O_j^1(\mathbf{r})|(x^2+y^2)|O_j^1(\mathbf{r})\rangle$  depends upon  $\Delta$  for each bond orientation, the sum of the contributions due to all the four bond orientations turns out to be independent of  $\Delta$  and equal to the corresponding crystalline value. As a result, we obtain almost no change in  $\chi_v(\Delta)$  with increase in  $\Delta$ . In  $\chi_p(\Delta)$  [Eq. (3.10)], we note that the change in the coefficient  $C_{jj'}(\Delta)$  is very small for different  $\Delta$ . The change in the values of  $|\langle O_j^1(\mathbf{r})|L_z|O_{j'}^1(\mathbf{r})\rangle|^2$  is also small and of the order  $0.07 \Delta$  from their crystalline values. Therefore, the reduction in  $\chi_p(\Delta)$  is almost due to the decrease in the values of the proportionality factor  $S_j^2(\Delta)/[1-S_j^2(\Delta)]$  with an increase in  $\Delta$ , unlike the earlier theories.<sup>13,14,24</sup>

We note that the values of  $\chi_v(o)$  and  $\chi_p(o)$  are individually large and nearly cancel in the case of the perfectly covalent tetrahedral semiconductors like Si and Ge. As ionicity increases,  $\chi_v$  increases in magnitude and  $\chi_p$  decreases and there is no longer a near-perfect cancellation as in the case of III-V semiconductors.<sup>11,14</sup> Therefore, as predicted by Fritzsche and Hudgens,<sup>25</sup> a small change in  $\chi_v$  and  $\chi_p$  drastically changes the total value of  $\chi$  of Si and Ge.

We note that since the change in the experimental value of  $\chi$  in the amorphous phase compared to the crystalline phase is 450% for Si and 270% for Ge, our results predict approximately a 50% enhancement in  $\chi$ . It may be noted that we have not included the effect of dihedral-angle disorder in our formulation. In fact, it has been shown that the effect of dihedral-angle disorder is important<sup>26</sup> in predicting the density of states near the top of the valence band of amorphous Si. We believe that our results would improve by considering the effect due to the dihedral-angle disorder. Further, we believe that our results would improve by considering the effect of bond-length disorder.

We shall now compare our results with the earlier results. We note that our formulation differs from the analysis of White and Anderson. White and Anderson have assumed that in the Van Vleck-type paramagnetic susceptibility  $\chi_p$  the matrix elements between the valence- and conduction-band states of the angular-momentum operator remain unchanged in the  $a$  phase relative to the  $c$  phase. Further, they have argued that if the band-gap minimum occurs in a restricted region of  $\mathbf{k}$  space, the value of the effective gap will be larger in the amorphous phase leading to reduction in  $\chi_p$ . On the other hand, in our formulation we have assumed that the average energy gap  $E_g$  remains unchanged in the  $a$  phase since the leading term in  $E_g$  in the Weaire-Thorpe model is  $2|V_2|$  and is not likely to change if the bond length remains the same. We have shown that the value of the matrix elements decreases in  $\chi_p$  with increase of disorder parameter  $\Delta$ , giving rise to large diamagnetic enhancement in  $\chi$  in the amorphous phase. In order to explain the lack of change in the dielectric constants of Si and Ge in the amorphous phase relative to the crystalline phase, we have shown<sup>16,27</sup> that the value of the matrix elements of the electric dipole operator between the valence- and conduction-band states changes very little with increasing disorder parameter  $\Delta$ , resulting in no change in  $\epsilon_0$ .

## V. SUMMARY AND CONCLUSION

We formulate a theory for the diamagnetic enhancement in amorphous semiconductors such as Si and Ge by analyzing the magnetic susceptibility ( $\chi$ ) of a tetrahedrally coordinated model amorphous semiconductor. We develop a method using a linear combination of hybrids to construct the valence- and conduction-band states and use them to derive expressions for  $\chi$  of the tetrahedral semiconductors in terms of matrix elements between intrasite hybrids and between hybrids of adjacent sites forming a bond. Our expression for  $\chi$  contains three terms: (i) a core diamagnetic term ( $\chi_c$ ), (ii) a Langevin-like diamagnetic term due to valence electrons ( $\chi_v$ ), and (iii) a Van Vleck-like paramagnetic term ( $\chi_p$ ). We construct an orthonormal set for the disordered network by introducing distortion in bond angles and use them to derive expressions for  $\chi(\Delta)$  of the model amorphous semiconductors in terms of bond-angle distortion parameter  $\Delta$ . An interesting feature of our result is that our expression for  $\chi_p$  is proportional to  $S^2/(1-S^2)$ , where  $S$  is the overlap integral. Since  $S$  decreases with increase of disorder, the value of  $\chi_p$  also decreases appreciably. We study the variation of  $\chi(\Delta)$  with  $\Delta$  by matching  $\chi_v(o)$  and  $\chi_p(o)$  (for  $\Delta=0.0$ ) with the experimental values<sup>15</sup> of  $\chi$  of

Si and Ge. There is essentially no change in  $\chi_v(\Delta)$  but appreciable reduction in  $\chi_p(\Delta)$  with increase of  $\Delta$  due to the proportionality factor  $S^2/(1-S^2)$ . Since  $\chi_v(o)$  and  $\chi_p(o)$  are individually large and nearly cancel each other for covalent semiconductors such as Si and Ge, we show that the large diamagnetic enhancement in the amorphous phase is mainly due to reduction in the Van Vleck-type paramagnetic susceptibility. From our analysis we note that there is approximately a 50% enhancement in  $\chi$  in the amorphous phase due to the effect of bond-angle disorder. Our results are expected to improve by considering the dihedral-angle disorder as well as bond-length disorder in our formulation.

We note that our theory can, in principle, be applied to nontetrahedral materials such as Se and Te as well, with suitable modifications. For these trigonal semiconductors, which are also covalent but do not show any diamagnetic enhancement in the amorphous phase, we believe that the values of  $\chi_v(o)$  and  $\chi_p(o)$  in these solids do not come close to canceling each other, unlike Si and Ge. Further, because of the anisotropy of the crystal structure,<sup>28,29</sup> and because of the fact that the valence band is constructed from the lone-pair  $p$ -type orbitals,<sup>30</sup> we believe that the expression for  $\chi$  of trigonal semiconductors should be different<sup>31</sup> from the expression for  $\chi$  of tetrahedral semiconductors.

## APPENDIX

For small deviations in the bond angles, i.e., for  $\alpha_j = \alpha_T + \gamma_j$ , the nonorthogonal set of hybrids for site I [Eq. (3.2)] can be expressed as

$$\begin{aligned} a_0^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) + \frac{\sqrt{3}}{2}p_z(\mathbf{r}), \\ a_1^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) + C_1(\gamma_1)\cos\psi_1 p_x(\mathbf{r}) - C_1(\gamma_1)\sin\psi_1 p_y(\mathbf{r}) + C_2(\gamma_1)p_z(\mathbf{r}), \\ a_2^1(\mathbf{r}) &= \frac{1}{2}s(\mathbf{r}) - \frac{1}{2}C_1(\gamma_2)(\cos\psi_2 + \sqrt{3}\sin\psi_2)p_x(\mathbf{r}) - \frac{1}{2}C_1(\gamma_2)(\sqrt{3}\cos\psi_2 - \sin\psi_2)p_y(\mathbf{r}) + C_2(\gamma_2)p_z(\mathbf{r}), \end{aligned} \quad (\text{A1})$$

and

$$a_3^1(\mathbf{r}) = \frac{1}{2}s(\mathbf{r}) - \frac{1}{2}C_1(\gamma_3)(\cos\psi_3 - \sqrt{3}\sin\psi_3)p_x(\mathbf{r}) + \frac{1}{2}C_1(\gamma_3)(\sqrt{3}\cos\psi_3 + \sin\psi_3)p_y(\mathbf{r}) + C_2(\gamma_3)p_z(\mathbf{r}),$$

where

$$C_1(\gamma) = -\frac{\sqrt{2}}{\sqrt{3}} + \frac{1}{2\sqrt{3}}\gamma + \frac{1}{\sqrt{6}}\gamma^2, \quad (\text{A2})$$

$$C_2(\gamma) = -\frac{1}{2\sqrt{3}} - \frac{\sqrt{2}}{\sqrt{3}}\gamma + \frac{1}{4\sqrt{3}}\gamma^2.$$

Similarly the nonorthogonal set of hybrids of site II at the nearest-neighbor vector  $\mathbf{d}_0$  [Eq. (3.3)] can be obtained by putting  $\beta = \alpha_T + \delta$ , where  $\delta$  is a small deviation, as

$$\begin{aligned}
a_0^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) - \frac{\sqrt{3}}{2}p_z(\mathbf{r}-\mathbf{d}_0), \\
a_1^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) - C_1(\delta_1)\cos\phi_1 p_x(\mathbf{r}-\mathbf{d}_0) + C_1(\delta_1)\sin\phi_1 p_y(\mathbf{r}-\mathbf{d}_0) - C_2(\delta_1)p_z(\mathbf{r}-\mathbf{d}_0), \\
a_2^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) + \frac{1}{2}C_1(\delta_2)(\cos\phi_2 + \sqrt{3}\sin\phi_2)p_x(\mathbf{r}-\mathbf{d}_0) \\
&\quad + \frac{1}{2}C_1(\delta_2)(\sqrt{3}\cos\phi_2 - \sin\phi_2)p_y(\mathbf{r}-\mathbf{d}_0) - C_2(\delta_2)p_z(\mathbf{r}-\mathbf{d}_0), \\
a_3^2(\mathbf{r}-\mathbf{d}_0) &= \frac{1}{2}s(\mathbf{r}-\mathbf{d}_0) + \frac{1}{2}C_1(\delta_3)(\cos\phi_3 - \sqrt{3}\sin\phi_3)p_x(\mathbf{r}-\mathbf{d}_0) \\
&\quad - \frac{1}{2}C_1(\delta_3)(\sqrt{3}\cos\phi_3 + \sin\phi_3)p_y(\mathbf{r}-\mathbf{d}_0) - C_2(\delta_3)p_z(\mathbf{r}-\mathbf{d}_0).
\end{aligned} \tag{A3}$$

We note that we have kept only terms up to second order in  $\gamma_j$  and  $\delta_j$  in Eqs. (A1) and (A3), respectively. In order to obtain the orthonormal set of hybrids at different sites, we obtain  $S_{jj'}^1$  and  $S_{jj'}^2$  [Eqs. (3.5) and (3.7)] as

$$\begin{aligned}
S_{jj'}^1 &= -\frac{1}{\sqrt{2}}\gamma_{j'} + \frac{1}{8}\gamma_j^2, j=0, j'=1,2,3, \\
&= \left[ \frac{1}{3} - \frac{1}{3\sqrt{2}}(\gamma_j + \gamma_{j'}) - \frac{1}{24}(\gamma_j^2 + \gamma_{j'}^2) + \frac{2}{3}\gamma_j\gamma_{j'} \right] \\
&\quad - \left[ \frac{1}{3} - \frac{1}{6\sqrt{2}}(\gamma_j + \gamma_{j'}) - \frac{1}{6}(\gamma_j^2 + \gamma_{j'}^2) + \frac{1}{24}\gamma_j\gamma_{j'} \right] [\cos(\psi_j - \psi_{j'}) - \sqrt{3}\sin(\psi_j - \psi_{j'})] \\
&\quad \text{for } j \neq j' \text{ and take cyclic permutations of the indices } 1,2,3. \tag{A4}
\end{aligned}$$

Similarly,

$$\begin{aligned}
S_{jj'}^2 &= -\frac{1}{\sqrt{2}}\delta_{j'} + \frac{1}{8}\delta_j^2, \text{ for } j=0 \text{ and } j'=1,2,3; \\
&= \left[ \frac{1}{3} - \frac{1}{3\sqrt{2}}(\delta_j + \delta_{j'}) - \frac{1}{24}(\delta_j^2 + \delta_{j'}^2) + \frac{2}{3}\delta_j\delta_{j'} \right] \\
&\quad - \left[ \frac{1}{3} - \frac{1}{6\sqrt{2}}(\delta_j + \delta_{j'}) - \frac{1}{6}(\delta_j^2 + \delta_{j'}^2) + \frac{1}{24}\delta_j\delta_{j'} \right] [\cos(\phi_j - \phi_{j'}) - \sqrt{3}\sin(\phi_j - \phi_{j'})] \\
&\quad \text{for } j \neq j' \text{ and take cyclic permutations of the indices } 1,2,3. \tag{A5}
\end{aligned}$$

We have also evaluated the following relations by keeping terms up to second order in  $\gamma_j$ :

$$S_{oj}^1 S_{jo}^1 = \frac{1}{2}\gamma_j^2, \tag{A6}$$

where  $j=1,2,3$ .

$$S_{oi}^1 S_{ij}^1 = - \left[ \frac{1}{3\sqrt{2}}\gamma_i + \frac{1}{8}\gamma_i^2 + \frac{1}{6}\gamma_i\gamma_j \right] + \left[ \frac{1}{3\sqrt{2}}\gamma_i - \frac{1}{8}\gamma_i^2 - \frac{1}{12}\gamma_i\gamma_j \right] [\cos(\psi_i - \psi_j) - \sqrt{3}\sin(\psi_i - \psi_j)], \tag{A7}$$

$$\begin{aligned}
S_{ij}^1 S_{jk}^1 &= \frac{1}{9} + \frac{1}{9\sqrt{2}}(\gamma_i + 2\gamma_j + \gamma_k) + \frac{1}{72}(-\gamma_i^2 + 2\gamma_j^2 - \gamma_k^2 + 20\gamma_i\gamma_j + 20\gamma_j\gamma_k + 4\gamma_k\gamma_i) \\
&\quad + \left[ -\frac{1}{9} + \frac{1}{18\sqrt{2}}(\gamma_i - \gamma_j - 2\gamma_k) - \frac{1}{72}(-4\gamma_i^2 - 7\gamma_j^2 - \gamma_k^2 - \gamma_i\gamma_j + 14\gamma_j\gamma_k - 2\gamma_k\gamma_i) \right] \\
&\quad \times [\cos(\psi_i - \psi_j) - \sqrt{3}\sin(\psi_i - \psi_j)] \\
&\quad + \left[ -\frac{1}{9} + \frac{1}{18\sqrt{2}}(-2\gamma_i - \gamma_j + \gamma_k) - \frac{1}{72}(-\gamma_i^2 - 7\gamma_j^2 - 4\gamma_k^2 + 14\gamma_i\gamma_j - \gamma_j\gamma_k - 2\gamma_k\gamma_i) \right] \\
&\quad \times [\cos(\psi_j - \psi_k) - \sqrt{3}\sin(\psi_j - \psi_k)] \\
&\quad + \left[ \frac{1}{9} - \frac{1}{18\sqrt{2}}(\gamma_i + 2\gamma_j + \gamma_k) + \frac{1}{72}(-4\gamma_i^2 - 7\gamma_j^2 - 4\gamma_k^2 + 2\gamma_i\gamma_j + 2\gamma_j\gamma_k + \gamma_i\gamma_k) \right] \\
&\quad \times [\cos(\psi_i - \psi_j) - \sqrt{3}\sin(\psi_i - \psi_j)][\cos(\psi_j - \psi_k) - \sqrt{3}\sin(\psi_j - \psi_k)], \tag{A8}
\end{aligned}$$



for  $i \neq j \neq k$ , and taking values 1,2,3 in cyclic order.

The expressions for  $S_{oj}^2 S_{jo}^2$ ,  $S_{oi}^2 S_{ij}^2$ , and  $S_{ij}^2 S_{jk}^2$  can also be obtained by keeping terms up to second order in  $\delta_j$ . These expressions can be written similarly to Eqs. (A6), (A7), and (A8), respectively, by replacing  $\gamma_j$  by  $\delta_j$  and  $\psi_j$  by  $\phi_j$ . Using the above relations in Eqs. (3.4) and (3.6), and after considerable algebra one can obtain the expressions for the orthonormal set of orbitals  $O_j^1(\mathbf{r})$  and  $O_j^2(\mathbf{r}-\mathbf{d}_0)$  for sites I and II, respectively, for the disordered network by keeping terms up to second order in  $\gamma_j$  and  $\delta_j$ .

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