

Diamagnetism of dielectrics

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An expression is derived for the magnetic susceptibility of an intrinsic semiconductor in a tight-binding basis that is valid for both crystalline and amorphous materials. In addition to diamagnetic intraband terms proportional to the square of the tight-binding radii there are interband terms involving intersite matrix elements. These additional terms are evaluated for a simple two-band model and found to be paramagnetic. It is shown that in an amorphous material these paramagnetic intersite contributions will be reduced, thereby producing a diamagnetic enhancement.

I. INTRODUCTION

The static magnetic susceptibility of dielectrics has never attracted a great deal of interest. The primary reason for this is that this quantity is very complex and the information contained in it is not readily apparent. Furthermore, the experimental susceptibility is often dominated by free carriers or impurities. However, recent work on amorphous systems reveals interesting diamagnetic behavior. For example, CdGeAs₂¹ and Ge² have significantly larger diamagnetic susceptibilities in their amorphous forms relative to their crystalline forms. The magnetic susceptibilities of S,³ Se,^{3,4} As₂S₃,⁵ and As₂Se₃,⁵ however, show little change upon going from crystal to glass. It would therefore appear that the magnetic susceptibility contains information relevant to our understanding of the electronic structure of solids and for this reason we have undertaken to examine this question. In molecular systems the magnetic susceptibility has already proven to be a useful parameter in studying chemical bonding.⁶ In combination with the molecular *g* factor, for example, it enables one to obtain a direct measurement of second moment of the electronic charge distribution in the molecule with respect to its center of mass.

In order to investigate the susceptibility of a dielectric solid, let us consider the case of an intrinsic two-band semiconductor. To our knowledge this problem has never been attacked di-

rectly, although much of the work on Bloch electrons in a magnetic field⁷ alludes to this case as a limit. These results often tend to be unnecessarily complex because they depend upon the representation used for this more difficult problem. The calculation itself of the magnetic response of a Bloch electron is also more complex because one is generally interested in phenomena involving closed electron orbits such as the de Haas-van Alphen effect which cannot be studied perturbatively. The static susceptibility, however, may be obtained from linear-response theory. Bardeen, for example, has demonstrated⁸ how one obtains the Landau diamagnetism of a free-electron gas using this approach. In this paper we derive an expression for the magnetic susceptibility of an intrinsic semiconductor that is applicable to both crystalline and amorphous materials.

II. LINEAR-RESPONSE THEORY

The susceptibility is defined as the ratio of the total induced magnetization to the applied field. To find this magnetization we must first compute the induced current density. The induced current density is related to the vector potential by

$$j_i(\vec{x}l) = -\frac{c}{4\pi} \int d^3x' dl' \mathcal{K}_{ij}(\vec{x}l; \vec{x}'l') \times A_j(\vec{x}'l'), \quad (1)$$

where the kernel is given by⁹

$$\mathcal{K}_{ij}(\vec{x}l; \vec{x}'l') = \frac{4\pi e^2}{mc^2} \langle \hat{n}_K(\vec{x}l) \rangle \delta(\vec{x} - \vec{x}') \delta(l - l') \delta_{ij} - i \frac{4\pi}{\hbar c^2} \langle [j_{Ki}^o(\vec{x}l), j_{Kj}^o(\vec{x}'l')] \rangle \Theta(l - l'). \quad (2)$$

This involves the commutator of the current operators for $\vec{A} = 0$ which have the form

$$j_{Ki}^o(\vec{x}l) = -\frac{e\hbar}{2mi} \left\{ \hat{\psi}_{K\alpha}^\dagger(\vec{x}l) \frac{\partial}{\partial x_i} \hat{\psi}_{K\alpha}(\vec{x}l) - \left[\frac{\partial}{\partial x_i} \hat{\psi}_{K\alpha}^\dagger(\vec{x}l) \right] \hat{\psi}_{K\alpha}(\vec{x}l) \right\}. \quad (3)$$

Here $\hat{\psi}_{K\alpha}(\vec{x}l)$ is a field operator in the Heisenberg representation,

$$\hat{\psi}_{K\alpha}(\vec{x}l) = e^{iKl/\hbar} \hat{\psi}_\alpha(\vec{x}) e^{-iKl/\hbar}, \quad (4)$$

where $K = \mathcal{H}_0 - \mu N$, \mathcal{H}_0 being the Hamiltonian and μ the chemical potential. The field operator is now expanded in the eigenstates of the system,

$$\hat{\psi}_\alpha(\vec{x}) = \sum_{\nu=0,1} \sum_k \psi_{\nu k \alpha}(\vec{x}) C_{\nu k \alpha}, \quad (5)$$

where ν is a band index, o referring to the valence band, and 1 to the conduction band, k refers to the states within the bands and α is a spin index. Using Eqs. (4) and (5) in (3) we obtain

$$j_{Ki}^o(\vec{x}t) = -\frac{e\hbar}{2mi} \sum_{\nu, \nu'} \sum_{k, k', \alpha} \left\{ \psi_{\nu k \alpha}^*(\vec{x}) \frac{\partial}{\partial x_i} \psi_{\nu' k' \alpha}(\vec{x}) - \left[\frac{\partial}{\partial x_i} \psi_{\nu k \alpha}^*(\vec{x}) \right] \psi_{\nu' k' \alpha}(\vec{x}) \right\} e^{iKt/\hbar} C_{\nu k \alpha}^\dagger C_{\nu' k' \alpha} e^{-iKt/\hbar}, \quad (6)$$

where

$$K = \sum_\nu \sum_{k, \alpha} (\epsilon_{\nu k} - \mu) C_{\nu k \alpha}^\dagger C_{\nu k \alpha}. \quad (7)$$

By integrating the equation of motion for the Heisenberg operator it is easy to show that

$$e^{iKt/\hbar} C_{\nu k \alpha}^\dagger e^{-iKt/\hbar} = e^{i(\epsilon_{\nu k} - \mu)t/\hbar} C_{\nu k \alpha}^\dagger. \quad (8)$$

This enables us to reduce the operator factor in Eq. (6) to

$$e^{iKt/\hbar} C_{\nu k \alpha}^\dagger C_{\nu' k' \alpha} e^{-iKt/\hbar} = e^{i(\epsilon_{\nu k} - \epsilon_{\nu' k'})t/\hbar} C_{\nu k \alpha}^\dagger C_{\nu' k' \alpha}. \quad (9)$$

The current-current commutator then involves

$$[C_{\nu k \alpha}^\dagger C_{\nu' k' \alpha}, C_{\nu'' k'' \beta}^\dagger C_{\nu''' k''' \beta}] = C_{\nu k \alpha}^\dagger C_{\nu'' k'' \beta} \delta_{k'' k'} \delta_{\nu'' \nu'} \delta_{\alpha \beta} - C_{\nu' k' \beta}^\dagger C_{\nu'' k'' \beta} \delta_{k'' k'} \delta_{\nu'' \nu'} \delta_{\alpha \beta}. \quad (10)$$

If we restrict ourselves to zero temperature then the averages indicated in Eq. (2) just become the expectation values in the ground state, which is the filled valence band. This is readily generalized to the case of multiple bands. It should be pointed out here that the assumption of a filled band excludes molecules such as benzene which are noted for their large diamagnetism. In benzene the "Fermi level" sits in the middle of the π -electron band and one does not have all the necessary "band" states available from which to construct localized states. The expectation value of Eq. (10) then becomes

$$\delta_{k'' k'} \delta_{k'' k'} \delta_{\alpha \beta} (\delta_{\nu'' \nu'} \delta_{\nu'' \nu' = \nu = 0} - \delta_{\nu'' \nu'} \delta_{\nu'' \nu' = \nu = 0}). \quad (11)$$

We see that if this expectation value is to be nonzero $\nu'' = \nu' = 1$ in the first term while $\nu''' = \nu = 1$ in the second.

Combining these results the expectation value of the current-current commutator is

$$\begin{aligned} \langle [j_{Ki}^o(\vec{x}t), j_{Kj}^o(\vec{x}'t')] \rangle = & -\frac{e^2 \hbar^2}{4m^2} \sum_{k, k', \alpha} \left\{ \psi_{0k\alpha}^*(\vec{x}) \frac{\partial}{\partial x_i} \psi_{1k'\alpha}(\vec{x}) - \left[\frac{\partial}{\partial x_i} \psi_{0k\alpha}^*(\vec{x}) \right] \psi_{1k'\alpha}(\vec{x}) \right\} \\ & \times \left\{ \psi_{1k'\alpha}^*(\vec{x}') \frac{\partial}{\partial x'_j} \psi_{0k\alpha}(\vec{x}') - \left[\frac{\partial}{\partial x'_j} \psi_{1k'\alpha}^*(\vec{x}') \right] \psi_{0k\alpha}(\vec{x}') \right\} e^{i(\epsilon_{0k} - \epsilon_{1k'}) (t-t')/\hbar} - (\text{c. c.}). \quad (12) \end{aligned}$$

In a similar manner the expectation value of the number operator appearing in the first term in the kernel, Eq. (2), becomes

$$\langle \hat{n}_K(\vec{x}t) \rangle = \sum_{k, \alpha} \psi_{0k\alpha}^*(\vec{x}) \psi_{0k\alpha}(\vec{x}). \quad (13)$$

The current, Eq. (1) becomes

$$\begin{aligned} j_i(\vec{x}t) = & -\frac{2e^2}{mc} \sum_k \psi_{0k}^*(\vec{x}) \psi_{0k}(\vec{x}) A_i(\vec{x}) - \frac{e^2 \hbar^2}{m^2 c} \text{Re} \sum_{k, k'} \left\{ \frac{\psi_{0k}^*(\vec{x}) (\partial/\partial x_i) \psi_{1k'}(\vec{x}) - [(\partial/\partial x_i) \psi_{0k}^*(\vec{x})] \psi_{1k'}(\vec{x})}{\epsilon_{1k'} - \epsilon_{0k}} \right\} \\ & \times \int d^3 x' \left\{ \psi_{1k'}^*(\vec{x}') \frac{\partial}{\partial x'_j} \psi_{0k}(\vec{x}') - \left[\frac{\partial}{\partial x'_j} \psi_{1k'}^*(\vec{x}') \right] \psi_{0k}(\vec{x}') \right\} A_j(\vec{x}'). \quad (14) \end{aligned}$$

As long as the induced current is small in comparison with the external current we may substitute for $\vec{A}(\vec{x})$ the value it would have in the absence of the medium. In the absence of the medium we just have a uniform magnetic field \vec{H} . Since the form for the kernel given by Eq. (2) assumed a transverse gauge, let us write

$$\vec{A}(\vec{x}) = \frac{1}{2} \vec{H} \times \vec{x}. \quad (15)$$

The integral d^3x' in Eq. (14) then gives

$$(i/\hbar) \langle 1k' | \vec{H} \cdot \vec{\Gamma} | 0k \rangle, \quad (16)$$

where $\vec{\Gamma}$ is the orbital angular-moment operator $\vec{x} \times \vec{p}$. The total magnetic moment is given by

$$\vec{M}V = \frac{1}{2c} \int d^3x [\vec{x} \times \vec{j}(\vec{x})] \quad (17)$$

from which we obtain the susceptibility

$$\chi_{ij} = -\frac{2e^2}{4mc^2V} \sum_k \langle 0k | [\vec{x} \times (\hat{H}_j \times \vec{x})]_i | 0k \rangle + \frac{2e^2}{2m^2c^2V} \sum_{k,k'} \frac{\langle 0k | l_i | 1k' \rangle \langle 1k' | l_j | 0k \rangle}{\epsilon_{1k'} - \epsilon_{0k}}, \quad (18)$$

where we have displayed the spin degeneracy explicitly by the factors of 2 in the numerators of the two coefficients.

Equation (18) is precisely what one would have expected in analogy with a molecule. Expressed in this form the susceptibility has a deceptively simple form. This deception arises from the fact that the states $\psi_{\nu k \alpha}(\vec{x})$ are the exact eigenstates of the finite system. We cannot, for example, use Bloch functions for these are the eigenfunctions of an infinitely periodic system, and therefore $\vec{x} \psi_{\nu k \alpha}(\vec{x})$ is not normalizable.¹⁰ If one wishes to use Bloch functions then the operators must be transformed in such a way as to make their matrix elements well defined. There have been many efforts in this direction and the results have generally been extremely complex. Blount,⁷ for example, finds that in the limit of an intrinsic semiconductor the Bloch representation gives in addition to the diamagnetic atomic and paramagnetic Van Vleck terms a third "pseudoatomic" term whose sign depends upon an effective mass. Fukuyama¹¹ has recently shown that the susceptibility of Bloch electrons can be expressed in a relatively simple form which allows reasonably simple calculations to be performed.¹²

The difference between the true states $\psi_{\nu k \alpha}$ and Bloch functions can be attributed to surface effects. Although the use of periodic, or Born-von Kármán, boundary conditions only affects certain quantities such as densities of states by the surface-to-volume ratio,¹³ this is not the case for matrix elements of "polarization" operators such

as occur in Eq. (18).

III. TIGHT-BINDING REPRESENTATION

In the case of an intrinsic semiconductor we might expect to avoid these difficulties by working in a tight-binding basis. Let us therefore introduce orbitals $|\nu, i, \alpha\rangle$, where ν is the band index, i is a site index, and α represents additional degrees of freedom. These might be Wannier functions or they might be the bonding and antibonding hybrid orbitals introduced by Heine¹⁴ in his treatment of Weaire's model¹⁵ of tetrahedrally bonded amorphous semiconductors. In this case there are four orbitals associated with the same index i , i. e., $\alpha = 1, 2, 3, \text{ or } 4$. The eigenfunctions of the valence and conduction band may then be expanded as

$$|\nu k\rangle = \sum_{i,\alpha} \langle \nu i \alpha | \nu k \rangle |\nu i \alpha\rangle. \quad (19)$$

For simplicity we shall assume that the index k includes the spin index. Having identified the coefficient in this expansion as the integral $\langle \nu i \alpha | \nu k \rangle$ assumes that the tight-binding basis is orthonormal. Also, notice that since these transformations are confined to each band separately, there will be closure relations for each of the function spaces characterized by the band indices, i. e.,

$$\sum_{k'} |1k'\rangle \langle 1k'| = 1, \quad (20)$$

when this operator acts on conduction band or antibonding states while it gives zero when it acts on valence band or bonding states.

The first step in transforming the susceptibility into this tight-binding basis is to remove the explicit dependence upon the exact eigenvalues in Eq. (18). This is accomplished by introducing an integral representation. Thus

$$\sum_k \sum_{k'} \frac{\langle 0k | l_\mu | 1k' \rangle \langle 1k' | l_\nu | 0k \rangle}{\epsilon_{1k'} - \epsilon_{0k}} = \sum_k \langle 0k | L_{\mu\nu} | 0k \rangle, \quad (21)$$

where $L_{\mu\nu}$ has the symmetrized form,

$$L_{\mu\nu} = \frac{1}{2} \sum_{k'} \int_0^\infty d\lambda (e^{\lambda x_0} l_\mu e^{-\lambda x_0} |1k'\rangle \langle 1k'| l_\nu + l_\mu |1k'\rangle \langle 1k'| e^{-\lambda x_0} l_\nu e^{\lambda x_0}). \quad (22)$$

Since the states in different bands are orthogonal the expansion coefficients in Eq. (19) satisfy

$$\sum_k \langle \nu i \alpha | \nu k \rangle \langle \nu k | \nu j \beta \rangle = \delta_{i,j} \delta_{\alpha,\beta}. \quad (23)$$

Therefore the sum over the intermediate states in Eq. (21) may be re-expressed in terms of the conduction band or antibonding orbitals,

$$\sum_{k'} |1k'\rangle\langle 1k'| = \sum_{j,\beta} |1j\beta\rangle\langle 1j\beta|. \quad (24)$$

Similarly, the sum over the initial states may be replaced by a sum over the valence band or bonding orbitals.

The advantage of this formulation is that we may now use a tight-binding form for the Hamiltonian \mathcal{H}_0 . However, the use of localized states presents an additional complication. This has to do with the fact that the values of coordinates or angular momenta are dependent upon the choice of origin. It can be shown that the susceptibility given by Eq. (18) is invariant of the origin. The proof is similar to that for a molecule¹⁶ involving the relation

$$\langle 1k' | p_\mu | 0k \rangle = i \frac{m}{\hbar} (\epsilon_{1k'} - \epsilon_{0k}) \langle 1k' | x_\mu | 0k \rangle. \quad (25)$$

It also involves the use of the closure relation given by Eq. (20). Our object now is to use similar arguments to express the susceptibility in the

tight-binding basis but such that the origin for each term coincides with the origin of the tight-binding wave function. There are a number of ways one might accomplish this. One would be to multiply the tight-binding basis functions by phase factors of the form $\exp[(ieH/\hbar c)X_i y]$. This corresponds to a gauge transformation which transforms the origin of the vector potential to the i th cell.¹⁷ We shall, however, employ a variation of Van Vleck's technique for proving the invariance of origin.¹⁶ Consider the diamagnetic term $\langle 0i\alpha | x^2 | 0i\alpha \rangle$. This may be written

$$\begin{aligned} \langle 0i\alpha | x^2 | 0i\alpha \rangle &= \langle 0i\alpha | (x - X_i)^2 | 0i\alpha \rangle \\ &+ 2X_i \langle 0i\alpha | x - X_i | 0i\alpha \rangle + X_i^2, \quad (26) \end{aligned}$$

where X_i is the x coordinate of site i . The first term has the desired form. The remaining two terms represent "divergences" whose compensation must come, as in the proof of the origin invariance, from the paramagnetic part. Consider

$$\begin{aligned} \langle 0i\alpha | L_{zz} | 0i\alpha \rangle &= \frac{1}{2} \int d\lambda \sum_k \sum_{k'} \sum_{k''} \langle 0i\alpha | 0k \rangle \langle 0k | e^{\lambda\mathcal{H}_0} [(x - X_i)p_y - (y - Y_i)p_x + X_i p_y - Y_i p_x] e^{-\lambda\mathcal{H}_0} | 1k' \rangle \\ &\times \langle 1k' | [(x - X_i)p_y - (y - Y_i)p_x + X_i p_y - Y_i p_x] | 0k'' \rangle \langle 0k'' | 0i\alpha \rangle + \dots \quad (27) \end{aligned}$$

Let us focus our attention on the term proportional to X_i^2 .

$$\begin{aligned} \frac{1}{2} \int d\lambda \sum_k \sum_{k'} \sum_{k''} \langle 0i\alpha | 0k \rangle \langle 0k'' | 0i\alpha \rangle [\langle 0k | e^{\lambda\mathcal{H}_0} p_y e^{-\lambda\mathcal{H}_0} | 1k' \rangle \langle 1k' | p_y | 0k'' \rangle \\ + \langle 0k | p_y | 1k' \rangle \langle 1k' | e^{-\lambda\mathcal{H}_0} p_y e^{\lambda\mathcal{H}_0} | 0k'' \rangle] X_i^2. \quad (28) \end{aligned}$$

Carrying out the integral and using Eq. (25) gives

$$-i \frac{m}{2\hbar} \sum_k \sum_{k'} \sum_{k''} \langle 0i\alpha | 0k \rangle \langle 0k'' | 0i\alpha \rangle [\langle 0k | y | 1k' \rangle \langle 1k' | p_y | 0k'' \rangle - \langle 0k | p_y | 1k' \rangle \langle 1k' | y | 0k'' \rangle] X_i^2. \quad (29)$$

Let us now add and subtract the following terms to those within the square brackets in Eq. (29),

$$\langle 0k | y | 0k' \rangle \langle 0k' | p_y | 0k'' \rangle - \langle 0k | p_y | 0k' \rangle \langle 0k' | y | 0k'' \rangle.$$

The added terms, when combined with those in Eq. (29), enable us to remove the sum over intermediate states by closure. These terms then collapse to $\langle 0k | [y, p_y] | 0k'' \rangle = i\hbar \delta_{k,k''}$. The resulting term just cancels the X_i^2 term in Eq. (26). Assuming the localized basis is real, the remaining terms from Eq. (29) may be written in the form

$$i \frac{m}{\hbar} \sum_i \left[\sum_j \langle 0i | y | 0j \rangle \langle 0j | p_y | 0i \rangle (X_i - X_j) \right] X_i. \quad (30)$$

The quantity within the square brackets clearly vanishes for $j=i$ and falls off exponentially as j moves away from i . If the material is reasonably homogeneous this quantity will be independent of i . Consequently, if we choose the origin for the site coordinates such that $\sum_i X_i = 0$, this term vanishes. This condition restricts us to large systems. Similar arguments may be applied to the other terms. For example, those terms proportional to $X_i Y_i$ involve the commutator $[y, p_x]$ and therefore vanish.

The total susceptibility therefore becomes

$$\chi_{xx} = -\frac{e^2}{4mc^2V} \sum_{i,\alpha} \langle 0i\alpha | (x-X_i)^2 + (y-Y_i)^2 | 0i\alpha \rangle + \frac{e^2}{4m^2c^2V} \sum_{i,\alpha} \sum_{j,\beta} \int_0^\infty d\lambda [\langle 0i\alpha | l_{zi}(\lambda) | 1j\beta \rangle \langle 1j\beta | l_{zi} | 0i\alpha \rangle + \langle 0i\alpha | l_{zi} | 1j\beta \rangle \langle 1j\beta | l_{zi}(-\lambda) | 0i\alpha \rangle]. \quad (31)$$

Notice that by removing the intermediate states in the second term by closure it may be written in the more compact form,

$$\frac{e^2}{2m^2c^2V} \sum_{i,\alpha} \int_0^\infty d\lambda \langle 0i\alpha | l_{zi} \left(-\frac{\lambda}{2}\right)^\dagger l_{zi} \left(-\frac{\lambda}{2}\right) | 0i\alpha \rangle,$$

where the angular-momentum operator l_z is now assumed to have the non-Hermitian matrix representation which only couples valence-band states to conduction-band states. Written this way shows that this term is manifestly positive and therefore paramagnetic.

Another point to keep in mind is that one cannot write the diamagnetic first term in a tight-binding basis as in Eq. (31) while writing the paramagnetic term in the "band" basis as in Eq. (18), although one often finds this done in the literature.

IV. DISCUSSION

We recognize the first group of terms in Eq. (31) as the diamagnetic contributions from the individual tight-binding states. The second group of terms represents the complicated effects of interband and, because of the presence of the Hamiltonian in the exponentials, of intersite contributions to the susceptibility. We can obtain some insight by considering a simple two-band model. Since the features we wish to explore are the roles of the energy gap and the overlap of the wave functions, let us consider the Hamiltonian,

$$\mathcal{H}_0 = t \sum_{i,\alpha} \sum_{\vec{\delta}} |0, i + \vec{\delta}, \alpha\rangle \langle 0, i, \alpha| + \Delta \sum_{i,\alpha} |1, i, \alpha\rangle \langle 1, i, \alpha|. \quad (32)$$

Here t is a transfer integral between a site i and one of its z nearest neighbors at $i + \vec{\delta}$. This model corresponds to a valence band of width $2zt$ and a narrow conduction band. Using the expansion,

$$e^A B e^{-A} = B + [A, B] + (1/2!)[A, [A, B]] + \dots, \quad (33)$$

we have evaluated the integrand in Eq. (31) to order λ^4 . We have made the simplifying assumption that the only nonzero matrix elements of the orbital angular momentum are between two states on the same site, i. e., $\langle 0, i, \alpha | l | 1, j, \beta \rangle = l_{01} \delta_{ij} \delta_{\alpha\beta}$. In the expansion one encounters terms involving sums of the form

$$\sum_{\vec{\delta}} \sum_{\vec{\delta}'} \langle 0, i | 0, i + \vec{\delta} + \vec{\delta}' \rangle.$$

Here $i + \vec{\delta}$ refers to one of the z nearest neighbors to i while $i + \vec{\delta} + \vec{\delta}'$ refers to one of the z nearest neighbors to $i + \vec{\delta}$. If we assume that our localized wave functions are orthogonal, as is the case with Wannier functions, then the only way that this sum can be nonzero is for $\vec{\delta}' = -\vec{\delta}$. Therefore, this particular sum has the value z . If we consider a simple cubic structure then terms of the form $\langle 0, i | 0, i + \vec{\delta} + \vec{\delta}' + \vec{\delta}'' \rangle$ will be zero. However, in fourth order we have an interesting situation. Terms involving combinations of four near-neighbor vectors can be nonzero in two distinctly different ways. One is for $\vec{\delta}'' = -\vec{\delta}'$ and $\vec{\delta}''' = -\vec{\delta}$. That is, one moves away from i and then returns over the same path. The quadruple sum gives z^2 in this case. However, it is also possible to return via a path that does not involve any retracing. The number of ways this can be done in a simple cubic system is $z(z-1)$. Thus, to fourth order the integrand in Eq. (31) becomes

$$2|l_{10}|^2 \left(1 - \lambda\Delta + \frac{\lambda^2\Delta^2}{2} - \frac{\lambda^3\Delta^3}{3!} + \frac{\lambda^4\Delta^4}{4!} + \dots + \frac{\lambda^2 z l^2}{2} - \frac{3\lambda^3 \Delta z l^2}{3!} + \frac{6\lambda^4 \Delta^2 z l^2}{4!} + \frac{\lambda^4 z^2 l^2}{4!} + \frac{z(z-1)\lambda^4 l^4}{4!} + \dots \right). \quad (34)$$

We recognize these terms as the leading terms in the expansion of

$$2|l_{10}|^2 \left(1 + \frac{1}{2} z l^2 \lambda^2 + \frac{z^2 l^4 \lambda^4}{4!} + \frac{z(z-1) l^4 \lambda^4}{4!} + \dots \right) e^{-\lambda\Delta}. \quad (35)$$

Carrying out the integral over λ , the second term in Eq. (31) becomes

$$\frac{N}{V} \frac{e^2 |l_{10}|^2}{m^2 c^2 \Delta} \left(\frac{\Delta^2}{\Delta^2 - z l^2} + \frac{z(z-1) l^4}{\Delta^4} + \dots \right). \quad (36)$$

The model, of course, is only valid as long as the valence band does not overlap the conduction band, i. e., $z l < \Delta$. The total susceptibility is the sum of diamagnetic $\langle r^2 \rangle$ terms plus the paramagnetic terms given by Eq. (36).

Notice that in the limit of vanishing overlap, i. e., $l \rightarrow 0$, Eq. (36) reduces to the Van Vleck paramagnetism associated with N independent sites. Therefore, the total susceptibility reduces to the sum of the susceptibilities associated with the constituents. Such an additivity has been recognized for a long time. However, we now have

TABLE I. Decomposition of the magnetic susceptibilities of group-IV and group-VI elements as well as As_2S_3 and CdGeAs_2 . All values are in units of 10^{-6} emu/mole.

	χ_{exp}	$\chi_{\text{core}}^{\text{a}}$	$r_{\text{covalent}}^{\text{b}}$ (Å)	$\chi_{(r^2)}$	$\chi_{\text{exp}} - (\chi_{\text{core}} + \chi_{(r^2)})$
C (diamond)	-5.8 ^c	-0.1	0.77	-6.64	+0.94
Si	-3.1 ^d	-1	1.17	-15.33	+13.2
Ge	-8.1 ^e	-7	1.22	-16.7	+15.6
S	-15.52	-1	1.04	-18.17	+3.65
Se (trig)	-21.48	-5	1.14	-21.83	+5.35
As_2S_3	-88.57	-21	As: 1.18	-77.90	+10.33
CdGeAs_2	-82.03	-47	Cd: 1.48	-52.33	+17.23

^aP. W. Selwood, Ref. 17, p. 78.

^bL. Pauling, *The Chemical Bond* (Cornell U. P., Ithaca, N. Y., 1967), p. 148.

^cM. Owen, Ann. Phys. (Leipz.) **37**, 657 (1912).

^dG. Busch, in *Halbeiter und Phosphore Kolloquium Garmisch-Partenkirchen*, 1956 (Vieweg, Braunschweig, 1956).

^eD. K. Stevens, J. W. Cleland, J. H. Crawford, and H. C. Schweinler, Phys. Rev. **100**, 1084 (1955); R. Bowers, *ibid.* **108**, 683 (1957).

an explicit representation for the bonding corrections or Pascal's constants as they are called.¹⁸

This model, characterized by the Hamiltonian of Eq. (32) with the additional "site approximations", is perhaps too simple to enable us to make any quantitative comparison with experimental data. Nevertheless, it is possible to qualitatively understand the difference between the group-IV elements and the group-VI elements.

Unfortunately, no one seems to have made a systematic study of the susceptibilities of the group-IV elements. The values found in the Landolt-Bornstein tables are listed in Table I. Note that the value for diamond is that given by Owen in 1912. Although a good natural diamond is probably the best sample one could hope for, this particular diamond did contain 15 ppm of iron. Since nonmagnetic impurities can also affect the susceptibility, one worries if such a value reflects the intrinsic susceptibility even though it is temperature independent. Let us therefore restrict our discussion to germanium and silicon for which efforts were made to remove the impurity contribution.

From experimental data on ionic compounds involving these elements it is possible, using the additivity which we have now established, to obtain the susceptibility associated with Si^{4+} and Ge^{4+} cores. These values as well as the total experimental susceptibilities are given in Table I. The fact that they are very close indicates that the diamagnetic and paramagnetic contributions from the four valence electrons must nearly cancel each other. To obtain an estimate of the diamagnetic contributions, we have used the square of the covalent radii in the first term in Eq. (31). These

results are given in the column labeled $\chi_{(r^2)}$, in Table I. The paramagnetic contribution is then given in the last column. The point to note here is the fact that this paramagnetic contribution from the valence electrons is large in comparison with the total measured susceptibility.

We have made a similar decomposition of the susceptibilities of sulfur and trigonal selenium. These are also given in Table I. Here we notice that the paramagnetic contributions are small in comparison with the measured values. We attribute these differences to the differences in the coordination of these two classes of materials. In the fourfold coordinated materials there are a greater variety of "paths" contributing to the interband terms. In trigonal selenium on the other hand the twofold coordination gives rise to a chain structure in which there are no "nonretracing" paths.

Let us now consider the implications of this model for an amorphous solid. One of the features of an amorphous solid is the possible appearance of localized states. If the energy of such a localized state is very close to the point at which the state becomes delocalized one might expect such a state to be characterized by a large orbit and thereby give a large diamagnetism. In fact, White and Anderson¹⁹ suggested this as a tentative explanation of the diamagnetic enhancement in amorphous materials. This, however, neglects any renormalization of the charge distribution associated with the delocalized states themselves. Kohn and Onffroy²⁰ have recently investigated this question in the context of a one-dimensional periodic lattice with a point defect. They find that even when the defect is strong enough to pull off a bound

state there is very little change in the Wannier functions associated with this system. This suggests to us that the diamagnetic term in Eq. (31) will not be greatly affected by disorder. Those terms involving intersite matrix elements however will be affected. To see how this occurs we note that in a disordered system we expect the transfer matrix elements to be different for different pairs of sites. Thus the fourth-order contribution, for example, would have the more general form

$$\sum_{\delta} \sum_{\delta'} \sum_{\delta''} \sum_{\delta'''} t_{\delta}^* t_{\delta'}^* t_{\delta''}^* t_{\delta'''}^* \times \langle 0, i | 0, i + \delta + \delta' + \delta'' + \delta''' \rangle .$$

Voids, dangling bonds, etc. will make some of these transfer matrix elements zero. One manifestation of this may be to restrict percolation paths to the extent that localized states are formed. It will also introduce an effective coordination number in Eq. (36) which will be less than that of the crystal, thereby reducing both terms in Eq. (36).

Various models have been proposed for amorphous semiconductors, particularly the fourfold coordinated semiconductors, which satisfy the local bonding requirements, i. e., do not introduce dangling bonds. Since the paramagnetic term in Eq. (31) becomes an expansion in the number of returning paths this becomes the quantity of interest in these models. The number of returning paths up to 18 steps has been tabulated by Thorpe *et al.*²¹ for the diamond lattice as well as the

Bethe lattice. The latter is an infinitely branching tree-like structure with no closed loops or rings. Since there are two sixfold rings per atom in the diamond lattice the number of returning paths associated with this structure exceeds those associated with the Bethe lattice for six steps and the difference grows rapidly with the number of steps. This suggests that the diamagnetic susceptibility of the Bethe lattice is larger than that of the diamond lattice. However, since the Bethe lattice is only one of many models suggested for amorphous materials, we cannot prove that this situation will always prevail.

Finally, let us consider the compounds As_2S_3 and CdGeAs_2 . In its crystalline form As_2S_3 has a layer structure. In such a two-dimensional system we would again expect the number of "non-retraceable" paths to be restricted. Consequently, the role of disorder would have less effect on the magnetic susceptibility as is observed.⁵ However, recent experiments²² indicate that if As_2S_3 is evaporated onto a cold substrate one can achieve enough disorder to affect the susceptibility. CdGeAs_2 on the other hand is a three-dimensional network and its susceptibility should therefore be sensitive to disorder according to our arguments above. This again is consistent with what is observed.¹

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