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Chemical-Bond Approach to the Magnetic Susceptibility of Tetrahedral Semiconductors*

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A chemical-bond theory of the magnetic susceptibility of tetrahedral semiconductors is presented. Starting from a Hall-Weaire–type Hamiltonian, we derive an expression for the susceptibility, whose diamagnetic and paramagnetic contributions are written in terms of gauge-invariant physical quantities. Our analysis confirms a recently postulated model for the susceptibility. Theory and experiment are in good agreement.

In a recent Letter,[1] Hudgens, Kastner, and Fritzsche (HKF) proposed a model susceptibility function for tetrahedral semiconductors of the form

$$\chi = \frac{-N_0 e^2}{6mc^2}\Big[\sum_{\text{core}}\langle r^2\rangle + \sum_{\text{val}}\langle r^2\rangle\Big] + \frac{|M|^2}{E_g}. \qquad (1)$$

They ascribed the first two diamagnetic terms in this formula, denoted by χ_c and χ_v, to core and valence electrons, respectively; the last term (χ_p) is a Van Vleck paramagnetic susceptibility arising from virtual interband transitions. HKF also measured the susceptibility, and its temperature dependence, for diamond, Si, Ge, GaAs, and GaP. From these data, they could then *separately* determine χ_v and χ_p. They find nearly complete cancelation between χ_v and χ_p, a constant interband matrix element ($|M|^2$) despite wide variations in E_g, and values of $\langle r^2\rangle_{\text{val}}{}^{1/2}$ that scale with lattice spacing. These results support their model, but leave several questions unanswered. In particular, the meaning of the various terms ($\langle r^2\rangle_{\text{val}}$, $|M|^2$, etc.) appearing in Eq. (1) remains unclear. It is not obvious, moreover, that such quantities are gauge invariant. The purpose of this Letter is to sketch a derivation of the HKF model which resolves these difficulties. We will show that Eq. (1) follows from a simple tight-binding picture, and we will present explicit expressions for the various terms in this formula, which do not depend on the choice of origin of the vector potential. The values of $\langle r^2\rangle_{\text{val}}$ and $|M|^2$ calculated from these expressions agree with those measured by HKF. These quantities have a chemical significance, and can be used (as HKF suggest) to characterize bonding in tetrahedral semiconductors. In this sense, the theory developed here is similar to recently proposed dielectric theories of chemical bonding.[2,3] On the other hand, our work is complementary to that of previous authors,[4] who have derived exact, but complicated, expressions for the magnetic susceptibility of crystals.

The Hall-Weaire (HW) model[5,6] is the starting point for our description of the magnetic properties of tetrahedrally bonded solids. This model has often been used to discuss the electronic structure of diamond-type semiconductors[5-7]. It is also the basis for one of the dielectric theories of bonding mentioned above.[3] To incorporate the effects of a magnetic field into the HW model, we introduce a basis set of gauge-invariant, sp^3, atomic orbitals of the form[8]

$$\psi_j(\vec{r}-\vec{R}_i)=\left\{\exp\left[\frac{ie}{2\hbar c}\vec{r}\cdot(\vec{B}\times\vec{R}_i)\right]\right\}\varphi_j(\vec{r}-\vec{R}_i). \quad (2)$$

Here $\varphi_j(\vec{r}-\vec{R}_i)$ is one of four ($j=1$ to 4) sp^3 atomic orbitals centered at site $\vec{R}_i$. Matrix elements are evaluated in the $\psi_j(\vec{r}-\vec{R}_i)$ representation, as discussed by Pople.[9] The results are best summarized by a tabulation of the magnetic field-induced modifications of the HW matrix elements. With reasonable approximations,[9] we find

$$E_0 \to E_0+(e^2B^2/8mc^2)\langle r_\perp{}^2(j)\rangle_{\mathrm{local}}\equiv\tilde{E}_0(j), \quad (3a)$$

$$V_2 \to e^{i\chi(i,i')}[V_2+(e^2B^2/8mc^2)\langle r_\perp{}^2(j)\rangle_{\mathrm{overlap}}]\equiv\tilde{V}_2(i,i',j), \quad (3b)$$

$$V_1 \to \{V_1+(3ie\hbar/8mc)[\vec{B}\cdot(\hat{\epsilon}_j\times\hat{\epsilon}_{j'})]\}\equiv\tilde{V}_1(j,j'), \quad (3c)$$

where

$$B^2\langle r_\perp{}^2(j)\rangle_{\mathrm{local}}=\int\varphi_j{}^*(\vec{r})(\vec{r}\times\vec{B})^2\varphi_j(\vec{r})\,d^3r, \quad (4a)$$

$$B^2\langle r_\perp{}^2(j)\rangle_{\mathrm{overlap}}=\int\varphi_j{}^*(\vec{r}-\vec{R}_i)\{[\vec{r}-\tfrac{1}{2}(\vec{R}_i+\vec{R}_{i'})]\times\vec{B}\}^2\varphi_j(\vec{r}-\vec{R}_{i'})\,d^3r, \quad (4b)$$

$$\chi(i,i')=(e/2\hbar c)\vec{B}\cdot(\vec{R}_i\times\vec{R}_{i'}), \quad (4c)$$

E_0 is the average energy of the sp^3 orbitals, V_2 and V_1 are the matrix elements defined by Weaire and Thorpe,[5] and $\hat{\epsilon}_j$ is a unit vector in the direction of the jth sp^3 orbital.

In the basis of gauge-invariant orbitals, the Hamiltonian takes the form

$$H=\{\sum_{i,j}\tilde{E}_0(j)|ij\rangle\langle ij|+\sum_{i,i',j}[\tilde{V}_2(i,i',j)|ij\rangle\langle i'j|+\mathrm{c.c.}]\}+\{\sum_{i,j,j'}[\tilde{V}_1(j,j')|ij\rangle\langle ij'|+\mathrm{c.c.}]\}\equiv(H_0+H_1). \quad (5)$$

Equation (5) is our starting point for calculation of the susceptibility. The complete problem is a difficult one,[4] so we use a perturbative approach leading to a power-series expansion of the susceptibility in the parameter V_1/V_2. This series converges rapidly, since $V_1/V_2<0.5$ is required to insure that the HW model represents an insulator.[5] We first diagonalize H_0. The resulting eigenfunctions are bonding and antibonding combinations of the states $\psi_j(\vec{r}-\vec{R}_i)$ and $\psi_j(\vec{r}-\vec{R}_{i'})$. These states may be used as a basis set for the operator H_1;

$$H_1=(H_{bb}+H_{aa})+(H_{ab}+H_{ba}), \quad (6)$$

where $(H_{bb}+H_{aa})$ is that portion of H_1 which couples bonding orbitals to bonding orbitals or antibonding orbitals to antibonding orbitals, whereas $(H_{ab}+H_{ba})$ mixes bonding and antibonding states. This separation is important, because the two types of terms play quite different roles in our calculation. We treat the operator $(H_{bb}+H_{aa})$ exactly, since it mixes degenerate orbitals, thus broadening the bonding and antibonding manifolds into the valence and conduction bands, respectively. However, $(H_{ba}+H_{ab})$ couples nondegenerate states whose energies differ by $2|V_2|$, and can legitimately be treated in perturbation theory.

To apply this argument, consider the truncated Hamiltonian

$$H_{\mathrm{diag}}=H_0+(H_{bb}+H_{aa}). \quad (7)$$

The diagonalization of even this reduced Hamiltonian is a difficult task. However, to evaluate the susceptibility, one does not require the individual eigenfunctions and eigenvalues of H_{diag}. For that purpose, it suffices to know the sum of *all* valence-band energies—a sum which can easily be calculated whenever the conduction and valence bands are decoupled. The total energy is then the trace of Eq. (7) over any complete set of valence-band states. It will prove convenient to use the bonding states for this purpose.

To calculate the susceptibility in powers of (V_1/V_2), we transform the complete Hamiltonian via successive canonical transformations, as follows:

$$H'=e^{iT}He^{-iT}, \quad (8)$$

and choose

$$i[T,H_{\mathrm{diag}}]+(H_{ba}+H_{ab})=0. \quad (9)$$

This procedure parallels that used in effective-mass theory. The new Hamiltonian, to second order in T, is

$$\langle \beta, b | H' | \beta', b\rangle = \langle \beta, b | H_{\mathrm{diag}} | \beta', b\rangle + \frac{1}{2}\sum_{\alpha}\left\{\frac{\langle \beta, b|H_{ba}|\alpha, a\rangle\langle \alpha, a|H_{ab}|\beta', b\rangle}{E_a(\alpha) - E_b(\beta)} + \frac{\langle \beta, b|H_{ba}|\alpha, a\rangle\langle \alpha, a|H_{ab}|\beta', b\rangle}{E_a(\alpha) - E_b(\beta')}\right\}, \tag{10}$$

where the labels β and α index the bonding ($|\beta, b\rangle$) and antibonding ($|\alpha, a\rangle$) eigenfunctions of H_{diag}. The valence and conduction bands are now decoupled to order $(V_1/V_2)^2$. In lowest approximation, $[E_a(\alpha) - E_b(\beta)] = 2|V_2|$ and the sum over intermediate states can immediately be evaluated. The total valence-electron energy (including magnetic-field-dependent terms) is the trace of Eq. (10) in the bonding representation. This expression contains both paramagnetic and diamagnetic terms. The former arise from the matrix elements of $H_{ab} + H_{ba}$; hence they depend upon bond angles and crystal coordination. The latter emerge from the H_{diag} term.

To extend this procedure to next order in (V_1/V_2), we keep higher powers of T in Eq. (8), and expand the energy denominator of Eq. (10) about the "average" gap $E_g \equiv 2|V_2|$. The result is a series of commutators of the form $H_{ba}[H_{\mathrm{diag}}, [H_{\mathrm{diag}} \cdots, [H_{\mathrm{diag}}, H_{ab}]]]$ which again can be evaluated with trace methods. To order $(V_1/V_2)^2$,

$$\chi = \frac{-Ne^2}{4mc^2}\sum_{j=1}^{4}\left\{\langle r_\perp^2(j)\rangle_{\mathrm{local}} + \langle r_\perp^2(j)\rangle_{\mathrm{overlap}}\left[1 - \frac{3}{4}\left(\frac{V_1}{V_2}\right)^2\right]\right\} + \frac{\frac{1}{2}N(e\hbar/mc)^2}{E_g}\left[1 + \frac{1}{4}\left(\frac{V_1}{V_2}\right)^2\right]. \tag{11}$$

Since $(V_1/V_2) < 0.5$,[5] the second-order terms in Eq. (11) are small and may be ignored. Equation (11) was derived on the assumption of zero overlap between orbitals that form a bond. With overlap, the expression is modified as follows[10]:

$$\chi = \frac{-Ne^2}{4mc^2}\left(\frac{1}{1+S}\right)\sum_{j=1}^{4}[\langle r_\perp^2(j)\rangle_{\mathrm{local}} + \langle r_\perp^2(j)\rangle_{\mathrm{overlap}}] + \frac{N}{2}\left(\frac{e\hbar}{mc}\right)^2\left(\frac{1}{1-S^2}\right)\frac{1}{\tilde{E}_g}, \tag{12}$$

where $\tilde{E}_g$ is the energy gap modified for overlap. Equation (12) is our final result, which we compare with the HKF model. Their diamagnetic and paramagnetic terms can now be identified with well-defined, gauge-invariant quantities: the orbital area $\langle r_\perp^2(j)\rangle_{\mathrm{local}}$, the overlap area $\langle r_\perp^2(j)\rangle_{\mathrm{overlap}}$, the overlap integral S, and the energy gap $\tilde{E}_g$. $|M|^2$, which depends only on the geometrical arrangement of the bonds, is given by

$$|M|^2 = (1 - S^2)^{-1}(e\hbar/mc)^2 N_0. \tag{13}$$

Here N_0 is Avogadro's number. This result implies that $|M|^2$ is constant for all covalent tetrahedrally bonded materials, as observed by HKF. With the value $S = 0.5$,[11] Eq. (13) gives $|M|^2 = 1.7 \times 10^{-4}$ eV cm^3/mole, in good agreement with the experimental values[1] 1.8 ± 0.6 (diamond), 1.8 ± 0.3 (Si), and 2.2 ± 0.2 (Ge) in units of 10^{-4} eV cm^3/mole.

To evaluate the diamagnetic terms in Eq. (12), we have used Herman-Skillman wave functions[12] to calculate $\langle r_\perp^2(j)\rangle_{\mathrm{local}}$. It can be shown[10] that $\langle r_\perp^2(j)\rangle_{\mathrm{overlap}} \lesssim (0.15)\langle r_\perp^2(j)\rangle_{\mathrm{local}}$. Our results[13] for $r_\perp$ agree with experimental values[1] (indicated in parentheses): diamond 0.84 Å (1.04 ± 0.15 Å), Si 1.23 Å (1.32 ± 0.1 Å), Ge 1.25 Å (1.48 ± 0.06 Å).

In conclusion, we have derived a particularly simple expression for the susceptibility of tetrahedral semiconductors in terms of gauge-invariant quantities characterizing the chemical bonding and the spatial structure of the solid. Work is presently under way to extend our formalism to differently coordinated solids and to amorphous materials.

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$$r_L = [\tfrac{1}{8}\sum_{\text{val}}\langle r^2\rangle]^{1/2} = [\langle r^2\rangle\sum_{\text{val}}]^{1/2}\,.$$

Theory of the Magnetic Susceptibility of Tetrahedral Semiconductors

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The magnetic susceptibility of an intrinsic tetrahedrally coordinated semiconductor is calculated using a tight-binding basis and approximations appropriate to the bond-orbital model. The susceptibility associated with the valence electrons is found to separate into a diamagnetic Langevin component and a paramagnetic Van Vleck component, both of which are found to be proportional to the square of the bond length, and nearly cancel in the homopolar semiconductors. The Langevin term is found to be approximately independent of polarity while the paramagnetic component varies with polarity, α_p, as $(1-\alpha_p^2)^{3/2}$.

The measured magnetic susceptibility, χ, of a large class of semiconductors shows variations which seem to be related to the nature of the chemical bonding and in some cases to the presence or absence of long-range order.[1,2] For example, the (diamagnetic) susceptibility of crystalline GaAs is about twice as large as that of crystalline Ge, and amorphous Ge is about 2.7 times more diamagnetic than crystalline Ge.[1]

The purpose of this Letter is to present a simple model which elucidates the nature of the relationship between χ and the chemical bond for the class of tetrahedrally coordinated crystals.

It is relatively easy to evaluate the orbital magnetic susceptibility of a solid in terms of the exact eigenfunctions of the solid. This corresponds to treating the solid as a giant "molecule." However, as soon as one attempts to express the susceptibility in a tight-binding basis the necessity of maintaining gauge invariance presents complications. A general tight-binding theory considering these complications was presented earlier.[3] The purpose of this Letter has been to evaluate the susceptibility obtained in Ref. 3 for a model which both is simple and yet contains enough information to enable us to understand variations from material to material. For this purpose we chose the bond-orbital model.[4,5] The advantage of this model lies in the fact that the coefficients of these hybrids involve parameters which have already been obtained for many semiconductors from dielectric and optical data. Furthermore, this model also allows a separate evaluation of the (valence electron) Langevin and Van Vleck contributions to χ. The calculation shows that whereas the main contribution to the Langevin-like terms χ_L is only weakly dependent on polarity, the paramagnetic contribution χ_p has a strong dependence. Our results indicate that the reduction of χ_p in the more polar crystals is caused not only by the larger gap between the valence and conduction states but also directly through a reduction of matrix elements in increasingly polar solids. This helps to explain the variation of the parameter B in the simple model for χ_p used by Hudgens, Kastner, and Fritzsche[1] to separate their measured susceptibilities into paramagnetic and diamagnetic com-