PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

Magnetic susceptibility of tetrahedrally coordinated solids

T. Sahu and P. K. Misra

Department of Physics, Berhampur University, Berhampur-760 007, Orissa, India

(Received 14 September 1981; revised manuscript received 27 May 1982)

We derive a general expression for the magnetic susceptibility (χ) of intrinsic semiconductors in the Bloch representation using finite-temperature Green's-function formalism. It is shown that terms of the same order have been missed in the earlier theories of χ. In order to apply our theory to tetrahedral semiconductors, we construct a basis set for the valence bands which is a linear combination of the sp^3 hybrids forming a bond in which their relative phase factors (heretofore neglected) have been properly included. We also construct a basis set for the conduction bands which are orthogonal to the valence-band functions. We construct Wannier functions for the valence bands from our Bloch functions and show that the bond orbitals used in the earlier chemical-bond theories are not the proper choice for the Wannier functions of the valence band. We use our basis functions in our general expression to obtain an expression for χ of tetrahedral semiconductors. Our expression for χ is origin independent and is free from any "scaling" parameter, unlike the earlier theories. A novel feature of our result is that our expressions for Van Vleck—type susceptibility is proportional to the overlap integral and tends to zero in the "no bonding" limit. We calculate χ of elemental and III-V tetrahedral semiconductors, and there is good agreement with experimental results.

I. INTRODUCTION

The chemical-bond approach[1-10] to the study of electronic properties of solids has recently been utilized to calculate the magnetic susceptibility (χ) of intrinsic tetrahedrally coordinated semiconductors. This approach, which is much simpler than band theory, emphasizes the bond aspect of the crystal structure and is valuable in studying chemical trends such as covalency, polarity, and metallicity. Further, this approach has a certain degree of flexibility and is well suited to the study of amorphous materials as well as periodic ones. In fact, recent experiments on the large diamagnetic enhancement of Ge (Ref. 11) and Si (Ref. 12) in the amorphous state relative to the crystalline state, which is one of the most fascinating and puzzling properties exhibited by many semiconductors, have generated widespread interest in these semiempirical chemical-bond theories of χ of tetrahedral semiconductors.

Hudgens, Kastner, and Fritzsche[13] (HKF) first showed that a simple chemical-bond model describes the magnetic susceptibility of $A^N B^{8-N}$ semiconductors. Sukhatme and Wolff[14] (SW) and Chadi, White, and Harrison[15] (CWH) have independently developed chemical-bond theories of χ of tetrahedral semiconductors. According to these theories, the magnetic susceptibility χ can be written

$$\chi=\chi_c+\chi_v+\chi_p \; , \tag{1.1}$$

where χ_c is the core-electron diamagnetism, χ_v is a Langevin-type diamagnetic component due to the valence electrons which is sensitive to the spatial extent of the valence charge density, and χ_p is a Van Vleck—type paramagnetic interband component arising from the virtual magnetic dipole transition between filled valence- and empty conduction-band states. SW have incorporated the effects of a magnetic field into the Hall-Weaire model[1,3,4] by introducing a basis set of gauge-invariant, sp^3, atomic orbitals.[16,17] They have used a perturbative approach leading to a power-series expansion of the susceptibility in the parameter V_1/V_2 where V_1 is the matrix element of the Hamiltonian between two orbitals of the same atom, and V_2 is the matrix element between two orbitals forming a bond. CWH have used a tight-binding basis[18] and approximations appropriate to the bond-orbital model,[7,8] which has also been used to calculate electric[19] and optical[20] susceptibilities, to obtain an expression for χ. They have used two "scaling" parameters γ_m and λ and determined these parameters by fitting to the experimentally separated values of χ_p and χ_v for Si. Then, assuming γ_m and λ to have the same values for other semiconductors, they have calculated χ of many average-valence-four semiconductors.

However, there is wide disagreement between the results of these chemical bond theories and the experimental results. The values of χ calculated from SW theory are -3.1 (-6.4) for Si, -12.4 (-15.7) for Ge, and -3.6 (-11.7) for C where the experimental results are given in the parentheses. The CWH theory seems to predict reasonably well the susceptibility of 26 semiconductors. However, in order to compare their theory with experiment, one must separate the diamagnetic (χ_L) and paramagnetic (χ_p) contribution since for covalently bonded tetrahedral semiconductors, χ_L and χ_p are both large and nearly cancel. Therefore, a theory which adequately predicts the total susceptibility may yield individual terms χ_L and χ_p in substantial disagreement with experiment. If we write $\chi_p^E = \chi_{\rm tot}^{\rm expt} - \chi_c - \chi_L^{\rm CWH}$ and compare χ_p^E with $\chi_p^{\rm CWH}$, we find that the difference is 100% or more for α-Sn, CdTe, HgS, HgSe, HgTe, and CuCl and is 40% or more for GaP, InAs, InSb, CdS, and CuBr.

In addition, as we shall show in detail later, there are other substantial deficiencies in these theories. Firstly, the value of χ_p in these theories is quite large even when the overlap integral S tends to zero, an unlikely result since one does not expect any significant Van Vleck—type contribution if there is no bonding. Secondly, the complete problem of the magnetic susceptibility of solids[21–24] has not been considered in these theories and we shall show that "terms of the same order" in χ have been omitted. Thirdly, in White's expression[18] for χ, χ_L, and χ_p are each origin dependent and contain divergent terms $\vec{R}_i$ and R_i^2, where $\vec{R}_i$ is the position of the midpoint of the bond. These divergent terms in $\chi_L + \chi_p$ cancel provided the localized states form a complete set for the conduction and valence bands. However, CWH have used as basis states the bonding and antibonding orbitals and have evaluated the matrix elements of White's expression for χ in the Hall-Weaire approximation.[1,3] Owing to these assumptions, the completeness criteria of the basis states is not satisfied and the divergent terms do not exactly cancel. Therefore, $\chi^{\rm CWH}$ is dependent on the choice of the local origin. Fourthly, in the CWH theory, a parameter λ, whose theoretical value varies from 0.52 to 0.71, has been arbitrarily "scaled" to 1.13. Since χ_p is proportional to λ^2, this "scaling" enhances their χ_p by a factor of 300% to 400% of its actual value. Finally, recent experiments[25] on the temperature dependence of magnetic susceptibility of materials of intermediate ionicity and highly ionic alkali halides indicate that these chemical-bond theories are either incorrect or incomplete and yield unphysical results for some materials.

In this paper we derive for the first time a general expression for the magnetic susceptibility of intrinsic semiconductors in the Bloch representation with the use of finite temperature Green's-function formalism. We show that terms of the same order have been missed in White's expression[18] for χ. In order to apply our theory to tetrahedral semiconductors, we construct a basis set for the valence bands which is a linear combination of sp^3 hybrids forming a bond in which their relative phase factors (heretofore neglected) has been properly included. We also construct a basis set for the conduction bands which are orthogonal to the valence-band functions.

In order to compare our basis functions with the bond orbitals[14,15] we construct Wannier functions[19] from our Bloch functions and show that the bond orbitals used in the earlier theories are not the proper choice for the Wannier functions of the valence band. We show that the basic assumption in the bond-orbital models, i.e., that the localized functions have the character of chemical bonds in the chemist's sense, is equivalent to ignoring the relative Bloch phase factors $e^{i\vec{k}\cdot\vec{d}_j}$ (where $\vec{d}_j$ is a bond length) between the hybrids forming a bond. However, since $\vec{d}_j - \vec{d}_{j'}$ is a lattice vector, this relative phase factor plays an important role in solids unlike in the case of molecules where it could be neglected.

We use our basis functions in our general expression for χ to obtain an expression for χ of tetrahedral semiconductors. Each term in our expression for χ is origin independent, unlike the earlier theories. A novel feature of our result is that our expression for χ_p is proportional to S and tends to zero in the "no bonding" limit. We calculate χ of a large number of semiconductors, and our results agree quite well with the experimental results. Our theory is free from any "scaling parameter" unlike the earlier theories.[15]

The organization of the paper is as follows. In Sec. II we derive a general theory for χ of intrinsic semiconductors. In Sec. III we construct a basis set in the Bloch representation both for the valence and conduction bands. We also construct Wannier functions from our Bloch functions and compare them with the bond orbitals. In Sec. IV we use our basis functions in our general expression for χ

to obtain an expression for χ of tetrahedral semiconductors. In Sec. V we numerically calculate χ of homopolar and III-V semiconductors and compare our results with the available theoretical and experimental results. In Sec. VI, we summarize our results.

II. MAGNETIC SUSCEPTIBILITY OF INTRINSIC SEMICONDUCTORS

A. Equation of motion in the Bloch representation

We shall derive[26] a general expression for the magnetic susceptibility of intrinsic semiconductors since no such theory is available. We consider an intrinsic semiconductor which has valence bands $(n,n',\ldots)$ and conduction bands $(m,m',\ldots)$. Using finite temperature Green's-function formalism, we obtain the thermodynamic potential $\Omega(T,V,\mu,\vec{B})$ for a noninteracting electron system in the presence of a periodic potential $V(\vec{r})$ and external magnetic field $\vec{B}$. Ω can be evaluated using Luttinger-Ward expression[27]

$$\Omega=\frac{1}{\beta}\mathrm{Tr}\ln(-G)\,, \tag{2.1}$$

where G is the exact one-particle Green's function. The trace involves summation over a complete one-particle set and over imaginary frequencies. G satisfies the equation

$$(\xi_l-H)G(\vec{r},\vec{r}\,',\vec{B},\xi_l)=\delta(\vec{r}-\vec{r}\,')\,, \tag{2.2}$$

where ξ_l is the complex energy

$$\xi_l=(2l+1)\frac{i\pi}{\beta}+\mu\,, \tag{2.3}$$

H is the one-particle Hamiltonian

$$H=\frac{1}{2m}\left[\vec{p}+\frac{e\vec{A}}{c}\right]^2+V(\vec{r})\,, \tag{2.4}$$

and $\vec{A}(\vec{r})$ is the vector potential. In the absence of the magnetic field, G has the symmetry

$$G(\vec{r},+\vec{R},\vec{r}\,'+\vec{R},\xi_l)=G(\vec{r},\vec{r}\,',\xi_l)\,, \tag{2.5}$$

where $\vec{R}$ is the crystal translation vector. The vector potential in the Hamiltonian destroys this symmetry but G can be written as the product of a "Peierls phase factor" and a part which has the above symmetry.[28,29] In the symmetric gauge $(\vec{A}=\frac{1}{2}\vec{B}\times\vec{r})$, we have

$$\begin{aligned}G(\vec{r},\vec{r}\,',\vec{B},\xi_l)&=\exp(i\vec{h}\cdot\vec{r}\times\vec{r}\,')\\&\quad\times\widetilde{G}(\vec{r},\vec{r}\,',\vec{B},\xi_l)\,,\end{aligned} \tag{2.6}$$

where $\vec{h}=e\vec{B}/2\hbar c$, and $\widetilde{G}$ satisfies crystal translational symmetry. Substituting Eqs. (2.4) and (2.6) in Eq. (2.2), commuting the differential operators through the Peierls phase factor, and then multiplying on the left by $\exp(-i\vec{h}\cdot\vec{r}\times\vec{r}\,')$, we obtain

$$\begin{aligned}&\left[\xi_l-\frac{1}{2m}[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^2-V(\vec{r})\right]\\&\qquad\times\widetilde{G}(\vec{r},\vec{r}\,',\vec{B},\xi_l)=\delta(\vec{r}-\vec{r}\,')\,.\end{aligned} \tag{2.7}$$

We can write the equation of motion in the Bloch representation, i.e., in terms of the basis functions $\psi_{n\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}U_{n\vec{k}}(\vec{r})$, where n is the band index and $\vec{k}$ is the reduced wave vector. Here $\psi_{n\vec{k}}(\vec{r})$ are the eigenfunctions of the Hamiltonian of the noninteracting electron in the absence of the magnetic field. With the use of the Bloch representation, Eq. (2.7) can be written

$$\begin{aligned}&\sum_{n'',\vec{k}\,',\vec{k}\,''}\int d\vec{r}\,d\vec{r}\,'d\vec{r}\,''e^{-i\vec{k}\cdot\vec{r}}U_{n\vec{k}}(\vec{r})\left[\xi_l-\frac{1}{2m}[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^2-V(\vec{r})\right]\\&\qquad\times\exp[i\vec{k}\,''\cdot(\vec{r}-\vec{r}\,'')]U_{n''\vec{k}''}(\vec{r})U^*_{n''\vec{k}''}(\vec{r}\,'')\widetilde{G}(\vec{r}\,'',\vec{r}\,',\vec{B},\xi_l)U_{n'\vec{k}'}(\vec{r}\,')e^{i\vec{k}\,'\cdot\vec{r}\,'}=\delta_{nn'}\,.\end{aligned} \tag{2.8}$$

By introducing change of variables $\vec{R}_1=\vec{r}\,''-\vec{r}\,',\vec{R}_2=\frac{1}{2}(\vec{r}\,'+\vec{r}\,'')$ and with the use of partial integration of the type

$$\begin{aligned}&\sum_{\vec{k}''}(\vec{r}-\vec{r}\,')\exp[i\vec{k}\,''\cdot(\vec{r}-\vec{r}\,')]\exp[i\vec{k}\,''\cdot(\vec{r}\,'-\vec{r}\,'')]U_{n''\vec{k}''}(\vec{r})U^*_{n''\vec{k}''}(\vec{r}\,'')\\&\qquad=\sum_{\vec{k}''}\exp[i\vec{k}\,''\cdot(\vec{r}-\vec{r}\,')]i\nabla_{\vec{k}''}\exp[i\vec{k}\,''\cdot(\vec{r}\,'-\vec{r}\,'')]U_{n''\vec{k}''}(\vec{r})U^*_{n''\vec{k}''}(\vec{r}\,'')\,,\end{aligned} \tag{2.9}$$

Eq. (2.8) can be written in the form

$$\sum_{n''}[\xi_l-H(\vec{K}',\xi_l)]_{n\vec{k},n''\vec{k}}\widetilde{G}_{n''\vec{k},n'\vec{k}}(\vec{k}',\xi_l)\,|_{\vec{k}'=\vec{k}}=\delta_{nn'}\,, \tag{2.10}$$

where

$$\vec{K}=\vec{k}+i\vec{h}\times\nabla_{\vec{k}}\ , \tag{2.11}$$

$$H(\vec{K},\xi_l)=\frac{1}{2m}(\vec{p}+\hbar\vec{K})^2+V(\vec{r})\ , \tag{2.12}$$

and

$$\begin{aligned}\widetilde{G}_{n''\vec{k},n'\vec{k}}(\vec{k}',\xi_l)&=\int d\vec{r}\,d\vec{r}\,'U^*_{n''\vec{k}}(\vec{r})\widetilde{G}(\vec{r},\vec{r}\,',\xi_l)\\&\quad\times\exp[-i\vec{k}'\cdot(\vec{r}-\vec{r}\,')]U_{n'\vec{k}}(\vec{r}\,')\ .\end{aligned} \tag{2.13}$$

Since the $U_{n\vec{k}}$'s form a complete set for periodic functions, Eq. (2.8) can be written in the alternate form

$$[\xi_l-H(\vec{K},\xi_l)]\widetilde{G}(\vec{k},\xi_l)=I\ . \tag{2.14}$$

We note that similar Green's-function equations for the orbital motion of Bloch electrons have been derived by Phillippas and McClure[28] in the Luttinger-Kohn representation[30] and Mohanty and Misra in the Bloch representation.[31]

B. Derivation of a general formula for χ

The magnetic susceptibility χ is calculated from the expression

$$\chi_{\mu\nu}=-\frac{1}{V}\lim_{B\to 0}\frac{\partial^2\Omega}{\partial B_\mu\partial B_\nu}\ . \tag{2.15}$$

In order to evaluate Ω, we write Eq. (2.12) in the form

$$H(\vec{K},\xi_l)=H_0(\vec{k},\xi_l)+H'(\xi_l)\ , \tag{2.16}$$

where $H_0(\vec{k},\xi_l)$ is the Hamiltonian in the absence of magnetic field,

$$H_0(\vec{k},\xi_l)=\frac{1}{2m}(\vec{p}+\hbar\vec{k})^2+V(\vec{r})\ , \tag{2.17}$$

$H'(\xi_l)$ is the operator

$$\begin{aligned}H'(\xi_l)=&-ih_{\alpha\beta}P^\alpha(\vec{k},\xi_l)\nabla^\beta_{\vec{k}}\\&-\frac{\hbar^2}{2m}h_{\alpha\beta}h_{\gamma\delta}\nabla^\beta_\kappa\nabla^\delta_\kappa\delta_{\alpha\gamma}\ ,\end{aligned} \tag{2.18}$$

and

$$\vec{P}=\frac{\hbar}{m}(\vec{p}+\hbar\vec{k})\ .$$

Here we have retained terms up to second order in the magnetic field and $h_{\alpha\beta}=\epsilon_{\alpha\beta\gamma}h^\gamma$, where $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor of the third rank and we follow Einstein summation convention. We make a perturbative expansion

$$\begin{aligned}\widetilde{G}(\vec{k},\xi_l)=&G_0(\vec{k},\xi_l)+G_0(\vec{k},\xi_l)H'G_0(\vec{k},\xi_l)\\&+G_0(\vec{k},\xi_l)H'G_0(\vec{k},\xi_l)H'G_0(\vec{k},\xi_l)\\&+\cdots\ ,\end{aligned} \tag{2.19}$$

where

$$G_0^{-1}(\vec{k},\xi_l)=\xi_l-H_0(\vec{k},\xi_l) \tag{2.20}$$

and is diagonal in the basis $U_{n\vec{k}}$. It can be easily shown that[29]

$$\nabla^\alpha_{\vec{k}}G_0(\vec{k},\xi_l)=G_0(\vec{k},\xi_l)P^\alpha G_0(\vec{k},\xi_l)\ , \tag{2.21}$$

and

$$\begin{aligned}\nabla^\alpha_{\vec{k}}\nabla^\gamma_{\vec{k}}G_0(\vec{k},\xi_l)&=\frac{\hbar^2}{m}G_0(\vec{k},\xi_l)G_0(\vec{k},\xi_l)\delta_{\alpha\gamma}\\&\quad+G_0(\vec{k},\xi_l)P^\alpha G_0(\vec{k},\xi_l)P^\gamma G_0(\vec{k},\xi_l)\\&\quad+G_0(\vec{k},\xi_l)P^\gamma G_0(\vec{k},\xi_l)P^\alpha G_0(\vec{k},\xi_l)\ .\end{aligned} \tag{2.22}$$

From Eqs. (2.19), (2.21), and (2.22) we obtain

$$\begin{aligned}\widetilde{G}(\vec{k},\xi_l)=&G_0(\vec{k},\xi_l)-ih_{\alpha\beta}G_0P^\alpha G_0P^\beta G_0\\&-h_{\alpha\beta}h_{\gamma\delta}G_0\left[\frac{\hbar^4}{2m^2}G_0\delta_{\alpha\gamma}\,\delta_{\beta\delta}+\frac{\hbar^2\delta_{\alpha\gamma}}{2m}(G_0P^\beta G_0P^\delta+G_0P^\delta G_0P^\beta+P^\beta G_0P^\delta G_0-2P^\beta G_0G_0P^\delta)\right.\\&\left.+2P^\alpha G_0P^\gamma G_0P^\beta G_0P^\delta\right]G_0+\cdots\ .\end{aligned} \tag{2.23}$$

The magnetic susceptibility $\chi_{\mu\nu}$ is calculated from Eqs. (2.1), (2.15), and (2.23). To carry out the frequency sums appearing in $\chi_{\mu\nu}$, we use the identity[27]

$$\frac{1}{\beta}\sum_{\xi_l}\ln\frac{1}{(H-\xi_l)}=-\frac{1}{2\pi i}\int_c\frac{d\xi}{\exp[\beta(\xi-\mu)]+1}\ln\frac{1}{(H-\xi)}\ , \tag{2.24}$$

where the contour c encircles the imaginary axis in counterclockwise direction. We define

$$\phi(\xi) = -\frac{1}{\beta}\ln\{1+\exp[-\beta(\xi-\mu)]\} \ . \tag{2.25}$$

From Eqs. (2.1), (2.24), and (2.25), we obtain

$$\Omega = \frac{1}{2\pi i}\mathrm{tr}\int_c \frac{d\phi(\xi)}{d\xi}\ln(H-\xi) \tag{2.26}$$

$$= -\frac{1}{2\pi i}\mathrm{tr}\int_c \phi(\xi)\tilde{G}(\xi)d\xi \ , \tag{2.27}$$

where the latter is obtained by an integration by parts, and tr is taken over one-particle states only. One can now substitute the results of Eq. (2.23) in Eq. (2.27) to obtain Ω. The results are precisely the same as obtained by using the inverse Laplace transform technique,[29] but the present technique is simpler.

The one-particle trace is evaluated over $U_{n\vec{k}}$ which are eigenfunctions of $H_0(\vec{k})$. After evaluating the trace, we perform the contour integration as prescribed in Eq. (2.27). We use the identity[24]

$$h_{\alpha\beta}h_{\gamma\delta}(M_1^\alpha M_2^\beta M_3^\gamma M_4^\delta + M_1^\alpha M_2^\gamma M_3^\delta M_4^\beta) = h_{\alpha\beta}h_{\gamma\delta}M_1^\alpha M_2^\gamma M_3^\beta M_4^\delta \ , \tag{2.28}$$

where M_1, M_2, M_3, and M_4 are matrix elements of $\vec{P}$ between $U_{n\vec{k}}$. We also adopt the convention that running index means that the sum over all the bands and all the spin indices shall be taken except that all band terms equal to s have been explicitly separated out. After some algebra we obtain

$$\begin{aligned}
\Omega = \sum_{\vec{k}} & i h_{\alpha\beta}P_{sq}^\alpha P_{qs}^\beta \left[\frac{f(E_s)}{E_{qs}} + \frac{2\phi(E_s)}{E_{qs}^2}\right] \\
& + h_{\alpha\beta}h_{\gamma\delta}\left[-\frac{1}{6}\frac{\hbar^2}{m}\delta_{\beta\delta}P_{ss}^\alpha P_{ss}^\gamma f''(E_s) - \frac{\hbar^4}{4m^2}\delta_{\alpha\gamma}\delta_{\beta\delta}f'(E_s)\right. \\
& \quad + P_{ss}^\alpha P_{ss}^\gamma P_{sq}^\beta P_{qs}^\delta\left[\frac{f''(E_s)}{3E_{qs}} + \frac{2f'(E_s)}{E_{qs}^2} + \frac{6f(E_s)}{E_{qs}^3} + \frac{8\phi(E_s)}{E_{qs}^4}\right] \\
& \quad + \frac{\hbar^2}{m}P_{sq}^\alpha P_{qs}^\gamma \delta_{\beta\delta}\left[\frac{f'(E_s)}{E_{qs}} + \frac{4f(E_s)}{E_{qs}^2} + \frac{8\phi(E_s)}{E_{qs}^3}\right] \\
& \quad - P_{sq}^\alpha P_{qs}^\gamma P_{sl}^\beta P_{ls}^\delta\left[\frac{f'(E_s)}{E_{qs}E_{ls}} + \frac{6f(E_s)}{E_{qs}^2E_{ls}} + \frac{8\phi(E_s)}{E_{qs}^3E_{ls}} + \frac{4\phi(E_s)}{E_{qs}^2E_{ls}^2}\right] \\
& \quad + P_{sq}^\alpha P_{ql}^\gamma P_{lt}^\beta P_{ts}^\delta\left[\frac{2f(E_s)}{E_{qs}E_{ls}E_{ts}} + \frac{4\phi(E_s)}{E_{qs}^2E_{ls}E_{ts}} + \frac{4\phi(E_s)}{E_{ts}^2E_{qs}E_{ls}}\right] \\
& \quad \left. + P_{ss}^\alpha P_{sq}^\gamma P_{ql}^\beta P_{ls}^\delta\left[\frac{-2f(E_s)}{E_{qs}E_{ls}^2} + \frac{2f(E_s)}{E_{qs}^2E_{ls}} - \frac{4\phi(E_s)}{E_{qs}E_{ls}^3} + \frac{4\phi(E_s)}{E_{qs}^3E_{ls}}\right]\right] \ ,
\end{aligned} \tag{2.29}$$

where sums are taken over all the repeated indices s, q, l, and t but $s \neq q,l,t$. Thus s takes all the values of n and m while q, l, and t each takes any of the values other than s. We have also used the notation $E_{qs} = E_q(\vec{k}) - E_s(\vec{k})$. By an integration by parts,[32] all the ϕ terms are converted to f terms. Similarly, some of the f terms are converted to f' terms. Setting $f'(E_s)$ and $f''(E_s)$ terms to be zero, $f(E_n)=1$ and $f(E_m)=0$ (for intrinsic semiconductors), we obtain from Eqs. (2.15) and (2.29)

$$\begin{aligned}
\chi_{\mu\nu} = \frac{h_{\alpha\beta}h_{\gamma\delta}(1+\delta_{\mu\nu})}{B^2}\sum_{n,\vec{k}} & \left[-\frac{\hbar^2}{m}\frac{P_{nm}^\alpha P_{mn}^\gamma}{E_{mn}^2}\delta_{\beta\delta} + \frac{P_{nm}^\alpha P_{mn'}^\gamma P_{n'm'}^\delta P_{m'n}^\beta}{E_{mn}E_{m'n}E_{mn'}}\right. \\
& + \frac{P_{nm}^\alpha P_{mn'}^\gamma P_{n'm'}^\beta P_{m'n}^\delta}{E_{m'n}E_{mn'}E_{m'n'}} - \frac{P_{nm}^\alpha P_{mn'}^\gamma P_{n'm'}^\beta P_{m'n}^\delta}{E_{mn}E_{m'n}E_{m'n'}} + \frac{2P_{nm}^\alpha P_{mn}^\beta P_{nm'}^\gamma P_{m'n}^\delta}{E_{mn}^2E_{m'n}} \\
& \left. - \frac{P_{nm}^\alpha P_{mm'}^\beta P_{m'm''}^\gamma P_{m''n}^\delta}{E_{mn}E_{m'n}E_{m''n}} + \frac{2P_{nn'}^\alpha P_{n'm}^\beta P_{mm'}^\gamma P_{m'n}^\delta}{E_{mn'}E_{m'n}E_{m'n'}} + \frac{P_{nn'}^\alpha P_{n'm}^\beta P_{mm'}^\gamma P_{m'n}^\delta}{E_{mn}E_{m'n}E_{mn'}}\right] \ ,
\end{aligned} \tag{2.30}$$

where repeated indices imply summation. We note that while summing over n', $n'=n$ is included and while summing over m', $m'=m$ is included but $n\neq m$. We further note that we have ignored all $P_{nn'}$ terms for $n\neq n'$ where no corresponding diagonal (P_{nn}) terms exist since these terms are small. It can be shown that Eq. (2.30), which is valid for any intrinsic semiconductor even when the bands are degenerate, is equivalent to the terms proportional to $f(E_n)$ in a general expression for diamagnetism of solids[33] [Eq. (5.36) of Ref. 33] if one ignores the $n'\neq n$ terms (since in the general theory of Bloch electrons[33] n is just a band index and the bands have not been grouped into two categories, i.e., valence bands $n,n',\ldots$ and conduction bands $m,m'\ldots$) and sums over all indices n, m, m' and m'' but $n\neq m,m',m''$. It can be shown that the Langevin term[18] is obtained from the first two terms and the Van Vleck term[18] is obtained from the sixth term. The other terms in Eq. (2.39) are extra terms obtained by us. It may be noted that each term in our expression for χ is origin independent.

III. LINEAR COMBINATION OF ATOMIC ORBITALS FORMALISM FOR TETRAHEDRAL SEMICONDUCTORS

We consider a zinc-blende structure where each atom is surrounded tetrahedrally by four identical atoms, which may be of a second type. The standard primitive cell contains two basic atoms at site i, with four sp^3 hybrids $h_j^1(\vec{r}-\vec{R}_i)$ pointing from atom I to the nearest neighbors (atom II) along the directions j ($j=1,\ldots,4$) and four other sp^3 hybrids $h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)$ pointing from these nearest neighbors to atom I. Here $\vec{R}_i$ is a lattice vector for site i and locates atoms of type I (we choose one of the atomic sites I as the origin) and $\vec{d}_j$ is a nearest-neighbor vector joining atom I with atom II. The hybrids can be expressed as

$$h_j^1(\vec{r}-\vec{R}_i)=\tfrac{1}{2}[s_1+\sqrt{3}(\zeta_j^x p_{x1}+\zeta_j^y p_{y1}+\zeta_j^z p_{z1})]\,, \tag{3.1}$$

and

$$h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)=\tfrac{1}{2}[s_2-\sqrt{3}(\zeta_j^x p_{x2}+\zeta_j^y p_{y2}+\zeta_j^z p_{z2})]\,, \tag{3.2}$$

where $\vec{\zeta}_1=1/\sqrt{3}(1,1,1)$, $\vec{\zeta}_2=1/\sqrt{3}(1,\bar{1},\bar{1})$, $\vec{\zeta}_3=1/\sqrt{3}(\bar{1},1,\bar{1})$, $\vec{\zeta}_4=1/\sqrt{3}(\bar{1},\bar{1},1)$, and s_1,p_{x1},p_{y1},p_{z1} and s_2,p_{x2},p_{y2},p_{z2} are the atomic orbitals at sites I and II, respectively. We construct Bloch-type tight-binding sums for valence-band basis functions by taking linear combination of the hybrids forming a bond,

$$\chi_j^v(\vec{r},\vec{k})=\sum_i f_j^v(\vec{k})e^{i\vec{k}\cdot\vec{R}_i}\times[h_j^1(\vec{r}-\vec{R}_i)+\lambda h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)\times e^{i\vec{k}\cdot\vec{d}_j}]\,, \tag{3.3}$$

where

$$f_j^v(\vec{k})=[N(1+\lambda^2+2\lambda S\cos\vec{k}\cdot\vec{d}_j)]^{-1/2}\,, \tag{3.4}$$

S is the overlap integral, and λ is related to Coulson's ionicity[19,34] f_c by the expression

$$f_c=\frac{(1-S^2)^{1/2}(1-\lambda^2)}{(1+\lambda^2+2\lambda S)}\,. \tag{3.5}$$

The basis functions for the conduction band χ_j^c are obtained by constructing functions orthogonal to $\chi_j^v(\vec{r},\vec{k})$:

$$\chi_j^c(\vec{r},\vec{k})=\sum_i f_j^c(\vec{k})e^{i\vec{k}\cdot\vec{R}_i}[(\lambda+Se^{i\vec{k}\cdot\vec{d}_j})h_j^1(\vec{r}-\vec{R}_i)-(\lambda S+e^{i\vec{k}\cdot\vec{d}_j})h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)]\,, \tag{3.6}$$

where

$$f_j^c(\vec{k})=\left[\frac{\lambda+Se^{-i\vec{k}\cdot\vec{d}_j}}{N(1-S^2)(1+\lambda^2+2\lambda S\cos\vec{k}\cdot\vec{d}_j)(\lambda+Se^{i\vec{k}\cdot\vec{d}_j})}\right]^{1/2}\,. \tag{3.7}$$

The Bloch eigenfunctions for the valence and conduction bands are

$$\psi_n(\vec{r},\vec{k})=\sum_j \alpha_{jn}^v(\vec{k})\chi_j^v(\vec{r},\vec{k})$$

and

$$\psi_m(\vec{r},\vec{k})=\sum_j \alpha_{jm}^c(\vec{k})\chi_j^c(\vec{r},\vec{k})\,. \tag{3.8}$$

Here α's are elements of (4×4) unitary matrices. We assume that the unitary properties of α^v and α^c separately hold good, i.e.,

$$\sum_n \alpha_{jn}^v(\vec{k})\alpha_{nj'}^{v\dagger}(\vec{k})=\delta_{jj'}$$

and

$$\sum_m \alpha_{jm}^c(\vec{k})\alpha_{mj'}^{c\dagger}(\vec{k})=\delta_{jj'}\,. \tag{3.9}$$

We note that our Bloch functions are different from the functions of Nucho *et al.*[19] in the sense that we have included a relative phase factor $e^{i\vec{k}\cdot\vec{d}_j}$ between the two hybrids forming a bond. Indeed, it may be argued that in the local representation the relative phase factors of the hybrids is included through their origin dependence. However, since the hybrids are bicentric, their relative phase factors must be properly taken into account while constructing the Bloch function in a linear combination of atomic orbitals formalism. If the localized functions (Wannier functions) constructed from these Bloch functions are written as $a_n=\sum_l c_l^n \phi_l$ where ϕ_l are the hybrids, the Bloch phase factors are included through c_l^n and not through the origin dependence of ϕ_l. The relative phase of the two hybrids which is introduced through their origin dependence arises due to the position of an atom relative to the others and would exist even when the atoms are independent.

In order to compare our basis functions with the bond orbitals,[14,15] we construct localized states from our Bloch functions. We define modified Wannier functions[19] by mixing valence-band states as

$$a_j^v(\vec{r}-\vec{R}_i)=\sum_{n\,\vec{k}}\frac{e^{-i\vec{k}\cdot\vec{R}_i}}{\sqrt{N}}\alpha_{nj}^{v+}(\vec{k})\psi_n(\vec{r},\vec{k}) . \tag{3.10}$$

From Eqs. (3.3) and (3.8)–(3.10), we obtain

$$\begin{aligned} a_j^v(\vec{r}-\vec{R}_i)=&T_j^1 h_j^1(\vec{r}-\vec{R}_i)+T_j^2 h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)\\ &+\sum_{j'\neq j} T_{jj'}^2 h_j^2(\vec{r}-\vec{R}_i-\vec{d}_{j'})\\ &+\cdots , \end{aligned} \tag{3.11}$$

where

$$\begin{aligned} T_j^1&=\frac{1}{\sqrt{N}}\sum_{\vec{k}} f_j^v(\vec{k}) ,\\ T_j^2&=\frac{\lambda}{\sqrt{N}}\sum_{\vec{k}} f_j^v(\vec{k})\cos\vec{k}\cdot\vec{d}_j ,\\ T_{jj'}^2&=\frac{\lambda}{\sqrt{N}}\sum_{\vec{k}} f_j^v(\vec{k})\cos\vec{k}\cdot\vec{d}_{j'} . \end{aligned} \tag{3.12}$$

As examples, we have calculated these coefficients for Si (the details of the calculation have been described later). We obtain $T_j^1=0.643$, $T_j^2=0.229$, and $T_{jj'}^2=0.291$. Thus the localized functions with site I as local origin are not the usual bonding orbitals[7,15,19] but there is a much greater admixture of $h_j^1(\vec{r}-\vec{R}_i)$ than $h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)$, as it should be. We have also calculated the Wannier functions $a_j^v(\vec{r}-\vec{R}_i-\vec{d}_j/2)$ from Eqs. (3.3) and (3.8)–(3.10) and we obtain

$$\begin{aligned} a_j^v(\vec{r}-\vec{R}_i-\vec{d}_j/2)&\\ =F_j[h_j^1(\vec{r}-\vec{R}_i)&+\lambda h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)]\\ +\sum_{j'\neq j}F_{jj'}[h_j^1(\vec{r}&-\vec{R}_i-\vec{d}_j+\vec{d}_{j'})\\ &+\lambda h_j^2(\vec{r}-\vec{R}_i-\vec{d}_{j'})]+\cdots , \end{aligned} \tag{3.13}$$

where

$$F_j=\frac{1}{\sqrt{N}}\sum_{\vec{k}} f_j^v(\vec{k})\cos(\vec{k}\cdot\vec{d}_j/2)$$

and

$$F_{jj'}=\frac{1}{\sqrt{N}}\sum_{\vec{k}} f_j^v(\vec{k})\cos\vec{k}\cdot(\vec{d}_{j'}-\vec{d}_j/2) . \tag{3.14}$$

For Si we obtain $F_j=0.513$ and $F_{jj'}=0.132$. We note that $a_j^v(\vec{r}-\vec{R}_i-\vec{d}_j/2)$ are essentially the bond orbitals[7,15,35] if we neglect the second term. Thus it appears that the relative phase of the bond orbitals is approximately included in the CWH theory if a bond center is chosen as the origin. However, since there are four bond orientations in a tetrahedral semiconductor, if we choose the center of one bond orientation (for example, j) as the lattice origin, the distance between the origin and the centers of the bonds in the other three orientations is not a lattice vector. In such cases the Wannier functions which have the centers of the bonds of j' orientation ($j'\neq j$) as local origin would be different in form from the CWH bonding orbitals,[7,15] i.e., from the Wannier functions which have the centers of the bonds of j orientations as local origin. Therefore, a more appropriate choice of the origin would be an atomic site in which case the Wannier functions would be of the same form in all the four bond orientations but which would be different from the CWH bond orbitals.

In order to make a comparison with the field-dependent basis functions used in SW theory,[14] we use the results of one of our earlier papers[36] in which it was shown that the set of magnetic Bloch functions $\psi_n^M(\vec{r},\vec{k})$ can be constructed from the zero-field Bloch functions $U_n(\vec{r},\vec{k})e^{i\vec{k}\cdot\vec{r}}$ with the use of the relation

$$\psi_n^M(\vec{r},\vec{k})=U_n(\vec{r},\vec{K}^*)e^{i\vec{k}\cdot\vec{r}}\,, \tag{3.15}$$

where $U_n(\vec{r},\vec{K}^*)$ is the operator obtained from $U_n(\vec{r},\vec{k})$ by replacing the wave vector $\vec{k}$ by the operator $\vec{K}^*$ symmetrically. From Eqs. (3.3), (3.8), and (3.15), we have

$$\begin{aligned}\psi_n^M(\vec{r},\vec{k})=&\sum_{i,j}\alpha_{jn}^{v}(\vec{k})f_j^{v}(\vec{k})e^{i\vec{k}\cdot\vec{R}_i}\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{R}_i\right]\\&\times\left[h_j^1(\vec{r}-\vec{R}_i)+\lambda e^{i\vec{k}\cdot\vec{d}_j}\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{d}_j\right]h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)\right]\,.\end{aligned} \tag{3.16}$$

From Eqs. (3.10) and (3.16), the magnetic Wannier functions a_{jv}^M for the valence band are obtained as

$$\begin{aligned}a_{jv}^M(\vec{r}-\vec{R}_i)=&\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{R}_i\right]\left[T_j^1h_j^1(\vec{r}-\vec{R}_i)+\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{d}_j\right]T_j^2h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)\right.\\&\left.+\sum_{j'\neq j}\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{d}_{j'}\right]T_{jj'}^2h_j^2(\vec{r}-\vec{R}_i-\vec{d}_{j'})\right]+\cdots\,.\end{aligned} \tag{3.17}$$

Thus the Wannier functions with site I as local origin are not the SW gauge-invariant bonding orbitals but there is a greater admixture of $h_j^1(\vec{r}-\vec{R}_i)$ than $h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)$ as it should be. Similarly we obtain from Eqs. (3.10) and (3.16) the valence-band Wannier functions $a_{jv}^M(\vec{r}-\vec{R}_i-\vec{d}_j/2)$ with the bond center as the local origin

$$\begin{aligned}a_{jv}^M(\vec{r}-\vec{R}_i-\vec{d}_j/2)=&\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{R}_i\right]\left\{F_j\left[h_j^1(\vec{r}-\vec{R}_i)+\lambda\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{d}_j\right]h_j^2(\vec{r}-\vec{R}_i-\vec{d}_j)\right]\right.\\&+\sum_{j'\neq j}F_{jj'}\left[\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times(\vec{d}_j-\vec{d}_{j'})\right]h_j^1(\vec{r}-\vec{R}_i-\vec{d}_j+\vec{d}_{j'})\right.\\&\left.\left.+\lambda\exp\left[-\frac{ie}{2\hbar c}\vec{r}\cdot\vec{B}\times\vec{d}_{j'}\right]h_j^2(\vec{r}-\vec{R}_i-\vec{d}_{j'})\right]\right\}+\cdots\,.\end{aligned} \tag{3.18}$$

We note that the first term in Eq. (3.18) gives essentially the SW gauge-invariant bonding orbitals. We further note that this gauge invariance was obtained because of the inclusion of the relative phase factors in our basis functions. However, for reasons explained earlier, the Wannier functions which have the centers of the bonds of j' orientations $(j'\neq j)$ as local origin would be different from a_{jv}^M.

IV. MAGNETIC SUSCEPTIBILITY OF TETRAHEDRAL SEMICONDUCTORS

We shall derive an expression for the magnetic susceptibility of tetrahedral semiconductors by using the Bloch functions obtained in Eq. (3.8). We simplify our results for χ in Eq (2.30) by using the relation

$$Q_{mn}=-\int U_m^*\nabla_{\vec{k}}U_n\,d\vec{r}=\frac{P_{mn}}{E_{mn}}\,. \tag{4.1}$$

From Eqs. (2.30) and (4.1), we obtain

$$\begin{aligned}\chi=&\frac{2h_{\alpha\beta}h_{\gamma\delta}}{B^2}\sum_{n\vec{k}}\left[-\frac{\hbar^2}{m}Q_{nm}^{+\alpha}Q_{mn}^{\gamma}\delta_{\beta\delta}+Q_{nm}^{+\alpha}Q_{mn'}^{\gamma}P_{n'm'}^{\delta}Q_{m'n}^{\beta}+P_{nm}^{\alpha}Q_{mn'}^{\gamma}Q_{n'm'}^{+\beta}Q_{m'n}^{\delta}-Q_{nm}^{+\alpha}P_{mn'}^{\gamma}Q_{n'm'}^{+\beta}Q_{m'n}^{\delta}\right.\\&\left.+2Q_{nm}^{+\alpha}Q_{mn}^{\beta}P_{nm'}^{\gamma}Q_{m'n}^{\delta}-\frac{Q_{nm}^{+\alpha}P_{mm'}^{\beta}P_{m'm''}^{\gamma}Q_{m''n}^{\delta}}{E_{m'n}}+\frac{2P_{nn'}^{\alpha}Q_{n'm}^{+\beta}P_{mm'}^{\gamma}Q_{m'n}^{\delta}}{E_{m'n'}}+\frac{P_{nn'}^{\alpha}Q_{n'm}^{+\beta}P_{mm'}^{\gamma}Q_{m'n}^{\delta}}{E_{mn}}\right]\\=&\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6+\chi_7+\chi_8\,.\end{aligned} \tag{4.2}$$

We note that we have the choice of evaluating these matrix elements by either directly using the Bloch functions, a procedure we have followed, or by making a unitary transformation to the local representation and by using the localized states obtained by us. We have used the Hall-Weaire approximation[1,3]; i.e., we have calculated only the matrix elements between hybrids at the same site and between hybrids of the same bond. Since the Hall-Weaire model yields a poor description of the conduction band, we have expressed the matrix elements of Eq. (4.2) in terms of valence-band functions by assuming the completeness relation

$$\sum_{m} |m\rangle\langle m| \cong \delta(\vec{r}-\vec{r}\,') - \sum_{n} |n\rangle\langle n| \ , \tag{4.3}$$

thereby neglecting the core states. In χ_6 and χ_7 since $E_{m'n}$ and $E_{m'n'}$ occur in the denominator, we sum over m states and in χ_8, since E_{mn} occurs in the denominator, we sum over m' states. We also use an average-energy-gap ansatz to evaluate χ_6, χ_7, and χ_8. Finally, we obtain

$$\chi_1+\chi_2+\chi_5=\chi_v^1+\chi_v^2 \ , \tag{4.4}$$

where

$$\chi_v^1=-\frac{4e^2}{mc^2}\sum_{\vec{k}} f_j[\langle x^2\rangle_1+\lambda^2\langle x^2\rangle_2+2\lambda\cos\vec{k}\cdot\vec{d}_j\langle x(x-d_x)\rangle_{12}] \ , \tag{4.5}$$

and

$$\begin{aligned}\chi_v^2=-\frac{4e^2}{mc^2}\sum_{\vec{k}}\{&\lambda A_j[\langle x^2-xy\rangle_1+\lambda^2\langle x^2-xy\rangle_2+2\lambda\cos\vec{k}\cdot\vec{d}_j\langle x(x-d_x-y+d_y)\rangle_{12}]\\&+[B_j(M_1-\lambda^2M_2)+C_j(P_1-\lambda^2P_2)]\} \ .\end{aligned} \tag{4.6}$$

In our approximation,

$$\chi_3+\chi_4=0 \ . \tag{4.7}$$

We also obtain

$$\chi_6+\chi_7+\chi_8=\chi_p^1+\chi_p^2 \ , \tag{4.8}$$

where

$$\chi_p^1=\frac{2e^2\hbar^2S^2}{m^2c^2E_g(1-S^2)}\sum_{\vec{k}}[(1+\lambda^2)^2-4\lambda^2\cos^2\vec{k}\cdot\vec{d}_{j'}]f_jf_{j'} \tag{4.9}$$

and

$$\begin{aligned}\chi_p^2=\frac{2e^2\hbar^2S}{m^2c^2E_g(1-S^2)}\sum_{\vec{k}}\Bigg\{&D_{jj'}+\Bigg[E_j\Bigg[2\langle x\rangle_{12}-\frac{Sd}{\sqrt{3}}\Bigg]+F_{jj'}(1-\lambda^2)-G_{jj'}(M_1-M_2)\\&+H_{jj'}(M_1-\lambda^2M_2)+J_{jj'}(P_1-\lambda^2P_2)\Bigg]\Bigg]\Bigg\} \ .\end{aligned} \tag{4.10}$$

Here j is chosen in the (111) direction, $j'\neq j$, and E_g is the average energy gap,

$$\langle 0\rangle_\alpha=\langle h_j^\alpha|0|h_j^\alpha\rangle \ ,$$

$$\langle 0\rangle_{12}=\langle h_j^1(\vec{r})|0|h_j^2(\vec{r}-\vec{d}_j)\rangle \ ,$$

$$M_\alpha=\langle s_\alpha|x|p_{x\alpha}\rangle \ ,$$

$$P_\alpha=\left\langle s_\alpha\left|\frac{d}{dx}\right|P_{x\alpha}\right\rangle \ ,$$

$$f_j=N|f_j^v(\vec{k})|^2 \ ,$$

A_j, B_j, C_j, $D_{jj'}$, E_j, $F_{jj'}$, $G_{jj'}$, $H_{jj'}$, and $J_{jj'}$ are functions of

$$\langle s_1|x^2|s_1\rangle+\lambda^2\langle s_2|x^2|s_2\rangle\ ,$$

$$\left\langle \frac{d}{dx}\right\rangle_{12}\ ,\ \left\langle (x-y)\frac{d}{dx}\right\rangle_{12}\ ,$$

and the above parameters.

We note that our χ_v^1 and χ_p^1 are the results which can be obtained by using our basis functions in the Langevin (χ_L) and Van Vleck (χ_p) terms of White.[18] χ_v^2 and χ_p^2 are new results obtained by us. We further note that the second group of terms in both χ_v^2 and χ_p^2 vanish for homopolar semiconductors (for which $\lambda=1$, $M_1=M_2$, $P_1=P_2$).

We shall now compare our results with the earlier results. We note that our expression for χ has been separated into Langevin-type susceptibility χ_v, which is the analog of the diamagnetic susceptibility of atoms (or hybrids) modulated by band effects, and Van Vleck—type susceptibility χ_p, which is the analogue of the Van Vleck susceptibility of molecules. Therefore, our χ qualitatively agrees with the HKF empirical results [their Eq. (3)]. Further, if we consider the extreme tight-binding case, our χ_v^1 agrees with the CWH results [their Eq. (6)] if we introduce their scaling parameters γ_m and with SW results [their Eq. (12)].

However, there is significant difference between our Van Vleck—type term (χ_p) and that of CWH and SW. We note that χ_p^1 and χ_p^2 are each proportional to S/E_g which decreases as the bonding decreases and becomes zero in the "no bonding" limit as it should since one does not expect Van Vleck—type susceptibility in such limit. In contrast, for homopolar semiconductors, the χ_p of both CWH and SW is quite large even when the overlap integral tends to zero, a result which is not physically satisfying.

An interesting point to note is that our expressions for χ_v and χ_p, which are free from any scaling parameters, are each independent of the choice of the local origin unlike the CWH results. We further note that the magnitudes of the diamagnetic terms ($\chi_v^1+\chi_v^2$), which are independent of E_g decrease slowly with increase of S. In contrast, the paramagnetic terms ($\chi_p^1+\chi_p^2$), which are inversely proportional to E_g, increase rapidly with increase of S. Therefore, χ becomes more diamagnetic when either S decreases or E_g increases. On the other hand, when λ increases, χ_v^1 slowly becomes more diamagnetic, χ_v^2 rapidly changes from diamagnetic to paramagnetic, χ_p^1 decreases, and χ_p^2 increases. It is therefore difficult to predict the variation of χ with λ.

Finally, we note that if we would calculate χ in a more realistic model than the Hall-Weaire approximation, we would have to consider matrix elements between the different hybrids, i.e., matrix elements between hybrids of one atom ($M_1,M_2,\ldots$), matrix elements between hybrids on adjacent atoms forming a bond ($N_1,N_2,\ldots$), matrix elements between hybrids on adjacent atoms not forming a bond ($P_1,P_2,\ldots$), and matrix elements between hybrids on further neighbors ($Q_1,Q_2,\ldots$). Only M and N are accounted for in the Hall-Weaire model. In general $N_i>Q_i>P_i$, a trend which is confirmed by the earlier calculations of matrix elements of the Hamiltonian.[19,37] Furthermore, N_i, Q_i, and P_i are all two-sited integral terms. In the Langevin-type terms [Eqs. (4.5) and (4.6)], the two-sited integrals are much smaller than the one-sited integrals. The major contribution to the Van Vleck—type terms [Eqs. (4.9) and (4.10)] are from terms which are proportional to the overlap integrals (S) but not to any other two-sited integrals. The two-sited integrals which we have neglected due to Hall-Weaire approximation would involve the overlap integrals between the hybrids not forming a bond, i.e., S_1, S_2, etc. We have calculated $S_1=0.093$ for Ge for P-type coupling while $S=0.662$. Thus the contribution to χ_p from these types of terms would be considerably reduced. In view of the above, we estimate the total error in making the Hall-Weaire approximation to be at most 10%.

V. RESULTS AND DISCUSSION

We have calculated the magnetic susceptibility of the homopolar semiconductors C, Si, and Ge and the III-V semiconductors BN, AlP, AlAs, GaP, and GaAs from our Eqs. (4.4) and (4.8). The Hartree-Fock atomic orbitals have been obtained from Clementi's table.[38] All the two-center integrals have been calculated with the use of the spheroidal coordinate transformation technique.[39] The integration over $\vec{k}$ was carried out over a sphere of volume equal to that of the Brillouin zone. The values of d, E_g f_c, and χ_c have been obtained[40,41] from Refs. 8, 15, and 25. In order to guard against rounding errors, the various one-sited and two-sited integrals and the summation over $\vec{k}$ were calculated in the computer using extended precision method. The various components of χ were calculated in one extended program with these results. In Table I we present our results of all the two-sited integrals. In Table II we present our results for the various components of χ and compare them with χ^{CWH} and the available experi-

TABLE I. Results of two-sited integrals used in χ.

Solid	S	L (A^{0-1})	$\langle x \rangle_{12}$ (A^0)	$\langle x(x-d_x) \rangle_{12}$ (A^{02})	$\langle x(y-d_y) \rangle_{12}$ (A^{02})	$\left\langle x\frac{d}{dx}\right\rangle_{12}$	$\left\langle x\frac{d}{dy}\right\rangle_{12}$
C	0.646	0.16	0.29	−0.02	−0.19	−0.249	
Si	0.67	0.15	0.454	−0.06	−0.42	−0.212	
Ge	0.662	0.15	0.465	−0.07	−0.44	−0.2	
BN	0.605	0.134	0.26	−0.025	−0.186	−0.17	0.062
AlP	0.63	0.113	0.408	−0.076	−0.415	−0.146	0.088
AlAs	0.641	0.113	0.436	−0.079	−0.447	−0.156	0.093
GaP	0.626	0.117	0.406	−0.093	−0.41	−0.147	0.087
GaAs	0.632	0.121	0.433	−0.085	−0.442	−0.151	0.097

mental results.

We note that our χ_v^1 is essentially equal to χ_L^{CWH} modulated by band effects. These effects increase the magnitude of the dominant $\langle h_j^1 | x^2 | h_j^1 \rangle$ term which is partially compensated by χ_v^2. Therefore, χ_L^{CWH} (scaled by γ_m) and our χ_v are nearly of the same magnitude for homopolar semiconductors. In fact, the two values are almost identical for Si, as they should, since CWH have obtained their "scaling parameter" γ_m in order to fit with the experimental results of Si. However, there is significant difference between χ_L^{CWH} and our χ_v for the III-V semiconductors.

The Van Vleck–type terms incorporate both the bonding effect (through S) and the band effect (through E_g) should provide a stringent test for any theory of χ. We note that our χ_p^1 is different from χ_p^{CWH}. However, χ_p^{CWH} and our χ_p are nearly equal for homopolar semiconductors although there is significant difference between them for III-V semiconductors. This agreement for homopolar semiconductors is not surprising since CWH have arbitrarily scaled a parameter λ, whose value varies from 0.52 to 0.71 to 1.13. Therefore, χ_p^{CWH}, which is proportional to λ^2, has been "scaled" by a factor between 300% to 400%. This scaling seems to compensate for the terms in χ_p missed by them as well as for the deficiencies in their bond-orbital model.

Finally, we note that there is good agreement between our results and the experimental results for all the semiconductors for which such results are available. It would be interesting to compare our predicted results for BN, AlP, and AlAs with experimental results, when available.

VI. SUMMARY AND CONCLUSION

The principal result of our work is the derivation of an expression for the magnetic susceptibility χ of tetrahedral semiconductors by using a basis set for the valence bands constructed from a linear combination of the hybrids forming a bond and a basis set for the conduction bands which are orthogonal to the valence-band basis functions. In the process we have also derived a general expression for χ of intrinsic semiconductors. We have

TABLE II. Magnetic susceptibility of tetrahedral semiconductors (χ in 10^{-6} cm^3/mole).

Solid	χ_c	χ_v^1	χ_v^2	χ_p^1	χ_p^2	χ_L^{CWH}	χ_p^{CWH}	χ_{tot} (present theory)	χ_{expt}[a]
C	−0.3	−19.2	1.7	4.4	3.5	−17.1	4.4	−9.9	−11.8
Si	−4.6	−42.9	3.5	14.0	22.5	−39.3	37.5	−7.5	−6.4
Ge	−14.0	−45.3	3.6	13.8	25.4	−42.7	38.5	−16.5	−15.7
BN	−0.3	−15.7	−3.6	6.8	4.0	−17.5	4.0	−8.8	
AlP	−4.8	−35.4	−12.0	22.9	10.3			−19.0	
AlAs	−11.2	−39.8	−11.6	24.3	13.2			−25.1	
GaP	−9.0	−34.7	−14.2	23.4	6.7	−39.6	23.7	−27.8	−30.0
GaAs	−14.0	−39.2	−14.3	24.4	8.0	−42.7	25.1	−35.1	−33.3

[a] Reference 13.

calculated the magnetic susceptibility of homopolar and III-V semiconductors and there is good agreement with experimental results.

It has been hitherto thought that the great virtue of Harrison's bond-orbital model[7,15] (BOM) is its simplicity and possibility of dealing with the problem analytically. In fact, the BOM has been used extensively for the calculation of the electric, magnetic, and optical properties of solids.[42] However, we have shown that the BOM in its present form is inadequate for calculation of χ of tetrahedral semiconductors mainly because the localized functions used as basis set in this model are not the proper choice for the Wannier functions of the valence band. We have also constructed Wannier functions from our Bloch functions for the valence bands. Our Wannier functions would be the appropriate choice for the localized basis set instead of the BOM. Recently we have formulated a theory for the electric susceptibility of tetrahedral semiconductors[43] by using these Wannier functions, and we have obtained good agreement with the experimental results.

ACKNOWLEDGMENTS

This research work was supported by the Council of Scientific and Industrial Research (India). We express our thanks to Dr. N. C. Mohapatra of our department for many helpful discussions.

---

[1] G. G. Hall, Philos. Mag. 43, 3381 (1952); 3, 429 (1958).

[2] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1960).

[3] D. Weaire and M. F. Thorpe, Phys. Rev. B 4, 2508 (1971).

[4] M. F. Thorpe and D. Weaire, Phys. Rev. Lett. 27, 1581 (1971).

[5] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[6] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York 1973).

[7] W. A. Harrison, Phys. Rev. B 8, 4487 (1973).

[8] W. A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1974).

[9] C. Huang, J. A. Moriarty, A. Sher, and R. A. Breckenridge, Phys. Rev. B 12, 5395 (1975).

[10] C. Huang, J. A. Moriarty, and A. Sher, Phys. Rev. B 14, 2539 (1976).

[11] S. J. Hudgens, Phys. Rev. B 7, 2481 (1973).

[12] H. Fritzsche and S. J. Hudgens, *Proceedings of the 6th International Conference on Amorphous and Liquid Semiconductors, Leningrad, 1975,* edited by B. T. Kolomiets (Nauka, Leningrad, 1976).

[13] S. Hudgens, M. Kastner, and H. Fritzsche, Phys. Rev. Lett. 33, 1552 (1974).

[14] V. P. Sukhatme and P. A. Wolff, Phys. Rev. Lett. 35, 1369 (1975).

[15] D. J. Chadi, R. M. White, and W. A. Harrison, Phys. Rev. Lett. 35, 1372 (1975).

[16] J. A. Pople, J. Chem. Phys. 37, 53 (1962); 37, 60 (1962).

[17] L. Salem, *Molecular Orbital Theory of Conjugated Systems* (Benjamin, Reading, Massachussetts, 1966).

[18] R. M. White, Phys. Rev. B 10, 3426 (1974).

[19] R. N. Nucho, J. G. Ramos, and P. A. Wolff, Phys. Rev. B 17, 1843 (1978); 17, 4835 (1978).

[20] K. Arya and S. S. Jha, Phys. Rev. B 20, 1611 (1979).

[21] E. I. Blount, Phys. Rev. 126, 1636 (1962).

[22] L. M. Roth, J. Phys. Chem. Solids 23, 433 (1962).

[23] J. E. Hebborn, J. M. Luttinger, E. H. Sondheimer, and P. J. Stiles, J. Phys. Chem. Solids 25, 741 (1964).

[24] P. K. Misra and L. Kleinman, Phys. Rev. B 5, 4581 (1972).

[25] R. M. Candea, S. J. Hudgens, and M. Kastner, Phys. Rev. B 18, 2733 (1978).

[26] A brief summary of the derivation has been published in T. Sahu and P. K. Misra, Phys. Lett. 85A, 165 (1981).

[27] J. M. Luttinger and J. C. Ward, Phys. Rev. 118, 1417 (1960).

[28] M. A. Philippas and J. W. McClure, Phys. Rev. B 6, 2051 (1972).

[29] N. C. Das and P. K. Misra, Solid State Commun. 22, 667 (1977).

[30] J. M. Luttinger and W. Kohn, Phys. Rev. 97, 869 (1955).

[31] S. P. Mohanty and P. K. Misra, Phys. Lett. 48A, 128 (1974).

[32] T. Sahu, Ph.D. thesis, Berhampur University, 1981 (unpublished).

[33] P. K. Misra and L. M. Roth, Phys. Rev. 177, 1089 (1969).

[34] C. A. Coulson, L. R. Redei, and D. Stocker, Proc. R. Soc. London 270, 357 (1962).

[35] The coefficient used in the bond-orbital model is $F_j=(1+\lambda^2+2\lambda S)^{-1/2}$, which is 0.547 for Si.

[36] P. K. Misra, Phys. Rev. B 2, 3906 (1970).

[37] K. C. Pandey and J. C. Phillips, Phys. Rev. B 13, 750 (1976); D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975).

[38] E. Clementi, *Table of Atomic Functions* (IBM, San Jose, California, 1965).

[39] J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

[40] C. A. Coulson, *Valence* (Oxford University Press, New York, 1972).

[41] Nucho *et al.* (Ref. 19) have shown that Coulson's ionicity (f_c) is identical, by definition, to Harrison's polarity (α_p).

[42] W. A. Harrison, *Electronic Structure and Properties of Solids—The Physics of the Chemical Bond* (Freeman, San Francisco, 1980).

[43] N. Panigrahi, T. Sahu, and P. K. Misra (unpublished).