Temperature dependence of the transition-metal magnetic susceptibilities

J. P. A. Charlesworth
Physics Department, Clark Hall, Cornell University, Ithaca, New York 14850

W. Yeung
Physics Department, Queen Mary and Westfield College, Mile End Road, London E1, England
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We present a method for calculating accurate Brillouin zone integrals of the Lindhard function at temperatures other than absolute zero. Within the linear tetrahedron method our expression is exact for the imaginary part and accurate to any arbitrary precision for the real part. We apply our method to calculate the temperature-dependent contribution to the bulk susceptibility for a range of transition metals as a function of temperature using linear muffin-tin orbital (LMTO) bands. For paramagnets our results follow the expected T^2 dependence. However our results for ferromagnets deviate qualitatively from the quadratic law. The different behavior is attributed to interband and matrix element effects. Our results for Fe exhibit two distinct behaviors. We discuss the implications for calculation of anomalies arising from spin fluctuations.

I. INTRODUCTION

With increasing understanding of the processes and physics of the ground state properties of condensed matter, experimenters are turning to excitation and correlation properties in their efforts to probe the physics of solid state materials. To the theorist the simplest quantities to calculate are the generalized susceptibilities χ^{+-} and the t matrix which deal with diagonal and off-diagonal long range orders, respectively. Although ground state calculations are now routinely performed within the local density approximation (LDA) in density functional theory (DFT), the correlation properties are a further level more complex and require parallel computing with supercomputers.[1,2] For the case of transition metals, the essential problems are the Brillouin zone sums and the treatment of the Fermi functions at finite temperatures.

In a recent paper[3] we presented a formulation of the tetrahedron method for calculating Lindhard sums at $T=0$. Using an analytic approach rather than the usual geometric interpretation, we obtained a general algebraic form for the integral which is much more compact and less complicated than the geometric approach and involves the minimum of calculation. With this form we were able to compute the enhanced dynamical susceptibilities $\chi^{+-}(\vec{q},\omega)$[1] using *ab initio* linear muffin-tin orbital (LMTO) band structures. Our calculational methods therefore now make it practicable to calculate from first principles a whole range of interesting physical properties dependent on Lindhard-like sums. For instance our recent calculations[2] show that, with LMTO band structures and the corresponding electron-hole interaction arising from the exchange and correlation potential, there is an optic branch for Fe but not for Ni in the spin wave spectra.

The stage is now set to compute from first principles physical quantities at finite temperatures. The importance of being able to calculate quantities at finite T cannot be overemphasized. For example the critical temperatures for magnetic and superconducting phase transitions are obtained from the divergence of the susceptibilities and the t matrix, respectively. For nearly and weakly ferromagnetic systems various authors[4–6] have discussed the specific heat anomalies due to spin fluctuations using the temperature dependence of χ derived from simple band structures. In addition, for magnetic systems the relative importance of collective (spin-wave) and single-particle (Stoner) excitations at nonzero temperatures is not well understood. The difficulty here arises because of a multitude of temperature behaviors the single-particle theories predict:[7,8] quadratic, T^2, for weak ferromagnets and paramagnets; exponential, $T^{3/2}\exp(-c/T)$, for strong ferromagnets; or fractional, $T^{3/2}$, for materials near the transition.

At finite temperatures, the geometric approach, which relies on a sharp Fermi cutoff in energy, is no longer applicable. Consequently there are few calculations done at $T \neq 0$. Indeed we know of no first principles susceptibility calculations done at finite temperatures. Our nongeometric approach, however, makes it generalizable to finite temperatures. In this paper we shall extend our work[9,3] on the linear-tetrahedron method to the case of a temperature-dependent Fermi function. To perform the tetrahedron integral we present an expansion of the Fermi function which is highly convergent for all energies in contrast with the very slowly convergent but commonly used Matsubara expansion. With our method we are able to calculate the dynamical susceptibilities $\chi^{+-}(\vec{q},\omega)$ at finite temperatures using first principles band structures. The approach we use is general and may be readily applied to a range of spectral functions beside the susceptibilities.

In this paper, as a test bed for our $T\neq 0$ formulas we shall also calculate T dependence of the bulk magnetic susceptibility of a number of transition metals and discuss the rela-

tive importance of the excitations. For metals at low temperatures a Sommerfeld expansion gives an αT^2 dependence for the temperature contribution of the bulk susceptibility. The coefficient α depends on the derivatives of the densities of states (DOS). For metals with narrow bands (e.g., transition metals) accurate determination of these derivatives is difficult and impractical due principally to the complexities arising from the range of possible inter- and intraband transitions. We shall investigate to what extent the quadratic behavior is valid and discuss the relationship between the T dependence and the structure of the DOS.

At this point, a brief discussion of the choice of materials we shall investigate is needed. Thermal effects in the susceptibility are likely to be most prominent when a flat band is coincident with the Fermi level. The Fermi level pinning position in transition metals may be considered to be one of two broad classes: The Fermi level is pinned at or near a maximum in the density of states; the Fermi level is pinned at a minimum in the DOS between two peaks. In the first of these the pinning position corresponds to the position of a very flat band and so the excitations are dominated by small energy (intraband) and small $\vec{q}$ transitions. These materials tend to be paramagnetic or ferromagnetic and exhibit a large susceptibility at $|\vec{q}|=0$ which asymptotically decreases with $|\vec{q}|$. When the Fermi level is pinned between peaks in the DOS, the susceptibility is dominated by larger energy (interband) and nonzero $\vec{q}$ transitions and the materials tend to be antiferromagnetic exhibiting a maximum in the susceptibility at $|\vec{q}|\neq 0$. The larger energies involved in the transitions result in an expected lesser dependence on temperature. For this reason, as well as the failure of LDA DFT to correctly obtain antiferromagnetic groundstates (see, e.g., Moruzzi and Marcus[10]), we will limit this investigation to paramagnetic and ferromagnetic materials.

In our investigation we will examine the fcc paramagnets Pd, Ag, and Cu and the ferromagnets bcc Fe and Mn as well as fcc Ni. Of particular interest among these is Ni. Examination of the magnetization of Ni at low temperatures has either been ambiguous[11] or has indicated that the Stoner excitations obey a T^2 law and so Ni is, contrary to de Haas–van Alphen experimental results,[12] in this respect a weak ferromagnet. For a more complete discussion of this problem see, for example, Mitchell and Paul.[13] The bcc Mn is chosen to allow an intermediate strength ferromagnet. Mn in the body-centered-cubic phase is predicted[14,15] to be ferromagnetic with a magnetic moment strongly dependent on the lattice parameter. In these calculations we use bcc Mn at the LMTO-DFT equilibrium spacing which results in a magnetic moment of $0.88\mu_B$.

II. FORMALISM

The general expression for the unenhanced transverse susceptibility may be written as a BZ integral

$$\chi^{+-}_{\vec{G},\vec{G}'}(\vec{q},\omega)=\frac{1}{N}\sum_{n,n'}\int_{\mathrm{BZ}} d^3k\left[\frac{f(\epsilon_{n'\vec{k}+\vec{q}})-f(\epsilon_{n\vec{k}})}{\epsilon_{n\vec{k}}-\epsilon_{n'\vec{k}+\vec{q}}+\omega+i0^+}\right]\langle n\vec{k}|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}\hat{s}_+|n'\vec{k}+\vec{q}\rangle\langle n'\vec{k}+\vec{q}|e^{+i(\vec{q}+\vec{G}')\cdot\vec{r}}\hat{s}_-|n\vec{k}\rangle, \tag{1}$$

where $\hat{s}_\pm$ are the spin ladder operators (whose action is simply to ensure that the n are associated with states of spin $\uparrow$ while the n' states are associated with spin $\downarrow$) and $f(\epsilon)$ is the Fermi function. In the future we will represent the product of the overlap matrices by $\mathscr{M}_{n,n'}(\vec{q};\vec{G},\vec{G}')$ for brevity.

The calculation of these *ab initio* matrix elements may be performed using eigenstates in a number of different representations. In our calculations we have used *ab initio* LMTO eigenstates evaluated within LDA DFT. The formalism for evaluating the overlap matrices, $\langle n\vec{k}\uparrow|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|n'\vec{k}+\vec{q}\downarrow\rangle$, using LMTO basis states has been presented by us before.[2] The Brillouin zone (BZ) integral is usually evaluated at $T=0$ K using the linear-tetrahedron method or the joint density of states (JDOS) method.[9] rahedron method, developed originally by Jepson and Andersen[16] and also Lehman and Taut[17] for calculating the density of states, the BZ is divided into a number of tetrahedra over which the eigenvalues are assumed to behave linearly and so are a simple function of the values at the vertices. For a sufficiently fine $\vec{k}$-point mesh[18] we may then make the approximation

$$\chi^{+-}_{\vec{G},\vec{G}'}(\vec{q},\omega)=-\frac{1}{N}\sum_{n,n'}\overline{\mathscr{M}}_{n,n'}(\vec{q};\vec{G},\vec{G}')\times\sum_t\int_t\frac{f(\epsilon_{n\vec{k}})-f(\epsilon_{n'\vec{k}+\vec{q}})}{\epsilon_{n\vec{k}}-\epsilon_{n'\vec{k}+\vec{q}}+\omega+i0^+}d^3k, \tag{2}$$

where t labels the individual tetrahedra comprising the BZ and $\overline{\mathscr{M}}_{n,n'}(\vec{q};\vec{G},\vec{G}')$ is the average of the matrix element over the tetrahedron.

At $T=0$ K this integral over the Lindhard term has been considered before using a geometric analysis by Rath and Freeman[19] and also by Lindgard.[20] Within their treatments the partial integral of a single Fermi function (taken to be a step function) is examined geometrically and the tetrahedron further subdivided into a number of smaller tetrahedra, all of which are fully occupied. The integral over the denominator in Eq. (2) is then performed analytically and the partial sums

added to give the integral for the entire original tetrahedron. The manner in which the Fermi surface cuts the original tetrahedron defines the number of smaller tetrahedra produced in this method, giving a maximum of three terms. For other topologies this approach becomes increasingly complex. The intersection of the Fermi surface with, e.g., a cubic microzone can be a still larger range of polygons up to a hexagon and consequently the approach is usually limited to tetrahedra.

The major drawback of the geometric approach for thermal excitations is its reliance on the Fermi function being a step function and cannot be extended to nonzero temperatures as the smooth Fermi function at $T\neq 0$ results in no unique method of defining occupied or unoccupied regions. In a recent work we have presented an alternative approach to the $T=0$ K tetrahedron method in which the integral is performed algebraically by converting the integrand into a sum over exponentials. For a step function, the algebraic approach proves a much more useful method, being less cumbersome, faster, and permitting a wider range of topologies. For nonzero temperature, we show here how the method may be extended to allow us to perform algebraic integration of the integrand.

We will consider the most general partial integral in Eq. (2) which we may write in a vector form as

$$I=\int_{\text{tet}} \frac{f(c_0+\vec{d}_0\cdot\vec{k})}{a_0+\vec{b}_0\cdot\vec{k}}d^3k. \tag{3}$$

The values of a_0, $\vec{b}_0$, c_0, and $\vec{d}_0$ are defined by the energies at the vertices of the tetrahedron. For brevity, we will consider a dimensionless Fermi function and hence treat the $1/k_BT$ coefficient as being subsumed within the c_0 and $\vec{d}_0$ values. The linearity of the functions with $\vec{k}$ means we may affine transform the tetrahedron to a unit right-handed tetrahedron

$$I=\Omega\int_{r_1=0}^{+1}\int_{r_2=0}^{1-r_1}\int_{r_3=0}^{1-r_1-r_2}\frac{f(c+\vec{d}\cdot\vec{r})}{a+\vec{b}\cdot\vec{r}}d^3r, \tag{4}$$

where $\Omega=\vec{k}_1\cdot(\vec{k}_2\times\vec{k}_3)$, $\{\vec{k}_i\}$ are the vector edges of the original tetrahedron and a, $\vec{b}$, c and $\vec{d}$ are defined to reproduce the energies at the vertices of the tetrahedron.

The Fermi function here must be written in a tractable form. A number of forms has been given for $f(\epsilon)$, e.g., Goedecker[21] and the Sommerfeld expansion,[22] of which, perhaps, the most commonly used is the Matsubara representation.[23] This form expands $f(\epsilon)$ as a sum over the poles of the function and although straightforward is very slowly convergent when $|\epsilon|\gg k_BT$. In our algebraic approach[3] to the $T=0$ K integral we convert the integrand to an integral over exponential functions and so here, following our previous work, we choose such a representation for the nonzero T Fermi function and write

$$f(x)=\frac{1}{1+e^x}\simeq\Theta(x)+\sum_{s=-}^{+} sf_N(sx)\Theta(-sx), \tag{5}$$

where $\Theta(x)$ is a step function defined to be 1 if $x<0$ and 0 otherwise and $f_N(x)$ is our approximation to the Fermi function defined for positive x in the Appendix to be a sum over exponentials.

We may thus write I in (4) as the sum of two parts I_1 and I_2,

$$I_1=\Omega\int_{r_1=0}^{+1}\int_{r_2=0}^{1-r_1}\int_{r_3=0}^{1-r_1-r_2}\frac{\Theta(c+\vec{d}\cdot\vec{r})}{a+\vec{b}\cdot\vec{r}}d^3r,$$

$$I_2=\Omega\sum_{s=-}^{+} s\int_{r1=0}^{+1}\int_{r_2=0}^{1-r_1}\int_{r_3=0}^{1-r_1-r_2}\times\frac{f_N(s(c+\vec{d}\cdot\vec{r}))\Theta(-s(c+\vec{d}\cdot\vec{r}))}{a+\vec{b}\cdot\vec{r}}d^3r. \tag{6}$$

The first of these, I_1, is simply the $T=0$ K form of the linear-tetrahedron integral and has been performed algebraically by the authors.[3] It reduces to

$$\begin{aligned}I_1=&\frac{\Omega\zeta}{2}\sum_{tuv}\epsilon_{tuv}\frac{b_u}{b_t}(a+b_t)^2[\Theta(c)\ln(|a|)-\Theta(c+d_t)\ln|a+b_t|]\\&-\frac{\Omega\nu}{2d_1d_2d_3}\sum_{tuv}\epsilon_{tuv}\frac{d_t}{b_t}\frac{b_u}{d_u}[\Theta(c)-\Theta(c+d_t)]\left(a-c\frac{b_t}{d_t}\right)^2\ln\left|a-c\frac{b_t}{d_t}\right|\\&+\frac{\Omega\xi}{2}\sum_{tuv}\epsilon_{tuv}\frac{1}{\mu_u}\frac{\Theta(c+d_t)}{d_t\mu_u-b_t}\left(\frac{d_u-d_v}{\mu_u-\mu_v}\right)[a+b_t-\mu_u(c+d_t)]^2\ln|a+b_t-\mu_u(c+d_t)|,\end{aligned} \tag{7}$$

where ϵ_{tuv} is the permutation tensor whose indices run from 1 to 3 and $\mu_i=(\Sigma_{jk}\epsilon_{ijk}b_j)/(\Sigma_{jk}\epsilon_{ijk}d_j)$. The constant prefactors are $1/\zeta=(b_1-b_2)(b_2-b_3)(b_3-b_1)$, $1/\xi=(d_1-d_2)(d_2-d_3)(d_3-d_1)$, and $1/\nu=(b_1/d_1-b_2/d_2)(b_2/d_2-b_3/d_3)$ $1/\nu=(b_1/d_1-b_2/d_2)(b_2/d_2-b_3/d_3)(b_3/d_3-b_1/d_1)$.

The second term may now be tackled by replacing all the functions by their exponential forms:

$$\Theta(x)=-\frac{i}{2\pi}\int_{p=-\infty}^{+\infty}\frac{e^{-ipx}}{p-i\delta_1}dp,$$

$$\frac{1}{x}=-\frac{i}{2}\sum_{z=-}^{+} z\int_{\lambda=0}^{+\infty}e^{\lambda(izx-\delta_2)}d\lambda,$$

$$f_N(x)=\sum_{n=1}^{N}\alpha_n e^{-nx}, \tag{8}$$

where the limit of $\delta_1\to 0$ and $\delta_2\to 0$ is implied throughout. Using these in I_2 gives us

$$I_2=-\frac{\Omega}{4\pi}\sum_{s=-}^{+}s\sum_{z=-}^{+}z\sum_{n=1}^{N}\alpha_n e^{-snc}\int_{\lambda=0}^{+\infty}e^{iz\lambda a-\lambda\delta_2}\int_{\eta=-\infty}^{+\infty}\frac{e^{isc\eta}}{\eta-i\delta_1}\mathscr{V}(iz\lambda\vec{b}+(is\eta-ns)\vec{d})d\eta d\lambda, \tag{9}$$

where $\mathscr{V}(\vec{x})$ is as defined below. The importance of the exponential form of the spatial integrand in this approach is that such an integral is readily performed using the identity

$$\mathscr{V}(\vec{v})=\int_{r_1=0}^{+1}\int_{r_2=0}^{1-r_1}\int_{r_3=0}^{1-r_1-r_2}e^{\vec{v}\cdot\vec{r}}d^3r=\frac{1}{(v_1-v_2)(v_2-v_3)(v_3-v_1)}\sum_{tuv}\epsilon_{tuv}\frac{v_u}{v_t}(1-e^{v_t}), \tag{10}$$

thus giving us

$$I_2=-\frac{i\xi\Omega}{4\pi}\sum_{s=-}^{+}\sum_{z=-}^{+}z\sum_{n=1}^{N}\alpha_n e^{-nsc}\sum_{tuv}\epsilon_{tuv}\frac{d_u}{d_t}\int_{\lambda=0}^{+\infty}e^{iza\lambda-\delta_2\lambda}I_\eta(s,z,n;\lambda)d\lambda,$$

$$I_\eta(s,z,n;\lambda)=\int_{\eta=-\infty}^{+\infty}\frac{e^{isc\eta}-e^{is(c+d_t)\eta+izb_t\lambda-nsd_t}}{(\eta-i\delta_1)\Pi_j(\eta+in+sz\lambda\mu_j)}\left(\frac{\eta+in+sz\lambda(b_u/d_u)}{\eta+in+sz\lambda(b_t/d_t)}\right)d\eta. \tag{11}$$

The evaluation of I_η is now performed by summing the poles in the upper or lower half-plane, giving us $I_2=I_2^{(1)}+I_2^{(2)}+I_3^{(3)}$, where

$$I_2^{(1)}=\frac{\xi}{2\mu_1\mu_2\mu_3}\sum_{s=-}^{+}s\sum_{z=-}^{+}\sum_{n=1}^{N}\alpha_n\sum_{tuv}\epsilon_{tuv}\frac{b_u}{b_t}\int_{\lambda=0}^{+\infty}\frac{1}{\Pi_j(\lambda+iszn/\mu_j)}\left(\frac{\lambda+iszn(d_u/b_u)}{\lambda+iszn(d_t/b_t)}\right)$$

$$\times[\Theta(-sc)e^{-nsc+iza\lambda}-\Theta(-s(c+d_t))e^{-ns(c+d_t)+iz\lambda(a+b_t)}]d\lambda, \tag{12}$$

$$I_2^{(2)}=\frac{\xi}{2}\sum_{s=-}^{+}s\sum_{z=-}^{+}\sum_{n=1}^{N}\alpha_n\sum_{tuv}\epsilon_{tuv}\frac{(b_u/b_t-d_u/d_t)}{\Pi_j(\mu_j-b_t/d_t)}[\Theta(sc)-\Theta(s(c+d_t))]\int_{\lambda=0}^{+\infty}\frac{1}{\lambda^2}\frac{e^{iz\lambda(a-cb_t/d_t)}}{\lambda+insz(d_t/b_t)}d\lambda, \tag{13}$$

and

$$I_2^{(3)}=-\frac{\xi\phi}{2}\sum_{s=-}^{+}s\sum_{z=-}^{+}\sum_{n=1}^{N}\alpha_n\sum_{tuv}\epsilon_{tuv}\sum_{pqr}\epsilon_{pqr}\frac{\mu_q}{\mu_p}\left(\frac{b_u-d_u\mu_p}{b_t-d_t\mu_p}\right)\int_{\lambda=0}^{+\infty}\frac{1}{\lambda^2}\frac{1}{\lambda+iszn/\mu_p}$$

$$\times[\Theta(sc)e^{iz\lambda(a-c\mu_p)}-\Theta(s(c+d_t))e^{iz\lambda(a+b_t-(c+d_t)\mu_p)}]d\lambda. \tag{14}$$

The λ integrals in these terms may be recognized as a number of exponential integral functions and the final forms are obtained by taking the limit as the lower range of the integral goes to zero. This leads us, after some rearrangement (see Appendixes B and C in Charlesworth and Yeung[3]), to the result $I_2=\Delta_1+\Delta_2$ where

$$\Delta_1=\xi\sum_{tuv}\frac{\epsilon_{tuv}\mu_u}{b_t-d_t\mu_u}\left(\frac{d_u-d_v}{\mu_u-\mu_v}\right)\mathrm{sgn}(c+d_t)\sum_{n=1}^{N}\frac{\alpha_n}{n^2}\Bigg[\ln|a+b_t-\mu_u(c+d_t)|$$
$$+e^{-n|c+d_t|}\mathscr{F}(-n\mathrm{sgn}(c+d_t)(a+b_t)/\mu_u)-\mathscr{F}\left(n\mathrm{sgn}(c+d_t)\left(\frac{1}{\mu_u}(a+b_t)-(c+d_t)\right)\right)\Bigg], \tag{15}$$

$$\Delta_2=\nu\frac{b_1b_2b_3}{d_1^2d_2^2d_3^2}\sum_{tuv}\epsilon_{tuv}\frac{d_u}{b_u}\sum_{n=1}^{N}\frac{\alpha_n}{n^2}\Bigg\{\mathrm{sgn}(c)\Bigg[\mathscr{F}\left(n\mathrm{sgn}(c)\left(a\frac{d_t}{b_t}-c\right)\right)-\ln\left|a-c\frac{b_t}{d_t}\right|$$
$$-e^{-n|c|}\mathscr{F}\left(-n\mathrm{sgn}(c)a\frac{d_t}{b_t}\right)\Bigg]-\mathrm{sgn}(c+d_t)\Bigg[\mathscr{F}\left(n\mathrm{sgn}(c+d_t)\left(a\frac{d_t}{b_t}-c\right)\right)$$
$$-e^{-n|c+d_t|}\mathscr{F}\left(-n\mathrm{sgn}(c+d_t)(a+b_t)\frac{d_t}{b_t}\right)-\ln\left|a-c\frac{b_t}{d_t}\right|\Bigg]\Bigg\}, \tag{16}$$

and $\mathscr{F}(x)=e^{-x}\mathrm{Ei}(x)$. We may finally rewrite this in a more compact form by noting that were we to have represented f_N by an infinite sum, then we would have a simple Taylor series for which $\alpha_n=(-1)^{n+1}$. The simple summation terms in Δ_1 and Δ_2 may thus be evaluated to give us

$$\Delta_1=\xi\sum_{tuv}\frac{\epsilon_{tuv}\mu_u}{b_t-d_t\mu_u}\left(\frac{d_u-d_v}{\mu_u-\mu_v}\right)\mathrm{sgn}(c+d_t)\Bigg\{\frac{\pi^2}{12}\ln|a+b_t-\mu_u(c+d_t)|+\sum_{n=1}^{N}\frac{\alpha_n}{n^2}$$
$$\times\Bigg[e^{-n|c+d_t|}\mathscr{F}(-n\mathrm{sgn}(c+d_t)(a+b_t)/\mu_u)-\mathscr{F}\left(n\mathrm{sgn}(c+d_t)\left(\frac{1}{\mu_u}(a+b_t)-(c+d_t)\right)\right)\Bigg]\Bigg\} \tag{17}$$

and

$$\Delta_2=\nu\frac{b_1b_2b_3}{d_1^2d_2^2d_3^2}\sum_{tuv}\epsilon_{tuv}\frac{d_u}{b_u}\Bigg(\frac{\pi^2}{12}[\mathrm{sgn}(c+d_t)-\mathrm{sgn}(c)]\ln\left|a-c\frac{b_t}{d_t}\right|+\sum_{n=1}^{N}\frac{\alpha_n}{n^2}$$
$$\times\Bigg\{\mathrm{sgn}(c)\Bigg[\mathscr{F}\left(n\mathrm{sgn}(c)\left(a\frac{d_t}{b_t}-c\right)\right)-e^{-n|c|}\mathscr{F}\left(-n\mathrm{sgn}(c)a\frac{d_t}{b_t}\right)\Bigg]-\mathrm{sgn}(c+d_t)$$
$$\times\Bigg[\mathscr{F}\left(n\mathrm{sgn}(c+d_t)\left(a\frac{d_t}{b_t}-c\right)\right)-e^{-n|c+d_t|}\mathscr{F}\left(-n\mathrm{sgn}(c+d_t)(a+b_t)\frac{d_t}{b_t}\right)\Bigg]\Bigg\}\Bigg). \tag{18}$$

It may be noted that the denominator $\mu_u-\mu_v$ does not pose a problem in Δ_1 as the permutation tensor does not permit $u=v$.

The corresponding imaginary part of the BZ of the Lindhard function, which is important for excited state lifetimes when $\omega\neq0$, may be readily deduced in the same manner. The general form of

$$\mathrm{Im}\left[\int_{\mathrm{tet}}\frac{f(\epsilon_{n\vec{k}})-f(\epsilon_{n'\vec{k}+\vec{q}})}{\epsilon_{n\vec{k}}-\epsilon_{n'\vec{k}+\vec{q}}+\omega+i0^+}d^3k\right] \tag{19}$$

may be written as

$$I=\int_{\mathrm{tet}}f(c_0+\vec{d}_0\cdot\vec{k})\,\delta(a_0+\vec{b}_0\cdot\vec{k})\,d^3k. \tag{20}$$

Replacing f in (20) with the form given in (5) and transforming the tetrahedron to a right-handed orthonormal basis, we may once more consider I to be made of two parts: I_1, the term involving the step function and essentially evaluated at $T=0$ K; the integral over the remaining correction to the Fermi function, I_2. The δ function may be written in an integral representation remarkably similar to that of the $1/x$ form in (8),

$$\delta(x)=\frac{1}{2\pi}\sum_{z=-}^{+}\int_{\lambda=0}^{+\infty}e^{\lambda(izx-\delta_2)}d\lambda, \tag{21}$$

and so little extra work need be performed. The equations for the imaginary part differ from those in (12) and (13) by simply a factor of iz/π and this requires just a different approach to the λ integrals.

As before, the integral for the $T=0$ K step function has been performed before[24] to give us

$$I_1=\frac{\xi}{4\mu_1\mu_2\mu_3}\sum_{tuv}\ \epsilon_{tuv}\frac{b_u}{b_t}[a^2\Theta(c)\mathrm{sgn}(a)-(a+b_t)^2\Theta(c+d_t)\mathrm{sgn}(a+b_t)]$$

$$-\frac{\xi}{4}\sum_{tuv}\ \frac{\epsilon_{tuv}\mu_v\mu_t/\mu_u}{b_t-\mu_u d_t}\left(\frac{d_u-d_v}{\mu_u-\mu_v}\right)\Theta(c+d_t)[a+b_t-\mu_u(c+d_t)]^2\mathrm{sgn}[a+b_t-\mu_u(c+d_t)]$$

$$-\frac{\nu}{4d_1d_2d_3}\sum_{tuv}\ \epsilon_{tuv}\frac{d_t}{b_t}\frac{b_u}{d_u}[\Theta(c)-\Theta(c+d_t)]\left(a-c\frac{b_t}{d_t}\right)^2\mathrm{sgn}\left(a-c\frac{b_t}{d_t}\right). \tag{22}$$

For the $T\neq 0$ K case, most of the derivation is similar to that of the real part and results in an *exact* result, I_2, comprising two parts $I_2=\Delta_1+\Delta_2$ with

$$\Delta_1=\frac{\nu b_1b_2b_3}{2d_1^2d_2^2d_3^2}\sum_{tuv}\ \epsilon_{tuv}\frac{d_u}{b_u}\left(\frac{\pi^2}{12}\mathrm{sgn}\left(a-c\frac{b_t}{d_t}\right)[\mathrm{sgn}(c+d_t)-\mathrm{sgn}(c)]\right.$$

$$\left.+2\mathrm{Li}_2(-e^{-|a\,(d_t/b_t)\,-c|})\left\{\mathrm{sgn}(c)\left[\Theta\left(a-c\frac{b_t}{d_t}\right)-\Theta(a)\right]+\mathrm{sgn}(c+d_t)\left[\Theta(a+b_t)-\Theta\left(a-c\frac{b_t}{d_t}\right)\right]\right\}\right) \tag{23}$$

and

$$\Delta_2=\frac{\xi}{2}\sum_{tuv}\ \frac{\epsilon_{tuv}\mu_u}{b_t-d_t\mu_u}\left(\frac{d_u-d_v}{\mu_u-\mu_v}\right)\mathrm{sgn}(c+d_t)\left[\frac{\pi^2}{12}\mathrm{sgn}[a+b_t-\mu_u(c+d_t)]\right.$$

$$\left.+2\mathrm{Li}_2(-e^{-|(a+b_t)/\mu_u-(c+d_t)|})[\Theta(a+b_t)-\Theta(a+b_t-\mu_u(c+d_t))-\mathrm{sgn}(\mu_u)\mathrm{sgn}(c+d_t)]\right], \tag{24}$$

where $\mathrm{Li}_2(x)$ is the second-order polylogarithm. The imaginary case, being a simpler integrand than that of the real one, is exact within the linear scheme of the tetrahedron approach. The nonzero temperature Fermi function is treated exactly and no series expansion is necessary as the Taylor series terms are resummable into polylogarithms.

Although in the calculations presented here we have concentrated on the real part of the integral, it has become customary in $T=0$ K susceptibility calculations to evaluate the simpler imaginary term and derive the real term through the Kramers-Kronig relationship. The exact result presented in (23) and (24) allows this method to be readily extended to nonzero temperatures.

We may note at this stage that for the temperature range which interests us (i.e., below a few hundred kelvin) the inclusion of the $1/k_BT$ term within c and $\vec{d}$ can lead to some numerical instability in the calculation due to the greatly differing magnitudes of, e.g., b_t/d_t and d_t/b_t. To avoid such an instability, we found it more prudent to observe that we could equally have incorporated the thermal energy scale in the n terms and consequently we may see that should we consider the c and $\vec{d}$ terms to give the energies at the tetrahedron vertices, then the temperature may be included in (17) and (18) and (23) and (24) by multiplying the Δ terms by $(k_BT)^2$ and replacing the n terms in the exponentials and $\mathscr{F}_0(nx)$ terms (but *not* the $1/n^2$ term) by n/k_BT.

For very low temperatures we were able to further simplify (17) and (18) by replacing $\mathscr{F}_0(x)$ with the first few terms of the asymptotic limit

$$\lim_{x\to\pm\infty}\mathscr{F}_0(x)\to\sum_{m=1}^{+\infty}\frac{(m-1)!}{x^m}\simeq\frac{1}{x}+\frac{1}{x^2}+\frac{2}{x^3}+\cdots. \tag{25}$$

These two corrections for nonzero temperatures, (17) and (18) and (23) and (24), in conjunction with the zero-temperature results, (7) and (22), give us a method to evaluate exactly the BZ integral at any temperature. In the case of the real integral, the accuracy is limited only by the size of the expansion used to represent the Fermi function which is shown in the Appendix to have exceedingly rapid convergence. For the imaginary case, even this limitation is not present and the integrals are exact.

The generality of this approach must be stressed. The integrals evaluated, (3) and (20), are due to the Green's function derivation of most excitation properties, a constituent of most excitation processes. Our results may be readily applied to, e.g., the superconductivity t matrix as well as the magnetic multilayer interaction function.

III. RESULTS AND DISCUSSION

As previously mentioned in the Introduction the formulas derived in the preceding section may be used to calculate the dynamical susceptibilities $\chi(\vec{q},\omega)$. For brevity and to communicate our results quickly, however, we shall only present here our calculations on the unenhanced bulk susceptibility for a number of transition metals. The parameters $\vec{G}$, $\vec{G}'$, $\vec{q}$, and ω are therefore all zero. In this particular case the overlap matrix element simplifies to $\langle n\vec{k}\uparrow|n'\vec{k}\downarrow\rangle$. For a paramagnet the up and down wave functions are the same and the overlap matrices are therefore diagonal in the band indices n and n' and the (unenhanced) bulk susceptibility is related to the density of states. Indeed using a Sommerfeld expansion one obtains for the temperature contribution[26]

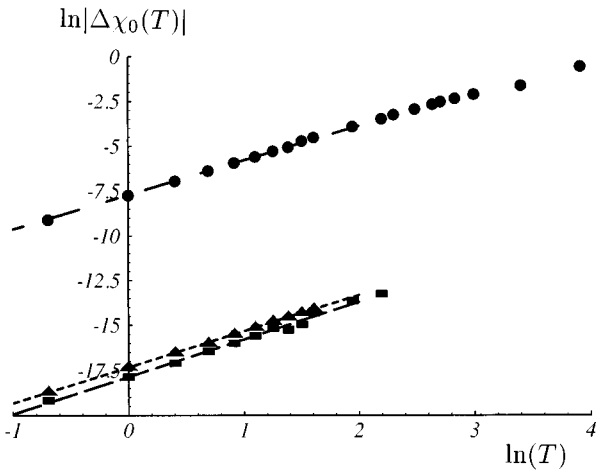

FIG. 1. Plot of $\ln(\Delta\chi^{+-})$ against $\ln(T)$ for the paramagnetic materials Pd (circles), Ag (triangles), and Cu (rectangles). The lines are aids to the eye showing the best linear fit.

$$\frac{\Delta\chi^{+-}(T)}{T^2}=\frac{\pi^2}{12}k_B^2\eta(\mu)\left.\frac{\partial^2\ln\eta(\epsilon)}{\partial\epsilon^2}\right|_{\epsilon=\mu}+\mathcal{O}(T^2), \quad (26)$$

where $\eta(\epsilon)$ is the density of states for a particular spin (half the total density of states).

The results for the paramagnets Pd, Ag, and Cu are given in Fig. 1. All calculations have been performed with the LMTO formalism using 19 683 $\vec{k}$ points in the BZ and were converged to rms errors in the charge density of less than 1 part in 10^8 to ensure full convergence. The formalism for such susceptibility calculations has been published before.[2] The lattice parameters used were 7.351, 7.729, and 6.822 a.u. for Pd, Ag, and Cu, respectively. The procedure we employed in our calculations was to use a converged LMTO band structure and Fermi level calculated at $T=0$ K and to evaluate the thermal deviation of the susceptibility assuming a fixed Fermi level. For comparison with the usual ussumed Sommerfeld result, (26), we have neglected the temperature dependence of the chemical potential. In principle this effect may be included by using our formulas (17) and (18), with a constant denominator in the self-consistent calculation of the DOS. However, we may observe that for materials such as Ag and Cu, the flat DOS results in a negligible dependence on μ and for Fe and Ni the high DOS near μ results in only a weak effect.

It is seen in Fig. 1 that the temperature contributions to the paramagnetic susceptibility obey the quadratic power law

TABLE I. The temperature parameter of paramagnetic and ferromagnetic materials. The susceptibilities are in units of μ_B/Ry and the temperatures are in units of K.

Metal	$\chi^{+-}(T=0)$	T_F^2
Ag	1.734	$-5.691\times10^{+7}$
Cu	2.017	$8.763\times10^{+7}$
Pd	16.198	$1.086\times10^{+5}$
Fe	14.550	N/A
Ni	13.433	$5.571\times10^{+6}$
Mn	13.204	$1.228\times10^{+7}$

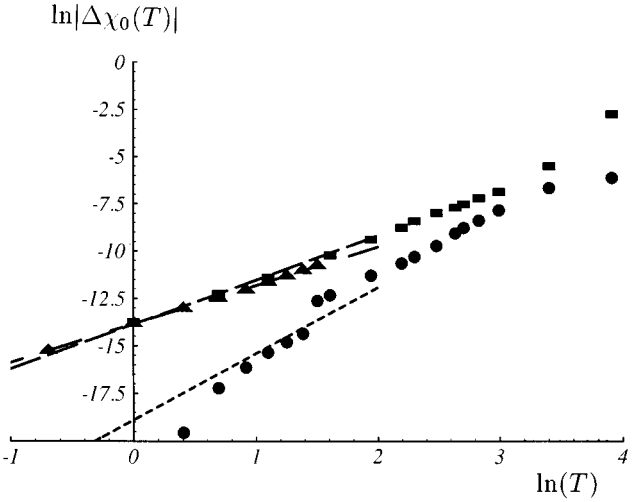

FIG. 2. Plot of $\ln(\Delta\chi^{+-})$ against $\ln(T)$ for the ferromagnetic materials Fe (circles), Mn (triangles), and Ni (rectangles). The lines are aids to the eye showing the best linear fit. That for Fe is for the entire range. At larger T the gradient becomes 3.

quite well. Fitting the data obtained to the formula $\chi^{+-}(T)=\chi^{+-}(0)(1-T^2/T_F^2)$, we obtain the T_F parameters given in Table I. We note the difference between Pd and Ag which have positive and negative coefficients T_F^2 coming from the differing signs of the logarithmic derivatives of the DOS at the Fermi energy.

For a ferromagnet the $|n\vec{k}\downarrow\rangle$ and $|n\vec{k}\uparrow\rangle$ wave functions in the overlap matrix elements, $\langle n\vec{k}\uparrow|n'\vec{k}\downarrow\rangle$, are different. This has essentially two effects: first, the off-diagonal elements for $n\neq n'$ no longer vanish and we have therefore interband effects. Second, these overlap matrix elements have a $\vec{k}$ and hence an energy dependence which profoundly modifies the temperature dependence. Therefore the bulk susceptibility is no longer simply related to the DOS and we can no longer expect a T^2 dependence. We compute the thermal contributions for χ for the ferromagnets Fe, Ni, and Mn. The lattice parameters used were 5.4057, 6.6520, and 5.2824, a.u., respectively. For the case of Mn, the lattice parameter was taken to be the equilibrium lattice spacing of the bcc structure as calculated by LMTO-DFT calculations. The magnetic moments of Fe, Mn and Ni were calculated to be $2.299\mu_B$/atom, $0.8855\mu_B$/atom, and $0.606\mu_B$/atom, respectively. The susceptibility calculations were performed using nonrelativistic LMTO theory; scalar relativistic LMTO theory typically changes the magnetic moment of ferromagnetic materials by $\sim$ 1–2%.

The temperature dependence of χ^{+-} for the ferromagnets is given in Fig. 2. The best fit gives temperature power laws of $T^{2.03}$ for Mn, $T^{2.34}$ for Ni. It is evident that the temperature dependences of these materials are completely different to that found for paramagnets. For Fe at low temperatures we could not fit its susceptibility to a single power law although at large T the susceptibility varies most closely to T^3.

If we ignore the overlap matrix elements, the Lindhard sum may be thought to be over two bands separated by an energy gap related to the magnetization. In this case we would expect an exponential type of temperature dependence. However, our results do not appear to fit easily to an

TABLE II. Comparison of the errors in the Matsubara and Taylor expansions of the Fermi function with our fitted form for a range of energies. All series consist of 15 terms. The relative percentage error is given and is defined to be $100\times|f_s(x)-f(x)|/f(x)$ where $f_s(x)$ is the series representation of the Fermi function, $f(x)$.

ϵ/k_BT	Matsubara	Taylor	Fitted
0	0.00×10^{0}	$1.00\times10^{+2}$	0.00×10^{0}
10^{-5}	4.47×10^{-4}	$9.99\times10^{+1}$	6.66×10^{-14}
10^{-3}	4.47×10^{-2}	$9.85\times10^{+1}$	4.63×10^{-12}
10^{-1}	4.70×10^{0}	$2.23\times10^{+1}$	6.22×10^{-13}
10^{0}	$8.28\times10^{+1}$	3.06×10^{-4}	8.85×10^{-10}
10^{+1}	$3.96\times10^{+6}$	2.22×10^{-14}	3.74×10^{-11}
10^{+2}	$7.32\times10^{+45}$	3.72×10^{-44}	2.23×10^{-37}

exponential form. This implies that the matrix elements have a profound influence[25] on the susceptibility even in the bulk case.

IV. SUMMARY

We have demonstrated in this paper how it is possible to perform accurate *ab initio* calculations of temperature-dependent correlation functions. This allows a number of problems to be addressed which have been, up until now, beyond the grasp of *ab initio* calculations. The method we have detailed here for performing the BZ integral of the Lindhard function is exact (within the linear tetrahedron method) for the imaginary part and accurate to any arbitrary precision for the real part.

Our susceptibility results suggest reasons for the difficulty solving the ''hidden excitation problem.'' The temperature dependence of the susceptibilities does not always fit the simple models of the Stoner excitations. For paramagnetic materials (which may be considered to be an infinitely weak ferromagnet), the temperature dependence of the Stoner excitations follows the T^2 dependence expected. But as the moment increases the deviation from the simple temperature dependence increases. For Ni, the dependence goes as $\sim T^{2.3}$ and for Fe the temperature dependence is much more involved. The latter has different behaviors for low and high temperatures with a distinct break at a certain temperature. The deviation from T^2 behavior is attributable to (1) an interband effect and (2) matrix element effects. Specific heat anomalies have been discussed in weak ferromagnets using temperature dependences of χ based on simple bands with no matrix elements. In light of our calculations in the previous section we believe that the temperature dependences would be rather different with more realistic bands. We propose that new calculations should be made using our method which is valid for all temperatures. It is well known that even a first principles band theory like LMTO theory does not give the correct critical temperature for itinerant magnets. This is usually attributed to the neglect of fluctuations. By using the coupling constant integration method one can write the free energy as an integral involving a susceptibilitylike type of correlation function (see, e.g., Moriya[26]). With this energy which includes the spin fluctuations Moriya was able to get a better value for the critical temperature. Since the latter based his calculations on a single band, we would expect to be able to do better with susceptibilities calculated with proper bands.

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APPENDIX: FERMI FUNCTION EXPANSION

The usual form of the dimensionless Fermi function,

$$f(x)=\frac{e^{-x}}{1+e^{-x}}, \tag{A1}$$

although compact, is not readily treatable within integrals. A number of approximations may be made to this function with different ranges of applicability. For a discussion of which see Goedecker.[21] The usual expansion of the Fermi function uses the Matsubara formula,

$$f(x)=\frac{1}{2}-2x\sum_{n=0}^{+\infty}\frac{1}{x^2+(2n+1)^2\pi^2}. \tag{A2}$$

Although a simple expression, the Matsubara expansion is very poorly convergent at larger values of x (or, equivalently, at $|\epsilon-\mu|\gg k_BT$).

In our approach we note that the symmetry of $f(x)$ means we may consider it to comprise a T-independent step function (already treatable) *plus* a T-dependent antisymmetric term. This antisymmetric term need only be defined in the region $x>0$ and consequently we will consider a series expansion for just the Fermi function in the region $x>0$ and write the full Fermi function as

$$f(x)\simeq\Theta(x)+\sum_{s=-}^{+} s\Theta(-sx)f_N(sx), \tag{A3}$$

where $f_N(x)$ is our series approximation to the Fermi function on the positive real axis and $\Theta(x)$ is the step function defined to be 1 for negative x and 0 elsewhere.

Along the positive axis the Fermi function is asymptoti-

cally decreasing from a value of $\frac{1}{2}$ at $x=0$ and may be expanded in a Taylor series in powers of e^{-x}, behaving as $\sim e^{-x}$ as $x\rightarrow+\infty$. This series form reproduces well the larger x region but due to the alternating signs of the expansion coefficients is poorly convergent for small x. However, each successive term in the exponential series expansion is significant over a successively smaller region and we may note that, provided $f_N(0)=\frac{1}{2}$ and $\lim_{x\rightarrow+\infty} f_N(x)\rightarrow e^{-x}$, we may fit a finite number of coefficients to $f(x)$ to achieve a greater accuracy than that of the Taylor series alone. We thus put

$$f_N(x)=\sum_{n=1}^{N}\alpha_n e^{-nx}, \tag{A4}$$

with $\alpha_1=1$ and $\alpha_N=\frac{1}{2}-\Sigma_{n=1}^{N-1}\alpha_n$. The remaining α coefficients are evaluated using the matrix equation

$$\vec{\alpha}=\mathscr{E}^{-1}\vec{f}, \tag{A5}$$

where $\mathscr{E}_{pq}=e^{-qx_p}$ and $f_p=f(x_p)$. The set of $\{x_p\}$ values at which the functional form is fitted is chosen to match the distribution of the basis states and thus in this case is chosen to have a logarithmic distribution.

The accuracy of this approach is vastly greater than that of either a truncated Taylor series or of the Matsubara expansion (see Table II). A 15-term expansion of our form is accurate to better than 10^{-8}% for all values of x whereas the Matsubara and Taylor expansions fail at large or small energies, respectively.

One interpretation of this scheme is of a dampening term placed within the Fermi function such that, rather than having $\alpha_n=(-1)^{n-1}$, we would have $\alpha_n=(-1+\delta)^{n-1}$. In our method, we also ensure a more rapid convergence at small x by having a dense set of fitting points in this region.

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