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LETTER TO THE EDITOR

A new algorithm for computing susceptibilities

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Abstract. We present a new algorithm for computing Lindhard sums in susceptibility calculations. Based on the joint density of states (JDOS) introduced by us some time ago our algorithm gives better control of convergence by decoupling the problems related to the mesh in k space and the mesh used for integrating over the energies. Our method is an extension of the usual tetrahedron method for densities of states. We find that, rather than complicating the problem, the presence of matrix elements helps in the computation of the JDOS. We use the method to calculate the JDOS and the unenhanced susceptibilities for a FCC model band structure. Since it is based on JDOS the method can be easily adapted to calculate the t-matrix which characterizes off diagonal long-range order. We also outline how we use the method to calculate susceptibilities for first principles band structures.

The generalized susceptibility $\chi(q+G,q,\omega)$ is fundamental to the study of the electronic properties of solids. It describes the response of the solid when probed by electromagnetic fields, light and neutrons. Its poles describe elementary excitations like spin waves for magnetic systems. Via the electron–phonon interactions it leads to the dynamical matrix and phonon spectra, and magnetoelasticity for magnetic systems. Its static value serves as a criterion for phase changes and the stability of the assumed ground state.

Besides the problem of generating the band structures, practical calculation of χ requires an efficient method of evaluating Brillouin zone sums. For q in special directions one can use group theory to exploit the lattice symmetry so that the sums need only be evaluated in an irreducible part of the Brillouin zone. Winter *et al* [1] used a scheme in which quantities are evaluated in an array of directions for k and an interpolation scheme is used for quantities dependent on $k+q$.

For q in a general direction group theory is not applicable and one has to consider other methods of dealing with the Brillouin zone sums. Most modern methods for dealing with such sums involve the division of the Brillouin zone into microcells and approximating the integrand within the cell usually via a linear scheme. For instance Lipton and Jacobs [2] used microcubes and linearized the energies within the cubes. A major advance in these linear methods was made by Jepson and Andersen [3] and Lehman and Taut [4] with the development of the tetrahedron method. From geometric considerations the latter authors obtained analytic formulae for the density of states (DOS) for each tetrahedron. Subsequently Rath and Freeman [5] and Per-Anker Lindgard [6] have adapted this method to calculate the unenhanced susceptibility χ. However none of the above methods can deal with rapidly varying

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matrix elements since they use either constant matrix elements or average values for them. For quantities which have the form of a simple spectral function Gilat and Bharatiya [7] have given an explicit formula which includes the matrix elements. In this letter we develop a method of calculating the unenhanced susceptibility which treat the matrix elements on a level with the band energies. Indeed our method is simpler with variable matrix elements.

Because the above methods integrate directly the Lindhard function special precautions need to be taken when the band energies are near the Fermi surface. The procedures adopted use extra k points or directions which involve either extrapolation for the extra k points or extra band calculations. In our method we first calculate the joint density of states (JDOS) recently introduced by us [8] for a fixed mesh of k points and then obtain the unenhanced susceptibility by multiplying the JDOS by a weighting function and integrating over energies. This disentangles the problems relating to (i) using a sufficient number of k points for the linear tetrahedron method to be valid and (ii) dealing with the principal part character of the integral entering through the weighting function. Since in a complex solid band structure calculations are computer intensive our method allows the use of a reasonable coarse mesh of k points while using a fine energy integration mesh around the Fermi surface. As a bonus our JDOS may also be used to calculate other quantities like the propagator for the t-matrix.

In this article we derive two alternative integral formulae for the JDOS. Within a tetrahedron where the various quantities may be linearized we derive analytic formulae for the JDOS. Our formulae show explicitly why problems arise when the gradients of the energies are parallel. In the final section we discuss our method, test it with a model FCC tight-binding band and outline how these may be implemented within a first-principles band structure program.

Below we develop our algorithm to calculate the unenhanced susceptibility, χ. In general this may be written as

$$\chi(q+G,q,\omega)=\int \mathrm{d}\epsilon'\mathrm{d}\epsilon J_{q+G,q}(\epsilon',\epsilon)W(\epsilon',\epsilon,\omega). \tag{1}$$

In (1), the Lindhard function W is defined by

$$W(\epsilon,\epsilon',\omega)=(f(\epsilon)-f(\epsilon')/(\epsilon-\epsilon'-\omega-\mathrm{i}\eta) \tag{2}$$

where η is a positive infinitesimal and $f(x)$ is a Fermi function. The computational problem is now relegated to (JDOS, J, defined by

$$J_{q+G,q}(\epsilon',\epsilon)=M_{n_1',n_1}(k_1;q,G)\delta(\epsilon'-\epsilon_{n_1'k_1+q})\delta(\epsilon-\epsilon_{n_1k_1}) \tag{3}$$

where G is a reciprocal lattice vector, n, n' are band indices and we have used a convention in which numerically subscripted variables are summed or integrated over their respective domains. The so-called matrix elements M are given by

$$M_{n',n}(k;q,G)=\mathcal{F}_{n'k+q,nk}(q+G)\mathcal{F}^*_{n'k+q,nk}(q). \tag{4}$$

In a tight-binding LMTO [9] formalism with basis states $\varphi_L, L\equiv(lm)$ and two centre integrals [10] $F_{L'L}$ defined by

$$F_{L'L}(p,R)=\int \varphi_{L'}(r)\mathrm{e}^{-\mathrm{i}p\cdot r}\varphi^*_L(r-R)\mathrm{d}r \tag{5}$$

the above form factors are given by

$$\mathcal{F}_{\kappa'\kappa}(p) = F_{L_1'L_1}(p, R_1)e^{-ik\cdot R_1} b_{L_1'\kappa'} b^*_{L_1\kappa} \tag{6}$$

where $b_{L\kappa}$ relate the band states ψ_κ to the LMTO orbitals φ_L. The composite index κ denotes the band n and the wave vector k.

In the usual DOS method we may write

$$J_{q+G,q}(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_{n'n} \int \frac{dS}{|\nabla \epsilon_{nk}|} M_{n',n}(k; q, G)\delta(\epsilon' - \epsilon_{n'k+q}) \tag{7}$$

where the integral is over the surface $\epsilon_n(k) = \epsilon$.

Exploiting the second delta function we obtain the following general expression for the joint density of states:

$$J_{q+G,q}(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_{n'n} \int_C \frac{dc}{|\nabla \epsilon_{nk} \times \nabla \epsilon_{n'k+q}|} M_{n',n}(k; q, G). \tag{8}$$

For each pair of bands n', n the integral is over the curve, C, where the surfaces $\epsilon_{nk} = \epsilon$ and $\epsilon_{n'k+q} = \epsilon'$ intersect.

Since we have a third function $M(k; \ldots)$ with surfaces defined by $M = M(k; \ldots)$ we can transform the integral over dc into an integral over dM. Indeed

$$J_{q+G,q}(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_{n'n} \int \frac{dM}{|\nabla M \cdot \nabla \epsilon_{nk} \times \nabla \epsilon_{n'k+q}|} M_{n',n}(k; q, G). \tag{9}$$

It will be seen that this last expression is easier to evaluate than the right hand side of (8).

The above expressions for the JDOS are valid in general. For simple bands one can obtain explicit formula for the JDOS. Let us consider the simple case of free electrons where $\epsilon_k = \hbar^2 k^2/2m$. In this case the band indices n, n' and the reciprocal lattice vector G are unnecessary and the matrix element is unity. The expression (8) reduces to

$$J_q(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \left(\frac{m}{\hbar^2}\right)^2 \int_C \frac{dc}{|k \times q|}. \tag{10}$$

The contour, C, of integration is a circle, the intersection of two spheres centred at the origin and at $-q$ with radii proportional to $\sqrt{\epsilon}$ and $\sqrt{\epsilon'}$, respectively. Integrating we obtain

$$J_q(\epsilon', \epsilon) = \begin{cases} \mathcal{V}/(2\pi)^3 (m/\hbar^2)^2 2\pi/q & \text{for } |\sqrt{\epsilon} - \sqrt{\epsilon_q}| < \sqrt{\epsilon'} < \sqrt{\epsilon_q} + \sqrt{\epsilon} \\ 0 & \text{otherwise} \end{cases} \tag{11}$$

where $\epsilon_q = \hbar^2 q^2/2m$. We have the remarkably simple result that for a parabolic band the JDOS is constant with respect to ϵ and ϵ'. In fact it is non zero within a parabola defined by $(\epsilon - \epsilon')^2 - 2\epsilon_q(\epsilon + \epsilon') + \epsilon_q^2 = 0$. This parabola is symmetrical about the line $\epsilon = \epsilon'$. If we substitute the expression (11) into the expression for χ and perform the double integral we obtain for free electrons the unenhanced susceptibility:

$$\chi_0(q, 0) = (\mathcal{V}/4\pi^2)(mk_F/\hbar^2)\left\{-1 + \left(\sqrt{\epsilon_F/\epsilon_q} - \tfrac{1}{4}\sqrt{\epsilon_q/\epsilon_F}\right) \times \left[\ln(2\sqrt{\epsilon_F\epsilon_q} - \epsilon_q)/(2\sqrt{\epsilon_F\epsilon_q} + \epsilon_q)\right]\right\} \tag{12}$$

which is the standard result [11] with the van Hove singularity at $q = 2k_F$.

In the more general case we would expect the JDOS to have more structure. In particular we would expect the quantity $M_{n'n}(k; q + G)$ to modify the results considerably. Indeed recently we have shown [12] that for a simple tight-binding band we can obtain almost analytic results for the JDOS and χ and that the variation of the matrix elements with k profoundly modify the behaviour of χ. With actual bands the symmetry of the lattice must be reflected in the JDOS and χ.

In general the integration in either (8) or (9) cannot be done analytically and one has to find efficient algorithms to do them numerically. In this section we shall now extend the tetrahedron method [3] normally used for calculating the JDOS

$$D(\epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_n \int \frac{\mathrm{d}S}{|\nabla \epsilon_{nk}|} \tag{13}$$

where the integral is over the surface $\epsilon_n(k) = \epsilon$. In this method the whole of k space is divided into tetrahedra and the integral is then a sum over the integrals for the tetrahedra. Within each tetrahedron a function $f(k)$ may be linearized, i.e.

$$f(k) \simeq f_1 + (k - k_1) \cdot \nabla f \tag{14}$$

where $f_\alpha = f(k_\alpha)$ and k_1, k_2, k_3 and k_4 are the vertices of the tetrahedron. If we define the matrix $\kappa^i_\alpha = (k_\alpha - k_1)^i$ for $\alpha = 2, 3, 4$ or

$$\kappa = \begin{pmatrix} k_2^x - k_1^x & k_2^y - k_1^y & k_2^z - k_1^z \\ k_3^x - k_1^x & k_3^y - k_1^y & k_3^z - k_1^z \\ k_4^x - k_1^x & k_4^y - k_1^y & k_4^z - k_1^z \end{pmatrix} \tag{15}$$

we may invert the equations to obtain the components of ∇f, namely

$$\nabla^i f = \sum_{\alpha=2}^{4} (\kappa^{-1})^i_\alpha (f_\alpha - f_1). \tag{16}$$

In the normal tetrahedron method the algorithm is considerably simplified by the simple analytic expressions, dependent only on the values, ϵ_α, of the energies at the vertices, obtained [3] the ratio of the surface $\mathrm{d}S$ and $\nabla \epsilon_{nk}$. Closer scrutiny shows that the simplification is due to the fact that the volume of the tetrahedron can be factored out of the cross-sectional area. Since one can choose tetrahedra with the same volume considerable computing is saved. We shall show that we can also factor out the tetrahedron volume in our expressions for the JDOS.

Let us consider the expression (9). Each of the gradients, $\nabla M, \nabla \epsilon_{nk}$ and $\nabla \epsilon_{n'k+q}$ may be written in the form (16) and the triple scalar product may be written as

$$\nabla M \cdot \nabla \epsilon_{nk} \times \nabla \epsilon_{n'k+q} = \det(\kappa^{-1} \cdot z_M)$$

where

$$z_M = \begin{pmatrix} M_2 - M_1 & \epsilon_2 - \epsilon_1 & \epsilon'_2 - \epsilon'_1 \\ M_3 - M_1 & \epsilon_3 - \epsilon_1 & \epsilon'_3 - \epsilon'_1 \\ M_4 - M_1 & \epsilon_4 - \epsilon_1 & \epsilon'_4 - \epsilon'_1 \end{pmatrix}$$

and the subscripted quantities denote the values of the functions evaluated at the tetrahedron vertices. From the properties of determinants we have

$$\det(\kappa^{-1} \cdot z_M) = \det(\kappa^{-1}) \det z_M = \det z_M / \det \kappa. \tag{17}$$

From the definition (15) of the matrix κ we observe that

$$\det(\kappa) = (k_2 - k_1) \cdot (k_3 - k_1) \times (k_4 - k_1) = 6\Omega_t$$

which is six times Ω_t, the volume of the tetrahedron. We thus obtain for the JDOS an expression which is analogous to the simple analytic one for the DOS. Apart from the volume the value of the JDOS for each tetrahedron is dependent only on the values of the matrix element and the energies $\epsilon_{nk}, \epsilon'_{n'k+q}$ at the vertices. This result was first derived by Long [13].

The above results are very useful when the band structure program producing the energies ϵ_{nk} and $\epsilon'_{n'k+q}$ also produce the matrix elements. However the calculation of the matrix elements is a time consuming process and sometimes one would like to ignore the k variation. If the matrix elements are constant then the expression (9) becomes singular since ∇M vanishes. We must revert to the expression (8). The denominator of (8) can also be written as a determinant but in order to have the desirable property of factorizing the tetrahedron volume we must find an appropriate expression for the unit vectors e_i spanning k space. Since $k_\alpha - k_1 = (k_\alpha - k_1)^i e_i$ we may invert this equation to write

$$e_i = \sum_{\alpha=2}^{4} (\kappa^{-1})^i_\alpha (k_\alpha - k_1). \tag{18}$$

The vector product in (8) may now be written

$$\nabla \epsilon_{nk} \times \nabla \epsilon_{n'k+q} = \det(\kappa^{-1} \cdot z)$$

where

$$z = \begin{pmatrix} k_2 - k_1 & \epsilon_2 - \epsilon_1 & \epsilon'_2 - \epsilon'_1 \\ k_3 - k_1 & \epsilon_3 - \epsilon_1 & \epsilon'_3 - \epsilon'_1 \\ k_4 - k_1 & \epsilon_4 - \epsilon_1 & \epsilon'_4 - \epsilon'_1 \end{pmatrix}.$$

The determinant may now be expanded to give

$$\det(\kappa^{-1} \cdot z) = \det(\kappa^{-1}) \det(z) = \det(z) / \det \kappa$$

and we again have the tetrahedron volume factored out.

We must now do the line integral specified by (8) or (9). In the spirit of the tetrahedron approximation the line integral in (8) is simply the distance between the two points at which the line of intersection of the surfaces $\epsilon = \epsilon_{nk}$ and $\epsilon' = \epsilon'_{n'k+q}$ hit the appropriate faces of the tetrahedron. For the integral (9) we require only the values of $M_{n'n}(k; q, G)$ at these points. To determine these end points we follow Long [13] by defining an alternate set of coordinates $\lambda_\alpha, \alpha = 1, 2, 3, 4$:

$$k = k_1 + \sum_{\alpha=2}^{4} \lambda_\alpha (k_\alpha - k_1) = \sum_{\alpha=1}^{4} \lambda_\alpha k_\alpha. \tag{19}$$

In the last sum we have the condition $\sum_\alpha \lambda_\alpha = 1$. We observe that k on a face opposite to vertex α have $\lambda_\alpha = 0$. Substituting for k into the linearized expression (14) for a general function $f(k)$ we have

$$f(k) = \sum_{\alpha=1}^{4} \lambda_\alpha f_\alpha .$$

Thus in terms of the λs the energy surfaces are given by

$$\sum_\alpha \lambda_\alpha \epsilon_\alpha = \epsilon \qquad \text{and} \qquad \sum_\alpha \lambda_\alpha \epsilon'_\alpha = \epsilon' . \tag{20}$$

Therefore the end point on face f is given by the solutions to the equations (20) and $\lambda_f = 0$. If we define

$$m_1 = \begin{pmatrix} 1 & \epsilon_2 & \epsilon'_2 \\ 1 & \epsilon_3 & \epsilon'_3 \\ 1 & \epsilon_4 & \epsilon'_4 \end{pmatrix} \qquad m_2 = \begin{pmatrix} 1 & \epsilon_1 & \epsilon'_1 \\ 1 & \epsilon_3 & \epsilon'_3 \\ 1 & \epsilon_4 & \epsilon'_4 \end{pmatrix}$$

$$m_3 = \begin{pmatrix} 1 & \epsilon_1 & \epsilon'_1 \\ 1 & \epsilon_2 & \epsilon'_2 \\ 1 & \epsilon_4 & \epsilon'_4 \end{pmatrix} \qquad m_4 = \begin{pmatrix} 1 & \epsilon_1 & \epsilon'_1 \\ 1 & \epsilon_2 & \epsilon'_2 \\ 1 & \epsilon_3 & \epsilon'_3 \end{pmatrix}$$

then the triplet of λ values defining k for the end point at the face f is given by $(1\ \epsilon\ \epsilon')m_f^{-1}$.

Assuming that the line of intersection C hits surfaces f and f' the JDOS is given by

$$J_{q+G,q}(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_{n'n\,t} \frac{3\Omega_t}{\det(z_M)} (M_f^2 - M_{f'}^2). \tag{21}$$

For the case where we have a constant matrix M we have the more complicated expression

$$J_{q+G,q}(\epsilon', \epsilon) = \frac{\mathcal{V}}{(2\pi)^3} \sum_{n'n\,t} \overline{M} \frac{6\Omega_t}{|\det(z)|} |k_f - k_{f'}| . \tag{22}$$

In the above the subscript t under the summation sign refer to the tetrahedra.

We have implemented the above method for calculating the JDOS and the unenhanced susceptibility using first-principles LMTO band structure program. Although our implementation uses parallel algorithms for both the tetrahedron sums and the band structure [14] the calculation of $\chi(q)$ is still a formidable undertaking requiring substantial computing resources. We shall report on the results obtained with this implementation using actual band structures in a future paper [15].

To calculate the unenhanced susceptibility χ we must calculate the JDOS for a sufficient number of values of ϵ and ϵ' so that we can integrate its product with the Lindhard function $W(\epsilon', \epsilon)$. The calculation of χ depends on two meshes (i) the mesh of k points used in evaluating the band structures and matrix elements and (ii) the integration mesh used for evaluating the double integral over the energies ϵ and

ϵ'. Since the Lindhard function possesses a singularity when ϵ and ϵ' approach each other from opposite sides of the Fermi energy, E_F one has to ensure a sufficiently fine mesh of energies near E_F. However this variation of energy may be done independently of the k mesh used in calculating the band structures. Our method allows the choice of a relatively coarse k mesh which is fixed throughout thereby offering savings of processing time.

In the standard discussion [16] of the instability of the normal phase with respect to superconductivity one looks for divergence of the t-matrix. The propagator for this quantity is given by

$$\mathcal{G}(q, q_0) = \sum_{n,n',k} \frac{1 - f(\epsilon_{nk}) - f(\epsilon_{n'k+q})}{q_0 - \epsilon_{nk} - \epsilon_{n'k+q}}.$$

This may be calculated by integrating the product of JDOS and an appropriate weighting function of ϵ' and ϵ. Indeed once the band energies are produced one can calculate criteria for instability with respect to both diagonal and off diagonal long-range order at the same time by evaluating respectively χ and the t-matrix, respectively.

We can test part of our algorithm by calculating the unenhanced susceptibility using a model band structure and comparing our results with those obtained previously by others. With a model band structure we are not restricted by the number of points we can afford to use in our k mesh. The results of such a calculation using a model FCC tight-binding band with nearest and next nearest neighbour overlap is shown in figure 1. Using the same band parameters as Lipton and Jacobs [2] we have reproduced the plots of $\chi(q)$ given in their paper.

In summary we have extended the tetrahedron method to compute the (JDOS). Employing this JDOS we present a new algorithm for calculating the unenhanced susceptibility and the propagator for the t-matrix. The matrix elements present no problems, in fact they make the calculation somewhat more straightforward. We have checked the method by computing $\chi(q)$ for a model FCC tight-binding band and produced results in agreement with previous calculations.

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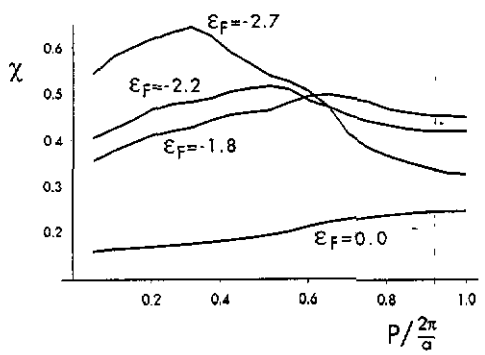

Figure 1. Unenhanced susceptibilities for a model FCC tight-binding band as a function of q for a series of Fermi energies.

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