Tetrahedron method of zone integration: Inclusion of matrix elements

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The tetrahedron method of Brillouin-zone integration is examined in comparison to the rectangular approach. Tetrahedrons are found to be more generally applicable, but they lack the simplicity provided by the symmetry inherent in the rectangular approach. In some earlier calculations of the magnetic susceptibility $\chi(\vec{q},\omega)$ the effect of the variation of the matrix elements throughout the Brillouin zone was not adequately accounted for. A method is described for incorporating this effect within the framework of the tetrahedron method. The possible effect of interpolation on the calculation of spectral functions is also discussed.

Very recently there has been interest in accurate calculations of the dynamical magnetic susceptibility $\chi(\vec{q}, \omega)$ in metals. Rath and Freeman[1] computed $\chi(\vec{q}, \omega)$ for Sc and Lindgård[2] calculated it for Gd, Tb, and Dy. In performing these calculations the so-called tetrahedron method was employed. This method was recently introduced by Jepson and Anderson[3] and independently by Lehman and Taut.[4]

$\chi(\vec{q}, \omega)$ is actually one particular case of a whole domain of spectral properties of solids (e.g., density of states, superconducting tunneling, vibronic transitions, infrared absorption, impurity modes, incoherent neutron scattering in solids, optical transitions, etc.), to which high-resolution methods of calculation can be applied. These methods have been recently discussed by one of these authors.[5,6] The tetrahedron method is actually one ramification of the so-called linear-analytic method.[5]

One purpose of this article is to assess the use of tetrahedrons as integration cells, especially in comparison with cubic and rectangular (orthorhombic) cells. Another objective is to incorporate in a systematic way the variations of matrix elements (also known as transition probabilities, coupling constants, oscillator strengths, etc.) within the framework of the tetrahedral approach. This effect has already been accounted for in the case of orthorhombic cells.[7,8]

The main idea behind the high-resolution method, first introduced by Gilat and Raubenheimer,[9,10] is to approximate a constant-energy surface $E_n(\vec{k})$ in reciprocal space by a plane and vary $E_n(\vec{k})$ linearly within a small volume (the integration cell) and then perform analytically the integration inside each cell. This approximation is known as the linear-analytic approach.[5,6]

There is a large variety of spectral properties in solids, but they are all closely related to either the imaginary part $I(E)$ of a spectral function

$$I(E) = \frac{V\pi}{(2\pi)^3} \int F(\vec{k}) \frac{dS}{|\vec{\nabla} E|} \ , \tag{1}$$

or to its real part $R(E)$,

$$R(E) = \frac{V}{(2\pi)^3} \int \frac{F(\vec{k})}{E(\vec{k}) - E} \, d^3k \ . \tag{2}$$

In these expressions $E(\vec{k})$ represents an energy band (dispersion relation), $F(\vec{k})$ is an appropriate matrix element that gives rise to the observed spectral property, and dS is a constant-energy-surface increment. V is the direct space volume (which can be lumped in the normalization constant). The magnetic susceptibility $\chi(\vec{q}, \omega)$ is related to $R(\omega)$ and is given by

$$\chi(\vec{q}, \omega) = \frac{V}{(2\pi)^3} \sum_{nn'} \int d^3k \, |\langle \vec{k}+\vec{q}| M_{nn'} |\vec{k}\rangle|^2 \times \frac{f(E_n(\vec{k}))[1 - f(E_{n'}(\vec{k}+\vec{q}))]}{E_{n'}(\vec{k}+\vec{q}) - E_n(\vec{k}) - \hbar\omega} \ , \tag{3}$$

where $M_{nn'}$ is the "matrix element" for $\chi(\vec{q}, \omega)$ and $f(E_n(\vec{k}))$ is the Fermi function, which is 1 or 0 for $E_n(\vec{k}) \leq E_F$ or $E_n(\vec{k}) > E_F$, respectively. A comparison of Eq. (3) with Eq. (2) shows the similarities as well as the differences between the functions $\chi(\vec{q}, \omega)$ and $R(E)$. The main difference is in the Fermi functions in Eq. (3) which limit $\vec{q}$ to scatterings between occupied and unoccupied states. Another difference is the interband transitions in Eq. (3).

The magnetic susceptibility serves here as a special example and the computational problem associated with the Fermi function can be tackled along the lines described by Rath and Freeman.[1] We next apply the zone-integration procedure to Eq. (1), by approximating the surfaces $S(E_n(\vec{k}) = E)$ by planes $S_i(E)$ within each integration cell. We obtain

$$I(E) = C \sum_i F(\vec{k}_i) \frac{S_i(E)}{|\vec{\nabla} E(\vec{k}_i)|} \ , \tag{4}$$

where $\sum_i$ is a summation over integration cells that fill the Brillouin zone exactly, and C is an appropriate normalization constant. Two problems emerge at the onset of this procedure: (a) what shapes to use for the cells and (b) how to account for $F(\vec{k})$?

In earlier calculations, cubic and later the more general orthorhombic[10] cells were chosen. For these shapes, $\vec{\nabla}E(\vec{k})$ is evaluated at the center point and integration is performed throughout the cell. More recently, Jepson and Anderson[3] and Lehman and Taut[4] chose tetrahedrons for integration cells. From data gathered so far[1-4] it seems that tetrahedrons have advantages as well as disadvantages in comparison to rectangular cells. The main advantage of tetrahedrons is that they are directly applicable to hexagonal and trigonal systems, whereas rectangular cells cause certain problems for these systems, which can however, be overcome.[10] Another important advantage of tetrahedrons is associated with integration over Fermi spheres. Whenever the Fermi surface intersects an integration cell, it divides it into an occupied and an unoccupied volume. For tetrahedral cells these volumes are either tetrahedrons themselves, or they can be split into tetrahedrons. This property does not readily apply to rectangular cells. Tetrahedrons are also somewhat more convenient because they have only three different integration ranges whereas orthorhombic cells have four. This in itself is a relatively minor advantage.

The disadvantages of tetrahedrons relative to rectangular cells are associated with their lower symmetry. It is very easy to attach a Cartesian system to rectangular cells whereas this very task causes some complications with tetrahedrons. This fact simplifies considerably the analytical integration procedure for rectangular cells.

This difficulty can be overcome for tetrahedrons by dispensing with the energy gradient $\vec{\nabla}E(\vec{k})$ and using instead the tetrahedron corner values of $E(\vec{k})$ to obtain expressions[1-4] for $S_i(E)$ in Eq. (4). The computational meaning of this is that one is using interpolation to determine $E_n(\vec{k})$ throughout the tetrahedron rather than extrapolation. This may cause a certain systematic error in the calculated $I(\omega)$ due to band crossings.[11] In a recent article, Cooke *et al.*[12] computed the density of states $N(E)$ for Nb and showed that interpolation did cause a spurious peak in $N(E)$. To rectify this, Cooke *et al.*[12] proposed to employ the Hellman-Feynman theorem[13] to obtain $\vec{\nabla}E_n(\vec{k})$ in an accurate and convenient manner. An equivalent approach was also used by Gilat and Dolling[14] in the case of the phonon spectrum of Na. Incidentally, it is still possible to apply extrapolation to tetrahedrons as well by using $\vec{\nabla}E_n(\vec{k})$ at the center to obtain corner values of $E_n(\vec{k})$. This procedure, however, is rather inefficient.

In view of all this, the use of the corner values of $E_n(\vec{k})$ for a tetrahedron should be considered more as a handicap rather than an advantage. In comparison, for rectangular cells it is a simple matter to use either the corner values of $E_n(\vec{k})$ or $\vec{\nabla}E_n(\vec{k})$ for spectral calculations, so that one has an option to choose between interpolation and extrapolation.

A second drawback of the tetrahedron method is associated with the incorporation of the variations of the matrix element $F(\vec{k})$ in the Brillouin zone. For rectangular cells, a Cartesian system is readily available, which enables application of Dalton's methods[15] to obtain all the expressions that account for the matrix-element variations. Moreover, owing to the high degree of symmetry of rectangular cells, many terms in these expressions, in particular for the real part $R(\omega)$, cancel out.[8]

Nevertheless, it is possible to incorporate variations in $F(\vec{k})$ within the tetrahedron version. The way we do this is first by making the observation that within the linear approximation $F(\vec{k}_i)$ in Eq. (4) must be calculated at the center of area of the constant-energy plane within each cell. This property can be used to derive the energy dependence of $F(\vec{k}_i)$ within each tetrahedron, where the corner values of $F(\vec{k})$ are assumed given. It is interesting to point out that contrary to the case of $E_n(\vec{k})$, interpolation for $F(\vec{k})$ could be a better procedure than extrapolation. The reason for this is that within the Hellman-Feynman scheme, eigenvectors are assumed to be constants throughout the cell, which may cause $F(\vec{k})$ to be constant. The use of corner values for $F(\vec{k})$ can override this assumption.

Let E_i and F_i $(i=1, 2, 3, 4)$ be the corner values of $E(\vec{k})$ and $F(\vec{k})$ respectively. We follow Lindgård's convention,[4] as well as most of his notation,

$$E_{\min}=E_1\le E_2\le E_3\le E_4=E_{\max}\ , \tag{5}$$

and obtain for the first range $(0\le X\le \Delta_{21})$

$$S(E)=(3V/D_1)X^2\ , \tag{6}$$

$$f(E)=\tfrac{1}{3}\epsilon_1 X\ , \tag{7}$$

where $D_1=\Delta_{41}\Delta_{31}\Delta_{21}$, $\Delta_{ij}=E_i-E_j$, $\epsilon_1=\epsilon_{21}+\epsilon_{31}+\epsilon_{41}$, $\epsilon_{ij}=(F_i-F_j)/\Delta_{ij}$, $X=E-E_1$, $f=F-F_1$, and V is the volume of the tetrahedron.

For the second range $(\Delta_{21}\le X\le\Delta_{31})$ we obtain

$$S(E)=(3V/D_1)X^2-(3V/D_2)(X-\Delta_{21})^2\ , \tag{8}$$

$$f(E)S(E)=\frac{\epsilon_1 V}{D_1}X^3-\frac{\epsilon_2 V}{D_2}(X-\Delta_{21})^3 - \frac{3\Delta_{21}\epsilon_{21}V}{D_2}(X-\Delta_{21})^2\ , \tag{9}$$

where $D_2=\Delta_{42}\Delta_{32}\Delta_{21}$ and $\epsilon_2=\epsilon_{21}+\epsilon_{32}+\epsilon_{42}$.

In the third range $(\Delta_{31}\le X\le\Delta_{41})$, S and f are given by

$$S(E)=(3V/D_4)(X-\Delta_{41})^2\ , \tag{10}$$

$$f(E)=\tfrac{1}{3}\Delta_4(X-\Delta_{41})+F_4-F_1\ , \tag{11}$$

where $D_4 = \Delta_{41}\Delta_{42}\Delta_{43}$ and $\epsilon_4 = \epsilon_{41} + \epsilon_{42} + \epsilon_{43}$.

The expressions for $S(E)$ were derived earlier,[1-4] but $f(E)$ is given here for the first time.

The expression for $R(\omega)$ can be found by applying the Kramers-Krönig relations to each tetrahedron. The total $R(\omega)$ which is closely related to the calculation of $\chi(\vec{q}, \omega)$ is given by

$$R(\omega) = C' \sum_i \int_{E_1}^{E_4} \frac{[F_1 + f_i(E)]S_i(E)}{E - \omega} dE , \qquad (12)$$

where i runs over all the tetrahedrons and C' is an appropriate normalization factor. F_1 is constant for each cell and the variations of $F(\vec{k})$ are accounted for by $f(E)$ in Eqs. (6)–(11). It should be pointed out that Eqs. (6)–(11) constitute the expressions for $I(\omega)$ for each cell, so that

$$I(E) = C' \sum_i [F_1 + f_i(E)]S_i(E) . \qquad (13)$$

The expressions for $R(\omega)$ for a single tetrahedron are now given

$$R_i(\omega) = R_{i0}(\omega) + R_{i1}(\omega) , \qquad (14)$$

where

$$R_{i0}(\omega) = \frac{3VF_1}{D_1}(E_1 - \omega)^2 \ln\left|\frac{E_3 - \omega}{E_1 - \omega}\right| - \frac{3VF_1}{D_2}(E_2 - \omega)^2 \ln\left|\frac{E_3 - \omega}{E_2 - \omega}\right| + \frac{3VF_1}{D_4}(E_4 - \omega)^2 \ln\left|\frac{E_4 - \omega}{E_3 - \omega}\right| \qquad (15)$$

and

$$\begin{aligned} R_{i1}(\omega) = {} & \frac{V\epsilon_1}{D_1}\left(\tfrac{1}{3}\Delta_{31}^3 - \tfrac{1}{2}(E_1 - \omega)\Delta_{31}^2 + (E_1 - \omega)^2\Delta_{31} - (E_1 - \omega)^3 \ln\left|\frac{E_3 - \omega}{E_1 - \omega}\right|\right) - \frac{V\epsilon_2}{D_2}\left(\tfrac{1}{3}\Delta_{32}^3 - \tfrac{1}{2}(E_2 - \omega)\Delta_{32}^2\right. \\ & \left. + (E_2 - \omega)^2\Delta_{32} - (E_2 - \omega)^3 \ln\left|\frac{E_3 - \omega}{E_2 - \omega}\right|\right) - \frac{3V\epsilon_{21}\Delta_{21}}{D_2}\left(\tfrac{1}{2}\Delta_{32}^2 - (E_2 - \omega)\Delta_{32} + (E_2 - \omega)^2 \ln\left|\frac{E_3 - \omega}{E_2 - \omega}\right|\right) \\ & + \frac{V\epsilon_4}{D_4}\left(\tfrac{1}{3}\Delta_{43}^3 + \tfrac{1}{2}(E_4 - \omega)\Delta_{43}^2 + (E_4 - \omega)^2\Delta_{43} - (E_4 - \omega)^3 \ln\left|\frac{E_4 - \omega}{E_3 - \omega}\right|\right) - \frac{3V\epsilon_{41}\Delta_{41}}{D_4}\left(\tfrac{1}{2}\Delta_{43}^2 + (E_4 - \omega)\Delta_{43}\right. \\ & \left. - (E_4 - \omega)^2 \ln\left|\frac{E_4 - \omega}{E_3 - \omega}\right|\right) . \end{aligned} \qquad (16)$$

The expression for $R_{i1}(\omega)$ of Eq. (16) which accounts for the linear variations in $F(\vec{k})$ is considerably lengthier and more complicated than the equivalent case for a rectangular cell [Eq. (12) of Gilat and Bohlin[8]]. This is another outcome of the less convenient shape of the tetrahedron.

Incidentally, it is possible to avoid altogether the direct calculation of $R(\omega)$ via Eqs. (15) and (16) and instead compute $I(\omega)$ from Eqs. (6)–(11) and then apply the Kramers-Krönig relations to $I(\omega)$ to obtain $R(\omega)$.

In conclusion, we have derived here the expressions necessary for the inclusion of matrix elements in the tetrahedron methods. These expressions should be helpful in evaluating spectral properties in solids, such as dynamical susceptibilities. We have also assessed the tetrahedron against the rectangular cell and found advantages as well as disadvantages for either cell.

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