General analytic method of zone integration for joint densities of states in metals

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A general method to calculate analytically the cross section of any shape of a microcell is presented. This method is the generalization of existing zone-integration methods based on the linear approximation. This method is useful for calculating joint densities of states in metals as well as dynamical susceptibilities and dielectric functions when the Fermi surface splits microcells into contributing and noncontributing volumes. It may also prove useful for calculating densities of states in crystals of lower symmetries.

The linear analytic method of Brillouin-zone integration has been developed and applied to many crystals. The main purpose of this method is to compute spectral functions of the type

$$I(\omega)=\frac{\Omega}{8\pi^2}\int_{\mathrm{BZ}}\delta(E(\vec{k})-\hbar\omega)A(\vec{k})\,d\vec{k}\,, \tag{1}$$

where $A(\vec{k})$ is the so-called "matrix element" and it is an analytic function of $\vec{k}$. Ω is the Wigner-Seitz cell volume. $I(\omega)$ can be transformed into the following integral

$$I(\omega)=\frac{\Omega}{8\pi^2}\int\frac{A(\vec{k})\,dS}{|\nabla E(\vec{k})|}\,, \tag{2}$$

where dS is an area increment of the constant-energy surface $E(\vec{k})=\hbar\omega$.

In the application of the linear analytic method, the irreducible part of the Brillouin zone (IBZ) is divided into small domains called microcells. These microcells can, in general, be any convex polyhedra but, in practice, mostly cubes and tetrahedra have been used. Within each microcell $E(\vec{k})$ is evaluated exactly at one point $\vec{k}_c$, and then approximated linearly at any other point by

$$E(\vec{k})=E(\vec{k}_c)+\vec{\nabla}E(\vec{k}_c)\cdot(\vec{k}-\vec{k}_c)\,. \tag{3}$$

The part of the constant-energy surface within every microcell is approximated by a constant-energy plane (CEP), being some polygon of area S, and the integral in Eq. (2) can be rewritten as

$$I(\omega)=\frac{\Omega}{8\pi^2}\sum_c\frac{A(\vec{k}_c)S_c(\omega)}{|\nabla E(\vec{k}_c)|}\,. \tag{4}$$

The summation is over all the microcells, and $S_c(\omega)$ is known analytically for cubic[1] (or orthorhombic) and tetrahedral[2,3] microcells. It is possible also to expand $A(\vec{k})$ linearly throughout the cells and the appropriate expressions for these cases are also known.[4,5] In many cases it is simpler to assume that $A(\vec{k})\cong$ const throughout the microcell.

In the present article the main interest is focused over the problem of calculating joint densities of states (JDOS) for metals. Here we have the problem that only transitions between an occupied state below Fermi level and an unoccupied state above Fermi level are allowed. The relevant integral is

$$I(\vec{q},\omega)=\frac{\Omega}{8\pi^2}\times\sum_{nl}\int_{\mathrm{BZ}}\frac{A(\vec{k}+\vec{q},\vec{k})[f_n(\vec{k}+\vec{q})-f_l(\vec{k})]\,ds}{|\nabla E_{nl}|}\,, \tag{5}$$

where n and l are band indices, $f_n(\vec{k}+\vec{q})$ and $f_l(\vec{k})$ are the Fermi occupation numbers, $E_{nl}=E_n(\vec{k}+\vec{q})-E_l(\vec{k})$ and the integral is carried over the constant-energy surface $E_{nl}=\hbar\omega$. $\vec{q}$ is a variable wave vector which is required in several calculations, such as the dielectric function $\epsilon(\vec{q},\omega)$ or the susceptibility function $\chi(\vec{q},\omega)$. In this article we are not concerned with problems involving $\vec{q}$. These are discussed in a previous paper[6] by the same author. This manuscript is mainly concerned with the problem caused by the Fermi surface. To appreciate this problem we notice that the Fermi surface $E(\vec{k})=E_F$ must split some microcells into two volumes, only one of which is contributing to the JDOS. The general shape of the contributing volume is a polyhedron that has at most 10 corners for a cubic microcell and 6 corners for a tetrahedron. What is necessary to find is the area of the polygon representing the CEP (constant-energy plane) within the contributing part of the microcell. This polygon is also the cross-section area of the contributing polyhedron when looking in the direction of $\vec{\nabla}E_{nl}$. Recently, a general method to find this area was proposed by Riedinger.[7]

In this approach it is necessary to locate all the corners of the polygon and compute its area as a sum of triangles. This method is numerically exact (within the linear approximation) but it does not yield the area of the polygon analytically. In the present article a general method is proposed that yields analytical expressions for the area of these polygons for any shape of the contributing microcell. Two different approaches are being adopted here: (a)

an approach using explicitly the gradient $\vec{\nabla} E_{nl}$ and the geometric properties of the polyhedra and the polygons involved; (b) an approach avoiding the use of $\vec{\nabla} E_{nl}$ and which employs only the corners' energies of the contributing polyhedron. The first approach suits the description of the original cubic microcell,[1] whereas the latter is more in line with energy interpolation.

a. Geometric approach. In each microcell the CEP forms a set of parallel planes perpendicular to the direction of the gradient $\vec{\nabla} E_{nl}$, the value of which is determined at $\vec{k}_c$, usually at the center of the microcell. The equation of this set of planes is given by

$$\vec{l} \cdot (\vec{k} - \vec{k}_0) - w = 0 , \tag{6}$$

where $\vec{l}$ is a unit vector along the direction of $\vec{\nabla} E_{nl}$ and w is a scale along this direction,

$$w = (\vec{k} - \vec{k}_0)_{\parallel} , \tag{7}$$

measured from the corner $\vec{k}_0$, for which the lowest value of $E_{nl}(\vec{k})$ is obtained throughout the microcell. The relation between $\hbar\omega$ and w is given by

$$w = \frac{\hbar\omega - E_{nl}(\vec{k}_0)}{|\nabla E_{nl}|} . \tag{8}$$

Next, the general properties of the contributing polyhedron are examined. Let p be the number of its corners, and they consist of two types: (a) corners of the original microcell; (b) corners generated by the Fermi surface (plane within the microcell) intersecting the edges of the original microcell. It is assumed that the coordinates $\vec{k}_i$ of all these corners can be found. For cubic microcells this can be easily accomplished. These corners can be arranged in an increasing order according to their relative distances w_i from the origin $\vec{k}_0$ by using the relation

$$w_i = \vec{l} \cdot (\vec{k}_i - \vec{k}_0) , \tag{9}$$

where $w_i \leq w_{i+1}$ and $i = 1, 2, \ldots, p$. In this manner the entire range of w is divided into $p-1$ ranges where the ith range is $w_i \leq w \leq w_{i+1}$. If $\vec{k}_0$ is included in the contributing polyhedron, then $\vec{k}_1 = \vec{k}_0$ and $w_1 = 0$. Now a general assumption is made about the topology of the contributing polyhedron, which maintains that every corner of the polyhedron is a junction of three edges only. Such a polyhedron is referred to as a regular polyhedron. To each of its corners $\vec{k}_i$, we relate three edges represented by unit vectors $\vec{\lambda}^i_\alpha$ along them ($\alpha = 1, 2, 3$). Next we look at the analytic properties of $S(w)$, the area of the cross-section polygon. There are two main properties: (i) $S(w)$ is a positively defined quadratic function of w, say,

$$S(w) = Aw^2 + Bw + C \geq 0 ; \tag{10}$$

(ii) S and dS/dw are both continuous functions of w over the entire range, but d^2S/dw^2 is discontinuous at w_i.

We begin with the evaluation of $S(w)$ at w_1. For $w = w_1 + dw$ the CEP is a triangle intersecting three infinitesimal segments of lengths du_α on the edges at $\vec{k}_1$, where du_α is

$$du_\alpha = \frac{dw}{\vec{\lambda}^1_\alpha \cdot \vec{l}} . \tag{11}$$

$\vec{\lambda}^1_\alpha \cdot \vec{l}$ is the cosine of the angle between $\vec{\nabla} E_{nl}$ and the αth edge at $\vec{k}_1$. These three segments form an infinitesimal tetrahedron, the volume dV of which is

$$dV = \frac{1}{6} (\vec{\lambda}^1_1 \times \lambda^1_2) \cdot \vec{\lambda}^1_3 \, du_1 \, du_2 \, du_3$$
$$= \frac{1}{6} \Lambda_1 \frac{(dw)^3}{(\vec{\lambda}^1_1 \cdot \vec{l})(\vec{\lambda}^1_2 \cdot \vec{l})(\vec{\lambda}^1_3 \cdot \vec{l})} , \tag{12}$$

where Λ_1 is the determinant of $\vec{\lambda}^1_\alpha$, namely,

$$\Lambda_1 = \begin{vmatrix} \lambda^1_{11} & \lambda^1_{12} & \lambda^1_{12} \\ \lambda^1_{21} & \lambda^1_{22} & \lambda^1_{22} \\ \lambda^1_{31} & \lambda^1_{32} & \lambda^1_{33} \end{vmatrix} , \tag{13}$$

and $dV = \frac{1}{3} dS \, dw$, so that

$$dS = \frac{1}{2} \Lambda_1 \frac{(dw)^2}{(\vec{\lambda}^1_1 \cdot \vec{l})(\vec{\lambda}^1_2 \cdot \vec{l})(\vec{\lambda}^1_3 \cdot \vec{l})} . \tag{14}$$

Because of condition (i) it is possible to find $S(w)$ in the first range where it is, actually, the area of a triangle:

$$S(w) = \frac{1}{2} \Lambda_1 \frac{(w - w_1)^2}{(\vec{\lambda}^1_1 \cdot \vec{l})(\vec{\lambda}^1_2 \cdot \vec{l})(\vec{\lambda}^1_3 \cdot \vec{l})} \tag{15}$$

and $w_1 \leq w \leq w_2$. In case that the first corner $\vec{k}_1$ happens to be a corner of a cube, then $\vec{\lambda}^1_\alpha$ form an orthogonal set and $S(w)$ reduces to

$$S(w) = \frac{w^2}{2 l_1 l_2 l_3} \qquad (0 = w_1 \leq w \leq w_2) . \tag{16}$$

If the original microcell is cubic but the first corner happens to be at a Fermi cut, then still one of the $\vec{\lambda}^1_\alpha$, say $\vec{\lambda}^1_1$, is along a Cartesian axis, and the other two are on the cube surface, so that $\Lambda_1 = \lambda^1_{22} \lambda^1_{33}$ and

$$S(w) = \frac{\lambda^1_{22} \lambda^1_{33} (w - w_1)^2}{2 l_1 (l_1 \lambda^1_{21} + l_2 \lambda^1_{22})(l_1 \lambda^1_{31} + l_3 \lambda^1_{33})} . \tag{17}$$

Now we proceed to the case of a general corner $\vec{k}_i$ of the contributing polyhedron characterized by w_i. Whenever the CEP crosses this corner in the range $w_i - dw \leq w \leq w_i + dw$, the number t of the corners of the cross-sectional polygon changes by 1,

$$\Delta t_i = \pm 1 . \tag{18}$$

For $\Delta t_i = 1$ the CEP is approaching the corner along one edge and departing from it along two edges. The situation is depicted in Fig. 1. The CEP represented by the angle $Q_1 P_1 R_1$ is approaching the corner A_i, and having traversed it, it is denoted by $Q_2 P_2 P_3 R_2$. The corner P_1 of the polygon along the polyhedron edge BA_i splits into two corners P_2 and P_3 along the

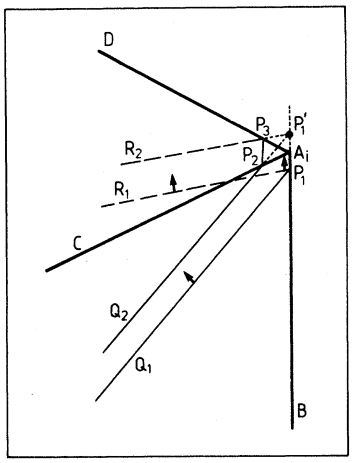

FIG. 1. The plane $Q_1P_1R_1$ approaches the corner A_i along the edge BA_i. After traversing the corners, it proceeds into the plane $Q_2P_1'R_2$, where it intersects the edges CA_i and DA_i at P_2 and P_3, respectively. The discontinuity in the area is described by $P_2P_1'P_3$.

two remaining edges. For the case $\Delta t_i = -1$ the opposite situation occurs, two corners of the CEP merge into one. What can also be observed in this figure is the discontinuity mentioned in (ii) of the CEP. This discontinuity is described by the area dS of the triangle $P_1^iP_2P_3$ of the infinitesimal tetrahedron $A_iP_1^iP_2P_3$. This area has already been calculated in Eq. (14) except for the index 1 that must now be replaced by i,

$$dS_i = \tfrac{1}{2}\Lambda_i \frac{(dw)^2}{(\vec{\lambda}_1^i\cdot\vec{\Gamma})(\vec{\lambda}_2^i\cdot\vec{\Gamma})(\vec{\lambda}_3^i\cdot\vec{\Gamma})} . \tag{19}$$

It is also obvious that the sign of the discontinuity depends on Δt, and it is positive for $\Delta t = -1$. At this point all the necessary elements for calculating $S(w)$ are at hand. Applying condition (i) for $S(w)$, its general expression for the range i for which $w_i \leq w \leq w_{i+1}$ is given by

$$S(w) = \tfrac{1}{2}\sum_{j=1}^{i\leq p-1} (-1)^{(1/2)(1+\Delta t_j)} \times \Lambda_j \frac{(w-w_j)^2}{(\vec{\lambda}_1^j\cdot\vec{\Gamma})(\vec{\lambda}_2^j\cdot\vec{\Gamma})(\vec{\lambda}_3^j\cdot\vec{\Gamma})} . \tag{20}$$

For a cubic microcell this general formula can be simplified according to Eqs. (16) and (17). Moreover, it is possible to begin the counting of i from the last to the first range and so obtain a different series for Eq. (20), which is also valid for $S(w)$, and, in fact, any linear combination of these two expressions is also a valid representation of $S(w)$. These tricks can help in circumventing possible singularities that may occur whenever $(\vec{\lambda}_\alpha^i\cdot\vec{\Gamma}) = 0$. These singularities, however, are accidental and they imply very special geometrical constraints for the Fermi plane or the cubes' edges with respect to the CEP. Such constraints seldom occur.

b. Energy approach. In this approach, the corners of the contributing polyhedron are characterized only by the energy values $E_{nl}(\vec{k}_i)$ at each corner rather than by the coordinates $\vec{k}_i$ themselves. The values of $E_{nl}(\vec{k}_i)$ can be obtained by solving the band-structure problem at each $\vec{k}_i$, and this is the method of interpolation, or rather by solving it at $\vec{k}_c$ and extrapolating for $E_{nl}(\vec{k}_i)$ with the aid of the gradient $\nabla E_{nl}(\vec{k}_c)$. Both ways are consistent and lead to the same dscription, although the respective values for $E_{nl}(\vec{k}_i)$ are somewhat different due to inaccuracies consistent with the linear approximation.

In this approach there is no reference to the scale on the coordinate axes and it is necessary therefore to know the volume V_c of each contributing polyhedron. This can be readily accomplished for tetrahedral microcells which are intersected by the Fermi plane, since at least one of the volumes generated by the Fermi surface is a tetrahedron and its edges can be calculated by using ratios of energy differences along the relevant edges. The value of V_c for orthorhombic (generalized cubic microcells) can also be found. Other microcells are of academic interest only. It is therefore assumed that V_c is known for every contributing polyhedron. p is, again, the number of corners of the polyhedron and $\epsilon_i = E_{nl}(\vec{k}_i)$, where ϵ_i are ordered in the fashion $\epsilon_1 \leq \epsilon_2 \leq \cdots \leq \epsilon_p$. Again it is assumed that all polyhedra are regular so that each corner ϵ_i is linked via three edges to three additional corners' energies ϵ_α where $\alpha = i_1, i_2, i_3$. It is necessary to find this triad of energies ϵ_α for each ϵ_i, in order to define D_i

$$D_i = |(\epsilon_i - \epsilon_{i_1})(\epsilon_i - \epsilon_{i_2})(\epsilon_i - \epsilon_{i_3})| . \tag{21}$$

Next an energy variable X is defined over the entire range $0 \leq X \leq \epsilon_p - \epsilon_1$ and there are $(p-1)$ ranges $\epsilon_i - \epsilon_1 \leq X \leq \epsilon_{i+1} - \epsilon_1$ at the boundaries of each of which the second-order discontinuity (ii) occurs. In the first range, the cross-section area of the CEP, being a triangle is given by

$$S(X) = \frac{3V_c}{D_1}X^2 , \quad 0 \leq X \leq \epsilon_2 - \epsilon_1 . \tag{22}$$

At each consecutive corner ϵ_i the expression for $S(X)$ undergoes a second-order discontinuity that can immediately be integrated due to condition (i), where the sign of this discontinuity is again positive or negative when the number of corners t of the polygon of the CEP decreases or increases by 1, respectively, so that $S(X)$ for the range $\epsilon_i - \epsilon_1 \leq X \leq \epsilon_{i+1} - \epsilon_1$ is given by

$$S(X) = 3V_c \sum_{j=1}^{i\leq p-1} \frac{(X - \Delta_{jj-1})^2}{D_j} (-1)^{(1/2)(1+\Delta t_j)} , \tag{23}$$

where $\Delta_{\alpha\rho\beta} = \epsilon_\alpha - \epsilon_\beta$ and $\epsilon_0 = \epsilon_1$. Also in this case it is possible to count the ranges backward from p to 1

and obtain an equivalent, though different, expression for $S(X)$ and employ it for circumventing accidential singularities. Equation (23) is somewhat simpler than Eq. (20) and, perhaps easier to apply in actual computation, which may give some marginal support to the tetrahedron microcell relative to the cubic one. On the other hand, there are certain inaccuracies that may occur for symmetry reasons[6] for $\vec{q} \neq 0$ in Eq. (5), which affect more the tetrahedral mesh of corners.

In this article the linearization of $A(\vec{k})$ in Eq. (4) is not considered but it can be incorporated into these approaches. One should note that, for each CEP, the value of $A(\vec{k})$ at the center of mass of the contributing polygon must be found. It is estimated that in most realistic cases $A(\vec{k})$ is not known in sufficient accuracy so that using $A(\vec{k}_c)$ for the entire contributing polyhedron is probably a good approximation.

Real-part calculations. The present approach allows also for the calculation of real-part integrals:

$$R(\alpha) = \frac{\Omega}{(2\pi)^3} \int \frac{A(\vec{k})\, d\vec{k}}{E(\vec{k}) - \hbar\alpha} , \tag{24}$$

which is related to real-part dielectric $\epsilon(\vec{q}, \omega)$ and dynamical susceptibility $\chi(\vec{q}, \omega)$ functions. Linear analytic methods for performing this integration were described by Gilat and Bohlin[8] for a cubic mesh and by Rath and Freemen[9] and Lindgård[10] for tetrahedron microcell. The expressions developed here allow now also for treating the case of JDOS in metals where the Fermi surface may intersect microcells into a contributing and noncontributing parts. It is possible to use either approach described in Eqs. (20) and (23) to integrate $R(\alpha)$ over the contributing part of the microcell. This procedure is briefly described here. In analogy to Eq. (5), $R(\vec{q}, \alpha)$ is written

$$R(\vec{q}, \alpha) = \frac{\Omega}{(2\pi)^3} \times \sum_{nl} \frac{A(\vec{k}+\vec{q}, \vec{k})[f_n(\vec{k}+\vec{q}) - f_l(\vec{k})]}{E_n(\vec{k}+\vec{q}) - E_l(\vec{k}) - \hbar\alpha} d\vec{k} , \tag{25}$$

and $d\vec{k}$ can be factorized into $d\vec{k} = dk_\perp dk_\parallel$, where these increments are perpendicular and parallel to the CEP, respectively. $dk_\parallel = dw$ and the integration over $dk_\perp$ yields $S(w)$, so that Eq. (25) reduces to

$$R(q, \alpha) = \frac{\Omega}{(2\pi)^3} \times \sum_c \sum_{nl} A(k_c) \int_{w_1}^{w_p} \frac{S(w)\, dw}{E_{nl}(k_0) + |\nabla E_{nl}|\, w - \hbar\alpha} , \tag{26}$$

where $\sum_c$ indicates a summation over the contributing parts of all microcells. Since $S(w)$ is known analytically from each c, Eq. (26) can be performed exactly in a straightforward manner, although the explicit expressions may be somewhat lengthy. It is also possible to reduce Eq. (26) to the approach described in Eq. (23), which uses the corners' energies. The appropriate expression for this case is

$$R(\vec{q}, \alpha) = \frac{\Omega}{(2\pi)^3} \sum_c \sum_{nl} A(\vec{k}_c) \int_0^{\epsilon_p - \epsilon_1} \frac{S(X)\, dX}{\epsilon_1 + X - \hbar\alpha} . \tag{27}$$

In conclusion, a new and general analytic method for incorporating transitions between above and below the Fermi level in metals for calculating JDOS and related properties has been presented. In fact, this method is a generalization of the linear analytic method to any shape of a microcell and therefore it is not limited to the calculation of JDOS only. For many cases, however, the tetrahedron or the cubic microcell, being just two variants of this general method, can serve as very useful microcells. In some cases, in particular in the calculation of direct densities of states of crystals of lower symmetries, it may be found useful to break up the irreducible Brillouin zone into a combination of microcells of different shapes, such as tetrahedra, orthorhombic cells, or wedges. In such cases, the general method presented here may prove useful to obtain the necessary expressions for the cross-section area of any shape. It is hoped to apply this approach in future calculations of dielectric matrices in metals.

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