

Fermi-surface harmonics: A general method for nonspherical problems. Application to Boltzmann and Eliashberg equations

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A set of functions called Fermi-surface harmonics (FSH's) are defined to be polynomials of the Cartesian components of the electronic velocity orthonormalized on the Fermi surface. These functions have many desirable properties, such as cell periodicity and a simple correspondence to spherical harmonics. However, there are many more linearly independent polynomials on a general surface than occur on a sphere. It is shown that this set is complete for simple Fermi surfaces; on general surfaces the mathematical question is not resolved but seems unlikely to cause physical difficulties. In the FSH representation, many problems take a particularly simple form. In particular the Boltzmann and Eliashberg equations are studied. By truncating at first-order polynomials, a slightly improved version of the usual variational solution for dc electrical conductivity is found. A convenient definition of Landau Fermi-liquid coefficients for anisotropic metals is suggested.

I. INTRODUCTION

Consider a property ϕ_k (such as a quasiparticle scattering rate $1/\tau_k$ or the superconducting energy gap Δ_k) which depends on the electron state with label k (shorthand for wave vector \vec{k} , band n , and spin) and energy ϵ_k . If the material is a metal it is often convenient to study separately the dependence of ϕ on energy ϵ near the Fermi energy and position \vec{k} on the Fermi surface. The reason for the desirability of separating energy and surface variables is the common occurrence of an energy such as $k_B T$ (temperature), $\hbar\Omega$ (phonon energy), or external potential which is very much smaller than 1 eV, the scale on which electron energy is measured. When k -space sums are required, energy integrals are simple to carry out, leaving complicated surface integrals. For a disem-bodied electron gas (or a metal like sodium) the Fermi surface is spherical and the angular variables θ and ϕ provide convenient coordinates for locating surface points. Functions like ϕ_k have expansions $\sum_L \phi_L(\epsilon) Y_L(\hat{k})$ in the spherical harmonics Y_L (where L is shorthand for lm). Matrix elements of spherically symmetric operators are diagonal in this representation (and depend only on l).

For certain solids (such as noble metals) the Fermi surface is still fairly simple, and can be specified by a "radius" $k_F(\theta, \phi)$ which is a single-valued function. The spherical harmonics are often still used to parameterize the behavior, for example, of scattering rates $1/\tau(\theta, \phi)$. However, for Fermi surfaces such as Cu, there is no reason to suppose that $1/\tau$ converges rapidly in spherical harmonics. The spherical harmonics have the advantages of being familiar and complete, but there are disadvantages: for example, they are not orthonormal when integrated over the Fermi sur-

face with any simple weight function. Worse problems arise in metals such as Mo where parts of the Fermi surface have "knobs" which makes $k_F(\theta, \phi)$ a multiple-valued function. It is difficult (but not impossible) to see how to construct a mapping between points on the surface and variables (θ, ϕ) . Another difficulty is that a physical property ϕ_k must be cell periodic in reciprocal space, and this is difficult to achieve with a non-periodic basis set such as $Y_L(\hat{k})$. These problems lead to frequent difficulties in such problems as the solution of Boltzmann equations. These difficulties have until now been solved only in a case-by-case fashion. This paper aims to remove all the above difficulties by describing a simple, infinite, orthonormal, and cell periodic basis set. These functions are given the name Fermi-surface harmonics (FSH's) and are labeled ψ_L . This set must necessarily be different not only for each crystal structure, but also for each band structure and for each constant energy surface of each band structure. Nevertheless, the functions are simple enough that they can be described and formally exhibited in a single nearly universal form.

The method consists simply of constructing all polynomials of the three Cartesian components of the velocity $\vec{v}_k = \nabla_{\vec{k}} \epsilon_k / \hbar$, and then orthonormalizing them on the constant energy surface. That is, we construct for each integer $N \geq 0$, all functions of the form $(v_{kx})^l (v_{ky})^m (v_{kz})^n$, (with all exponents l, m, n non-negative and $l + m + n = N$) and proceeding from $N=0$ on upwards, orthonormalize them according to the rule

$$\begin{aligned} \sum_k \psi_L(k) \psi_{L'}(k) \delta(\epsilon_k - \epsilon) & \Big/ \sum_k \delta(\epsilon_k - \epsilon) = \delta_{LL'}, \\ & = \int \frac{dS_k}{|\vec{v}_k|} \psi_L(k) \psi_{L'}(k) \Big/ \int \frac{dS_k}{|\vec{v}_k|}, \quad (1) \end{aligned}$$

where L is a convenient set of labels, which includes possibly a spin variable, and δ is the Dirac δ function. For an energy surface of one sheet (such as the Fermi surface of Na or Cu) there will be one such function for each set of integers (l, m, n) , while for a two-sheeted surface there will be two, and so on. The functions ψ_L are cell periodic because the velocity is cell periodic. This is the principal reason for using \vec{v}_k instead of \vec{k} to construct the polynomials. Completeness is a more difficult question which is discussed (but not laid to rest) in the Appendix. The principal conclusions are that polynomials in the wave vector components k_x, k_y, k_z are surely complete. The same arguments extend to the velocity polynomials for simple surfaces, but the situation for complicated surfaces is not obvious. In the bulk of this paper, completeness will be assumed, although it may not in fact always be true.

There still remains arbitrariness in the specific form of the functions ψ_L . Much of this arbitrariness is removed by choosing ψ_L to transform as basis functions for the irreducible representations Γ_i of the point group of the crystal. For spherical symmetry, i. e., $\epsilon_k \propto k^2$, the spherical harmonics immediately evolve from these specifications. However, for nonspherical symmetry the functions ψ_L are more numerous [there are $\frac{1}{2}(N+1)(N+2)$ independent polynomials of order N but only $2N+1$ spherical harmonics]. Such properties are most easily explained by example, and this will be done in Sec. II.

It is interesting to note that these specifications are not restricted to Fermi-surface problems. The procedure is equally applicable to an arbitrary surface in a space of dimension ν provided the surface is defined by a formula $\rho(x_1, x_2, \dots, x_\nu) = \text{const}$. Polynomials can then be generated either from the spatial variables x_i or from the gradients $d\rho/dx_i$. The generalization of Eq. (1) is obvious. It seems possible that the procedure described here has been used elsewhere in the literature of applied mathematics, but a complete search has not been attempted. In the literature on Fermi-surface problems, several authors have used methods which have features in common with the present method, but are less general. In particular, Kagan and Flerov¹ choose a mixed basis set of polynomials in the wave-vector \vec{k} with essentially the orthogonality relation (1). In order to have cell periodicity the first-order polynomials are made piecewise continuous over sheets which intersect zone boundaries. Aoi and Swihart² have discussed a possible expansion set orthonormalized on the Fermi surface, but failed to find a convenient explicit realization. Many other authors have described schemes for improving on the spherical-harmonic basis set. Extensive formal

work for the Boltzmann equation has been done by Bross,³ his functions being related to the well-known cubic harmonics defined by Von der Lage and Bethe.⁴ The cubic harmonics are equal in number to the spherical harmonics and are orthonormal on a sphere. The present choice of orthonormality [Eq. (1)] drastically alters the properties of the functions.

The plan of the paper is to exhibit the functions in Sec. II, describe their properties in Sec. III, and to demonstrate their application to the Boltzmann and Eliashberg equations in Secs. IV and V, respectively. Section VI serves as a summary and presents a brief discussion of Landau Fermi-liquid theory of anisotropic metals. The Appendix is devoted to the questions of completeness.

II. EXPLICIT FUNCTIONS FOR CUBIC SYMMETRY

A. Single sheet

The high symmetry of cubic crystals makes construction of orthogonal polynomials for small N very easy. For larger N or lower symmetry the problem becomes more tedious but no more difficult in principle. The polynomials are exhibited in Table I for polynomials up to order $N=3$. The first nine entries are entirely straightforward. They are the familiar cubic harmonics with the velocity instead of position or wave vector. The normalization of Eq. (1) leads to the particularly simple choice $\psi_0 = 1$ for the $N=0$ function. The Kramers symmetry between $(\vec{k} \uparrow)$ and $(-\vec{k} \downarrow)$ is sufficient to guarantee that v_{kx} is orthogonal to 1 (provided the system is nonmagnetic; otherwise inversion symmetry is needed). Orthorhombic symmetry is necessary to have v_{ky} orthogonal to v_{kx} ; in lower symmetry the Schmidt procedure can be used to orthogonalize v_{ky} to v_{kx} . The function v_{kx} is normalized by dividing by $\langle v_{kx}^2 \rangle^{1/2}$ or $\frac{1}{3}\langle v^2 \rangle^{1/2}$, the root-mean-square Fermi velocity. Bracket notation is used with the meanings

$$\langle \phi \rangle \equiv \sum_k \phi_k \delta(\epsilon_k - \epsilon) / \sum_k \delta(\epsilon_k - \epsilon), \quad (2)$$

$$\langle \phi \chi \rangle \equiv \langle \phi | \chi \rangle \equiv \sum_k \phi_k \chi_k \delta(\epsilon_k - \epsilon) / \sum_k \delta(\epsilon_k - \epsilon).$$

The irreducible representations are labeled in the convention of Bouchaert, Smoluchowski, and Wigner.⁵ Functions belonging to different representations (or different rows of the same representation) are automatically orthogonal. The only surprising feature in Table I is the appearance of a Γ_0 function in second order and an extra set of Γ_{15} functions in third order. The necessity for these "extra" polynomials can be seen in the following way. There are $\frac{1}{2}(N+2)(N+1)$ polynomials of x, y, z of order N . [This result can be found by counting the number of inequivalent terms in the

TABLE I. Fermi-surface harmonics for cubic symmetry, single sheet. For order 3, the labels of all ten functions are given but the explicit form of the functions is complicated and therefore omitted.

Order of polynomial	Irreducible representation	Label of function	Explicit form for cubic symmetry
$N=0$	Γ_0	ψ_0	1
$N=1$	Γ_{15}	ψ_x	$v_{kx}/\langle v_x^2 \rangle^{1/2}$
		ψ_y	$v_{ky}/\langle v_y^2 \rangle^{1/2}$
		ψ_z	$v_{kz}/\langle v_z^2 \rangle^{1/2}$
$N=2$	$\Gamma_{25'}$	ψ_{xy}	$v_{kx}v_{ky}/\langle v_x^2 v_y^2 \rangle^{1/2}$
		ψ_{yz}	$v_{ky}v_{kz}/\langle v_y^2 v_z^2 \rangle^{1/2}$
		ψ_{zx}	$v_{kz}v_{kx}/\langle v_z^2 v_x^2 \rangle^{1/2}$
	Γ_{12}	$\psi_{x^2-y^2}$	$(v_{kx}^2 - v_{ky}^2)/\langle (v_x^2 - v_y^2) \rangle^{1/2}$
		$\psi_{3x^2-r^2}$	$(3v_{kx}^2 - v_k^2)/\langle (3v_{kx}^2 - v_k^2) \rangle^{1/2}$
	Γ_0	ψ_{r^2}	$(v_k^2 - \langle v^2 \rangle)/\langle (v_k^2 - \langle v^2 \rangle)^2 \rangle^{1/2}$
$N=3$	$\Gamma_{2'}$	ψ_{xyz}	$v_{kx}v_{ky}v_{kz}/\langle v_x^2 v_y^2 v_z^2 \rangle^{1/2}$
	Γ_{25}	$\psi_x(y^2-z^2)$, and 2 similar	
	Γ_{15}	$\psi_x(y^2+xz^2)$, and 2 similar	
	Γ_{15}	ψ_x^3 , and 2 similar	

expansion of $(x+y+z)^N$.] On the surface of a sphere, $r^2 = x^2 + y^2 + z^2$ is constant and therefore proportional to ψ_0 : similarly xr^2 is proportional to ψ_x . Thus certain polynomials disappear in spherical symmetry. However, on the Fermi surface v_k^2 is not constant. The only constants are functions of ϵ_k which in general cannot be expressed as a *finite* polynomial of \vec{v}_k . Therefore on a general surface, all distinct polynomials are linearly independent. The occurrence of extra polynomials of low order is actually quite advantageous for numerical applications. Consider the energy gap Δ_k of a cubic superconductor. This function has full cubic symmetry (in the usual s-wave Cooper pairing). To represent cubic anisotropy using cubic harmonics requires polynomials of minimum order 4, i.e., $x^4 + y^4 + z^4$. However, using FSH's there is a completely symmetric function ψ_{r^2} of order 2 which has as many nodes as the Fermi surface has bulges. This is illustrated schematically in Fig. 1. The capability of parameterizing complicated anisotropy with a low-order polynomial is an obvious advantage.

B. Two sheets

The results given so far are easily generalized to Fermi surfaces of more than one sheet. A brief discussion is given here of a two-sheeted example.

It is assumed that the sheets are not related by symmetry. The indices a and b are used to denote the two surfaces (which may belong to different bands or to the same band). There are two different ways to construct polynomials ψ_L for this case, each of which has advantages. We can construct one set of functions for each sheet (the "disjoint" representation), the functions ψ_{La} vanishing on sheet b and conversely for ψ_{Lb} . Then the functions ψ_{La} and ψ_{Lb} are automatically orthogonal to each other. Alternatively we can construct two sets ψ_{Lg} and ψ_{Lu} where (g, u) stand for (even, odd) and ψ_{0g} has the value 1 on both sheets (the "symmetric" representation). Using the partial densities of states

$$N_{a,b}(\epsilon) = \sum_k^{\text{sheet } a,b} \delta(\epsilon_k - \epsilon), \quad (3)$$

where $N_a + N_b = N$ (the total density of states), we can write out orthonormalized functions in either representation

$$\begin{aligned} \text{disjoint} & \begin{cases} \psi_{0a} = [N(\epsilon)/N_a(\epsilon)]^{1/2} \delta_{ka}, \\ \psi_{0b} = [N(\epsilon)/N_b(\epsilon)]^{1/2} \delta_{kb}, \end{cases} \\ \text{symmetric} & \begin{cases} \psi_{0g} = 1, \\ \psi_{0u} = [N_b(\epsilon) \delta_{ka} - N_a(\epsilon)] \delta_{kb} / \\ [N_a(\epsilon) N_b(\epsilon)]^{1/2}, \end{cases} \end{aligned} \quad (4)$$

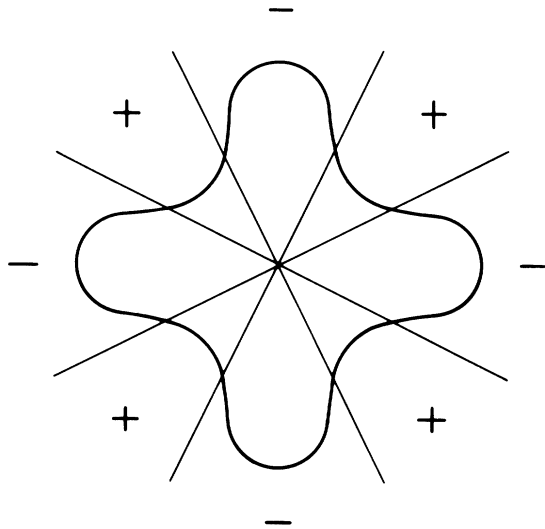


FIG. 1. Hypothetical Fermi surface in two dimensions with square symmetry illustrating the many nodes available in the surface harmonic $\psi_{r2} \propto v_k^2 - \langle v^2 \rangle$. Four nodal lines are drawn which separate the positive from the negative regions. The bulges are regions of lower velocity than average while the depressions have higher velocity. In three dimensions the analogous surface is a distorted octahedron (such as the hole surface of Nb, Ref. 6) with six negative bulges and eight positive depressions, separated by complicated nodal surfaces. Similar behavior on a sphere is exhibited by the cubic harmonic of order 4, $\frac{3}{2}r^4 - x^4 - y^4 - z^4$.

where δ_{ka} is unity if k is on sheet a and zero otherwise. The disjointed representation is algebraically simpler, but the symmetric representation will clearly be better for describing properties which are nearly constant on the Fermi surface.

C. Multiple sheets related by symmetry

Frequently closed sheets of Fermi surface occur in multiples which are related to each other by the symmetry operations of the crystal. The most familiar examples occur in conduction bands of semiconductors, such as degenerate n -type Si which has six ellipsoidal surfaces located along the $\langle 100 \rangle$ directions in the Brillouin zone, or Ge which has eight half ellipsoids or four whole ones located around the $(2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ points. Other examples among cubic materials are Nb,⁶ where the Fermi level intersects two bands which give rise to two centrosymmetric surfaces and one set of six ellipsoids, or Cr, Mo, and W,⁷ where three bands give rise to a total of fourteen distinct pieces of Fermi surface. In all these cases the multiplicity of linearly independent polynomials increases in proportion to the number of distinct pieces of Fermi surface, as can easily be seen by construction. However, the complexity of the mathematics can be greatly reduced by the use of group theory.

The simplest construction of orthonormal polynomials is again the disjoint representation with a distinct set of functions for each distinct piece of surface. However, in general these will be basis functions for a *reducible* representation of the group, if several pieces are related by symmetry. It is a standard exercise to transform to a representation which is irreducible. The resulting FSH's are linear combinations of simple polynomials on each surface with amplitudes and phases determined by group theory. The resulting choice of FSH's is not the symmetric representation of Sec. II B (which involves even and odd combinations of functions on two unrelated surfaces). It is more properly regarded as a special degenerate case of a single sheet which forms a proper starting point for either symmetric or disjoint representations when other unrelated sheets also occur.

Among the various basis functions which occur for multiple sheets, one in particular is worth mention. Namely, there always occurs in each order a set of functions of exactly the same form and symmetry as would occur for a single sheet. For example, in first order, the function defined as $v_{kx}/\langle v_{kx}^2 \rangle^{1/2}$ on all symmetry-related pieces is the logical choice for one of three Γ_{15} partners (in cubic symmetry). However, there are many other distinct first-order functions. For example, on the silicon $[100]$ ellipsoid, v_{kx} is invariant under the subgroup that leaves the ellipsoid invariant. Therefore a Γ_0 basis function can be constructed by applying to v_{kx} the six operations that transform the ellipsoids into each other, and adding the results in phase. This function looks like $\pm v_{kx}$ on the $[\pm 100]$ ellipsoids, $\pm v_{ky}$ on the $[0\pm 10]$ ellipsoids, and so forth.

III. GENERAL PROPERTIES

In this section rules are given for expanding functions in Fermi-surface harmonics, and the Clebsch-Gordan coefficients are defined and discussed. First consider functions h_k or $A_{kk'}$ of one or two variables which are defined for wave vector \vec{k} , \vec{k}' in the first Brillouin zone and possibly individually for electron bands n , n' , and spin orientations σ , σ' . (For example, $A_{kk'}$ may be a scattering matrix element squared.) Actually the functions h and A need only be defined over a limited energy range within the Brillouin zone. We assume we can expand these functions in Fermi-surface harmonics

$$h_k = \sum_L h_L(\epsilon) \psi_L(\vec{k}),$$

$$A_{kk'} = \sum_{LL'} A_{LL'}(\epsilon, \epsilon') \psi_L(\vec{k}) \psi_{L'}(\vec{k}').$$
(5)

The inverse relations are easily found from the orthonormality relation (1):

$$h_L(\epsilon) = \sum_k \delta(\epsilon_k - \epsilon) \psi_L(k) h_k / \sum_k \delta(\epsilon_k - \epsilon), \quad (6)$$

$$A_{LL'}(\epsilon, \epsilon') = \sum_{kk'} \delta(\epsilon_k - \epsilon) \delta(\epsilon_{k'} - \epsilon') \psi_L(k) \psi_{L'}(k') A_{kk'}$$

$$\times \left(\sum_{kk'} \delta(\epsilon_k - \epsilon) \delta(\epsilon_{k'} - \epsilon') \right)^{-1}.$$

Group theory can be used to obvious advantage to simplify the coefficients $A_{LL'}$. For example, if $A_{kk'}$ is invariant under simultaneous operations of the group on both \vec{k} and \vec{k}' , then $A_{LL'}$ has no off-diagonal elements connecting different irreducible representations or different partners in the same representation. An explicit proof is given by Aoi and Swihart² for the Landau f function. Using the expansions (5), Brillouin-zone sums can be easily converted to energy integrals and discrete angular sums. For example, in Eq. (2) an inner product $\langle \phi | \chi \rangle$ is defined as the normalized Fermi-surface integral of the functions ϕ_k and χ_k . If we expand in FSH's according to Eq. (5), the inner product gets transformed from the k representation (2) into the L representation:

$$\langle \phi | \chi \rangle = \sum_L \phi_L(\epsilon) \chi_L(\epsilon). \quad (7)$$

To illustrate how Brillouin-zone sums are handled, we use Eq. (5) to rewrite a simple inhomogeneous linear integral equation

$$h_k = \sum_{k'} A_{kk'} g_{k'}. \quad (8)$$

It is convenient to introduce on the right-hand side of (8) a factor $1 = \int d\epsilon' \delta(\epsilon_{k'} - \epsilon')$ which separates the k' sum into energy and surface parts. The using Eqs. (1) and (5) we easily find that Eq. (8) is equivalent to

$$h_L(\epsilon) = \int d\epsilon' N(\epsilon') \sum_{L'} A_{LL'}(\epsilon, \epsilon') g_{L'}(\epsilon'). \quad (8')$$

As a final example of transforming from k to L space, suppose we wish to expand the product function $g_k h_k$ in FSH's. This can be done in terms of Clebsh-Gordan coefficients $C_{LL'L''}$,

$$g_k h_k = \sum_{LL'L''} C_{LL'L''} g_L(\epsilon) h_{L'}(\epsilon) \psi_{L''}(k), \quad (9)$$

where the coefficient C is defined by

$$\psi_L(k) \psi_{L'}(k) \equiv \sum_{L''} C_{LL'L''} \psi_{L''}(k),$$

$$C_{LL'L''} = \sum_k \delta(\epsilon_k - \epsilon) \psi_L(k) \psi_{L'}(k) \psi_{L''}(k) \quad (10)$$

$$\times \left(\sum_k \delta(\epsilon_k - \epsilon) \right)^{-1}$$

These coefficients are real numbers, and completely symmetric in the indices L, L', L'' .

Some simple properties can easily be verified:

$$C_{00L} = \delta_{L0}, \quad C_{0LL'} = \delta_{LL'}, \quad (11)$$

$$C_{LL'L''} = 0 \text{ unless } |N_L - N_{L'}| \leq N_{L''} \leq N_L + N_{L'},$$

where N_L is the order of the polynomial ψ_L . Slight ambiguities arise when applying these relations to multisheeted surfaces, but these are easily resolved by inspection. For example, in the disjointed representation the relations (11) are individually true on each sheet, and the coefficients all vanish unless all three functions are on the same sheet. In the symmetric representation the notation ψ_0 must be taken to mean ψ_{0g} . The last of the relations (11) follows by observing that $\psi_L \psi_{L'}$ is a polynomial of order $N_L + N_{L'}$, and by the completeness of the polynomials this can be expanded in polynomials of order $N_L + N_{L'}$, or less. This proves the upper bound on $N_{L''}$. The lower bound follows because two other upper bound relations symmetric in $LL'L''$ also hold. Group theory can be used to find additional symmetry-induced selection rules on the coefficients C .

IV. BOLTZMANN EQUATION

We examine only the problem of electrical conductivity of a metal in a homogeneous dc external electric field E assumed for definiteness to be directed along the \hat{x} axis. The distribution function F_k is written in the usual form as $f_k + \phi_k$ ($\partial f / \partial \epsilon_k$), where f_k is the Fermi factor ($e^{\beta \epsilon_k} + 1$)⁻¹ and the zero of energy is taken at the chemical potential. The current is given by

$$\vec{j} = - \sum_k e \vec{v}_k \phi_k \frac{\partial f}{\partial \epsilon_k}$$

$$= e \int d\epsilon \left(- \frac{\partial f}{\partial \epsilon} \right) N(\epsilon) \langle \vec{v} | \phi \rangle, \quad (12)$$

where the inner-product notation (2) has been used to express the surface integral. The Boltzmann equation has the form

$$-eE v_{kx} \left(\frac{\partial f}{\partial \epsilon_k} \right) = \sum_{k'} Q_{kk'} \phi_{k'}, \quad (13)$$

$$Q_{kk'} = \frac{1}{kT} \left(\delta_{kk'} \sum_{k''} P_{kk''} - P_{kk'} \right),$$

where $Q_{kk'}$ is the scattering operator which is decomposed into scattering in and scattering out components. This form is quite general provided the phonons or other dynamical scatterers are assumed in thermal equilibrium, and requires only minor modification to deal with electron-electron Coulomb scattering. The factor $P_{kk'}$ is the equilibrium transition probability. For elastic impurity scattering $P_{kk'}$ has the form

$$P_{kk'}^{imp} = (2\pi n_i / \hbar) |T_{kk'}|^2 \delta(\epsilon_k - \epsilon_{k'}) f_k (1 - f_{k'}), \quad (14)$$

where T is the T matrix for impurity scattering and n_i is the impurity density. If we expand $P_{kk'}^{\text{imp}}$ in FSH's, the result can be written

$$P_{LL'}^{\text{imp}}(\epsilon, \epsilon') = -kT \left(\frac{\partial f}{\partial \epsilon} \right) \left(\frac{1}{\tau(\epsilon)} \right)_{LL'} \frac{\delta(\epsilon - \epsilon')}{N(\epsilon)},$$

$$\left(\frac{1}{\tau(\epsilon)} \right)_{LL'} = \sum_{kk'} \delta(\epsilon_k - \epsilon) \delta(\epsilon_{k'} - \epsilon) \psi_L(k) \psi_{L'}(k') \quad (15)$$

$$\times \left(\frac{2\pi n_i}{h} \right) |T_{kk'}|^2 \left(\sum_k \delta(\epsilon_k - \epsilon) \right)^{-1}.$$

The left-hand side of the Boltzmann equation (13) is proportional to $\psi_{xg} = v_{kx} / \langle v_x^2 \rangle^{1/2}$. Then combining Eqs. (13)–(15) and transforming to the FSH representation, the Boltzmann equation becomes

$$X_L \equiv eE \langle v_x^2 \rangle^{1/2} \delta_{Lxg} = \sum_{L'} Q_{LL'} \phi_{L'}$$

$$Q_{LL'} = \sum_{L''} C_{LL'L''} \left(\frac{1}{\tau} \right)_{L''0} - \left(\frac{1}{\tau} \right)_{LL'} \quad (16)$$

where the scattering in term involves Clebsch-Gordan coefficients while the scattering out term does not. There is a well-known variational procedure⁸ for solving Eq. (16) which relies on the fact that $Q_{LL'}$ is symmetric and positive definite. This method bears repeating as there are some slightly unfamiliar results that can be derived from it. The procedure is to find a trial vector ξ_L which does not necessarily solve (16) but which contains free parameters that can be so varied as to approach the true solution ϕ_L . A theorem exists that provided ξ_L satisfies

$$\langle \xi | X \rangle = \langle \xi | Q | \xi \rangle \quad (17)$$

[in particular ϕ satisfies this because of Eq. (16)], then

$$\langle \xi | X \rangle \leq \langle \phi | X \rangle. \quad (18)$$

The version (7) of the inner-product definition (2) has been used here. The right-hand side of (18) is proportional to $\langle \phi | v \rangle$ which according to (12) measures the contribution to the current from electrons with energy ϵ . Thus a solution to (17) gives a lower bound on the current. One unfamiliar feature of this analysis is that we are maximizing the current *at each energy* rather than the total current as is more often done. Clearly for otherwise equivalent trial solutions, we get higher current (lower resistance) than is found in the usual method. The second less familiar observation is that if we truncate Eq. (16) at polynomials of some order N_{max} , the resulting exact solution ϕ_L^t of the truncated equations also satisfies Eq. (17) and so gives a lower bound on the current.

Let us now solve Eq. (16) approximately by truncating at order 1 polynomials. In order to simplify the algebra we assume a single-sheeted Fermi surface. The generalization to more com-

plicated cases or larger N_{max} is straightforward but tedious. First note that the elements $Q_{L0} = Q_{0L}$ of the scattering operator vanish for all L because of the second relation (11) and the symmetry of $\tau_{LL'}$ in L and L' . Now write out explicitly the component $L = x$ of Eq. (16), truncating at first-order polynomials

$$eE \langle v_x^2 \rangle^{1/2} = Q_{xx} \phi_x + Q_{xy} \phi_y + Q_{xz} \phi_z. \quad (19)$$

We now assume cubic symmetry to further simplify the algebra. This makes Q diagonal in the indices (x, y, z) . The solution is

$$\phi_x = eE \langle v_x^2 \rangle^{1/2} \tau,$$

$$\frac{1}{\tau} = Q_{xx} = \sum_L C_{xxL} \left(\frac{1}{\tau} \right)_{L0} - \left(\frac{1}{\tau} \right)_{xx} \quad (20)$$

$$= \langle \psi_x^2 | 1/\tau | \psi_0 \rangle - \langle \psi_x | 1/\tau | \psi_x \rangle,$$

where the definition (10) of the Clebsch-Gordan coefficients has been used in the last line. Finally, it is easy to show that Eq. (20) can be re-written

$$\frac{1}{\tau(\epsilon)} = \frac{1}{2} \sum_{kk'} (\vec{v}_k - \vec{v}_{k'})^2 \frac{2\pi}{h}$$

$$\times n_i |T_{kk'}|^2 \delta(\epsilon_k - \epsilon) \delta(\epsilon_{k'} - \epsilon) \left(\sum_k v_k^2 \delta(\epsilon_k - \epsilon) \right)^{-1}, \quad (21)$$

which has the form of the standard lowest-order variational solution. This illuminates somewhat the nature of the usual solution by showing that it is an exact solution for velocity polynomials up to order 1. This result would be very hard to obtain by truncated solution using any basis set not beginning with functions like \vec{v}_k . The specific elements of $1/\tau_{LL'}$, which enter for cubic symmetry are

$$1/\tau = 1/\tau_{00} + C_{xxr}^2 (1/\tau_{r20}) - 1/\tau_{xx}, \quad (22)$$

$$C_{xxr}^2 = (\langle v^4 \rangle - \langle v^2 \rangle^2)^{1/2} / \langle v^2 \rangle.$$

As already noted, ψ_{r2} has many nodes, corresponding in spherical harmonics to terms at least of $l=4$. Equation (22) expresses quite economically exactly which information about the scattering matrix elements $|T_{kk'}|^2$ is contained in the approximate dc electrical conductivity. A somewhat different combination of the coefficients $1/\tau_{LL'}$ will determine the thermal conductivity.

The final result for the conductivity $\sigma = j/E$ is

$$\sigma(T) = e^2 \int d\epsilon \left(- \frac{\partial f}{\partial \epsilon} \right) N(\epsilon) \langle v_x^2 \rangle \tau(\epsilon). \quad (23)$$

Recently there have been theoretical claims^{9,10} that fine structure in the electronic density of states $N(\epsilon)$ can be manifested as an unusual T dependence of the electrical resistance. In this context it is interesting to compare (23) with the

more standard form of the variational solution

$$\sigma_v(T) = \left\{ e^2 \left[\int d\epsilon N(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) \langle v_x^2 \rangle_\epsilon \right]^2 \right\} \\ \times \int d\epsilon N(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right) \langle v_x^2 \rangle \left(\frac{1}{\tau(\epsilon)} \right). \quad (24)$$

At $T=0$ only a very narrow energy interval of electrons are involved and the two formulas are equivalent. At higher temperatures these formulas differ in the fashion in which electrons of energy ϵ are regarded as contributing to the current. Both formulas give rigorous lower bounds on σ , but Eq. (23) must give a higher (and therefore better) estimate as each energy has had its current separately maximized. Indeed the Schwartz inequality can be used to show that (23) gives a higher σ at finite T than does (24). If the assumptions are made that v_k and $T_{kk'}$ vary slowly with ϵ as compared with the variation of $N(\epsilon)$, then Eq. (21) implies $1/\tau(\epsilon) \sim N(\epsilon)$ and (23) implies $\sigma(T) = \sigma(0)$, while Eq. (24) would predict

$$\frac{\sigma_v(T)}{\sigma_v(0)} = \left[\int d\epsilon N(\epsilon) \left(-\frac{\partial f}{\partial \epsilon} \right)^2 \right] \\ \times \left[\int d\epsilon N(\epsilon)^2 \left(-\frac{\partial f}{\partial \epsilon} \right)^{-1} \right], \quad (25)$$

which implies $\sigma_v(T) < \sigma_v(0)$. The conclusion to be drawn is that a correct analysis of higher-order T dependence requires a careful solution for the energy dependence of ϕ_k . Apparently if $N(\epsilon)$ is structured, $\phi_x(\epsilon)$ can adjust itself to account for this and maximize the current. Therefore results such as those of Refs. 9 and 10 should be re-examined. This last conclusion does not specifically rely on the FSH representation and could equally well have been derived by other methods.

These results retain much of their validity for multi-sheeted Fermi surfaces. However, we no longer have an exact treatment for polynomials up to order one, having effectively truncated away all noneven polynomials of zeroth and first order.

V. ELIASHBERG EQUATIONS

There has been much interest, both experimental and theoretical, in discovering the degree of anisotropy that the superconducting energy gap Δ_k will manifest as k varies on the Fermi surface.¹¹ It is known¹² that anisotropy in Δ_k will cause the transition temperature T_c to be higher than in an isotropic superconductor with $\Delta = \langle \Delta_k \rangle$. The most widely studied model is the "two-band" model¹³ where it is assumed that Δ_k is separately constant on two sheets of Fermi surface but Δ_a is not assumed equal to Δ_b . The technique of FSH's allows a unified discussion of two-band effects and single- (or multi-) band anisotropy. The simplest question is the influence of anisotropy

on T_c , and this is the only one specifically addressed in this paper. At T_c , the BCS¹⁴ or Eliashberg¹⁵ integral equations become linear equations for Δ_k . At lower temperatures, the nonlinearity of the theory will cause the anisotropy effects to be much harder to handle exactly. However, unless the coupling is very strong, the nonlinearity is only weakly coupled to the anisotropy, and the anisotropic part of the equations can be approximately linearized as first discussed by Anderson and Morel.¹⁶ Thus although only the linear theory at $T = T_c$ is explicitly discussed here, the approximate nonlinear theory for $T < T_c$ will have the same structure.

A completely general starting point is the formula for the self-energy $\underline{\Sigma}$ in the Nambu tensor notation, where the off-diagonal part of $\underline{\Sigma}$ is the "anomalous" or "pairing" self-energy:

$$\underline{\Sigma}(k, i\omega_n) = -\frac{1}{\beta} \sum_{k'n'} \int d\epsilon' \delta(\epsilon_{k'} - \epsilon') \\ \times V(k, k'; n, n') \underline{\tau}_3 \underline{G}(k', i\omega_{n'}) \underline{\tau}_3. \quad (26)$$

In this equation, $\underline{\tilde{G}}$ is the Green's function given by $(i\omega_n \underline{1} - \epsilon_k \underline{\tau}_3 - \underline{\Sigma})^{-1}$, V includes all the interactions between electrons k and k' , $i\omega_n$ is a Matsubara frequency $i\pi(2n+1)/\beta$, β is $(k_B T)^{-1}$, $\underline{\tau}_i$ are the Pauli matrices, and $\hbar = 1$. The energy integral over $\delta(\epsilon'_k - \epsilon')$ has been inserted to separate surface from energy variables. The only rapid dependence on ϵ' comes from the energy explicitly occurring in the denominator of G . All other dependence on ϵ' is weak in comparison to ω'_n or Σ which are small energies. Therefore $\delta(\epsilon'_k - \epsilon')$ can be replaced by $\delta(\epsilon'_k) = \delta(\epsilon'_k - \epsilon_F)$ when the k' summation is done, except for keeping the energy ϵ' correctly in the denominator of G . This allows the ϵ' integration to be performed. If we decompose $\underline{\Sigma}$ into diagonal and off-diagonal components (to define the renormalization Z and pair field ϕ)

$$\underline{\Sigma} = [1 - Z(k, i\omega_n)] i\omega_n \underline{1} + \phi(k, i\omega_n) \underline{\tau}_1, \quad (27)$$

the resulting equation is

$$(1 - Z) i\omega_n \underline{1} + \phi \underline{\tau}_1 = \frac{i\pi}{\beta} \sum_{k'n'} \delta(\epsilon_{k'}) \\ \times V(k, k'; n, n') \left(\frac{i\omega'_n Z' \underline{1} - \phi' \underline{\tau}_1}{[(i\omega'_n Z')^2 - \phi'^2]^{1/2}} \right). \quad (28)$$

This equation is accurate to order $(m/M)^{1/2}$ for electron-phonon mechanisms as shown by Migdal's analysis,¹⁷ and forms a starting point for virtually any microscopic examination of superconductivity. At $T = T_c$, the pair field ϕ' becomes infinitesimal and can be dropped from the denominator of (28). Writing out the diagonal part of (28) explicitly we find

$$i\omega_n Z = i\omega_n - \frac{i\pi}{\beta} \sum_{k'n'} \delta(\epsilon_{k'}) V(k, k'; n, n') \omega_{n'} / |\omega_{n'}|, \quad (29)$$

which is the normal-state mass renormalization and self-energy function. The off-diagonal part of (28) is a homogeneous linear integral equation for the pair field ϕ . It is standard to define the gap function Δ as ϕ/Z , but more convenient, following Bergmann and Rainer,¹⁸ to modify this to $\bar{\Delta} = \phi / |\omega_n| Z$. Then using Eq. (29) we get an integral equation for $\bar{\Delta}$:

$$\frac{\beta |\omega_n|}{\pi} \bar{\Delta}(kn) = \sum_{k'n'} \delta(\epsilon_{k'}) V(k, k'; n, n') \times [\text{sgn} n' \bar{\Delta}(kn) - \bar{\Delta}(k'n')]. \quad (30)$$

Let us now specialize to the case where V includes only electron-phonon interactions. The Coulomb interaction as well as other effects such as impurity scattering can easily be added in, but make the resulting equations too cumbersome to display explicitly. The Eliashberg form of the electron-phonon interaction is $|M_{kk'}|^2 D(k-k'; i\omega_n - i\omega_{n'})$, where M is the electron-phonon matrix element and D is the phonon Green's function. Using the phonon spectral function B , this can be written

$$V_{ep}(k, k'; n, n') = |M_{kk'}|^2 \int_0^\infty d\Omega B(k-k', \Omega) \frac{2\Omega}{(i\omega_n - i\omega_{n'})^2 - \Omega^2}. \quad (31)$$

It has already been assumed that the interaction V varies slowly as \vec{k} or \vec{k}' moves away from the Fermi surface. Therefore Eqs. (29) and (30) describe the variation of Z and Δ as \vec{k} varies on the Fermi surface; the variation as ϵ_k departs from ϵ_F is weak and is being neglected. Therefore, when we expand these equations in FSH's, we need only do so directly at the Fermi energy. The expansion for Δ is written

$$\Delta(kn) = \sum_L \Delta_{Ln} \psi_L(k), \quad (32)$$

$$\Delta_{Ln} = \frac{1}{N(0)} \sum_k \delta(\epsilon_k) \Delta(kn) \psi_L(k).$$

A similar pair of equations relate $Z(kn)$ to Z_{Ln} . Let us write out explicitly the expansion of the Eliashberg interaction (31):

$$\alpha_{LL'}^2 F(\Omega) \equiv \frac{1}{N(0)} \sum_{kk'} \delta(\epsilon_k) \delta(\epsilon_{k'}) |M_{kk'}|^2 \times B(k-k', \Omega) \psi_L(k) \psi_{L'}(k'), \quad (33)$$

$$V_{ep}(kk', nn') = -\frac{1}{N(0)} \sum_{LL'} \lambda_{LL'}(n-n') \psi_L(k) \psi_{L'}(k'), \quad (34)$$

$$\lambda_{LL'}(n-n') \equiv \int_0^\infty d\Omega \alpha_{LL'}^2 F(\Omega) \frac{2\Omega}{\Omega^2 + (\omega_n - \omega_{n'})^2}. \quad (35)$$

The isotropic components ($L=0, L'=0$) of $\alpha_{LL'}^2 F$ and $\lambda_{LL'}(n-n')$ are the functions $\alpha^2 F$ and $\lambda(n-n')$ of the usual isotropic strong-coupling theory, and $\lambda_{00}(0)$ is the usual coupling constant and mass enhancement parameter λ . In terms of these definitions (32)–(35), the integral Eq. (30) becomes a matrix equation

$$|2n+1| \Delta_{Ln} = \sum_{L'n'} \left(\lambda_{LL'}(n-n') - \delta_{nn'} \right) \times \sum_{L''n''} C_{LL'L''} \lambda_{L''0}(n-n'') \text{sgn} n'' \Delta_{L'n''}. \quad (36)$$

This equation is now in a form which permits rapid computer calculations to find T_c . Such calculations have been done by several authors^{18–20} in the isotropic approximation, which is equivalent to assuming $\lambda_{LL'}(n-n') = \lambda(n-n') \delta_{L0} \delta_{L'0}$ (in the “symmetric” representation). If the isotropic approximation is made, Eq. (36) becomes equivalent to Eq. (7) of Bergmann and Rainer,¹⁸ Eqs. (1) and (2) of Owen and Scalapino,¹⁹ or Eqs. (14) and (15) of Allen and Dynes.²⁰

The most familiar solutions for T_c are those of McMillan²¹ who used an altogether different representation of the same equations, namely one where the gap function Δ had been analytically continued from the imaginary Matsubara frequencies to the real (and physical) frequencies ω . McMillan's starting equations can easily be derived by the standard procedure of analytically continuing Eq. (28) and then taking the limit as $T \rightarrow T_c$. The resulting equations can be written in the FSH representation as

$$[Z(\omega)\Delta(\omega)]_L = \sum_{L'L''} C_{LL'L''} Z_{L'}(\omega) \Delta_{L''}(\omega) = - \sum_{L'} \int_{-\infty}^\infty \frac{d\omega'}{\omega'} \int_0^\infty d\Omega \alpha_{LL'}^2 F(\Omega) \times \text{Re}[\Delta_{L'}(\omega')] K(\omega, \omega', \Omega), \quad (37)$$

$$\omega[\delta_{L0} - Z_L(\omega)] = \int_{-\infty}^\infty d\omega' \int_0^\infty d\Omega \alpha_{L0}^2 F(\Omega) K(\omega, \omega', \Omega), \quad (38)$$

where the function K is defined as

$$K(\omega, \omega', \Omega) \equiv \frac{f(\omega') + N(\Omega)}{\omega - \omega' + \Omega} + \frac{f(-\omega') + N(\Omega)}{\omega - \omega' - \Omega}, \quad (39)$$

and f and N are the Fermi and Bose functions. In the isotropic approximation these equations reduce to Eq. (2) of McMillan's paper. At temperatures below T_c , Eq. (37) is modified by replacing $\text{Re}[\Delta_{L'}(\omega')]/\omega'$ by the L' component of the function $\text{Re}[\Delta(\omega')]/(\omega'^2 - \Delta'^2)^{1/2}$. The combination of non-linear and anisotropic effects in this expression is hard to handle numerically. Fortunately in most cases it is adequately accurate to approximate this by $\text{Re}[\Delta_{L'}(\omega')]/(\omega'^2 - \Delta_0'^2)^{1/2}$ which effectively de-

couples nonlinear from anisotropic effects.

The Eqs. (33)–(39) set out here form a simple and rigorous basis for the discussion of anisotropy in superconductors. The explicit solution of these equations for T_c is reserved for a future publication.²²

VI. SUMMARY

A new basis set of polynomials orthogonalized on the Fermi surface has been described in this paper. These polynomials (FSH's) have some desirable properties such as cell periodicity, and a simple relationship with spherical harmonics. However, some important questions have not been adequately answered. There is the difficult mathematical question of completeness, discussed in the Appendix. There is also a related question which is best answered by experience, namely whether physically significant properties can be adequately represented by a few low-order FSH's. In this regard it is encouraging to observe that most work done to date on the problem of dc conductivity can be reproduced by truncating the Boltzmann equation at FSH's of order 1. The important unanswered question is whether extension to order 2 gives a major reduction of the error committed by truncating at order 1. If the answer turns out to be yes, then we have a powerful tool for handling many previously messy problems. For example, Landau Fermi-liquid theory has proved to be a powerful method for summarizing the results of many experiments in a small number of empirical parameters. In spherical symmetry (as in ³He or Na) these parameters are the coefficients f_l of a spherical harmonic expansion of the Landau f -function $f_{kk'}$. There has been relatively little extension of this work to anisotropic metals, partly because of the lack of a simple set of theoretically defined parameters to serve as guidelines. It seems likely that the FSH basis set described here will give the best possible such set of parameters, namely the matrix elements $f_{LL'}$. For a single-sheeted Fermi surface of cubic symmetry these parameters will be only twice as great in number as in spherical symmetry. Specifically, in spherical symmetry the parameters are f_0, f_1, f_2 (with higher than $l=2$ parameters ignored out of ignorance or convenience; spin symmetric, and antisymmetric components are implied for each l .) In cubic symmetry the analogous set of parameters is six in number, five being diagonal elements (namely $f_{0,0}, f_{x,x}, f_{xy,xy}, f_{x^2-y^2,x^2-y^2}, f_{r^2,r^2}$) and one off-diagonal (f_{0,r^2}), or twelve counting the spin degree of freedom. For multisheeted Fermi surfaces the number increases rapidly because there will be additional off-diagonal terms as well as additional diagonal ones. However, it is likely that most of these parameters will be irrelevant for most experiments. Hope-

fully, many experiments will probe only one or a few parameters. For example, the inverse of the optical mass (or the Drude plasma frequency squared) is altered by a factor $1+A$, where the Silin parameter^{23–25} A is given by

$$A = \sum_{kk'} f_{kk'} \vec{v}_k \cdot \vec{v}_{k'} \delta(\epsilon_k) \delta(\epsilon_{k'}) / \sum_k v_k^2 \delta(\epsilon_k). \quad (40)$$

In cubic symmetry this is simply the spin-symmetric parameter $f_{x,x}$, a result that remains true even for multisheeted Fermi surfaces if ψ_x is the symmetric function equal to $v_{kx}/\langle v_x^2 \rangle^{1/2}$ on all sheets; in spherical symmetry this becomes f_1 .

In summary it appears that many anisotropic problems take a particularly simple form when expressed in the basis set of Fermi-surface harmonics described here. Although it has not been proved, one can be optimistic that a rapidly convergent expansion in FSH's will occur for most physical variables and will greatly assist the solution of problems in anisotropic Fermi systems.

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APPENDIX

We wish to examine the question of completeness. The specific literature on orthogonal functions in more than one dimension is sparse.²⁶ First a suitable definition is needed. We define a space $L^2(|\nabla\epsilon(\vec{k})|^{-1}, S)$ as all functions f such that the integral

$$\int_S \frac{dS_k}{|\nabla\epsilon_k|} |f(\vec{k})|^2$$

exists and is finite. The surface S is defined by $\epsilon(\vec{k}) = \epsilon_F$ and \vec{k} in the first Brillouin zone. The property of completeness is often called in the mathematical literature "closure in $L^2(|\nabla\epsilon|^{-1}, S)$." A set of functions ψ_L is complete if for every f in $L^2(|\nabla\epsilon|^{-1}, S)$ and every $\epsilon > 0$, there exists a function of the form

$$\phi_n = \sum_{L=1}^n C_L \psi_L$$

with n finite such that

$$\int_S \frac{dS}{|\nabla\epsilon|} |f - \phi_n|^2 < \epsilon. \quad (A1)$$

If this property holds for some nonorthogonal set ψ_L , then it remains after orthogonalization.

A very powerful result, known as the Stone-

Weierstrass theorem,²⁷ is helpful in demonstrating the property (A1). We first need to establish that the velocity polynomials are an algebra. First we define $C(S)$ as the set of continuous real valued functions on the space S (which we will take to be the Fermi surface). An "algebra A in $C(S)$ " is a set of functions such that if f and g are in A , and a and b are any real numbers, then $af + bg$ and fg are both also in A . It is clear that polynomials in the wave vector (k_x, k_y, k_z) , in the velocity $[v_x(\vec{k}), v_y(\vec{k}), v_z(\vec{k})]$, or in any functions of \vec{k} . The Stone-Weierstrass theorem says that if A is an algebra in $C(S)$ and (i) S is a compact space, (ii) A contains the constant functions, and (iii) A "separates the points of S ," then A is a dense subset of $C(S)$. This means that for any function f in $C(S)$, and any $\epsilon > 0$, there exists a function g in A such that for all points \vec{k} in S

$$|g(\vec{k}) - f(\vec{k})| < \epsilon. \quad (\text{A2})$$

The property (A2) is called uniform approximation, and is stronger than the property (A1), called approximation in the mean. It is easy to show that (A1) holds provided (A2) holds and the integral over S of $\int dS/|\nabla\epsilon|$ is finite, i.e., the density of states at the Fermi energy should not diverge.

Thus it remains to show that the velocity polynomials satisfy the requirements (i), (ii), and (iii) of the Stone-Weierstrass theorem. Properties (i) and (ii) are trivially satisfied but condition (iii) generally is not. A family of functions A on S is said to "separate the points of S " if given any two distinct points \vec{k}_1 and \vec{k}_2 of S , there exists a function f in A such that $f(\vec{k}_1) \neq f(\vec{k}_2)$. This property is clearly manifested by the coordinates k_x, k_y, k_z . Thus a complete set of polynomials orthogonal on the Fermi surface can be constructed from the wave-vector components. However, for many Fermi surfaces there are pairs of points where $\vec{v}(\vec{k}_1) = \vec{v}(\vec{k}_2)$ so the velocity does not in general separate the points of S . Thus the velocity cannot be used to specify a coordinate system for all Fermi surfaces. If a function $\phi(k)$ has the property $\phi(\vec{k}_1) \neq \phi(\vec{k}_2)$ for points \vec{k}_1 and \vec{k}_2 where $\vec{v}(\vec{k}_1) = \vec{v}(\vec{k}_2)$, then it is obvious that a uniform approximation (A2) to ϕ cannot be made with a polynomial $p(\vec{v}(\vec{k}))$. This does not necessarily imply that an approximation in the mean (A1) fails, but it does destroy the proof. On the other hand, there are many simple Fermi surfaces where $\vec{v}(\vec{k})$ does separate the points of S and therefore on these surfaces the FSH's are complete. A general proof (or disproof) of completeness remains to be found.

Let us analyze in more detail the possible occurrence of points where the velocity vectors are identical. We consider only a single-sheeted sur-

face. It is only necessary for $\vec{v}(\vec{k})$ to separate points on each sheet separately. If we consider an arbitrary point \vec{k}_1 on S , there may in general exist one or more arbitrary isolated points \vec{k}_2 where $\vec{v}(\vec{k}_2) = \vec{v}(\vec{k}_1)$. Since \vec{k}_1 was arbitrarily chosen on S , it is highly improbable that \vec{k}_2 also lies on S . Generally $\vec{v}(\vec{k})$ is smooth and differentiable (except on isolated lines in the zone where degeneracies occur; these will have undefined velocities but these lines intersect the Fermi surface only in points which will cause no problem). If we consider points \vec{k}'_1 near \vec{k}_1 with velocities $\vec{v}(\vec{k}'_1) \approx \vec{v}(\vec{k}_1) + [(\vec{k}'_1 - \vec{k}_1) \cdot \nabla] \vec{v}(\vec{k}_1)$, then in general there is a one-to-one mapping to other points \vec{k}'_2 near \vec{k}_2 with velocity $\vec{v}(\vec{k}'_2) = \vec{v}(\vec{k}'_1)$. This result holds provided the effective-mass tensors $m_{\alpha\beta}^{-1}(k_1) = \partial V_\alpha(k_1)/\partial k_\beta$ and $m_{\alpha\beta}^{-1}(k_2)$ have nonvanishing determinants. (Otherwise the one-to-one mapping occurs only from a two-dimensional manifold near \vec{k}_1 to one near \vec{k}_2 .) If we consider a two-dimensional neighborhood on S near \vec{k}_1 , this maps into a two-dimensional neighborhood near \vec{k}_2 on which partner points of equal velocity are found. This second surface can possibly intersect S on a line. Thus there may occur isolated lines L_1 and L_2 on S where for each point on L_1 , a partner point on L_2 occurs with equal velocity. We do *not* expect to find areas a_1, a_2 with partner points. Thus the failure of $\vec{v}(\vec{k})$ to separate points on S is restricted to isolated lines. Since these constitute a set of measure zero, the possibility of approximating in the mean [Eq. (A1)] is not ruled out.

In spherical symmetry, the velocities $\vec{v}(\vec{k})$ on S all have the same length but two points on S never have parallel velocity. For general surfaces two or more points with parallel velocity can be found over finite fractions of the surface, but usually the lengths are not equal. Two cases can be distinguished: accidental equality and symmetry-related equality. The former case is not prevented on isolated lines but seems unlikely to occur on an arbitrary given surface, whereas the latter case occurs more commonly. Let us take Cu as an example. The Fermi surface is known from many experiments to be a single sheet which intersects zone boundaries in the $\langle 111 \rangle$ directions. One can identify regions of parallel velocities by finding magnetic field directions in which more than one cyclotron orbit is observed. For example both a neck and a belly orbit are seen when the field is along $\langle 111 \rangle$. Thus there is a line on the neck with $\vec{v}(\vec{k})$ perpendicular to $\langle 111 \rangle$ and a similar line around the belly. For each point on one line, a corresponding point on the other line has a parallel velocity. Then one could expect that somewhere along these lines occur points where the magnitudes of \vec{v} are (accidentally) equal. However it is known²⁸ that the neck velocities are

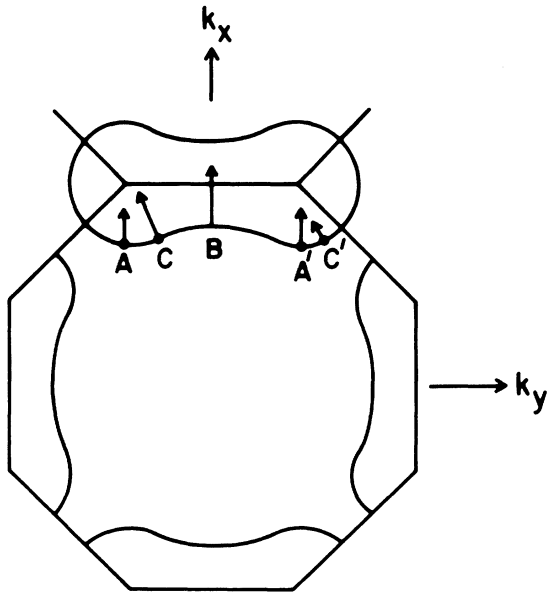


FIG. 2. $k_x=0$ slice of a hypothetical Fermi surface reminiscent of copper. Velocity vectors are shown for five points A, A', B, C, C'. The points A and A' are symmetry related and have identical velocity vectors.

smaller in magnitude than the belly velocities, so accidental equality of \vec{v} between neck and belly points does not occur. It seems that accidental equalities of \vec{v} do not occur at all in Cu.

However, symmetry-related equality does occur in Cu. For example, on the $k_x=0$ plane the Fermi surface points are described by their wave vectors $(k_x, k_y, 0)$ and have velocities $(v_x, v_y, 0)$. There are corresponding points $(k_x, -k_y, 0)$ obtained by reflection in the $k_y=0$ plane for which $\vec{v}=(v_x, -v_y, 0)$. There is also a special point where v_y vanishes (accidentally). The corresponding point has an identical velocity. This is illustrated somewhat schematically in

Fig. 2, where the pair of symmetry related points is labeled A, A'. A point B is also shown where \vec{v} is parallel but larger in magnitude. The points A and A' lie on lines L, L' which are the loci of points for which $v_y=0$. These symmetry related lines contain corresponding pairs of points for which $\vec{v}=\vec{v}'$. There are no other pairs of points in the $k_x=0$ plane (except for other points obtained from A, A' by rotations) for which $\vec{v}=\vec{v}'$. For example the points C, C' have parallel but unequal velocities.

In general points \vec{k} may occur where the vector \vec{v} has (accidentally) higher symmetry than \vec{k} has. Whenever this occurs, there will be other points obtained from \vec{k} by symmetry operations which leave \vec{v} invariant. It is worth mentioning that functions like $1/\tau_{\vec{k}}$ and $\Delta_{\vec{k}}$ which have the full symmetry of the crystal take the same value at symmetry related points. In order to have uniform approximations (A2) to such functions, it is only necessary for $\vec{v}(\vec{k})$ to separate points in the irreducible wedge of the Brillouin zone. This apparently holds in Cu and quite likely also for most Fermi surfaces. Even in the dc conductivity problem where the distribution function $\phi_{\vec{k}}$ has lower symmetry, errors do not seem to arise from symmetry-related equality of \vec{v} 's. For example the lines L, L' in Cu will have equal value of $\phi_{\vec{k}}$ at corresponding points if the field is in the x or z direction. Only if the field is in the y direction will $\phi_{\vec{k}}$ be different on corresponding points. However, v_y vanishes on L and L' so these points do not contribute any current if \vec{E} points in the y direction.

In conclusion, although a general proof of completeness is lacking, it is also not ruled out. Even if completeness fails on many Fermi surfaces, this may not present real difficulties for most physical problems and most Fermi surfaces.

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