From here, $\vec{q}_1 = \vec{q}_c = (\frac{1}{8}a, \frac{1}{8}a, \frac{1}{8}a)$. Similarly, from the relations (10) and (11) we find $\vec{q}_2 = C_2^x \vec{q}_c = (\frac{1}{8}a, -\frac{1}{8}a, -\frac{1}{8}a)$, $\vec{q}_3 = C_2^y \vec{q}_c = (-\frac{1}{8}a, \frac{1}{8}a, -\frac{1}{8}a)$, and $\vec{q}_4 = C_2^z \vec{q}_c = (-\frac{1}{8}a, -\frac{1}{8}a, \frac{1}{8}a)$. This result shows that the values of the band quasicoordinates $\vec{q}_n$ for the valence band of Ge coincide with the vectors of the star for the symmetry center $\vec{q}_c$ of the space group O_h^7. In proving this result no use was made of the explicit form of the periodic potential. What this means is that the band quasicoordinates $\vec{q}_n$ for any composite band of the $(c, 1)$ symmetry will reproduce the star of $\vec{q}_c$ for O_h^7. It can be checked that the values of $\vec{q}_s$ in Eq. (11) will reproduce the star of the symmetry center for any of the irreducible band representations of the space group O_h^7. This result can be generalized to any composite band with given symmetry of a solid belonging to any space group: The eigenvalues of the BC operator will give the symmetry centers of the space group of the solid and vice versa (if the latter are given we also know the possible eigenvalues of the BC operator).

In summary, it has been shown that for each band in a solid one can define a band-center operator which is a conserved quantity. Its eigenvalues are the average position of the electron in different bands, and they also coincide with the symmetry centers of the space group for the particular solid.

The author enjoyed discussions on the subject with Professor R. Barrie and Professor W. Opechowski. It is a pleasure to thank the Physics Department of the University of British Columbia for its kind hospitality.

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[1]F. Bloch, Z. Phys. 52, 555 (1928).
[2]C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
[3]E. N. Adams, J. Chem. Phys. 21, 2013 (1953).
[4]E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13.
[5]J. Des Cloizeaux, Phys. Rev. 129, 554 (1963), and 135, A685, A689 (1964).
[6]J. Zak, Phys. Rev. Lett. 45, 1025 (1980), and Phys. Rev. B 23, 2824 (1981).
[7]*International Tables of X-ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch, Birmingham, 1952), Vol. 1.
[8]J. Zak, Phys. Rev. B 20, 2228 (1979); J.-P. Rouyet and J. Zak, Phys. Rev. B 23, 561 (1981); J. Zak, Phys. Lett. 83A, 287 (1981).
[9]W. Kohn, Phys. Rev. 115, 809 (1959).
[10]J. Zak, Phys. Rev. Lett. 47, 450 (1981).

Fermi-Surface Sum Rule and its Consequences for Periodic Kondo and Mixed-Valence Systems

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(Received 24 July 1981)

The Friedel sum rule for impurities is related to the Luttinger requirement that the volume of the Fermi surface of a crystal is independent of interactions. As a consequence important results derived by use of the Friedel sum rule, e.g., the $T \rightarrow 0$ properties of the Kondo problem, can be extended to periodic cases. Considered explicitly are the remarkable consequences for Fermi surfaces and Fermi-liquid properties of periodic Kondo and mixed-valence systems.

PACS numbers: 71.45.Gm, 72.15.Qm, 75.20.Hr

There are two well-known sum rules which relate properties of states at the Fermi energy μ to the number of fermions, the Friedel sum rule[1] on phase shifts at μ caused by an impurity and the Luttinger sum rule[2] on the volume enclosed by the Fermi surface in a perfect crystal. The derivation by Luttinger showed that the sum rule[2] is a rigorous result of the analytic properties of Fermi liquids,[2,3] including interactions between fermions to all orders. The same techniques were used by Langer and Ambegaokar[4] to provide a general proof of the Friedel sum rule. In subsequent years Fermi-liquid theory including the Friedel sum rule has been one of the most powerful tools in theoretical physics—among its consequences are rigorous expressions for impurity scattering at $T=0$,[4] the "orthogonality catastrophe" and the resulting forms for x-ray edges,[5] and the low-temperature properties of the impurity Kondo problem.[6-8] In the last case the sum rule and the Fermi-liquid analysis have been confirmed in detail by exact solutions[9,10] of the simplest Hamiltonians describing the Kondo problem; even at this stage, however, the sum rule is the only rigorous justification that the results apply to real metals.[7]

The subject of this Letter is the relation of the Friedel and Luttinger sum rules and the consequences of the unified sum rule for periodic systems with strong interactions. The relation is implicit in the work of Langer and Ambegaokar,[4] but apparently it has neither been stated explicitly nor has its importance been realized in the intervening twenty years. The central point of the present work is that the extensive work on impurities[4-10] can be mapped onto periodic systems with consequences of particular significance because of the requirements of translational symmetry. We shall consider explicitly the unsolved problems of much current interest for periodic Kondo and mixed-valence systems[11,12] and we shall see that the sum rule leads to remarkable consequences for the Fermi surface and resulting physical properties.

The Fermi-surface sum rule can be derived in terms of the exact one-electron Green's function[2-4,13] $G_\alpha(z)=\{z-H_\alpha^0-\Sigma_\alpha(z)\}^{-1}$, where H^0 is a noninteracting Hamiltonian, Σ is the proper self-energy, and α is a symmetry label. The basis of Fermi-liquid theory at $T=0$ is that quasiparticle states are well defined at the Fermi energy μ, i.e., that $\Sigma_\alpha(\mu)$ is Hermitian for each α.[2,3] From the analytic conditions which follow for $\Sigma(z)$, the analysis of Luttinger[2] leads directly to the general form of the sum rule,

$$N=(2\pi i)^{-1}\sum_\alpha \mathrm{Tr}\{\ln[-G_\alpha(\mu-i\eta)]-\ln[-G_\alpha(\mu+i\eta)]\}, \tag{1}$$

where N is the number of electrons and the right-hand side is a sum over the phases of $G_\alpha(\mu)$.[2-4,13] Since $\Sigma_\alpha(\mu)$ is Hermitian, the right-hand side can be evaluated in terms of the eigenvalues E_α^n of $H_\alpha^0+\Sigma_\alpha(\mu)$, counting unity for each $E_\alpha^n<\mu$, zero for $E_\alpha^n>\mu$, and a fractional value for $E_\alpha^n=\mu$. In the periodic case the translational symmetry of the many-body system leads to conservation of momentum k within the Brillouin zone; then $\alpha\to k$ and n denotes bands and spin. The Fermi surface of the interacting system is defined by $E_k^n=\mu$, and (1) becomes the Luttinger sum rule,[2,3,13]

$$N=\sum_{kn}\theta(\mu-E_k^n)\equiv V_{\mathrm{FS}}, \tag{2}$$

which equates the volume of the exact Fermi surface V_{FS} in one Brillouin zone to the number of electrons per cell. The Friedel sum rule can be derived[4] from the difference in (1) caused by a localized perturbation in an infinite system: α labels the states in the point symmetry of the impurity and the changes are described by phase shifts $\delta_\alpha(z)$, which at μ are given by[4]

$$2i\delta_\alpha(\mu)=\Delta\,\mathrm{Tr}\{\ln[-G_\alpha(\mu-i\eta)]-\ln[-G_\alpha(\mu+i\eta)]\}.$$

Thus (1) leads directly to the Friedel sum rule for interacting electrons,[1,4]

$$\Delta N=\pi^{-1}\sum_\alpha\delta_\alpha(\mu). \tag{3}$$

The utility of the sum rule can be illustrated by the simplest Hamiltonian which contains the essence of Kondo and mixed-valence effects,[11-19]

$$H=\sum_{k\sigma}\epsilon_k d_{k\sigma}^\dagger d_{k\sigma}+\sum_{i\sigma}\{\epsilon_f f_{i\sigma}^\dagger f_{i\sigma}+\tfrac{1}{2}Un_\sigma^f n_{-\sigma}^f+V(f_{i\sigma}^\dagger d_{i\sigma}+d_{i\sigma}^\dagger f_{i\sigma})\}. \tag{4}$$

Here d labels a simple band with dispersion ϵ_k and width W, f an atomiclike state with no degeneracy except for spin and having a Coulomb interaction U, and V the small f-d hybridization, taken to be site diagonal. For large U the f spectral weight is split into two parts at ϵ_f and ϵ_f+U, each with width $\sim\Delta\sim V^2/W$. Equation (4) describes the Kondo regime for $\epsilon_f\ll\mu$ and $\epsilon_f+U\gg\mu$, where both f peaks are well removed from μ and the f occupation is 1. There is a continuous variation as $\epsilon_f\to\mu$ to the mixed-valence regime with nonintegral f occupation. In the impurity case where the f state is restricted to a single site i, Eq. (4) is the Anderson Hamiltonian[14] and the large-U symmetric case (a half-filled d band with $\epsilon_f=-U/2$, $\epsilon_f+U=U/2$) is equivalent[9] to a spin-$\frac{1}{2}$ Kondo model with $J\sim V^2/U$. The Friedel sum rule (3) can be applied using only the condition that the ground state is a nonmagnetic singlet.[6-9] It follows that $\delta_0(\mu)=\pi/2$ for each spin, i.e., the maximum effect upon the

Fermi surface allowed by the unitarity limit, even if the f spectral weight is almost completely removed from μ by a large U and the coupling V is small. This occurs because of a many-body resonance at μ, having height $1/\Delta$ to satisfy the sum rule[6-8,15] and width[6-10] $T_K \sim \exp(-W/J)$. The solution evolves continuously to $T_K \sim \Delta$ in the mixed-valence regime.[9,15] Furthermore, Nozières[7] and others[6-8,15,16] have derived the low-T properties from Fermi-liquid theory of the states near μ, which has now been verified by exact solutions.[10] This establishes the applicability of Fermi-liquid theory to such impurity problems with strong interactions and forms the basis for understanding more general cases.

The periodic version of Eq. (4), the Anderson lattice,[11,12] has been studied extensively in the case with one f site i and two electrons per unit cell.[13,17-19] If $U = 0$ the solution is an insulator with a gap; therefore for $U \neq 0$, so long as there is no new long-range order, the sum rule requires that $V_{FS} = C$. This can be satisfied either by an insulating gap or, if any states cross μ, by a semimetallic Fermi surface with equal electron and hole contributions.[13] There is now strong evidence that the ground state is a nonmagnetic insulator, based upon numerical calculations on finite cells,[17] renormalization-group results on the one-dimensional Kondo lattice,[18] and coherent-potential approximation[13] and variational[19] calculations for mixed valence. The sum rule is satisfied because for large U there is a many-body resonance[17] at μ in complete analogy with the impurity case. The special feature caused by periodicity is structure in the resonance density of states, which results in the insulating gap for this Hamiltonian.

The new results of this paper are for periodic cases where there is no insulating gap. The sum rule leads to properties not found in any theoretical calculation to date because it has not yet been possible to produce a complete description reconciling the strong local correlations in the f states with a Fermi surface obeying the sum rule. Figure 1 shows schematically energy vs k in a case with *two* wide d bands spanning the Fermi surface and the f spectral weight at ϵ_f and $\epsilon_f + U$. If the d and f electrons were decoupled, then the total Fermi surface counting both d bands would contain n^d electrons. The true Fermi surface, however, must contain $n^d + n^f$ electrons according to the Luttinger sum rule. This is accomplished via a many-body resonance in $\Sigma_k(z)$ near μ giving renormalized Fermi wave vectors k_F, as shown in

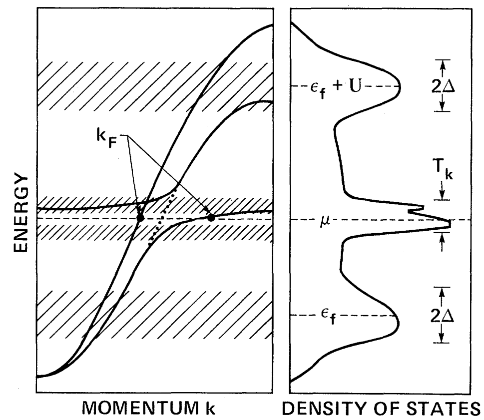

FIG. 1. Schematic spectrum of the Kondo lattice including split-off bands at ϵ_f and $\epsilon_f + U$, the many-body resonance of width $\sim T_K$, and the well-defined renormalized Fermi surface. The scale T_K is expanded for clarity. A case with two wide bands is shown, one hybridized with the f and one not for this direction of k. The dotted line shows the decoupled band ϵ_k, and the solid lines and crosshatching, the effects of coupling to the f. The density of states is similar to the impurity Kondo case (see Fig. 20 of Ref. 8) except that periodicity leads to structure in the many-body resonance.

Fig. 1 for one band (which changes from electronlike to holelike). The other band is shown unaffected to illustrate the fact that along high-symmetry directions the d-band states at μ may be decoupled from the f states. On the right is shown the schematic density of states, which is similar to that for an impurity[7,8] with a resonance at μ of width $\sim T_K$. In addition, however, periodicity leads to structure in the resonance including critical points and a tendency to form the gap which actually occurs for Eq. (4). This tendency suggests that the "four-peak" structure of Fig. 1 is characteristic of the periodic Kondo problem just as three peaks are characteristic of the impurity case.[7,8] So long as the symmetry does not change, the results vary continuously to the mixed-valence limit, as in the impurity case.

The essential conclusion is that, for the *anomalous* cases where there are fractionally occupied f states which act in many ways as localized and atomiclike *but nevertheless do not order magnetically*, then the many-body states at and near the Fermi energy are modified coherently by their presence: (1) The volume of the Fermi surface is the same as if the f states formed simple extended bands at μ, and (2) states near μ are described by an interacting Fermi liquid having a characteristic energy scale $\sim T_K$. This is particularly significant in the periodic case since it shows that the low-energy excitations behave like those of narrow extended bands whether or not the f states are "at" the Fermi energy. In fact, narrow-band behavior, on an energy scale much less than Δ, is direct evidence for Kondo-like effects with the split f spectral weight and the many-body resonance as illustrated in Fig. 1.

There is now a large literature which shows that Kondo and mixed-valence effects occur in many anomalous rare-earth solids.[11,12] Perhaps the most significant recent results are for crystals involving Ce, where the Kondo-like situation has been demonstrated by photoemission[20] experiments on γ-Ce, $CeAl_2$, etc. Narrow-band Fermi-liquid behavior has been observed in many cases,[11,12] and in $CeSn_3$ the Fermi surface has been studied using the de Haas–van Alphen effect[21]; some parts are similar to its normal analog $LaSn_3$ and other parts are qualitatively different with high masses, exactly like the extended narrow-band behavior discussed above and shown in Fig. 1. A more detailed analysis of this and other anomalous crystals will be given elsewhere.[22]

The relations between impurity and periodic cases can be clarified further by general considerations. One primary difference is the possibility of a phase transition to a state of different symmetry and we can identify three situations: (1) If ordering occurs with $T_c \gg T_K$, as in ordinary rare earths, application of the sum rule to the ordered state is completely consistent with ordinary Fermi surfaces. (2) If ordering occurs with $T_c < T_K$, each phase is anomalous and acts as an interacting Fermi liquid of the correct symmetry. (3) If there is no new order, then the present work leads also to the result that certain average properties are independent of the symmetry, so that impurity results apply to general solids, crystalline or disordered. For example, the well-known ratio[7-10,16] χ/γ of enhancements of susceptibility χ and specific heat γ is a general property of Fermi liquids, which has been confirmed experimentally for a large number of anomalous rare-earth crystals.[16]

In summary, I have presented a unified sum rule which encompasses the Friedel sum rule[1] on impurity phase shifts and the Luttinger condition[2] on the volume of the Fermi surface in a crystal. This relation and the extensive previous work on impurities[4-10,14-16] lead directly to interesting properties of periodic Kondo and mixed-valence systems and provide the first step in understanding the low-temperature properties of such strongly interacting periodic systems.

The author gratefully acknowledges many valuable conversations with R. Jullien, A. Blandin, J. Friedel, C. Herring, J. W. Allen, and P. Pfeuty, a useful comment by P. W. Anderson, and partial support by the National Science Foundation.

[1] J. Friedel, Philos. Mag. 43, 153 (1952).

[2] J. M. Luttinger, Phys. Rev. 119, 1153 (1960).

[3] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice Hall, Englewood Cliffs, N.J., 1980).

[4] J. S. Langer and V. Ambegaokar, Phys. Rev. 121, 1090 (1961).

[5] P. W. Anderson, Phys. Rev. Lett. 18, 1049 (1967).

[6] D. C. Langreth, Phys. Rev. 150, 516 (1966).

[7] P. Nozières, J. Phys. (Paris) 39, 1117 (1978); P. Nozières and A. Blandin, J. Phys. (Paris) 41, 193 (1980).

[8] G. Gruner and A. Zawadowski, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1978), Vol. VIIB, p. 591.

[9] K. G. Wilson, Rev. Mod. Phys. 47, 773 (1975); H. R. Krishnamurthy, K. G. Wilson, and J. W. Wilkins, Phys. Rev. B 21, 1044 (1980).

[10] P. B. Weigmann, Pis'ma Zh. Eksp. Teor. Fiz. 31, 392 (1980) [JETP Lett. 31, 364 (1980)]; N. Andrei, Phys. Rev. Lett. 45, 379 (1980).

[11] J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. 44, 1 (1981).

[12] See papers in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. P. Maple (North-Holland, Amsterdam, 1981).

[13] R. M. Martin and J. W. Allen, J. Appl. Phys. 50, 7561 (1979), and Ref. 12, p. 85.

[14] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[15] F. D. M. Haldane, Ref. 12, p. 153.

[16] H. Lustfeld and A. Bringer, Solid State Commun. 28, 119 (1980); D. M. Newns and A. C. Hewson, J. Phys. F 10, 2429 (1980).

[17] R. Jullien and R. M. Martin, to be published.

[18] R. Jullien, P. Pfeuty, and B. Coqblin, Ref. 12, p. 169.

[19] B. H. Brandow, Int. J. Quantum Chem. 13, 423 (1979).

[20] J. W. Allen, S.-J. Oh, I. Lindau, J. M. Lawrence, L. I. Johansson, and S. B. Hagstrom, Phys. Rev. Lett. 46, 1100 (1981).

[21] W. R. Johansson, G. W. Crabtree, A. S. Edelstein, and O. D. McMasters, Phys. Rev. Lett. 46, 504 (1981).

[22] R. M. Martin, in Proceedings of the 27th Annual Conference on Magnetism and Magnetic Materials, 10–13 November 1981, Atlanta, Georgia (J. Appl. Phys., to be published).