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Effective-Mass Parameters for Electronic Energy Bands*

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The continuation of electronic energy bands in the neighborhood of symmetry points is discussed in terms of explicit expressions derived within the Green's-function method. The accuracy and convenience of these formulas are demonstrated in the calculations of specific band parameters at various symmetry points of the Brillouin zone for degenerate as well as nondegenerate states in both nonrelativistic and relativistic problems. Applications of this approach are briefly discussed.

Methods of continuing the band structure $E_n(\vec{k})$ in the neighborhood of a point $\vec{k}_0$ at which $E_n(\vec{k}_0)$ is known are of considerable interest both in theoretical and semiempirical contexts. Standard $\vec{k}\cdot\vec{p}$ perturbation theory gives a straightforward expansion for a nondegenerate Bloch state of band index n and wave vector $\vec{k}_0$ in terms of the momentum matrix elements, $\vec{p}_{nn'}(\vec{k}_0)$, and the inverse effective-mass tensor, which is given by the well-known f-sum rule[1]

$$\left(\frac{m}{m^*}\right)^{(n)}_{ij} = \delta_{ij} + \left(\frac{2}{m}\right) \mathrm{Re} \sum_{n'}{}' \frac{p_{i,nn'}(\vec{k}_0)\, p_{j,n'n}(\vec{k}_0)}{E_n(\vec{k}_0) - E_{n'}(\vec{k}_0)} . \quad (1)$$

This result and the corresponding formulas for degenerate band parameters are quite general and they have been useful in many aspects of solid-state theory. Nevertheless, they do not provide a practical means for accurately calculating the band parameters since the evaluation of the sum over excited states in (1) requires, in general, an appreciable number of energy eigenvalues and a large number of interband momentum matrix elements which are generally unavailable.

A more tractable result for the effective mass at the center of the Brillouin zone was obtained by Bardeen[2] within the spherical approximation. Bardeen's formula is accurate and simple since it involves only the logarithmic derivatives of the s and p radial functions evaluated on the equivalent sphere at the energy of the lowest Γ_1 state. The spherical approximation, however, used in this approach is inapplicable to states other than the s-like Γ_1 state of monatomic cubic crystals. In contrast, the generalization of Bardeen's formula given by Cohen and Ham[3] applies to any symmetry state; however, the evaluation of the surface integral, which appears in their formula to replace the sum over excited states in (1), appears to be a difficult computational task and to our knowledge it has not been carried out for any specific calculations.

In this paper we present and evaluate explicit expressions for the effective-mass parameters at various symmetry points in the Brillouin zone for degenerate as well as nondegenerate bands in both nonrelativistic and relativistic problems. These results, which are derived within the framework of the Green's-function method[4] (GFM), are both very accurate and very convenient to evaluate and, we believe, will be quite useful. That the GFM should be useful in this connection is not surprising in view of its unsurpassed effectiveness in determining $E(\vec{k})$ for crystal potentials which can be approximated by the muffin-tin form.

The GFM dispersion relation is given by

$$\det[B_{LL'}(E, \vec{k}) + \delta_{LL'}E^{1/2}\cot\eta_l] = 0 , \tag{2}$$

where the index $L(\equiv l, m)$ labels the partial-wave components employed in the expansion of the wave function inside the inscribed sphere. Two features of (2) are to be noted here. First, the effects of the potential on the dispersion law, which are incorporated in the phase shifts η_l, are completely separated from the effects of crystal structure, which are described by the structure-dependent terms $B_{LL'}(E, \vec{k})$. Second, as has been amply demonstrated,[5] only the angular momentum components with $l \leq 2$ are necessary to achieve high accuracy in the calculation of $E(\vec{k})$; only these components will be retained in the results of this work. This rapid convergence resulting in a secular determinant of very small order, which can be reduced even further by symmetry, together with the separation of the potential- and structure-dependent terms make the GFM dispersion relation an ideal base for accurate and convenient expansions near symmetry points. In order to achieve the desired results it is only necessary to suitably expand the secular equation about the eigenvalue at $\vec{k}_0$, which we take to be a symmetry point. We define the expansion of the $B_{LL'}$ in a given direction $\delta\vec{k}$ (chosen to best exploit symmetry) by

$$B_{LL'}(E, \vec{k}_0 + \delta\vec{k}) = B_{LL'} + \delta k B_{LL'}^{(1)} + \delta k^2 B_{LL'}^{(2)} + \cdots , \tag{3}$$

where the expansion coefficients $B_{LL'}^{(1,2)}$, etc., evaluated at $\vec{k}_0$ can be computed (and tabulated once and for all for a given crystal structure[6]) as easily as the structure constants themselves.

The expansion of (2) about the s-like Γ_1 state at the bottom of the conduction band for monatomic cubic crystals yields the following simple expression for the effective mass:

$$\frac{m^*(\Gamma_1)}{m} = \left(\frac{F_{10}\,\partial F_{00}/\partial E}{(B_{00,10}^{(1)})^2 - F_{10}B_{00,00}^{(2)}} \right)_{E(\Gamma_1)} , \tag{4}$$

where $F_{lm} \equiv B_{lm,lm} + E^{1/2}\cot\eta_l$ and the expansion coefficients $B_{LL'}^{(1,2)}$ are to be calculated in the direction of any internal symmetry axis. This result, which expresses $m^*(\Gamma_1)$ in terms of only the s and p phase shifts, is as convenient as Bardeen's formula once the structure terms are evaluated. Moreover, this formula is more accurate than Bardeen's result in that the anisotropic Bloch boundary conditions are properly taken into account within the GFM. In fact, this result and all those to be reported below are *exact* expressions of the band parameters for the $E(\vec{k})$ given by the GFM when only the $l = 0$, 1, and 2 angular momentum components are included in the trial functions.

Of more significance than the improved accuracy for $m^*(\Gamma_1)$ is the fact that by the same approach similar results can readily be obtained for symmetry states other than Γ_1. For example, the effective-mass parameters for the X_2 and X_3 states for fcc crystals are simply given by

$$\frac{m^*(X_2)}{m} = -\frac{\partial F_{22s}/\partial E}{B_{22s,22s}^{(2)}} \quad \text{and} \quad \frac{m^*(X_3)}{m} = -\frac{\partial F_{22c}/\partial E}{B_{22c,22c}^{(2)}} , \tag{5}$$

where the various terms are to be evaluated at $\vec{k} = 2\pi/a(1, 0, 0)$ and $E(X_2)$ and $E(X_3)$, respectively. Here, the $B_{LL'}^{(2)}$ are to be calculated in the [100] direction, and the extra subscripts c and s (for cosine and sine) indicate that the appropriate lattice harmonics for these states are of the form $Y_{lmc,s} \propto (Y_{lm} \pm Y_{lm}^*)$, where the Y_{lm}'s are spherical harmonics. These formulas express the effective-mass parameters of these d-like states quite naturally in terms of the $l = 2$ phase shifts.

The extension to degenerate bands is quite straightforward. Here the parameters needed to describe the band structure in the neighborhood of an n-fold degenerate level are contained in a determinantal equation (of order n) of the form $\det(H_{ij} - \lambda\delta_{ij}) = 0$. By way of an example, the three band parameters L, M, and N[1,7] for the three-fold Γ'_{25} state of fcc crystals enter the above secular equation through $H_{11} = Lk_1^2 + M(k_2^2 + k_3^2)$ and $H_{12} = Nk_1k_2$ (and cyclic permutations) with $\lambda = E - k^2$ (in a.u.). These parameters are given in degenerate $\vec{k}\cdot\vec{p}$ perturbation theory in terms of complicated expressions of the type appearing in (1).[7] However, within the GFM we obtain very simply

$$L + 1 = \left(\frac{B_{22c,22c}}{\partial F_{22c}/\partial E} \right)_{E(\Gamma'_{25})} , \tag{6}$$

with similar expressions for M and N. Here $B_{22c,22c}^{(2)}$ is to be calculated in the [100] direction. Details will be published elsewhere.

The extension to the relativistic problem is also quite straightforward, using the relativistic generalization of the dispersion relation (2).[8] In this case the wave function is expanded in terms of spin angular momentum functions labeled by the relativistic quantum numbers κ and μ. The effective mass for the Γ_{6+} state (corresponding to the nonrelativistic Γ_1 state) of fcc crystals is found to be

$$\frac{m^*(\Gamma_{6+})}{m} = \left(\frac{\Phi_{-2}\Phi_1\,\partial\Phi_{-1}/\partial E}{(\Phi_1 + \frac{1}{2}\Phi_{-2})|A_{-1,2}^{(2)}|^2 - A_{-1,-1}^{(2)}\Phi_{-2}\Phi_1} \right)_{E(\Gamma_{6+})} , \tag{7}$$

where $\Phi_K = A_{K,K} + E^{1/2}\cot\eta_\kappa$ and $A_{K,K'} \equiv A_{\kappa\mu,\kappa'\mu}$ with $\mu = \frac{1}{2}$. Here the $A_{\kappa\mu,\kappa'\mu'}$ are linear combinations of the $B_{lm,l'm'}$ appearing in (2) with appropriate Clebsch-Gordan coefficients, while the η_κ are the appropriate relativistic phase shifts.

In Table I we compare the band parameters for a number of different metals, as calculated by formulas of the type discussed above, versus the

TABLE I. Band parameters for various symmetry states of various metals.

Symmetry state	m^*/m by GFM formula	m^*/m by fitting $E(\vec{k})$
Γ_1, Cu	0.9415	0.9414
Γ_{25}', Cu, L[a]	−1.298	−1.298
M	−0.7308	−0.731
N	2.799	2.78
Γ_{12}, Cu, L[a]	−0.6475	−0.648
J	−0.4389	−0.439
X_1, Cu, along Δ	4.450	4.45
X_3, Cu, along Δ	3.519	3.52
X_2, Cu, along Δ	−9.015	−9.01
X_5, Cu, along Δ	−2.320	−2.32
X_4', Cu, along Δ	−0.1155	−0.12
L_2', Cu, along Λ	−0.1405	−0.145
$\perp$ to Λ	0.2486	0.25
Γ_1, Li	1.293	1.293 (1.321)[b]
Γ_1, Na	0.9701	0.970 (0.967)[b]
Γ_1, K	0.8726	0.8725 (0.867)[b]
Γ_{6+}, Pb	0.9555	0.9554

[a] See Ref. 7.

[b] See Ref. 9, Table VI.

same quantities obtained by numerically fitting $E(\vec{k})$, calculated by the GFM for the same potential, (i.e., phase shifts), over a suitable range of $\vec{k}$ in the vicinity of the symmetry point in question. In cases where we can obtain accurate fitted values with a reasonable effort the agreement is excellent; however, in those cases where $E(\vec{k})$ is parabolic only over a small region, as in the vicinity of X_4' and L_2', the numerical fitting requires very precise eigenvalues in order to yield values as accurate as those in the second column. Included in Table I are the Γ_1 masses for the first three alkali metals using the phase shifts obtained by Ham through the quantum defect method and employed by him in his comprehensive GFM study of the alkali metal family.[9] While the alkali masses obtained from (4) agree with the fitted values to within less than 0.1%, they differ from the values (in brackets) given by Ham by as much as 3% in the case of Li. This is explained by the fact that Ham's m^* values were obtained from a least-squares fit of the expression $E_0+E_2k^2+E_4k^4$ to the calculated $E(\vec{k})$ over a large range of k (sometimes as large as $\frac{5}{8}$ of the zone dimension), while our values give the curvature of $E(\vec{k})$ at $\vec{k}=0$. Thus, they are somewhat different quantities, and this difference is largest in the case of Li, where the deviation from parabolicity is the greatest.

To illustrate the results of Table I we have plotted in Fig. 1 the band structure of Cu in the [100] direction from the bottom of the s-p conduction band to energies well above the d bands and the Fermi level. The dotted curves represent the parabolic expansions about Γ and X using the band parameters of the second column of Table I. The solid curves are the energies obtained by the standard GFM. The substantial range of $\vec{k}$, over which there is close agreement between the two sets of curves for this relatively complicated band structure, is to be noted. The band which has the smallest range over which there is close agreement is understandably the Δ_1 band connecting with the p-like X_4' state. In this case, where the curvature of $E(\vec{k})$ changes from negative to positive at a value of k very close to the zone face, one should not expect a quadratic expansion to be faithful over a large range of $\delta\vec{k} = \vec{k}-\vec{k}(X)$. Improved expansions can be achieved by including the δk^4 (and higher-order) terms and by other variations of the approach, which we are presently investigating.

In this paper we have outlined a procedure for expanding energy bands near symmetry points and we have demonstrated that it is almost trivial to

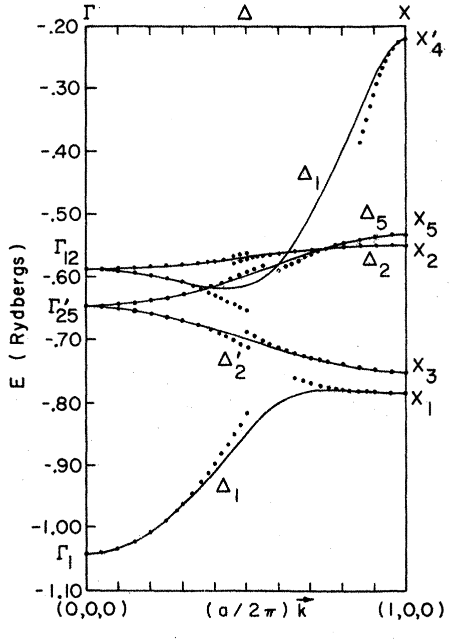

FIG. 1. Band structure of Cu (Chodorow potential) in the [100] direction. Solid curves were calculated by the standard GFM; dotted curves were calculated by using the effective-mass parameters of the second column of Table I.

apply this method in actual calculations of the band structure over most of the zone using only the second-order parameters. In fact, one would be able to obtain a complete picture of the whole spectrum by making use of the higher-order expansion parameters and, if needed, by calculating $E(\vec{k})$ separately only at a few points and in those portions of the zone that might be inaccessible by the expansion parameters. Such expansions will give the band structure itself [rather than an interpolation Hamiltonian whose secular determinant still needs to be evaluated in order to get $E(\vec{k})$] in terms of only a small number of parameters. This in turn will greatly simplify the calculation of such quantities as the density of states, etc. In addition, this procedure is well suited to accurately resolve the detailed band structure of "pockets" of states in those regions of the zone which are of particular physical importance. Here we note that expansions with the relativistic coefficients will accurately determine the small spin-orbit coupling parameters which are of critical importance in such contexts as magnetic breakdown, g factors, etc. Also, with appropriate modifications for nonmuffin-tin potentials, it might not be too optimistic, perhaps, to extend even to semiconductors these selective studies of important regions of the zone.

What is more important, however, than the calculational merits of this expansion procedure is the fact that it can be used in semiempirical contexts as an interpolation scheme. Moreover, in contrast with other interpolation schemes where the adjustable parameters are of no direct physical significance, the fitting parameters of this scheme are the effective-mass parameters of this work which are expressed explicitly in terms of the phase shifts of the *real* (rather than pseudo) crystal potential. Therefore, blending these first-principles formulas with empirical information will put useful constraints on the phase shifts and thus, in turn, will provide specific information about the underlying crystal field.

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Cyclotron Resonance from a Fractional Orbit in Silver†

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Cyclotron resonance has been observed from a fraction of a dog's-bone orbit in silver under conditions where the carriers are effectively prevented from making more than two transits through the skin layer. In the high-$\omega_c\tau$ limit, the properties of such a resonance are shown to differ significantly from those of a conventional cyclotron-resonance spectrum. The requirements on the alignment of the sample surface relative to the crystal axis and on the flatness of the sample are very severe when the magnetic field points in a symmetry direction. These requirements are relaxed by an order of magnitude by a slight misorientation of the magnetic field.

A conventional Azbel'-Kaner[1] cyclotron-resonance experiment measures the cyclotron mass associated with a closed orbit in k space. A steady magnetic field is applied parallel to a flat metal surface, and the resonance is caused by the multiple interaction between the electromagnetic field and electrons passing through the skin layer once per revolution. In the case of a concave orbit, a situation may arise