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Note

Analytical Wavefunction Normalization Procedure in KKR-Method

I. Introduction

The KKR-method is a well-known technique for investigating the band structure of crystals [1–3]. This method exactly solves the eigenvalue problem for a one-electron Schrödinger equation with a given crystal potential. Segall and Juras [4] and Chen and Segall [5] obtained (using the KKR-method) the exact expressions for the derivatives of the one-electron energy $E(\mathbf{k})$ with respect to the wave vector $\mathbf{k}$ and the potential shift. The latter is used for normalization of the one-electron wavefunctions. A direct computation of the linear energy shift caused by the finite potential shift for the normalization procedure [3] requires additional computing effort. Another approach to the normalization problem is described by Janak *et al.* [6].

In this paper a new normalization procedure, the expressions for the group velocity $\mathbf{V} = \partial E/\partial \mathbf{k}$ and the inverse mass tensor $1/m_{ij} = \partial^2 E/\partial k_i \, \partial k_j$ are presented. The technique for evaluating the derivatives of the normalization factor and the expansion coefficients of the wavefunction are also described. The latter can be used to extrapolate both $E(\mathbf{k})$ and the wavefunction in the neighbourhood of each KKR-point. This procedure decreases computing requirements for self-consistent band calculations.

All the expressions for the above-mentioned derivatives are exact within the framework of the KKR-method. They may be obtained analytically (i.e., without using numerical differentiations) and, unlike [4], have a simple form for an arbitrary $\mathbf{k}$-point in the Brillouin zone.

In Section II the basic equations of the KKR-method and the wavefunction normalization procedure from [3] are described. An analytic normalization procedure is derived in Section II. Expressions for the group velocity and the inverse mass tensor are presented in Section IV.

II. Basic Equations

The KKR-method is a "cellular" one. Solutions of Schrödinger's equation are found only within a single unit cell. The crystal potential is represented approximately in the "muffin-tin" form as a spherically symmetric $U(r)$ within the sphere inscribed in the cell and a constant U_{out} elsewhere. Denote the region of a cell within

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the inscribed sphere as Ω_{I} and that outside the spherical region as Ω_{II}. The radius of the sphere equals "b."

The wavefunction $\Psi_{\mathbf{k}}(\mathbf{r})$ within a cell is represented in the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_L (i)^l \cdot C_L \cdot R_L(r) \cdot Y_L(\mathbf{r}), & \text{if} \quad r \leqslant b \\ \sum_L (i)^l \left[A_L \cdot n_l(\kappa r) + B_L \cdot j_l(\kappa r)\right] \cdot Y_L(\mathbf{r}), & \text{if} \quad r > b. \end{cases} \tag{1}$$

The functions $Y_L(\mathbf{r})$ are linear combinations of spherical harmonics. The combinations are chosen such that they transform under the irreducible representations of the symmetry group of the wave vector $\mathbf{k}$. "L" is a set of orbital quantum numbers (l, m). $R_l(r)$ is a radial function which satisfies the radial differential equation in Ω_I

$$\frac{d^2R_l(r)}{dr^2} + \frac{2}{r} \cdot \frac{dR_l(r)}{dr} + \left(E - U(r) - \frac{l(l+1)}{r^2}\right) \cdot R_l(r) = 0, \tag{2}$$

where $n_l(x)$ and $j_l(x)$ are spherical Neuman and Bessel functions. κ is determined by the relation:

$$\kappa^2 = \begin{cases} E - U_{\text{out}}, & \text{if} \quad E > U_{\text{out}}, \\ U_{\text{out}} - E, & \text{if} \quad E < U_{\text{out}}. \end{cases} \tag{3}$$

When $E < U_{\text{out}}$, the factors $(i)^l$ in Eq. (1) are deleted and the substitutions $n_l(x) \to k_l^{(1)}$, $j_l(x) \to i_l(x)$ are performed. Here $i_l(x) = (i)^{-l} j_l(ix)$, $k_l^{(1)}(x) = -(i)^{-l} h_l^{(1)}(ix)$ and $h_l^{(1)}(x)$ is the spherical Hankel function.

Note that the original KKR equation assumes U_{out} is identically zero. The shift of the crystal potential by a constant amount, however, generates a constant shift for all energy levels. Hence, all the KKR equations with an arbitrary constant U_{out} will be valid, if, in an expression for the Green's function, the substitution $E \to E - U_{\text{out}}$ is performed.

The coefficients C_L, B_L are determined by the relations

$$C_L = \frac{A_L}{\kappa b^2 \left[j_l(\kappa b) \cdot \dfrac{\partial R_l(b)}{\partial b} - R_l(b) \cdot \dfrac{\partial j_l(\kappa b)}{\partial b} \right]}, \tag{4}$$

$$B_L = \sum_L G_{LL'}(\kappa, \mathbf{k}) \cdot A_L, \tag{5}$$

where $G_{LL'}(\kappa, \mathbf{k})$ are coefficients derived from a Green's function, and are distinguished from $B_{LL'}$ in [3] by $G_{LL'}(\kappa, \mathbf{k}) = \kappa \cdot B_{LL'}$. The coefficients A_L are solutions of the system of linear homogeneous equations

$$A_L \cdot \frac{R_l(b) \cdot \dfrac{\partial n_l(\kappa b)}{\partial b} - n_l(\kappa b) \cdot \dfrac{\partial R_l(b)}{\partial b}}{j_l(\kappa b) \cdot \dfrac{\partial R_l(b)}{\partial b} - R_l(b) \cdot \dfrac{\partial j_l(\kappa b)}{\partial b}} - \sum_{L'} G_{LL'}(\kappa, \mathbf{k}) A_{L'} = 0. \tag{6}$$

For a fixed $\mathbf{k}$ the value E is determined by the requirement that the determinant of the system of Eqs. (6) must equal zero. For self-consistent calculations the wavefunction has to be normalized:

$$N \cdot \int_{\Omega_I + \Omega_{II}} \kappa^2 \cdot |\psi_{\mathbf{k}}(\mathbf{r})|^2 \cdot d\tau = 1. \tag{7}$$

N is a normalization factor. Integrating over Ω_I leads to an expression for the non-normalized charge of Ω_I:

$$q = \sum_L q_L, \tag{8}$$

$$q_L = \kappa^2 \cdot |C_L|^2 \cdot \int_0^b R_l^2(r)\, r^2\, dr. \tag{9}$$

The factor κ^2 is inserted for convenience.

Instead of integrating over the complex region Ω_{II}, one may find the normalized charge of Ω_I by shifting the potential for $r < b$ by a small constant amount ΔU_{out}. The corresponding shifted eigenvalue $\tilde{E} = E + \Delta E$ can be found by a standard method. The difference ΔE is given in first-order perturbation theory by

$$\Delta E \cdot \int_{\Omega_I + \Omega_{II}} |\psi_{\mathbf{k}}(\mathbf{r})|^2\, d\tau = \Delta U_{\text{out}} \cdot \int_{\Omega_I} |\psi_{\mathbf{k}}(\mathbf{r})|^2 \cdot d\tau.$$

The normalized charge q_N and N are now determined by the relationships

$$q_N = \Delta E / \Delta U_{\text{out}}, \tag{10}$$

$$N = q_N / q. \tag{11}$$

This normalization procedure requires repeated evaluation of the determinant of the system of Eqs. (6), in order to determine $\tilde{E}$. Moreover, large accuracy is required to minimize computational error of numerical differentiation (10).

III. Analytical Normalization Procedure

Equation (6) may be written in a form which reflects the continuity of the logarithmic derivative of $\psi_{\mathbf{k}}(\mathbf{r})$ on the sphere:

$$\frac{\partial R_l(b)}{\partial b} \Big/ R_l(b) = \frac{A_L \cdot \dfrac{\partial n_l(\kappa b)}{\partial b} + B_l \cdot \dfrac{\partial j_l(\kappa b)}{\partial b}}{A_L \cdot n_l(\kappa b) + B_L \cdot j_l(\kappa b)}. \tag{12}$$

Consider an infinitesimal constant shift δU_{out} for the potential in Ω_{II}.

Equation (12) will be satisfied by new values $\tilde{E} = E + \delta E$, $\tilde{A} = A_L + \delta A_L$, $\tilde{\kappa} = \kappa + \delta\kappa$, where

$$\delta\kappa = \begin{cases} (\delta E - \delta U_{\text{out}})/2\kappa, & \text{if} \quad E > U_{\text{out}} \\ (\delta U_{\text{out}} - \delta E)/2\kappa, & \text{if} \quad E < U_{\text{out}}. \end{cases} \tag{13}$$

First consider the case $E > U_{\text{out}}$. The right- and left-hand sides of Eq. (12) may be expanded for the original E, A_L, κ and multiplied by the same factor

$$\begin{aligned} \rho &= (\kappa b)^2 \cdot |C_L|^2 \cdot R_l^2(b)/\delta E \\ &= (\kappa b)^2 \cdot [A_L \cdot n_l(\kappa b) + B_L \cdot j_l(\kappa b)]^2/\delta E. \end{aligned} \tag{14}$$

A direct calculation and using relationship

$$j_l(x) \cdot \frac{dn_l(x)}{dx} - n_l(x)\frac{dj_l(x)}{dx} = \frac{1}{x^2}$$

leads to

$$\left(\frac{\partial^2 R_l(b)}{\partial E\,\partial b} \cdot R_l(b) - \frac{\partial R_l(b)}{\partial b} \cdot \frac{\partial R_l(b)}{\partial E}\right) \cdot |C_L|^2 \cdot (\kappa b)^2$$

$$= Q_L \left(1 - \frac{\delta U_{\text{out}}}{\delta E}\right) + \kappa A_L \cdot \sum_{L'} G_{LL'}(\kappa, \mathbf{k})\, A_{L'} + 0(\delta U_{\text{out}}^2), \tag{15}$$

$$Q_L = \frac{|A_L|^2 \cdot \left[\left(\dfrac{l(l+1)}{b^2} - E + U_{\text{out}}\right) \cdot R_l(b) - \dfrac{\partial R_l(b)}{\partial b}\left(\dfrac{\partial R_l(b)}{\partial b} + R_l(b)/b\right)\right]}{2 \cdot b \cdot \left[j_l(\kappa b)\dfrac{\partial R_l(b)}{\partial b} - R_l(b) \cdot \dfrac{\partial j_l(\kappa b)}{\partial b}\right]}$$

$$- \frac{1}{2} A_L \cdot \sum_{L'} \frac{\partial G_{LL'}(\kappa, \mathbf{k})}{\partial \kappa} \cdot A_{L'}. \tag{16}$$

The relation

$$\begin{aligned} \frac{\partial^2 n_l(\kappa b)}{\partial\kappa\,\partial b} &= \frac{b}{\kappa}\frac{\partial^2 n_l(\kappa b)}{\partial b^2} + \frac{1}{\kappa}\frac{\partial n_l(\kappa b)}{\partial b} \\ &= \frac{b}{\kappa}\left[\left(\frac{l(l+1)}{b^2} - \kappa^2\right) n_l(\kappa b) - \frac{\partial n_l(\kappa b)}{\partial b}\right] \end{aligned} \tag{17}$$

and a similar relation for $\partial^2 j_l(\kappa \cdot b)/\partial\kappa\,\partial b$ were also used. The continuity of the wavefunction and its derivative on the sphere allows the substitution of $R_l(b)$ for $n_l(\kappa b)$ and $j_l(\kappa b)$.

The left-hand side of Eq. (15) can be related to the non-normalized charge of Ω_l [7]. Following [7], take the derivatives of both sides of equation

$$\nabla^2 \psi_{\mathbf{k}}(\mathbf{r}) = (U(\mathbf{r}) - E)\, \psi_{\mathbf{k}}(\mathbf{r})$$

with respect to E in the form

$$\int_{\Omega_I} \bar{\psi}_{\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial E} \nabla^2 \psi_{\mathbf{k}}(\mathbf{r})\, d\tau = \int_{\Omega_I} \bar{\psi}_{\mathbf{k}}(\mathbf{r}) \left[(U(\mathbf{r}) - E) \frac{\partial \bar{\psi}_{\mathbf{k}}(\mathbf{r})}{\partial E} - \psi_{\mathbf{k}}(\mathbf{r}) \right] d\tau, \tag{18}$$

which reduces to

$$\int_{\Sigma_I} d\mathbf{s} \left[\bar{\psi}_{\mathbf{k}}(\mathbf{r}) \frac{\partial}{\partial E} \nabla \psi_{\mathbf{k}}(\mathbf{r}) - \frac{\partial \psi_{\mathbf{k}}(\mathbf{r})}{\partial E} \cdot \nabla \bar{\psi}_{\mathbf{k}}(\mathbf{r}) \right] = - \int_{\Omega_I} |\psi_{\mathbf{k}}(\mathbf{r})|^2\, d\tau. \tag{19}$$

Here Σ_I is the surface which covers the region Ω_I, i.e., the spherical surface.

Using the explicit expression for $\psi_{\mathbf{k}}(\mathbf{r})$, we get

$$|C_L|^2 \cdot b^2 \left[\frac{\partial^2 R_l(b)}{\partial b\, \partial E} \cdot R_l(b) - \frac{\partial R_l(b)}{\partial b} \cdot \frac{\partial R_l(b)}{\partial E} \right] = - \frac{q_L}{\kappa^2}. \tag{20}$$

When $\delta U_{\text{out}} \to 0$, Eq. (15) transforms to

$$Q_L \cdot X_0 + \kappa A_L \cdot \sum_{L'}{}' G_{LL'}(\kappa, \mathbf{k})\, X_{L'} - \kappa X_L \cdot \sum_{L'}{}' G_{LL'}(\kappa, \mathbf{k})\, A_{L'} = q_L, \tag{21}$$

where $X_0 = 1/Q_N - 1$, $X_L = \partial A_L / \partial E$; $Q_N = \partial E / \partial U_{\text{out}}$ is the normalized charge of Ω_{II}. We are restricted to the case of $\delta A_0 = 0$ (one coefficient in a system of linear homogeneous Eqs. (6) may be considered arbitrary).

The system of Eqs. (21) determines Q_N and $\partial A_L / \partial E$, whereas

$$N = \frac{1 - Q_N}{q}. \tag{22}$$

Consider the case where

$$G_{LL'}(\kappa, \mathbf{k}) = G_{L'L}(\kappa, \mathbf{k}). \tag{23}$$

Using the summation of Eqs. (21) over all "L" and Eq. (23) gives

$$X_0 \cdot \sum_L{}' Q_L = \sum_L{}' q_L. \tag{24}$$

Hence,

$$Q_N = \frac{\sum_L Q_L}{\sum_L Q_L + q_L}, \tag{25}$$

$$q_N = \frac{\sum_L q_L}{\sum_L Q_L + q_L}. \tag{26}$$

It is not essential to solve the system of Eqs. (21). The value of $Q = \sum_L Q_L$ may be interpreted as the non-normalized charge of Ω_{II}. The expression for Q_L would be obtained if the same method used in deriving Eq. (20) is used with the replacement: $\Omega_I \to \Omega_{II}$, $\Sigma_I \to \Sigma_{II}$. Σ_{II} represents the inscribed sphere and the complex surface of the crystal cell boundary. In cases of special cell symmetry, when condition (23) applies (for example, simple cubic, "bcc," and "fcc" lattices), integration over the complex surface vanishes. The wavefunction and its derivatives on those cell boundary planes related to each other by symmetry transformations will be the same in accord with periodic boundary conditions for $\psi_{\mathbf{k}}(\bar{r})$, as long as the directions of normals of these planes are opposite. Hence, the integral over the complex part of Σ_{II} vanishes and the expression for Q_L coincides with (16).

Note that Eq. (16) is similar to Eq. (A10) in Ref. [8], which uses augmented spherical waves and the periodicity of $\psi_{\mathbf{k}}$ and $\partial\psi_{\mathbf{k}}/\partial E$, so that the integral over the surface of the unit cell vanishes.

When $E < U_{\text{out}}$, Eq. (6) is transformed by the substitutions: $n_l(x) \to k_l^{(1)}(x)$, $j_l(x) \to i_l(x)$, $G_{LL'}(\kappa, \mathbf{k}) \to (-1)^{l'+1} G_{LL'}(\kappa, \mathbf{k})$. The expression for Q_L in this case coincides with (16), except for the opposite sign. Equations (20)–(26) are unaltered. The opposite sign in Eq. (16) is due to the opposite sign of κ^2. The factor $(-1)^{l'+1}$ before $G_{LL'}(\kappa, \mathbf{k})$ is compensated by the same factor in the relationship

$$i_l(x)\frac{dk_l^{(1)}(x)}{dx} - k_l^{(1)}(x)\cdot\frac{di_l(x)}{dx} = \frac{(-1)^{l+1}}{x^2},$$

which is used in deriving Q_L.

For "complex" lattices Q_L and q_L are obtained by summing over all spherical regions, i.e., over basis of the unit cell. The expression for Q_N, when Eq. (23) is true, is analogous to the result of [9] for a normalized charge outside the spherical regions obtained in the scattering-waves method. The analogy will be complete if the external sphere contribution is neglected.

A test calculation of q_N from (26) with the Mathieu potential for (2) gives a result coinciding with Eq. (10).

IV. Group Velocity and Inverse Mass Tensor

Consider an infinitesimal shift $\mathbf{k} \to \mathbf{k} + \delta\mathbf{k}$. Using a technique similar to that used in developing Eq. (21), we find

$$(Q_L + q_L)\frac{\partial E}{\partial \mathbf{k}} + \kappa \cdot \sum_{L'} G_{LL'}(\kappa, \mathbf{k})\left(A_{L'}\frac{dA_L}{d\mathbf{k}} - A_L \cdot \frac{dA_{L'}}{d\mathbf{k}}\right)$$
$$= \kappa \cdot A_L \cdot \sum_{L'} \frac{\partial G_{LL'}(\kappa, \mathbf{k})}{\partial \mathbf{k}} \cdot A_{L'}. \tag{27}$$

Direct differentiation of Eq. (27) gives

$$(Q_L + q_L) \cdot \frac{\partial^2 E}{\partial k_i \partial k_j} + \sum_{L'} G_{LL'}(\kappa, \mathbf{k}) \cdot \left(\frac{dZ_{Li}}{dk_j} A_{L'} - A_L \frac{dZ_{L'i}}{dk_j} \right)$$

$$= -V_i \frac{d}{dk_j}(Q_L + q_L) + \sum_{L'} \frac{d}{dk_j} \frac{\partial G_{LL'}(x, \mathbf{k})}{\partial k_i} A_L A_{L'}$$

$$+ \sum_{L'} \frac{dG_{LL'}(\kappa, \mathbf{k})}{dk_j} (A_L \cdot Z_{L'i} - A_{L'} \cdot Z_{Li})$$

$$+ \sum_{L'} \frac{\partial G_{LL'}}{\partial k_i} \left(A_L Z_{L'j} + Z_{Lj} A_{L'} + A_L A_{L'} V_j \frac{\partial \kappa}{\partial E} \right), \tag{28}$$

where $Z_{Li} \equiv \kappa(dA_L/dk_i)$. From a comparison of (22) with (25)–(26)

$$N = \frac{1}{\sum_L Q_L + q_L}. \tag{29}$$

Hence,

$$\frac{dN}{d\mathbf{k}} = -N^2 \cdot \sum_L \frac{d}{d\mathbf{k}}(Q_L + q_L), \tag{30}$$

$$\frac{d^2 N}{dk_i\, dk_j} = -N^2 \cdot \sum_L \frac{d^2}{dk_i\, dk_j}(Q_L + q_L) - \frac{2}{N} \frac{dN}{dk_i} \cdot \frac{dN}{dk_j}. \tag{31}$$

Equations (28)–(31) require knowledge of $\partial^n R_l(b)/\partial E^n$ and $(\partial^n/\partial E^n)(\partial R_l(b)/\partial b)$ for $n = 0, 1, 2$. These derivatives are determined by Eq. (2) and

$$\left(\nabla^2 + E - U(r) - \frac{l(l+1)}{r^2} \right) \frac{\partial R_l(r)}{\partial E} = -R_l(r), \tag{32}$$

$$\left(\nabla^2 + E - U(r) - \frac{l(l+1)}{r^2} \right) \cdot \frac{\partial^2 R_l(r)}{\partial E^2} = -2 \cdot \frac{\partial R_l(r)}{\partial E}. \tag{33}$$

Equations (27)–(33) determine $\mathbf{V} = \partial E/\partial \mathbf{k}$, $1/m_{ij} = \partial^2 E/\partial k_i\, \partial k_j$ and the derivatives of the normalized expansion coefficients $\tilde{A}_L = \sqrt{N} \cdot A_L$. This permits extrapolation of $E(\mathbf{k})$ and $\psi_{\mathbf{k}}(\mathbf{r})$ between two neighbouring $\mathbf{k}$-points and, therefore, decreases the total number of points determined by the KKR-method. When Eq. (23) is valid, the summation Eqs. (27), (28) over all "L" gives

$$\mathbf{V} = \kappa \cdot N \sum_{L,L'} A_L \frac{\partial G_{LL'}(\kappa, \mathbf{k})}{\partial \mathbf{k}} \cdot A_{L'}, \tag{34}$$

$$\frac{1}{m_{ij}} = \frac{V_i}{N} \cdot \frac{dN}{dk_j} + \sum_{L,L'} \frac{\partial G_{LL'}(\kappa, \mathbf{k})}{\partial k_i} \left(2 \cdot A_{L'} \cdot Z_{Lj} + A_L \cdot A_{L'} \frac{\partial \kappa}{\partial E} V_j \right)$$

$$+ \kappa A_L A_{L'} \frac{d}{dk_j} \left(\frac{\partial G_{LL'}(\kappa, \mathbf{k})}{\partial k_i} \right). \tag{35}$$

Equations (27)–(35) are exact within the framework of the KKR-method which uses the derivatives of the $G_{LL'}$-coefficients obtained analytically from equations of [3]. Accurate evaluation of the above and higher derivatives of $\mathbf{V}$, A_L and N depends on convergence of the series for $\partial^i G_{LL'}/\partial\kappa^j\,\partial\mathbf{k}^{i-j}$ and the accuracy of the numerical calculation of Eqs. (32)–(37).

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