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The Korringa–Kohn–Rostoker method and momentum density calculations in solids

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Abstract. We point out an omission in an often used form of the variational functional in the Korringa–Kohn–Rostoker method of electronic band structure calculation. This omission does not affect the results of Kohn and Rostoker, but leads to incorrect results for matrix elements calculated from the variational functional for a crystal with more than one atom per unit cell and muffin-tin spheres of unequal sizes. We also discuss the form of the momentum density and its behaviour in the vicinity of free-electron energies.

1. Introduction

A few years ago Mijnaerends and Rabou (1986, hereafter referred to as MR) published a method for calculating the momentum density based on the Korringa–Kohn–Rostoker (KKR) method of electronic band structure calculation. The MR scheme has been applied to a number of solids and has proved to be a reliable way to compute momentum densities for Compton scattering and two-photon annihilation of thermalised positrons (e.g. Hanssen and Mijnaerends 1986). However, when the method was implemented recently for use in high- T_c ceramic superconductors (Bansil *et al* 1988; this reference of course presents the results based on the correct formulae for a general lattice) it was found to yield incorrect results for the momentum density; unphysical discontinuities appeared to occur in the momentum density of these materials in the vicinity of band energies accidentally degenerate with the free-electron energy at a specific wave vector k . It became clear that the problems were caused by the unwarranted presence in the wave functions of factors of $r_{i\mu}^2$, where $r_{i\mu}$ denotes the muffin-tin radius of an atom of type μ . The error is somewhat subtle and may affect other calculations based on KKR theory, since it could be traced to the omission of factors r_i^2 from the expression for the variational functional Λ given by Kohn and Rostoker (1954, hereafter denoted by KR) and found in textbooks (e.g. Jones and March 1973). This functional forms the basis for conventional KKR theory and several later developments (Segall 1957, MR). We emphasise that the omission of these factors in the variational functional affects the wave functions but not the secular equation, and thus not the eigenvalues. For monatomic crystals discussed in KR these differences are of no consequence: the wave function given by KR contains a spurious factor r_i^2 , but this factor is cancelled out when the wave function is normalised. However, for crystals with more than one atom per unit cell in which muffin-tin spheres

of unequal sizes are admitted (Segall 1957, MR), these factors do not cancel and erroneous wave functions are produced.

The outline of this article is as follows. Section 2 discusses the KKR wave function. To avoid excessive formalism, the notation of KR and MR is closely followed and frequent reference to the equations in these papers is made. The correct formulae for the electron momentum density and the electron-positron momentum density are presented in section 3. In section 4 the behaviour of the momentum density in the vicinity of free-electron energies $E = p^2$ is investigated. Since the KKR theory involves functions that are singular at these energies, care is necessary in evaluating the momentum density. By expanding the relevant quantities in powers of $E - p^2$ we show that the momentum density is well-behaved near $E = p^2$ and that the formulae derived in this paper facilitate numerical computation also in the close vicinity of free-electron energies. A short discussion completes the article.

2. Wave functions in the KKR formalism

For notational convenience we consider a monatomic system, even though our primary interest is in crystals with more than one atom per unit cell. Kohn and Rostoker (1954) have shown that the band structure problem is equivalent to the variational principle $\delta\Lambda = 0$, where

$$\Lambda = \lim_{\varepsilon \rightarrow 0} \Lambda_\varepsilon$$

with (KR (3.12))

$$\Lambda_\varepsilon = \int_{r < r_i - 2\varepsilon} ds \int_{r' < r_i - \varepsilon} ds' \left(\frac{\partial \psi^*(\mathbf{r})}{\partial r} - \psi^*(\mathbf{r}) \frac{\partial}{\partial r} \right) \left(\psi(\mathbf{r}') \frac{\partial}{\partial r'} G(\mathbf{r}, \mathbf{r}') - G(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial r'} \psi(\mathbf{r}') \right). \quad (1)$$

For a system of spherically symmetric non-overlapping muffin-tin potentials of radius r_i , the functional Λ_ε can be evaluated by expanding the Green function $G(\mathbf{r}, \mathbf{r}')$ and the wave function $\psi(\mathbf{r})$ in the form (KR (3.13) and (3.7))

$$G(\mathbf{r}, \mathbf{r}') = \sum_{LL'} (A_{LL'} j_l(\kappa r) j_{l'}(\kappa r') + \kappa \delta_{LL'} j_l(\kappa r) n_{l'}(\kappa r')) \times Y_L^*(\hat{r}) Y_{L'}(\hat{r}') \quad r < r' < r_i \quad (2)$$

and†

$$\psi(\mathbf{r}) = \sum_L i^l C_L R_l(r) Y_L(\hat{r}). \quad (3)$$

Here $\kappa = E^{1/2}$, the composite index L stands for (l, m) , the $A_{LL'}$ are the familiar KKR structure functions (KR (A2.5)), the R_l denote regular solutions of the radial Schrödinger

† The use of i^l in the wave function allows the use of real spherical harmonics, but otherwise is of no consequence.

equation, and the other quantities have their conventional meaning. If the expansions (2) and (3) are substituted into (1) and the limit $\varepsilon \rightarrow 0$ is taken, one readily finds

$$\Lambda = \sum_{LL'} C_L^* r_l^2 (R_l' j_l - R_l j_l') \left(i^{-l+l'} A_{LL'} + \kappa \delta_{LL'} \frac{R_l n_l' - R_l' n_l}{R_l j_l' - R_l' j_l} \right) \times (R_l' j_l' - R_l j_l) r_l^2 C_{L'}. \quad (4)$$

The right-hand side of (4) differs from the equivalent expression in KR (3.15) in the presence of two factors r_l^2 which stem from the two surface integrations in (1).

The Wronskians in (4) can be evaluated in terms of the phase shifts η_l by using the relations

$$R_l' j_l - R_l j_l' = (\tan \eta_l) / \kappa r_l^2 \quad (5)$$

$$R_l' n_l - R_l n_l' = 1 / \kappa r_l^2. \quad (6)$$

Equations (5) and (6) implicitly require that the wave functions are normalised such that $R_l = j_l(\kappa r) - (\tan \eta_l) n_l(\kappa r)$ for $r > r_i$; equation (4) on the other hand is valid for any normalisation of R_l . By inserting (5) and (6) into (4) and introducing new coefficients \bar{C}_L according to ((cf KR (3.21), MR (8), MR (10))

$$C_L = (\bar{C}_L / r_l^2) (R_l' j_l - R_l j_l')^{-1} \quad (7)$$

or

$$C_L = \kappa (\cot \eta_l) \bar{C}_{L'} \quad (8)$$

equation (4) may be written as

$$\Lambda = - \sum_{LL'} \bar{C}_L^* M_{LL'} \bar{C}_{L'} \quad (9)$$

where the elements of the matrix **M** are defined by the expression between large brackets on the right-hand side of (4).

Application of the variational principle to (9) leads to the system of homogeneous equations (KR (3.21), MR (7))

$$\sum_{LL'} M_{LL'} \bar{C}_{L'} = 0 \quad (10)$$

which may be solved by searching for the zeros of the determinant of **M**. Normalisation of the wave function belonging to eigenvalue E_j can be obtained in terms of the energy derivative of the functional Λ (Hubbard and Mijnaerends 1972)

$$\int_{\tau} |\psi(\mathbf{r})|^2 d\mathbf{r} = \left. \frac{\partial \Lambda}{\partial E} \right|_{E=E_j} \quad (11)$$

whence, with (9),

$$\int_{\tau} |\psi(\mathbf{r})|^2 d\mathbf{r} = N \int_{\tau} |\psi(\mathbf{r})|^2 d\mathbf{r} = - \frac{1}{\tau} \sum_{LL'} \bar{C}_L^* \dot{M}_{LL'} \bar{C}_{L'}. \quad (12)$$

Here N is the number of unit cells per unit volume, τ the volume of the unit cell, and **M** denotes the energy derivative of **M** evaluated at $E = E_j$. As shown by MR, equations (3), (8), (10) and (12) provide a method for calculating normalised Bloch functions in the KKR formalism.

The foregoing discussion is straightforwardly generalised to treat crystals with a basis following Segall (1957) or MR. A calculation of the Bloch wave function with the aid of equations similar to (3), (8), (10) and (12) then yields (MR (21))

$$\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{4\pi}{\tau} \sum_n (\sum_{\mu} \exp[i\mathbf{k}_n \cdot (\mathbf{r} - \mathbf{b}_{\mu})]) / (E - k_n^2) \sum_L \bar{C}_{L\mu}(\mathbf{k}) S_{L\mu}(\mathbf{k}_n, E). \quad (13)$$

Here $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$, where \mathbf{K}_n is a reciprocal lattice vector, and $S_{L\mu}$ are Fourier transforms of $R_{l\mu}$ as defined in MR. The normalisation according to equation (12) now takes the form

$$\int |\psi(\mathbf{r})|^2 d\mathbf{r} = N \int |\psi(\mathbf{r})|^2 d\mathbf{r} = -\frac{1}{\tau} \sum_{\mu\nu} \sum_{LL'} \bar{C}_{L\mu}^* \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} \quad (12')$$

where μ and ν label the atoms of the basis. Equations (7), (8), (12) and (13) differ from previously published equations (e.g. KR (3.21), MR (16), MR (21)) by factors of squares of muffin-tin radii. In monatomic crystals, or in the special case of a polyatomic crystal with muffin-tin spheres of equal radii, these factors have no influence on the normalised KKR wave functions and hence on the physical properties. This, however, is not true for crystals with a basis and muffin-tin spheres of unequal sizes.

3. Momentum density in a crystal with a basis

In the independent particle approximation, the electron momentum density $\rho(\mathbf{p})$ is given by

$$\rho(\mathbf{p}) = \text{constant} \sum_j f(E_j) \left| \int \exp(-i\mathbf{p} \cdot \mathbf{r}) \psi_{\mathbf{k},j}(\mathbf{r}) d\mathbf{r} \right|^2 \quad (14)$$

where \mathbf{k} is the reduced wave vector corresponding to the momentum \mathbf{p} , the summation extends over all eigenvalues E_j belonging to \mathbf{k} , and $f(E)$ is the Fermi-Dirac occupation function. Following MR, the use of the KKR wave function derived above can be shown to lead to the expression

$$\rho(\mathbf{p}) = -\frac{(4\pi)^2}{\tau} \sum_j \frac{f(E)}{(E - p^2)^2} \left| \frac{\sum_{\mu} \exp(-i\mathbf{p} \cdot \mathbf{b}_{\mu}) \sum_L \bar{C}_{L\mu}(\mathbf{k}) S_{L\mu}(\mathbf{p}, E)}{\sum_{\mu\nu} \sum_{LL'} \bar{C}_{L\mu}^*(\mathbf{k}) \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu}(\mathbf{k})} \right|_{E=E_j}^2 \quad (15)$$

Here \mathbf{b}_{μ} denotes the position of the μ th atom in the unit cell. Expression (15) differs from the corresponding equation (MR (22)) in that the latter contains factors of squares of muffin-tin radii under the summation sign in the numerator as well as the denominator[†]. The formula for the electron-positron momentum density $\rho_{2\gamma}(\mathbf{p})$, rel-

[†] That the normalisation of the wave functions is treated properly in (15) can be shown independently by following the Green function approach described by Mijnaerends and Bansil (1976), where an explicit reference to wave functions is not required.

evant for two-photon annihilation, is similarly shown to be

$$\begin{aligned} \rho_{2\gamma}(\mathbf{p}) &= \frac{(4\pi)^4}{\tau^2} \sum_{k_+} f^+(E^+) \sum_j f(E) \\ &\times \left| \sum_n \sum_\mu \exp[-i(\mathbf{p} - \mathbf{k}_+ - \mathbf{K}_n) \cdot \mathbf{b}_\mu] \sum_L \bar{C}_{L\mu}(\mathbf{k}) \frac{S_{L\mu}(\mathbf{p} - \mathbf{k}_+ - \mathbf{K}_n, E)}{E - |\mathbf{p} - \mathbf{k}_+ - \mathbf{K}_n|^2} \right. \\ &\times \sum_\nu \exp[-i(\mathbf{k}_+ + \mathbf{K}_n) \cdot \mathbf{b}_\nu] \sum_{L'} \bar{C}_{L'\nu}^+(\mathbf{k}_+) \frac{S_{L'\nu}^+(\mathbf{k}_+ + \mathbf{K}_n, E^+)}{E^+ - |\mathbf{k}_+ + \mathbf{K}_n|^2} \left. \right|^2 \\ &\times \left(\sum_{\mu\nu} \sum_{LL'} \bar{C}_{L\mu}^*(\mathbf{k}) \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu}(\mathbf{k}) \sum_{\sigma\tau} \sum_{\Lambda\Lambda'} \bar{C}_{\Lambda\sigma}^{+\sigma\tau}(\mathbf{k}_+) \dot{M}_{\Lambda\Lambda'}^{+\sigma\tau} \bar{C}_{\Lambda'\tau}^+(\mathbf{k}_+) \right)^{-1} \Big|_{E=E_j} \end{aligned} \quad (16)$$

where all positron-related quantities have been given the superscript + and f^+ represents the Maxwell–Boltzmann distribution for the low-density positron state.

4. The form of the momentum density near free-electron poles

For a given \mathbf{k} , in a perfect crystal, the momentum density is non-zero only for $\mathbf{p} = \mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$. Expressions (15) and (16) for the momentum density need to be evaluated only at the actual band energies E_j , and thus, excepting accidental degeneracies, the free-electron energies do not actually occur in the calculations.

At the free-electron energies $E = k_n^2 \equiv |\mathbf{k} + \mathbf{K}_n|^2$ the KKR structure functions $A_{LL'}$, and hence the matrix elements $M_{LL'}$, are singular. Therefore, if for a given momentum $\mathbf{p} = \mathbf{k}_0 \equiv \mathbf{k} + \mathbf{K}_0$, say, one of the eigenvalues E is at or near the free-electron energy $E_0 = k_0^2 \equiv |\mathbf{k} + \mathbf{K}_0|^2$, then it is sensible to expand the numerator and denominator in expression (15) into powers of $E - k_0^2$. To this end, consider the structure function $A_{LL'}^{\mu\nu}$ in a crystal with a basis (Segall 1957)

$$\begin{aligned} A_{LL'}^{\mu\nu} &= \frac{(4\pi)^2}{\tau} i^{l-r} \sum_n \frac{j_l(k_n r) j_{l'}(k_n r') \exp[i\mathbf{k}_n \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)]}{j_l(\kappa r) j_{l'}(\kappa r')} \frac{1}{E - k_n^2} \\ &\times Y_L^*(\hat{k}_n) Y_{L'}(\hat{k}_n) - \kappa \delta_{LL'} \delta_{\mu\nu} \frac{n_l(\kappa r)}{j_l(\kappa r)}. \end{aligned} \quad (17)$$

Using (17), the matrix \mathbf{M} is split as

$$M_{LL'}^{\mu\nu} = \bar{M}_{LL'}^{\mu\nu} + \frac{(4\pi)^2}{\tau} \frac{j_l(k_0 r) j_{l'}(k_0 r') \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)]}{j_l(\kappa r) j_{l'}(\kappa r')} \frac{1}{E - k_0^2} Y_L^*(\hat{k}_0) Y_{L'}(\hat{k}_0) \quad (18)$$

where $\bar{\mathbf{M}}$ is the regular part of \mathbf{M} . Multiplying (18) by $\bar{C}_{L\mu}^*$ on the left and by $\bar{C}_{L'\nu}$ on the right, and summing over the indices, one finds, using (10)

$$\begin{aligned} &\frac{(4\pi)^2}{\tau} (E - k_0^2)^{-1} \sum_{\mu\nu} \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)] \sum_{LL'} \bar{C}_{L\mu}^* Y_L^*(\hat{k}_0) \bar{C}_{L'\nu} Y_{L'}(\hat{k}_0) \\ &+ \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \bar{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} = 0 \end{aligned} \quad (19)$$

with all quantities implicitly evaluated at the eigenvalues $E = E_j$. It is useful to rearrange (19) in the form

$$\begin{aligned} \sum_{\mu\nu} \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)] \sum_{LL'} \bar{C}_{L\mu}^* Y_L^*(\hat{k}_0) \bar{C}_{L'\nu} Y_{L'}(\hat{k}_0) \\ = \frac{-\tau}{(4\pi)^2} (E - k_0^2) \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu}. \end{aligned} \tag{20}$$

The numerator in (15) can be expanded by invoking the following relations for the functions $S_{L\mu}$ (MR equations (15), (A1) and (A2))

$$\begin{aligned} S_{L\mu}(\mathbf{k}_0, E) &= -\kappa \cot \eta_{l\mu} Y_L(\hat{k}_0) \int_0^{r_1} j_l(k_0 r) V_\mu(r) R_{l\mu}(r, E) r^2 dr \\ &= Y_L(\hat{k}_0) [1 - \kappa(E - k_0^2) F_{l\mu}(k_0, E)] \end{aligned} \tag{21}$$

with

$$F_{l\mu}(k, E) \equiv \cot \eta_{l\mu} \int_0^{r_1} j_l(kr) R_{l\mu}(r, E) r^2 dr. \tag{22}$$

This together with (20) yields

$$\begin{aligned} \left| \sum_{\mu} \exp(-i\mathbf{k}_0 \cdot \mathbf{b}_\mu) \sum_L \bar{C}_{L\mu} S_{L\mu}(\mathbf{k}_0, E) \right|^2 \\ = -\frac{\tau}{(4\pi)^2} (E - k_0^2) \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} - \kappa(E - k_0^2) \\ \times \sum_{\mu\nu} \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)] \sum_{LL'} \bar{C}_{L\mu}^* Y_L^*(\hat{k}_0) \bar{C}_{L'\nu} Y_{L'}(\hat{k}_0) \\ \times (F_{l\mu}^*(k_0, E) + F_{l'\nu}(k_0, E)) + \text{higher order terms.} \end{aligned} \tag{23}$$

By using (18) the denominator in (15) can be similarly expanded as

$$\begin{aligned} \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} &= \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \dot{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} + \frac{(4\pi)^2}{\tau} \sum_{\mu\nu} \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)] \\ &\times \sum_{LL'} \bar{C}_{L\mu}^* Y_L^*(\hat{k}_0) \bar{C}_{L'\nu} Y_{L'}(\hat{k}_0) \left[\frac{-1}{(E - k_0^2)^2} - \frac{1}{E - k_0^2} \right. \\ &\times \left. \left(\frac{1}{j_l(kr)} \frac{d}{dE} j_l(kr) + \frac{1}{j_{l'}(kr)} \frac{d}{dE} j_{l'}(kr) \right) \right]. \end{aligned} \tag{24}$$

Using (20), and taking into account the extra factor $(E - k_0^2)^2$ in the denominator of (15), it is clear that all three terms inside the large square brackets contribute to the

lowest order term, which is proportional to $E - k_0^2$:

$$\begin{aligned}
 (E - k_0^2)^2 \sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \bar{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} \\
 = (E - k_0^2) \left[\sum_{\substack{LL' \\ \mu\nu}} \bar{C}_{L\mu}^* \bar{M}_{LL'}^{\mu\nu} \bar{C}_{L'\nu} - \frac{(4\pi)^2}{\tau} \sum_{\mu\nu} \exp[i\mathbf{k}_0 \cdot (\mathbf{b}_\mu - \mathbf{b}_\nu)] \right] \\
 \times \sum_{LL'} \bar{C}_{L\mu}^* Y_L^*(\hat{\mathbf{k}}_0) \bar{C}_{L'\nu} Y_{L'}(\hat{\mathbf{k}}_0) \\
 \times \left(\frac{1}{j_l(kr)} \frac{d}{dE} j_l(kr) + \frac{1}{j_{l'}(kr)} \frac{d}{dE} j_{l'}(kr) \right) \Big] + \text{higher order terms.} \quad (25)
 \end{aligned}$$

Equations (23) and (25) show explicitly that the numerator as well as the denominator of (15) go to zero linearly in $E - k_0^2$; hence, their quotient is smooth and well behaved near free-electron singularities. A suitable formula for the momentum density may now be obtained by the substitution of (23) and (25) into (15); we avoid writing it out in detail in the interest of brevity. The preceding discussion is straightforwardly generalised to investigate the behaviour of the electron–positron momentum density (16) near the free-electron poles.

5. Discussion

The question of numerical implementation of the momentum density formulae presented in this article deserves further comment. Strictly speaking, one should cut out an energy window in the vicinity of the free-electron energies and use well-behaved formulae in this region. Our experience, however, has been that if the $S_{L\mu}$ functions are programmed in the form (21)–(22) which explicitly displays the correct behaviour near $E = k_0^2$, and double precision (i.e. 64-bit) arithmetic is used consistently, satisfactory results can be obtained, excepting accidental degeneracies.

In summary, we have pointed out an omission in an often published form of the variational functional in the KKR method of band structure computation. This omission is of no physical consequence, except in crystals with more than one atom per unit cell in which muffin-tin spheres of unequal sizes are used, where it leads to incorrect wave functions.

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