Korringa-Kohn-Rostoker Spectral-Band Theory for General Potentials

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(Received 25 April 1990)

Korringa-Kohn-Rostoker (KKR) theory is formulated in a way that is independent of the assumption that the potential is of the muffin-tin type. The resulting form of the KKR equation retains the separation of its dependence on the lattice structure and on the potential.

PACS numbers: 71.25.Cx, 71.25.Pi, 72.15.Eb

One of the most useful tools in the calculation of the band structure of the energy spectrum of electrons in solids is the KKR equation due to Korringa[1] and Kohn and Rostoker.[2] This equation was first formulated for muffin-tin models, in which there is a sphere S in each unit cell of the periodic crystal such that the potential is spherically symmetric (central) in S and constant outside S. The first of these assumptions fails, for example, for molecular crystals with covalent bonds, and the second also is often unrealistic. (Both assumptions fail for a single-site potential whose range is larger than the interior radius of the unit cell, even if that potential is central, because the effective potential in each cell, which is the sum of the single-site potentials from all cells, is then noncentral.)

In recent years a number of efforts have been made to extend the KKR theory beyond the muffin-tin model, to allow the potential to be noncentral in S (this might be called a *banged-up muffin tin*) and to drop the assumption of an interstitial region in which it has a constant value.[3-12] These attempts have been beset by the use of awkward and inappropriate mathematical techniques.[13]

The purpose of the present Letter is to formulate the KKR theory in a manner that is independent of the basis vectors chosen and independent of whether the potential is of the muffin-tin kind or not. The derivation is also applicable if the molecular potentials overlap; the potential in the unit cell then includes that from the interior molecule and all the tails of those originating from the outside. This paper does not claim to provide direct assistance to numerical band calculations, which are important for applications; its aim, rather, is to provide an unambiguous and well-defined basis from which to start studies of band properties and approximation schemes. While the resulting equation itself is not new, its derivation is considerably simpler than those given by others.[3-10]

It is *a priori* clear that the use of spherical harmonics as basis functions is not well suited to a scattering problem in which the potential has no spherical symmetry.[14] An operator formulation lends itself, in actual calculations, to the use of any convenient choice of basis. It is therefore best to leave that choice until the end, rather than start out with it. There will be no approximations in the derivation and formulation of our general version of the KKR equation, and that equation cleanly separates the dependence on the lattice structure and on the potential.

The basic equation of Ref. 2 for the electronic Bloch wave function in a crystal is the homogeneous linear integral equation

$$\psi(\mathbf{r})=\int_{\Omega} d\tau' G(\mathbf{r},\mathbf{r}')V_{\Omega}(\mathbf{r}')\psi(\mathbf{r}')\,, \tag{1}$$

where Ω is the unit cell of the crystal, $d\tau'$ is the volume element, and $G(\mathbf{r},\mathbf{r}')$ is the Hermitian Green's function

$$G(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\sum_{\mathbf{R}\in\mathcal{T}}\frac{\cos(\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{R}|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{R}|}e^{i\mathbf{k}\cdot\mathbf{R}}. \tag{2}$$

Here $\kappa=\sqrt{E}$ and the sum runs over the set $\mathcal{T}$ of lattice translations

$$\mathcal{T}:=\{\mathbf{R}\in\mathbb{R}^3:\mathbf{R}=s_1\mathbf{a}_1+s_2\mathbf{a}_2+s_3\mathbf{a}_3,\ s_i=0,\pm1,\pm2,\ldots\},$$

where $\mathbf{a}_i$ are three fundamental translation vectors of the lattice.

It was shown in Ref. 2 that if $\psi(\mathbf{r})$ is a solution of the Schrödinger equation with the potential

$$\begin{aligned}&V(\mathbf{r})=V_{\Omega}(\mathbf{r}),\quad \mathbf{r}\in\Omega\,;\\&V(\mathbf{r}+\mathbf{R})=V(\mathbf{r}),\quad \forall\mathbf{R}\in\mathcal{T}\end{aligned} \tag{3}$$

and the property that $\psi(\mathbf{r}+\mathbf{R})=e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$, $\forall\mathbf{R}\in\mathcal{T}$, then it satisfies (1). Conversely, Eq. (1) is an integral equation for $\psi(\mathbf{r})$, $\mathbf{r}\in\Omega$. Given a solution ψ_Ω of (1) for $\mathbf{r}\in\Omega$, Eq. (1) at the same time explicitly defines a function $\psi(\mathbf{r})$ for all $\mathbf{r}\in\mathbb{R}^3$ in terms of ψ_Ω. The function thus defined coincides with ψ_Ω for $\mathbf{r}\in\Omega$, it has the periodicity property $\psi(\mathbf{r}+\mathbf{R})=e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$, $\forall\mathbf{R}\in\mathcal{T}$, and it satisfies the Schrödinger equation with the periodic potential (3). Thus a necessary and sufficient condition for ψ to be a Bloch solution of the Schrödinger equation with the potential (3) is that it satisfies Eq. (1).

Following Kohn and Rostoker we write

$$G=G_0+D\,, \tag{4}$$

where G_0 is the principal-value Green's function

$$G_0(\mathbf{r},\mathbf{r}')=-\frac{1}{4\pi}\frac{\cos(\kappa|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

and D is a solution of the free Schrödinger equation for $\mathbf{r} \in \Omega$. We may then write in operator notation

$$\mathbb{1} - GV_\Omega = [\mathbb{1} - DV_\Omega(\mathbb{1} - G_0V_\Omega)^{-1}](\mathbb{1} - G_0V_\Omega) .$$

Since E is assumed to be positive, the operator $\mathbb{1} - G_0V_\Omega$ is invertible. Thus (1) is equivalent to the equation

$$(\mathbb{1} - DK)\varphi = 0 , \tag{5}$$

where $\varphi = (\mathbb{1} - G_0V_\Omega)\psi$ and $K = V_\Omega(\mathbb{1} - G_0V_\Omega)^{-1}$ is the usual K operator for scattering by the potential V_Ω, which vanishes outside the unit cell Ω. The necessary and sufficient condition for the existence of a nontrivial solution of Eq. (5) is that

$$\det(\mathbb{1} - DK) = 0 , \tag{6}$$

where det is the Fredholm determinant. (Precise conditions on V_Ω under which this Fredholm determinant is well defined as an absolutely convergent series will be proved elsewhere.[15])

Now it is only the restriction of D to the interior Ω of the first unit cell that enters into Eq. (6). For $\mathbf{r},\mathbf{r}' \in \Omega$ the function $D(\mathbf{r},\mathbf{r}')$ satisfies the free Schrödinger equation both as a function of $\mathbf{r}$ and as a function of $\mathbf{r}'$; therefore it must be expressible in the form

$$D(\mathbf{r},\mathbf{r}') = \frac{1}{(4\pi)^2} \int d\hat{\mathbf{n}} \int d\hat{\mathbf{n}}' \mathcal{D}(\hat{\mathbf{n}},\hat{\mathbf{n}}') e^{i\kappa(\hat{\mathbf{n}}\cdot\mathbf{r} - \hat{\mathbf{n}}'\cdot\mathbf{r}')} , \quad \mathbf{r},\mathbf{r}' \in \Omega , \tag{7}$$

where both integrals extend over all solid angles. The Fredholm determinant $\det(\mathbb{1} - DK)$ can be expressed entirely in terms of $\operatorname{tr}(DK)^n$, $n = 1,2,\ldots$ (see, for example, Ref. 16). If we insert (7) into these traces, we obtain

$$\operatorname{tr}(DK)^n = \operatorname{tr}\left[-\frac{1}{4\pi}\mathcal{D}\mathcal{K}\right]^n ,$$

where the trace on the right-hand side is only over the unit sphere (that is, integrations over all solid angles) and $\mathcal{K}$ is the *on-the-energy-shell* K matrix

$$\mathcal{K}(\hat{\mathbf{n}},\hat{\mathbf{n}}') = -\frac{1}{4\pi} \int d\mathbf{r} \int d\mathbf{r}' K(\mathbf{r},\mathbf{r}') e^{i\kappa(\hat{\mathbf{n}}'\cdot\mathbf{r}' - \hat{\mathbf{n}}\cdot\mathbf{r})} .$$

Therefore (6) becomes

$$\mathfrak{D}(E,\mathbf{k}) := \det\left[\mathbb{1} + \frac{1}{4\pi}\mathcal{D}\mathcal{K}\right] = 0 . \tag{8}$$

This equation is the general version of the KKR equation. The K matrix depends on the potential in a single cell only and it is a function of the energy E; on the other hand, $\mathcal{D}$ depends on the structure of the lattice only and is a function of both E and $\mathbf{k}$, as (2) shows. Thus (8) determines the relation between E and $\mathbf{k}$, and the dependence on the lattice structure, on the one hand, and the potential, on the other hand, are separated.[17]

Since $D(\mathbf{r},\mathbf{r}')$ is a function of $\mathbf{r} - \mathbf{r}'$ only, it is also expressible in the simpler form

$$D(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi} \int d\hat{\mathbf{n}} \mathcal{D}(\hat{\mathbf{n}}) e^{i\kappa\hat{\mathbf{n}}\cdot(\mathbf{r}-\mathbf{r}')} . \tag{9}$$

However, this representation is valid only inside a sphere inscribed in the unit cell and cannot be used unless the potential is assumed to be constant in the interstitial region.

The on-shell K matrix can always be expanded in a series (which converges strongly in the mathematical sense) on the basis of its orthonormal eigenfunctions $\mathcal{Y}_n$ in the form

$$\mathcal{K}(\hat{\mathbf{n}},\hat{\mathbf{n}}') = \frac{4\pi}{\kappa} \sum_n \mathcal{Y}_n(\hat{\mathbf{n}}) \tan\delta_n \mathcal{Y}_n^*(\hat{\mathbf{n}}') . \tag{10}$$

Here the δ_n are the eigenphase shifts, which are real and depend on the energy only.[18] The functions $\mathcal{Y}_n$ are the same as the eigenfunctions of the S matrix, and some of their properties are discussed in Ref. 19; they will also generally depend on the energy.

If we then define the infinite-dimensional matrix $\mathcal{A}$ with elements

$$\mathcal{A}_{nm} := \int d\hat{\mathbf{n}} \int d\hat{\mathbf{n}}' \mathcal{Y}_n^*(\hat{\mathbf{n}}) \mathcal{D}(\hat{\mathbf{n}},\hat{\mathbf{n}}') \mathcal{Y}_m(\hat{\mathbf{n}}') , \tag{11}$$

then Eq. (8) becomes

$$\mathfrak{D}(E,\mathbf{k}) = \det(\mathbb{1} + \kappa^{-1}\mathcal{A}\tan\delta) = 0 , \tag{12}$$

where δ is the diagonal matrix with the eigenphase shifts on the diagonal. The diagonal elements of $\tan\delta$ tend to zero as $n \to \infty$ (nonuniformly in the energy); if they are set equal to naught for $n > N$ for some N (which may have to depend on the energy), then $\mathfrak{D}(E,\mathbf{k})$ becomes the ordinary determinant of a finite matrix and (12) is equivalent to the equation

$$\det(\mathcal{A} + \kappa\cot\delta) = 0 . \tag{13}$$

In the case of a central potential the eigenfunctions of $\mathcal{K}$ are the spherical harmonics, the eigenphase shifts are the ordinary phase shifts, and the matrix $\mathcal{A}$ becomes the matrix $\mathbf{A}$ with elements $A_{lm;l'm'}$ of Ref. 2. In that case Eq. (13) is identical with Korringa's version of the KKR equation.[1]

There remains the question of how to calculate the kernel $\mathcal{D}(\hat{\mathbf{n}},\hat{\mathbf{n}}')$. Let us define the family of normal[20] Hilbert-Schmidt operators $T(\alpha)$: $L^2(\mathbb{S}^2) \to L^2(\mathbb{S}^2)$, where $\mathbb{S}^2$ is the unit sphere, so that $T(\alpha)f = g$ stands for

$$\frac{1}{4\pi} \int d\hat{\mathbf{n}} e^{i\alpha\hat{\mathbf{n}}\cdot\hat{\mathbf{n}}'} f(\hat{\mathbf{n}}) = g(\hat{\mathbf{n}}') .$$

The eigenfunctions of $T(\alpha)$ are the spherical harmonics and its eigenvalues are $i^l j_l(\alpha)$, where j_l is a spherical Bessel function. If we regard $D(\mathbf{r},\mathbf{r}') := D(r,r';\hat{\mathbf{r}},\hat{\mathbf{r}}')$ and $\mathcal{D}(\hat{\mathbf{n}},\hat{\mathbf{n}}')$ as the integral kernels of operators and r and r' as parameters, then Eq. (7) can be written in the form

$$D(r,r') = T(\kappa r)\mathcal{D}T^\dagger(\kappa r') ,$$

which would be formally solved by

$$\mathcal{D}=T^{-1}(\kappa r)D(r,r')T^{\dagger -1}(\kappa r') . \tag{14}$$

However, since the operator T is compact, its eigenvalues accumulate at the origin and thus zero is in its spectrum. Therefore its inverse, if it exists, is not a bounded operator. What is more, if α is such that for some nonnegative integer l we have $j_l(\alpha)=0$, then zero is a point eigenvalue of $T(\alpha)$ and thus an inverse of $T(\alpha)$ does not exist. Note that contrary to its appearance the left-hand side of (14) is independent of r and r'. Therefore r and r' may be chosen so that zero is not a point eigenvalue of $T(\kappa r)$ or $T(\kappa r')$.

Expansion of the directional dependences of D and $\mathcal{D}$ on the basis of the eigenfunctions of T, the spherical harmonics, leads to the expression (A2.5) of Ref. 2 for the infinite matrix $\mathbf{A}$ with elements $\mathbf{A}_{lm;l'm'}$. It is the presence of the factor $[j_l(\kappa r)j_{l'}(\kappa r')]^{-1}$ in that expression which produces an element of possible instability in the series

$$\mathcal{D}(\hat{\mathbf{n}},\hat{\mathbf{n}}')=\sum_{l,l'=0}^{\infty}\sum_{m=-l}^{l}\sum_{m'=-l'}^{l'} Y_l^m(\hat{\mathbf{n}})A_{lm;l'm'}Y_{l'}^{m'*}(\hat{\mathbf{n}}') . \tag{15}$$

At the same time, it means that the truncation at maximal angular momentum L may be sensitive to the choice of L. In other words, the problem of using the formal inverse of $T(\alpha)$ given by its expansion

$$T^{-1}(\alpha,\hat{\mathbf{n}},\hat{\mathbf{n}}')=\sum i^{-l}[j_l(\alpha)]^{-1}Y_l^m(\hat{\mathbf{n}})Y_l^{l*}(\hat{\mathbf{n}}') \tag{16}$$

is the same as the problem that arises in the use of the matrix $\mathbf{A}$ of Ref. 2.

Using the expansion (15) and defining the matrix $\mathbf{K}$ with elements

$$K_{lm,l'm'}=\frac{4\pi}{\kappa}\sum_n U_{lm,n}\tan\delta_n U^*_{n,l'm'} ,$$

where

$$U_{lm,n}:=\int d\hat{\mathbf{n}}\, Y_l^{m*}(\hat{\mathbf{n}})\mathcal{Y}_n(\hat{\mathbf{n}}) ,$$

we may also write Eq. (12) in the form

$$\mathfrak{D}(E,\mathbf{k})=\det(\mathbb{1}+\kappa^{-1}\mathbf{A}\mathbf{K})=0 . \tag{17}$$

We may similarly proceed with (9). Set $D(\mathbf{r},\mathbf{r}'):=D(\mathbf{r}-\mathbf{r}')$, $D(\mathbf{r}):=D(r,\hat{\mathbf{r}})$, and regard $D(r,\hat{\mathbf{r}})$ and $\mathcal{D}(\hat{\mathbf{n}})$ as vectors, so that in operator notation

$$D(r)=T(\kappa r)\mathcal{D} .$$

Use of the eigenfunction expansion (16) then leads to the inversion

$$\mathcal{D}(\hat{\mathbf{n}})=\sum_{LM} D_{LM}Y_L^M(\hat{\mathbf{n}}) ,$$

where the coefficients $\mathcal{D}_{LM}$ are given by Eq. (A2.9) of Ref. 2.

It should be noted, however, that use of an angular momentum basis for non-muffin-tin potentials leads to a variety of known convergence problems[21] about which this paper has nothing to say. It would clearly be desirable to find a representation of the function $\mathcal{D}$ that does not rely on an angular momentum expansion.

I am indebted to Professor James Swihart for Ref. 11 and other references that led to, and to Professor Allan MacDonald for a useful conversation. Part of this work was supported by a grant from the National Science Foundation.

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[12] See especially Refs. 7 and 10 for further references to controversies surrounding the handling of the interstitial region, and Refs. 8 and 11 for references to controversies concerning the general separability of the dependence on the lattice structure and the potential.

[13] Some of the procedures used in Refs. 4, 8, and A. Ziegler [Am. J. Phys. **57**, 518-524 (1989)] can be mathematically justified only under very restrictive conditions that have never been stated accurately. Numerical calculations usually employ models for which these conditions are satisfied and thus give reliable results. But these methods are not useful for general studies of mathematical properties of the needed functions.

[14] Contrary to an assertion in the first part of Ref. 3, a noncentral potential is not the same as a potential of the form $\sum_{lm} W_{lm}(r)P_{lm}$, where P_{lm} is a projection on the spherical harmonic Y_l^m.

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[17] Contrary to an assertion in the third part of Ref. 8, an additional matching condition is not needed. It is automatically satisfied by the Block functions generated by any solution of

(1), and the necessary and sufficient condition for the existence of the latter is (6). See also Ref. 11.

[18] This is in contrast to the phases used in the first part of Ref. 3, which depend on $\hat{\mathbf{n}}$. See also the second part of Ref. 3 for the use of eigenphase shifts.

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[20] That is, their Hermitian and skew-Hermitian parts commute.

[21] The calculation of $\mathcal{D}$ by (17), i.e., on an angular momentum basis, is beset with convergence problems that result in part from the difficulties mentioned in connection with Eq. (15). One of these problems, which arises when (17) is used for potentials that are not of the banged-up muffin-tin type, is known as *near-field corrections* and studied in detail in the third part of Ref. 6.