Relativistic Formulation of the Green's Function Method in Periodic Lattices

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A relativistic formulation of the Kohn-Rostoker Green's function method is developed in the Dirac formalism. The result is very simple. The matrix elements of the secular equation have the same form as the nonrelativistic matrix elements, and the relativistic structure constant consists of the summation of the products of a nonrelativistic structure constant and a Clebsch-Gordan coefficient over spin $\pm 1/2$. Hence, a calculation of the relativistic matrix elements can be performed as easily as the nonrelativistic calculation, and the only problem is a significant increase in computing time which results from the doubling of the dimensions of the secular equation and the complex property of the matrix elements. The present paper also contains a brief discussion of the relativistic formulation of the APW method, and an expression for the matrix element corresponding to the nonrelativistic matrix element is proposed.

§ 1. Introduction

Recently, many authors have studied the band structures of metals and semiconductors composed of heavy elements, and attempted to include relativistic effects.

Most of these studies were carried out in Pauli's spinor formalism, mainly by using the perturbation method.[1] However, there is a case for a free-electron-like band in which the relativistic effects have the same order as the crystal potential effects, and in that case it is not appropriate to treat the relativistic effects by the perturbation method.[2] In addition, in the perturbation method there is a problem how to choose the wave functions.

More recently, a relativistic formulation of the OPW method[2] and of the APW method[3] have been developed in the Dirac formalism. In both cases, the expressions for the matrix elements of the secular equations are similar to those of the nonrelativistic theory. Therefore, a calculation of the matrix elements can be performed as easily as the nonrelativistic calculation. The only problem found in the relativistic theory is a significant increase in computing time, which results from the doubling of the basis set and the complex property of the matrix elements.

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On the other hand, the Green's function method is the most useful method in the nonrelativistic band theory because of its rapid convergence and generality.[4],[5] Hence we can expect that the Green's function method has its advantages also in the relativistic theory. In particular, its rapid convergence is expected to make it the most powerful one in the relativistic theory. For this reason, we have studied the relativistic formulation of the Green's function method in the Dirac formalism.

§ 2. Basic formulation

Our eigenvalue problem is expressed as follows:

$$H|\Psi(r)\rangle = W|\Psi(r)\rangle, \tag{1}$$

$$|\Psi(r+R_n)\rangle = \exp(i k \cdot R_n)|\Psi(r)\rangle, \tag{2}$$

where W is an energy eigenvalue for the wave vector k. R_n is any translation vector of the lattice. H is the Dirac Hamiltonian:[*]

$$H = \boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta + V. \tag{3}$$

Corresponding to the Kohn-Rostoker nonrelativistic formalism, we introduce the relativistic Green's function

$$G(r, r') = -\frac{1}{\tau} \sum_{n,m} \frac{|\Psi^0_{nm}(r)\rangle \langle \Psi^0_{nm}(r')|}{k_n^* - W}, \tag{4}$$

where τ is the volume of the unit cell of the lattice. $|\Psi^0_{nm}(r)\rangle$ is the Dirac plane wave with wave vector k_n expressed in the form[6]

$$|\Psi^0_{nm}(r)\rangle = \left(\frac{k_n^*+1}{2k_n^*}\right)^{1/2} \cdot \left(\begin{array}{c} |\chi(m)\rangle \\ \dfrac{\boldsymbol{\sigma} \cdot k_n}{k_n^*+1}|\chi(m)\rangle \end{array}\right) \exp(ik_n \cdot r), \tag{5}$$

where

$$k_n = k + K_n, \qquad k_n^* = (k_n^2 + 1)^{1/2}.$$

K_n is the reciprocal lattice vector. $\boldsymbol{\sigma}$ is the Pauli matrix, and $|\chi(\pm 1/2)\rangle$ are the Pauli spinors. $|\Psi^0_{nm}(r)\rangle$ satisfies the Dirac equation for a free particle:

$$(\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta)|\Psi^0_{nm}(r)\rangle = k_n^*|\Psi^0_{nm}(r)\rangle. \tag{6}$$

The Green's function $G(r, r')$ satisfies

$$(\boldsymbol{\alpha} \cdot \boldsymbol{p} + \beta - W)G(r, r') = -\delta(r - r'), \tag{7}$$

$$G(r + R_n, r') = \exp(ik \cdot R_n)G(r, r'). \tag{8}$$

By using the Green's function, our eigenvalue problem is replaced by

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[*] Units are $m = c = \hbar = 1$.

$$|\Psi(r)\rangle = \int_\tau G(r, r') V(r') |\Psi(r')\rangle, \tag{9}$$

where the volume integral is taken over the unit cell.

The integral equation (9) is equivalent to the variational principle

$$\delta \Lambda = 0, \tag{10}$$

where

$$\Lambda \equiv \int_\tau \langle \Psi(r) | V(r) | \Psi(r) \rangle d\tau$$

$$- \int\int_{\tau\ \tau} \langle \Psi(r) | V(r) G(r, r') V(r') | \Psi(r') \rangle d\tau d\tau'. \tag{11}$$

In this variational principle, k and W are variational for arbitrary trial functions $|\Psi(r)\rangle$ as indicated by Kohn and Rostoker.[4]

For simplicity, we restrict our attention to a simple lattice. The generalization to complex lattices is easily carried out as in the nonrelativistic case.[7] Further we restrict our discussion to a potential of the "muffin-tin" form, that is, the potential V is spherically symmetric about each atom within the sphere inscribed in the unit cell and constant elsewhere:

$$V(r) = V(r), \qquad r \le R$$
$$= 0, \qquad r > R. \tag{12}$$

This assumption is necessary for the Green's function method so that the practical calculation may be carried out without formidable labor.

We notice from (11) that the contribution to Λ comes only from the sphere $r < R$, $r' < R$ and the calculation of Λ is greatly simplified.

Following Kohn and Rostoker we deal with the singularity of G as follows:

$$\Lambda = \lim_{\varepsilon \to 0} \Lambda^\varepsilon, \tag{13}$$

where

$$\Lambda^\varepsilon \equiv \int_{r \le R-2\varepsilon} d\tau \ \langle \Psi(r) | V(r) | \Psi(r) \rangle$$

$$- \int_{r \le R-2\varepsilon} d\tau \int_{r' \le R-\varepsilon} d\tau' \ \langle \Psi(r) | V(r) G(r, r') V(r') | \Psi(r') \rangle. \tag{14}$$

Using the hermitian property of the operators and the divergence theorem, the volume integral in (14) can be transformed into the following surface integral form. (Appendix A)

$$\Lambda^\varepsilon = - \int_{r=R-2\varepsilon} ds \int_{r'=R-\varepsilon} ds' \ \langle \Psi(r) | \alpha \cdot \hat{r} \, G(r, r') \alpha \cdot \hat{r}' | \Psi(r') \rangle, \tag{15}$$

where $\hat{r}$ represents the unit vector along r.

In order to calculate the surface integral, it is sufficient to know the wave function $|\Psi(r)\rangle$ inside the sphere. Then we expand $|\Psi(r)\rangle$ in the central field orbitals $|\Psi_\chi{}^\mu(r)\rangle$:[6]

$$|\Psi(r)\rangle = \sum_{\chi\mu} C_{\chi\mu} |\Psi_\chi{}^\mu(r)\rangle, \tag{16}$$

where

$$|\Psi_\chi{}^\mu(r)\rangle = \begin{pmatrix} g_\chi(r) & |\chi_\chi{}^\mu(\hat{r})\rangle \\ if_\chi(u) & |\chi_{-\chi}^\mu(\hat{r})\rangle \end{pmatrix}. \tag{17}$$

$|\Psi_\chi{}^\mu\rangle$ is taken as the eigenfunction of our Hamiltonian inside the sphere with the energy eigenvalue W which we are seeking.

$$H|\Psi_\chi{}^\mu(r)\rangle = W|\Psi_\chi{}^\mu(r)\rangle. \tag{18}$$

By using the Clebsh-Gordan coefficients, the spin angular functions $|\chi_\chi{}^\mu(\hat{r})\rangle$ are expressed in the form[6]

$$|\chi_\chi{}^\mu(\hat{r})\rangle = \sum_{m=\pm 1/2} C(l\,1/2\,j\,;\,\mu-m,\,m) Y_l^{\mu-m}(\hat{r}) |\chi(m)\rangle. \tag{19}$$

The radial functions are the solutions of the following coupled linear differential equations:

$$\frac{df_\chi}{dr} = \frac{x-1}{r} f_\chi - (W-V-1) g_\chi, \tag{20}$$

$$\frac{dg_\chi}{dr} = -\frac{x+1}{r} g_\chi + (W-V+1) f_\chi. \tag{21}$$

Substituting (16) into (14) and using the variational principle (10), we reach the desired secular equation

$$\text{Det}\, \Lambda_{\chi\mu,\chi'\mu'} = 0, \tag{22}$$

where

$$\Lambda_{\chi\mu,\chi'\mu'} = \lim_{\varepsilon \to 0} \Lambda_{\chi\mu,\chi'\mu'}^\varepsilon \tag{23}$$

$$\Lambda_{\chi\mu,\chi'\mu'}^\varepsilon \equiv -\int_{r=R-2\varepsilon} ds \int_{r'=R-\varepsilon} ds'$$

$$\times \langle \Psi_\chi{}^\mu(r) | \boldsymbol{\alpha} \cdot \hat{r}\, G(r \cdot r') \boldsymbol{\alpha} \cdot \hat{r}' | \Psi_{\chi'}^{\mu'}(r') \rangle. \tag{24}$$

§ 3. Relativistic Green's function

In this section, we derive a simplified expression for the relativistic Green's function, which consists of the nonrelativistic Green's function operated on by a matrix whose elements include operators.

Substituting the expression for the Dirac plane wave (5) into (4) and replacing wave vectors $\boldsymbol{k}_n$ by momentum operators $\boldsymbol{p}$ and $\boldsymbol{p}'$, the relativistic Green's function is expressed in the symmetric form

$$G(\boldsymbol{r}, \boldsymbol{r}') =$$

$$
\begin{pmatrix}
-\dfrac{1}{\tau}\sum_n \dfrac{k_n{}^*+1}{2k_n{}^*}\dfrac{\exp ik_n(\boldsymbol{r}-\boldsymbol{r}')}{k_n{}^*-W} & -\boldsymbol{\sigma}'\cdot\boldsymbol{p}'\left[-\dfrac{1}{\tau}\sum_n\dfrac{1}{2k_n{}^*}\dfrac{\exp ik_n(\boldsymbol{r}-\boldsymbol{r}')}{k_n{}^*-W}\right] \\[2ex]
\boldsymbol{\sigma}\cdot\boldsymbol{p}\left[-\dfrac{1}{\tau}\sum_n\dfrac{1}{2k_n{}^*}\dfrac{\exp ik_n(\boldsymbol{r}-\boldsymbol{r}')}{k_n{}^*-W}\right] & -\boldsymbol{\sigma}\cdot\boldsymbol{p}\,\boldsymbol{\sigma}'\cdot\boldsymbol{p}'\left[-\dfrac{1}{\tau}\sum_n\dfrac{1}{2k_n{}^*(k_n{}^*+1)}\dfrac{\exp ik_n(\boldsymbol{r}-\boldsymbol{r}')}{k_n{}^*-W}\right]
\end{pmatrix}
$$

$$\times \sum_{m=\pm 1/2}|\varkappa(m))\,(\varkappa(m)|, \tag{25}$$

where $\sum|\varkappa(m))\,(\varkappa(m)|$ is operated on as a scalar by the matrix [ ]. $\boldsymbol{\sigma}$ operates on $|\varkappa(m))$ and $\boldsymbol{\sigma}'$ on $(\varkappa(m)|$.

Because of the linear property of the operators, we can take the summation over n in each element before $\boldsymbol{\sigma}\cdot\boldsymbol{p}$ and $\boldsymbol{\sigma}'\cdot\boldsymbol{p}'$ operate on them. The summation over n in each element of Eq. (25) is carried out as follows. For this purpose we use the two relations:

$$\frac{1}{(2\pi)^3}\int \exp[i(\boldsymbol{K}_n+\boldsymbol{k}-\boldsymbol{K})\rho]\,d^3\rho = \delta(\boldsymbol{K}_n+\boldsymbol{k}-\boldsymbol{K}), \tag{26}$$

$$\frac{1}{\tau}\sum_n \exp(i\boldsymbol{K}_n\rho) = \sum_s \delta(\rho-\boldsymbol{R}_s). \tag{27}$$

For the first element, for example, we also use the relation

$$-\frac{1}{(2\pi)^3}\int \frac{k^*+1}{2k^*}\frac{e^{ikR}}{k^*-(W+i\varepsilon)}\,d^3k = (W+1)\left(-\frac{1}{4\pi}\frac{e^{i\eta R}}{R}\right) \tag{28}$$

where

$$\eta = (W^2-1)^{1/2} = (E^2+2E)^{1/2} = ((E/c)^2+E)^{1/2}. \tag{29}$$

The relation (28) is easily derived by means of complex integration. In (29) E is the energy measured with respect to the rest mass and the last expression is expressed in Rydberg units.

Using (26)–(29) we can carry out the summation over n for the first element of (25) as follows:

$$-\frac{1}{\tau}\sum_n \frac{k_n{}^*+1}{2k_n{}^*}\frac{\exp(ik_nR)}{k_n{}^*-(W+i\varepsilon)}$$

$$= -\frac{1}{\tau}\sum_n \frac{1}{(2\pi)^3}\iint d^3K\,d^3\rho\,\exp[i(\boldsymbol{K}_n+\boldsymbol{k}-\boldsymbol{K})\rho]\frac{K^*+1}{2K^*}\frac{\exp(i\boldsymbol{K}R)}{K^*-(W+i\varepsilon)}$$

$$= -\frac{1}{(2\pi)^3}\sum_s \iint d^3K\,d^3\rho\,\delta(\rho-\boldsymbol{R}_s)\exp[i(\boldsymbol{k}-\boldsymbol{K})\rho]$$

$$\times \frac{K^*+1}{2K^*} \frac{\exp(i\boldsymbol{KR})}{K^*-(W+i\varepsilon)}$$

$$= -\sum_s \exp(i\boldsymbol{kR}_s) \frac{1}{(2\pi)^3} \int d^3K \frac{K^*+1}{2K^*} \frac{\exp[i\boldsymbol{K}(\boldsymbol{R}-\boldsymbol{R}_s)]}{K^*-(W+i\varepsilon)}$$

$$= (W+1)\left(-\frac{1}{4\pi}\sum_s \exp(i\boldsymbol{kR}_s) \frac{\exp(i\eta|\boldsymbol{R}-\boldsymbol{R}_s|)}{|\boldsymbol{R}-\boldsymbol{R}_s|}\right). \tag{30}$$

Putting $\boldsymbol{R}=\boldsymbol{r}-\boldsymbol{r}'$ in the last expression of (30) we get the first element of (25) in simplified form. Calculating each element of (25) similarly, we get the relativistic Green's function in the simplified symmetric form:

$$\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}') = \begin{bmatrix} W+1 & -\boldsymbol{\sigma}'\boldsymbol{p}' \\ \boldsymbol{\sigma p} & -\dfrac{(\boldsymbol{\sigma p})(\boldsymbol{\sigma}'\boldsymbol{p}')}{W+1} \end{bmatrix} \times \sum_{m=\pm 1/2} |\chi(m))\,(\chi(m)|$$

$$\times G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}'), \tag{31}$$

where

$$G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}') = -\frac{1}{4\pi}\sum_s \exp(i\boldsymbol{kR}_s) \frac{\exp[i\eta|\boldsymbol{r}-\boldsymbol{r}'-\boldsymbol{R}_s|]}{|\boldsymbol{r}-\boldsymbol{r}'-\boldsymbol{R}_s|}. \tag{32}$$

It should be noted that $G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}')$ has the same form as the nonrelativistic Green's function, and in fact it becomes the nonrelativistic Green's function itself in the nonrelativistic limit $(c\to\infty)$. The relativistic Green's function (31) has a form which consists of the nonrelativistic Green's function operated on by the matrix whose elements include the operators $\boldsymbol{\sigma p}$ and $\boldsymbol{\sigma}'\boldsymbol{p}'$. If we note the relation between the upper component and the lower component of a wave function in the relativistic theory, and note that the upper component becomes the nonrelativistic wave function in the nonrelativistic limit, we can easily appreciate that this result is natural.

To calculate the surface integral (24), we need the value of $G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}')$ in the region of $r<r'$. As was shown by Kohn and Rostoker, $G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}')$ can be written in the form[4]

$$G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}') = \sum_{\substack{lm \\ l'm'}} [A_{lm,l'm'}\, j_l(\eta r) j_{l'}(\eta r')$$

$$+ \eta\delta_{ll'}\delta_{mm'}\, j_l(\eta r) n_l(\eta r')] Y_l^m(\hat{r}) Y_{l'}^{m'+}(\hat{r}'). \tag{33}$$

The "structure constants" $A_{lm,l'm'}$ are functions of E and $\boldsymbol{k}$, and are characteristic for the lattice independent of the potential. The calculation of $A_{lm,l'm'}$ can be carried out to any desired accuracy by the Ewald summation procedure, as was shown by Ham and Segall.[5]

Using the transformation inverse to (19), we get

$$\sum_{m=\pm 1/2} |\chi(m))\,(\chi(m)| G^{N\cdot R}(\boldsymbol{r},\boldsymbol{r}')$$

$$= \sum_{\substack{\chi,\mu \\ \chi'\mu'}} [B_{\chi\mu,\chi'\mu'} j_l(\eta r) j_{l'}(\eta r') + \eta \delta_{\chi\chi'}\delta_{\mu\mu'}$$

$$\times j_l(\eta r)\eta_l(\eta r')] \times |\chi_\chi^\mu(\hat{r}))(\chi_{\chi'}^{\mu'}(\hat{r}')|, \tag{34}$$

where

$$B_{\chi\mu,\chi'\mu'} = \sum_{m=\pm 1/2} C(l\,1/2\,j\,;\ \mu-m,\,m)C(l'\,1/2\,j'\,;\ \mu'-m,\,m)$$

$$\cdot \times A_{l\mu-m,\,l'\mu'-m}\ . \tag{35}$$

Substituting (34) into (31), we obtain the final expression for the relativistic Green's function

$$G(r, r') = \begin{bmatrix} W+1 & -\boldsymbol{\sigma'p'} \\ \\ \boldsymbol{\sigma p} & -\dfrac{(\boldsymbol{\sigma p})\,(\boldsymbol{\sigma'p'})}{W+1} \end{bmatrix}$$

$$\times \sum_{\substack{\chi\mu \\ \chi'\mu'}} [B_{\chi\mu,\chi'\mu'} j_l(\eta r) j_{l'}(\eta r') + \eta \delta_{\chi\chi'}\delta_{\mu\mu'}$$

$$\times j_l(\eta r)n_l(\eta r')] \times |\chi_\chi^\mu)(\chi_{\chi'}^{\mu'}|. \tag{36}$$

§ 4. Calculation of the matrix elements

, In calculating the surface integral (24), we must deal with the operators $\boldsymbol{\sigma p}$ and $\boldsymbol{\sigma'\hat{r}'}$. For this purpose we use the relations for relativistic operators,[6]

$$\boldsymbol{\sigma p} = -i(\boldsymbol{\sigma \hat{r}})\left(\frac{\partial}{\partial r}+\frac{x+1}{r}\right), \tag{37}$$

where

$$x = -(\boldsymbol{\sigma l}+1),$$

$$x|\chi_\chi^\mu) = \chi|\chi_\chi^\mu), \tag{38}$$

$$\boldsymbol{\sigma\hat{r}}|\chi_\chi^\mu) = -|\chi_{-\chi}^\mu), \tag{39}$$

and the relations for spherical Bessel functions,

$$\frac{d}{d\rho}j_l(\rho) = \frac{1}{2l+1}[l\,j_{l-1}(\rho) - (l+1)j_{l+1}(\rho)], \tag{40}$$

$$\frac{j_l(\rho)}{\rho} = \frac{1}{2l+1}[j_{l-1}(\rho) + j_{l+1}(\rho)]. \tag{41}$$

From (37)–(41), we get

$$\boldsymbol{\sigma p}j_l(\eta r)|\chi_\chi^\mu) = i\eta S_\chi j_{\bar{l}}\ (\eta r)|\chi_{-\chi}^\mu), \tag{42}$$

$$\boldsymbol{\sigma p}n_l(\eta r)|\chi_\chi^\mu) = i\eta S_\chi n_{\bar{l}}\ (\eta r)|\chi_{-\chi}^\mu), \tag{43}$$

where S_χ is the sign of χ. j, l and $\bar{l}$ are specified by χ according to the rule

$$j=l-1/2\,;\ l=\chi\,; \qquad \bar{l}=l-1\ (\chi>0),$$

$$j = l + 1/2 \, ; \quad l = -\varkappa - 1 \, ; \quad \bar{l} = l + 1 \quad (\varkappa < 0) \, . \tag{44}$$

Substituting $G(\boldsymbol{r}, \boldsymbol{r}')$ (Eq. (36)) and $|\varPsi_\varkappa{}^\mu\rangle$ (Eq. (17)) into the surface integral (24), and using the relations (39), (42) and (43), we obtain $\varLambda_{\varkappa\mu\,;\,\varkappa'\mu'}$ in the following form:

$$\varLambda_{\varkappa\mu\,;\,\varkappa'\mu'} = (W + 1) g_\varkappa g_{\varkappa'} \left(L_\varkappa j_l - \frac{S_\varkappa \eta}{W + 1} j_{\bar{l}} \right)$$

$$\times \left[B_{\varkappa\mu,\varkappa'\mu'} \left(\frac{S_{\varkappa'} \eta}{W + 1} j_{\bar{l}'} - j_{l'} L_{\varkappa'} \right) \right.$$

$$\left. + \eta \delta_{\varkappa\varkappa'} \delta_{\mu\mu'} \left(\frac{S_\varkappa \eta}{W + 1} n_{\bar{l}} - n_l L_\varkappa \right) \right], \tag{45}$$

where

$$L_\varkappa = \frac{f_\varkappa(R)}{g_\varkappa(R)}, \quad g_\varkappa = g_\varkappa(R), \quad j_l = j_l(\eta R), \quad \text{etc.}$$

Dividing each row and each column of $\varLambda_{\varkappa\mu\,;\,\varkappa'\mu'}$ by the proper factors before equating the determinant of (45) to zero, and neglecting terms of the order of $(E/c)^2$ ($\sim 10^{-5}$), we obtain the desired secular equation

$$\mathrm{Det} \left| B_{\varkappa\mu,\varkappa'\mu'} + \eta \delta_{\varkappa\varkappa'} \delta_{\mu\mu'} \frac{L_\varkappa n_l - \eta S_\varkappa n_{\bar{l}}}{L_\varkappa j_l - \eta S_\varkappa j_{\bar{l}}} \right| = 0 \, . \tag{46}$$

We can convert (46) to an expression in Rydberg units by replacing $L_\varkappa = \dfrac{f_\varkappa(R)}{g_\varkappa(R)}$ with $\dfrac{c f_\varkappa(R)}{g_\varkappa(R)} = L_\varkappa$.

§ 5. Relation to the nonrelativistic theory

To compare the relativistic secular equation (46) with the nonrelativistic equation, let us refer to the nonrelativistic secular equation

$$\mathrm{Det} \left| A_{lm,l'm'} + \eta \delta_{ll'} \delta_{mm'} \frac{L_l n_l - n_l'}{L_l j_l - j_l'} \right| = 0, \tag{47}$$

where

$$L_l = \frac{d \ln R_l(r)}{dr} \bigg|_{r=R}, \quad j_l' = \frac{d}{dr} j_l(\eta r), \quad \text{etc.}$$

Comparing (46) with (47), we notice that the relativistic secular equation has the same form as the nonrelativistic equation. We can then reach the relativistic secular equation (46) by replacing each factor in the matrix elements as follows:

$$A_{lm,l'm'} \longrightarrow B_{\varkappa\mu,\varkappa'\mu'}$$

$$\delta_{ll'} \delta_{mm'} \longrightarrow \delta_{\varkappa\varkappa'} \delta_{\mu\mu'},$$

$$j_l', n_l' \longrightarrow \eta S_x j_{\bar{l}}, \, \eta S_x n_{\bar{l}},$$

$$L_l \longrightarrow L_x. \tag{48}$$

The reason for this analogy is apparent. Because of the mixing of the "up spin" ($m = 1/2$) with "down spin" ($m = -1/2$) in the same ($\varkappa$, μ), the relativistic structure constants $B_{\varkappa\mu, \varkappa'\mu'}$ consist of a summation of the product of the nonrelativistic structure constant $A_{lm, l'm'}$ and the Clebsh-Gordan coefficient over spin $\pm 1/2$. (see 35). The derivatives of Bessel functions change the form, since in the relativistic theory the momentum operator appears in the form of $\boldsymbol{\sigma p}$. The logarithmic derivatives $L_l = \dfrac{d \ln R_l}{dr}\bigg|_{r=R}$ become $L_x = \dfrac{c f_x(R)}{g_x(R)}$.

In fact, it can easily be shown that in the nonrelativistic limit ($c \to \infty$) the relativistic secular equation (46) becomes the nonrelativistic secular equation (47) except for the spin degeneracy.

From (20) and (21), we have in the nonrelativistic limit

$$\lim_{c \to \infty} \frac{c f_x(r)}{g_x(r)} = \frac{d \ln g_x(r)}{dr} + \frac{\varkappa + 1}{r}. \tag{49}$$

Since the upper component of the relativistic wave function becomes the nonrelativistic wave function in the limit of $c \to \infty$, $\dfrac{d \ln g_x(r)}{dr}$ in (49) is nothing but the usual logarithmic derivative $\dfrac{d \ln R_l(r)}{dr}$ appearing in the nonrelativistic theory.

From (49) and (40)–(43), we obtain the following relations in the limit of $c \to \infty$:

$$\lim_{c \to \infty} (L_x j_l - \eta S_x j_{\bar{l}}) = L_l j_l - j_l', \tag{50}$$

$$\lim_{c \to \infty} (L_x n_l - \eta S_x n_{\bar{l}}) = L_l n_l - n_l'. \tag{51}$$

Substituting (50) and (51) into (46) and transforming ($\varkappa$, μ) into (l, $\mu - m$, m), we get the nonrelativistic secular equation (47) except for the spin degeneracy.

§ 6. Remarks

We have shown that the matrix elements of the relativistic secular equation have the same form as the nonrelativistic matrix elements. Thus the calculations of the relativistic matrix elements are not complicated compared with the nonrelativistic calculations. The only problem found in the relativistic calculation is a significant increase in computing time which results from the doubling of the basis set, the complex property of the matrix elements and the double roots of the secular equation in crystals with inversion symmetry according to

the time reversal symmetry. This problem arising from the relativistic band theory is shared with other methods.[2],[3] Because of its rapid convergence, the Green's function method is more advantageous than other methods for relativistic calculations.

Together with the Green's function method, the APW method seems to be a powerful method also in the relativistic theory because of its rather good convergence and generality. The APW method is similar to the Green's function method in that the wave function is expanded in the central field orbitals inside the sphere and its matrix elements include the logarithmic derivatives on the sphere. Hence, as in the case of the Green's function method, its relativistic matrix elements are expected to have a form corresponding to the nonrelativistic matrix elements. However, Loucks' expression for the relativistic APW matrix elements is not expressed in the same form as the nonrelativistic matrix elements, and Loucks did not show the relation between the relativistic formulation and the nonrelativistic formulation.[3] In Appendix B we give a brief discussion of the relativistic APW formalism and derive the matrix elements in the same form as the nonrelativistic matrix elements by replacing the factors of the nonrelativistic matrix elements with the proper factors.[*] Our expression for the matrix elements is more compact than Loucks' expression, although it can easily be derived from his expression.

It should be noted that besides their convergence and generality both the Green's function method and the APW method have the advantage, for relativistic calculations, that the wave functions are comparatively exact in the neighborhood of the atoms.

Acknowledgements

Appendix A

Derivation of (15)

Using the hermitian property of $\boldsymbol{\alpha}$ and the divergence theorem, we have

$$\int_{r \leq R} \langle \Psi | \boldsymbol{\alpha} \boldsymbol{p} | \Phi \rangle d\tau = \int_{r \leq R} \langle \Phi | \boldsymbol{\alpha} \boldsymbol{p} | \Psi \rangle^* d\tau$$

$$- i \int_{r=R} \langle \Psi | \boldsymbol{\alpha} \hat{r} | \Phi \rangle ds. \qquad (\text{A} \cdot 1)$$

From (A·1), we get

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*) A complete formulation and discussion of the relativistic APW method is presented in the author's thesis.[8]

$$\int_{r'\leq R} G(r, r')\alpha p' |\Psi(r')\rangle d\tau' = \int_{r'\leq R} \{\langle\Psi(r')|\alpha p'G(r', r)\}^\dagger d\tau'$$

$$-i\int_{r'=R} G(r, r')\alpha\hat{r}'|\Psi(r')\rangle dS' . \qquad (A\cdot2)$$

From (A·2), (1) and (3) we derive the relation

$$\int_{r'\leq R} G(r, r') V(r') d\tau'$$

$$= \int_{r'\leq R} \{\langle\Psi(r')|(\alpha p' + \beta - W) G(r', r)\}^\dagger d\tau'$$

$$-i\int_{r'=R} G(r, r')\alpha\cdot\hat{r}'|\Psi(r')\rangle dS'$$

$$= |\Psi(r)\rangle\int_{r'\leq R} \delta(r-r') d\tau' - i\int_{r'=R} G(r, r')\alpha\hat{r}'|\Psi(r')\rangle dS' \qquad (A\cdot3)$$

and the conjugate relation for (A·3)

$$\int_{r\leq R} \langle\Psi(r)|V(r) G(r, r') d\tau$$

$$= \langle\Psi(r')|\int_{r\leq R} \delta(r-r') d\tau + i\int_{r=R} \langle\Psi(r)|\alpha\hat{r}G(r, r') dS . \qquad (A\cdot4)$$

Substituting (A·3) and (A·4) into (14), we obtain the surface integral (15) as follows:

$$\Lambda^\varepsilon = \int_{r\leq R-2\varepsilon} d\tau \langle\Psi(r)|V(r)$$

$$\times [|\Psi(r)\rangle - \int_{r'\leq R-\varepsilon} d\tau'G(r, r') V(r')|\Psi(r')\rangle]$$

$$= i\int_{r\leq R-2\varepsilon} d\tau \int_{r'=R-\varepsilon} dS'\langle\Psi(r)|V(r) G(r, r')\alpha\hat{r}'|\Psi(r')\rangle$$

$$= -\int_{r=R-2\varepsilon} dS \int_{r'=R-\varepsilon} dS'\langle\Psi(r)|\alpha\hat{r}G(r, r')\alpha\hat{r}'|\Psi(r')\rangle. \qquad (A\cdot5)$$

Appendix B

On the relativistic formulation of the APW method

Loucks[3] constructed the relativistically argumented plane wave (RAPW), which consists of an expansion of the central field orbitals $|\Psi_\chi^\mu\rangle$ (Eq. (17))

inside the sphere and a Dirac plane wave (5) outside the sphere. The expansion coefficients are chosen such that the upper components of the wave functions in each region are continuous on the sphere. As a result the lower components of RAPW are discontinuous on this boundary. Using RAPW as the basis function, Loucks derived the secular equation for the Hamiltonian (3) with the "muffin-tin" potential (12).

First, let us prove that RAPW exactly corresponds to APW.

The lower components $|\Phi_2\rangle$ of the relativistic wave function $|\Psi\rangle$ can be expressed in terms of the upper component $|\Phi_1\rangle$:

$$|\Psi\rangle = \begin{pmatrix} |\Phi_1\rangle \\ |\Phi_2\rangle \end{pmatrix} = \begin{bmatrix} |\Phi_1\rangle \\ \dfrac{1}{W-V+1}\boldsymbol{\sigma p}|\Phi_1\rangle \end{bmatrix}. \qquad (A\cdot6)$$

We notice from this expression that the discontinuity of the lower component is nothing but the discontinuity of the derivative of the upper component and the contribution from the surface integral in the matrix elements is due to this discontinuity. Thus if we note that the upper component is the nonrelativistic wave function in the nonrelativistic limit, it is apparent that Loucks' formalism exactly corresponds to the nonrelativistic APW formalism. Hence we expect that the RAPW matrix elements have a form corresponding to the APW matrix elements, just as in the Green's function method. In fact we can obtain the relativistic matrix elements by replacing the factors of the nonrelativistic matrix elements with the proper factors, as in the case of the Green's function method.

The nonrelativistic APW matrix elements[9] are written in the form

$$\mathrm{APW}\binom{n}{N} = (\boldsymbol{k}_N\boldsymbol{k}_n - E)\,\Omega_{nN}$$

$$+ 4\pi R^2 \sum_{l=0}^{\infty} D_l\binom{n}{N} j_l(k_nR) j_l(k_NR) L_l, \qquad (A\cdot7)$$

where

$$\Omega_{nN} = \tau\delta_{nN} - 4\pi R^2 \frac{j_1(|\boldsymbol{k}_N - \boldsymbol{k}_n|R)}{|\boldsymbol{k}_N - \boldsymbol{k}_n|}, \qquad (A\cdot8)$$

$$D_l\binom{n}{N} = (2l+1)P_l(\hat{k}_n\hat{k}_N)$$

$$= 4\pi \sum_{m=-l}^{l} Y_l^{m\dagger}(\hat{k}_N) Y_l^m(\hat{k}_n), \qquad (A\cdot9)$$

$$L_l = \frac{d\ln R_l(r)}{dr}\bigg|_{r=R}. \qquad (A\cdot10)$$

Taking into account the spin, and noting that the quantum number in the relativistic central field problem is $(\varkappa, \mu)$ and referring to the relation between

the relativistic matrix elements and the nonrelativistic matrix elements in the Green's function method, we replace the factors in (A·12) as follows:

$$\Omega_{nN} \longrightarrow \Omega_{nN}\delta_{mM},$$

$$D_l\binom{n}{N} \longrightarrow D_x\binom{n\ m}{N\ M},$$

$$L_l \longrightarrow L_x = \frac{cf_x(R)}{g_x(R)}, \qquad (A·11)$$

where

$$D_x\binom{n\ m}{N\ M} = 4\pi\sum_{\mu}C(l\,1/2\,j\,;\ \mu-m,\ m)C(l\,1/2\,j\,;\ \mu-M,\ M)$$

$$\times Y_l^{\mu-M\dagger}(\hat{k}_N)\,Y_l^{\mu-m}(\hat{k}_n), \qquad (A·12)$$

where m, M specify the spins of RAPW. In (A·11), we neglect the relativistic effects on the plane wave part, since its effect is of the order of $(k_n/c)^2$.

From (11), we get the relativistic matrix elements

$$\text{RAPW}\binom{n\ m}{N\ M} = (\boldsymbol{k}_n\cdot\boldsymbol{k}_N - E)\,\Omega_{nN}\delta_{mM}$$

$$+ 4\pi R^2\sum_{x}D_x\binom{n\ m}{N\ M}\,j_l(k_nR)j_l(k_NR)\,L_x. \qquad (A·13)$$

In fact, if we calculate the surface integral by the same procedure as in the nonrelativistic case, we can get (A·13) neglecting terms of the order of $(k_n/c)^{2}.$[8]

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