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Korringa–Kohn–Rostoker Method

1. Brief summary of the theory of scattering

1.1. Radial Schrödinger equation

The Schrödinger equation describing the motion of the particle scattered by a central, spherical potential in units of $\hbar/2m = 1$ is

$$\left[-\nabla^2 + V(r)\right] \psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}), \tag{1.1}$$

where the Laplacian operator ∇^2 in spherical coordinate is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{L^2}{r^2}, \tag{1.2}$$

with

$$L^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}. \tag{1.3}$$

A solution of eq.(1.1) is then expressed in terms of a solution of the radial Schrödinger equation $u_l(r)$ as

$$\psi_{lm}(\boldsymbol{r}) = \frac{u_l(r)}{r} Y_{lm}(\theta, \varphi), \tag{1.4}$$

where $u_l(r)$ satisfies

$$\frac{d^2 u_l(r)}{dr^2} + \left[E - V(r) - \frac{l(l+1)}{r^2}\right] u_l(r) = 0 \tag{1.5}$$

and $Y_{lm}(\theta, \varphi)$ are the spherical harmonics defined to be eigenfunctions of L^2 and L_z.

1.2. Boundary condition and the phase shifts

Outside the potential range ($r > r_0$), the radial Schrödinger equation reduced to that of the free space and its solution may be any linear combinations of the two independent solutions (one regular, the other irregular) of

$$\frac{d^2 w_l(r)}{dr^2} + \left[E - \frac{l(l+1)}{r^2}\right] w_l(r) = 0. \tag{1.6}$$

The two solutions P and Q of eq.(1.6) are related to the spherical Bessel (regular solution) and Neumann (irregular solution) functions, $j_l(z)$ and $n_l(z)$, respectively, by

$$P_l(r;E) = \sqrt{E} r j_l(\sqrt{E} r) \tag{1.7}$$

and

$$Q_l(r;E) = -\sqrt{E} r n_l(\sqrt{E} r). \tag{1.8}$$

The negative sign is attached to the definition of Q_l for the later convenience. At large distances, these functions behave as

$$P_l(r;E) \longrightarrow \sin(\sqrt{E} r - \frac{l\pi}{2}) \tag{1.9}$$

and

$$Q_l(r;E) \longrightarrow \cos(\sqrt{E} r - \frac{l\pi}{2}). \tag{1.10}$$

The asymptotic form of the solution of eq.(1.4) at large distances is therefore

$$\begin{aligned} u_l(r) &\overset{r \gg r_0}{\longrightarrow} A \cos(\sqrt{E} r - \frac{l\pi}{2}) + B \sin(\sqrt{E} r - \frac{l\pi}{2}) \\ &= \sqrt{A^2 + B^2} \sin(\sqrt{E} r - \frac{l\pi}{2} + \eta_l). \end{aligned} \tag{1.11}$$

Here the so-called phase shift η_l is introduced. The regularity of u_l at the origin determines the ratio B/A and the asymptotic boundary condition at $r \gg r_0$ determines the normalization $\sqrt{A^2 + B^2}$. In the theory of scattering, the proper asymptotic boundary condition for the wave function is

$$\psi(r) \overset{r \gg r_0}{\longrightarrow} \mathrm{e}^{i\sqrt{E} z} + \frac{\mathrm{e}^{i\sqrt{E} r}}{r} f(\theta, \varphi). \tag{1.12}$$

Correspondingly, the condition on the normalization of the radial wave function is

$$u_l(r) \overset{r \gg r_0}{\longrightarrow} \mathrm{e}^{i\eta_l} \sin(\sqrt{E} r - \frac{l\pi}{2} + \eta_l) \tag{1.13}$$

or equivalently

$$u_l(r) = \mathrm{e}^{i\eta_l} \left[\cos\eta_l P_l(r;E) + \sin\eta_l Q_l(r;E) \right], \qquad r > r_0. \tag{1.14}$$

1.3. t-matrix

A more familiar expression of $u_l(r)$ with the same normalization as implied by eq.(1.14) may be

$$u_l(r) = P_l(r;E) - \sqrt{E}t_l(E)R_l^+(r;E), \qquad r > r_0, \tag{1.15}$$

where $R_l^+ = Q_l + iP_l$ is related to the spherical outgoing Hankel function $h_l^{(1)}(z) = j_l(z) + in_l(z)$ by

$$R_l^+(r;E) = i\sqrt{E}rh_l^{(1)}(\sqrt{E}r) \tag{1.16}$$

and t_l is the so-called atomic t-matrix defined by

$$t_l(E) = -\frac{1}{\sqrt{E}}\sin\eta_l\, \mathrm{e}^{i\eta_l}. \tag{1.17}$$

It is also possible to express $u_l(r)$ in terms of the k-matrix (corresponding to eq.(1.14)) or s-matrix (if R_l^+ and $R_l^- = Q_l - iP_l$ are used instead of P_l and Q_l).

Practically, the phase shift η_l is calculated in the following way. First, given a potential $V(r)$ and an energy parameter E, we integrate the radial Schrödinger equation numerically from the origin with the regular boundary condition to obtaine a solution $u_l(r)$, which satisfies

$$\frac{u_l'(r)}{u_l(r)} = \frac{P_l'(r) + \tan\eta_l\, Q_l'(r)}{P_l(r) + \tan\eta_l\, Q_l(r)}. \tag{1.18}$$

at $r > r_0$ irrespective of the normalization, Now, equation (1.18) is readily solved with respect to η_l.

1.4. Integral expression for the t-matrix

Another expression of the phase shifts, or equivalently the t-matrices, is obtained from the integral form of the Schrödinger equation. The expression is never used for actual calculations but is often useful in formal discussions. First we define a normalization constant Λ_l by

$$\Lambda_l = \lim_{r\to 0} \frac{(2l+1)!!\, u_l(r)}{(\sqrt{E}r)^{l+1}}. \tag{1.19}$$

Then from the Wronskian relation between u_l and w_l, which is a direct consequence of the Schrödinger eqs.(1.5) and (1.6),

$$\begin{aligned} W[w_l(r), u_l(r)]\Big|_{r_1}^{r_2} &= \{w_l(r)u_l'(r) - w_l'(r)u_l(r)\}\Big|_{r_1}^{r_2} \\ &= \int_{r_1}^{r_2} dr\, w_l(r)V(r)u_l(r), \end{aligned} \tag{1.20}$$

where w_l is either P_l or Q_l, it follows that

$$t_l(E) = \frac{E^{-1}\int_0^\infty dr\, P_l(r;E)V(r)u_l(r)}{\Lambda_l + E^{-1/2}\int_0^\infty dr\, R_l^+(r;E)V(r)u_l(r)}. \tag{1.21}$$

If u_l is normalized as eq.(1.13), the denominator of eq.(1.21) simply gives a unity. Similarly, k-matrix (or s-matrix) is obtained if R_l^+ (or P_l) is suitably replaced by a linear combination of P_l and Q_l (or R_l^+ and R_l^-).

2. Radial Green's functions

2.1. Integral form of the Schrödinger equation

From the Wronskian relation eq.(1.20), it follows that

$$W[P_l(r), u_l(r)] = \int_0^r dr\, P_l(r)V(r)u_l(r) \tag{2.1}$$

and

$$C - W[Q_l(r), u_l(r)] = \int_r^\infty dr\, Q_l(r)V(r)u_l(r), \tag{2.2}$$

where the constant C depends on the normalization of u_l. For the normalization implied by eq.(1.13), C satisfies

$$\begin{aligned} C &= W[Q_l(r), u_l(r)]_{r>R} = W[Q_l, P_l]\, \mathrm{e}^{i\eta_l} \cos\eta_l \\ &= \sqrt{E}\, \mathrm{e}^{i\eta_l} \cos\eta_l, \end{aligned} \tag{2.3}$$

where the relation $W[j(z), n(z)] = 1/z^2$ is used. In the following, we adopt this normalization for u_l. Now we multiply eq.(2.1) by Q_l, multiply eq.(2.2) by P_l and add them, obtaining

$$u_l(r) = \mathrm{e}^{i\eta_l} \cos\eta_l\, P_l(r) - \frac{1}{\sqrt{E}} \int_0^\infty dr'\, Q_l(r_>)P_l(r_<)V(r')u_l(r'), \tag{2.4}$$

where $r_<$ and $r_>$ denote the smaller and the greater of r and r'. Equation (2.4) is reduced to the expression given by eq.(1.14) when $r > r_0$ is satisfied.

2.2. Green's function

The quantity

$$g(r, r') = -\frac{P_l(r_<)Q_l(r_>)}{\sqrt{E}} \tag{2.5}$$

appearing in eq.(2.4) is a radial Green function.

The expression which is reduced to eq.(1.15) for $r > r_0$ is also obtained by replacing Q_l with $R_l^+ - iP_l$:

$$u_l(r) = P_l(r) - \frac{1}{\sqrt{E}} \int_0^\infty dr' \, R_l^+(r_>) P_l(r_<) V(r') u_l(r') \tag{2.6}$$

Here the relation eq.(1.21), with the denominator of r.h.s. being a unity, is used. The quantity

$$g^+(r, r') = -\frac{P_l(r_<) R_l^+(r_>)}{\sqrt{E}} \tag{2.7}$$

in eq.(2.6) again is a radial Green function.

2.3. Boundary condition

The difference between two Green functions, $g(r, r')$ (standing wave Green function) and $g^+(r, r')$ (outgoing wave Green function), becomes clear if we consider the integral equation of the form

$$u_l(r) = P_l(r) + \int_0^\infty dr' \, g^+(r, r') V(r') u_l(r'). \tag{2.8}$$

The solution will satisfy eq.(1.14). On the other hand, if we use g, instead of g^+, in eq.(2.8), the solution will satisfy $u_l(r) = P_l(r) + \tan \eta_l \, Q_l(r)$ for $r > r_0$. This means that the difference between g and g^+ is only in the normalization of the solution or, in other words, in the asymptotic boundary conditions. Note that the analytic properties of g and g^+ nevertheless are quite different. For example, g^+ is analytic in the upper half complex plane of the physical energy-sheet while g is not.

2.4. Differential equation for the Green function

We introduce a Green function which satisfies an inhomogeneous differential equation as is the case of usual Green functions for the linear differential equations;

$$\frac{d^2 g_l(r, r')}{dr^2} + \left[E - \frac{l(l+1)}{r^2} \right] g_l(r, r') = \delta(r - r'). \tag{2.9}$$

The discontinuity arising at $r = r'$ in the first derivative $P_l(r_<) Q_l(r_>)$ yields the δ-function on the r.h.s. of eq.(2.9).

2.5. Eigenfunction expansion

Seemingly a quite different expression of the radial Green function is obtained by introducing an eigenfunction expansion of the Green function. A set of eigenfunctions $\{P_l(r;E_n)\}$ are defined by the radial Schrödinger equation eq.(1.6) with a boundary condition $w_l(R) = 0$ at $r = R > r_0$. In the limit $R \gg 1$, the energy eigenvalues E_n's of $P_l(r;E_n)$ satisfy (see eq.(1.9))

$$\sqrt{E_n}\,R = n\pi + \frac{l\pi}{2}. \tag{2.10}$$

Expanding $g(r,r')$ as

$$g(r,r';E) = \sum_n G_n(r')P_l(r;E_n) \tag{2.11}$$

and inserting it into eq.(2.9), we obtain

$$g(r,r';E) = \sum_n \frac{P_l^*(r';E_n)P_l(r;E_n)}{E - E_n}, \tag{2.12}$$

where we assume that P_l is normalized as

$$\int_0^R |P_l(r;E_n)|^2\,dr = 1. \tag{2.13}$$

2.6. Radial Green function in general cases

Though all the arguments so far have regarded the free space as the reference system, the whole story goes as well for any other choice of the reference system. Thus if we take the system described by the Schrödinger equation with a potential term, eq.(1.5), as a reference system, we will obtain the Green function describing the propagation of the electron waves in the system with a central, spherical potential. The expression for such Green functions clearly has the same form as that for the free space Green function. In the later sections we will refer to such general cases by the same formulae, simply replacing $P_l(r;E)$, $Q_l(r;E)$ and $R_l^{\pm}(r;E)$ by the corresponding radial wave functions obtained in each case.

3. Free space Green's function

3.1. Real space representation

The free space Green function is defined by the differential equation

$$(\nabla^2 + E)g(\boldsymbol{r}, \boldsymbol{r}'; E) = \delta(\boldsymbol{r} - \boldsymbol{r}'), \tag{3.1}$$

whose momentum space representation

$$(-k^2 + E)g(\boldsymbol{k}; E) = 1 \tag{3.2}$$

readily gives the solution

$$g(\boldsymbol{r}, \boldsymbol{r}'; E) = \int \frac{d^3k}{(2\pi)^3} \frac{\exp\left[i\boldsymbol{k} \cdot (\boldsymbol{r} - \boldsymbol{r}')\right]}{E - k^2}. \tag{3.3}$$

Equation (3.3) is nothing but the eigenfunction expansion of the Green function. The integration on the r.h.s is easily performed as

$$\begin{aligned} (\text{r.h.s. of eq.(3.3)}) &= \frac{1}{(2\pi)^3} \int_0^\infty k^2 dk \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi \, \frac{\exp(ik|\boldsymbol{r} - \boldsymbol{r}'|\cos\theta)}{E - k^2} \\ &= \frac{1}{4\pi^2 |\boldsymbol{r} - \boldsymbol{r}'|} \int_{-\infty}^\infty kdk \, \frac{\sin(k|\boldsymbol{r} - \boldsymbol{r}'|)}{E - k^2} \\ &= -\frac{\exp(i\sqrt{E}|\boldsymbol{r} - \boldsymbol{r}'|)}{4\pi|\boldsymbol{r} - \boldsymbol{r}'|}. \end{aligned} \tag{3.4}$$

In the last expression the limit $E + i\delta \quad (\delta \to 0)$, corresponding to the outgoing-wave boundary condition (retarded Green function), is assumed.

3.2. Partial wave expansion

Partial wave expansion of the free space Green function is obtained from the similar expansion of the plane waves:

$$\exp(i\boldsymbol{k} \cdot \boldsymbol{r}) = 4\pi \sum_L i^l j_l(kr) Y_L(\hat{\boldsymbol{k}}) Y_L(\hat{\boldsymbol{r}}) = 4\pi \sum_L i^l \frac{P_l(r; E)}{kr} Y_L(\hat{\boldsymbol{k}}) Y_L(\hat{\boldsymbol{r}}) \tag{3.5}$$

(notice: P_l in eq.(3.5) are not the Legendre polynomials.) Here Y_L are the *real* spherical harmonics with the usual notation (use $\cos m\phi$ and $\sin m\phi$ instead of $\exp(im\phi)$ for real harmonics) and L represents (l, m). By substituting the exponential term in eq.(3.3) and performing the angular part integration, we obtain

$$
\begin{aligned}
g(\boldsymbol{r}, \boldsymbol{r}'; E) &= \frac{2}{\pi r r'} \sum_L \int_0^\infty dk \frac{P_l(r;E) Y_L(\hat{\boldsymbol{r}})\, P_l(r';E) Y_L(\hat{\boldsymbol{r}}')}{E - k^2} \\
&= \sum_L Y_L(\hat{\boldsymbol{r}}) G_L(r, r'; E) Y_L(\hat{\boldsymbol{r}}')
\end{aligned}
\tag{3.6}
$$

By expanding the radial Green function $g(r, r'; E)$ by the radial eigenfunctions $P_L(r; E_n)$ satisfying the boundary condition $P_L(R; E_n) = 0$, where R is some fixed large value ($R \gg 1$, see Sec. 2), and using the relation

$$
\sum_n \longrightarrow \frac{R}{\pi} \int_0^\infty dk \qquad \text{and} \qquad \int_0^R P_L^2(r; k^2) dr \longrightarrow \frac{R}{2},
\tag{3.7}
$$

where $k = \{n\pi + (l\pi/2)\}/R$, both being valid for $R \gg 1$, we find

$$
G_L(r, r'; E) = \frac{g(r, r'; E)}{r r'}.
\tag{3.8}
$$

Finally, using the expression for $g(r, r; E)$ given in Sec. 2 we obtain the partial wave expansion of $g(\boldsymbol{r}, \boldsymbol{r}'; E)$:

$$
\begin{aligned}
g(\boldsymbol{r}, \boldsymbol{r}'; E) &= -\sqrt{E} \sum_L Y_L(\hat{\boldsymbol{r}}) \left(\frac{P_l(r_<; E)}{\sqrt{E} r_<} \right) \left(\frac{R_l^+(r_>; E)}{\sqrt{E} r_>} \right) Y_L(\hat{\boldsymbol{r}}') \\
&= -i\sqrt{E} \sum_L J_L(r_<; E) H_L(r_>; E),
\end{aligned}
\tag{3.9}
$$

where we define

$$
J_L(r; E) = j_l(\sqrt{E} r) Y_L(\hat{\boldsymbol{r}})
\tag{3.10}
$$

and

$$
H_L(r; E) = h_l^{(1)}(\sqrt{E} r) Y_L(\hat{\boldsymbol{r}}).
\tag{3.11}
$$

3.3. General cases

Similarly the Green function of the system with a central, spherical potential may be expressed (see the last paragraph of Sec. 2) as

$$
\begin{aligned}
G(\boldsymbol{r}, \boldsymbol{r}'; E) &= -\sqrt{E} \sum_L Y_L(\hat{\boldsymbol{r}}) \left(\frac{\mathcal{P}_l(r_<; E)}{\sqrt{E} r_<} \right) \left(\frac{\mathcal{R}_l^+(r_>; E)}{\sqrt{E} r_>} \right) Y_L(\hat{\boldsymbol{r}}') \\
&= -i\sqrt{E} \sum_L \mathcal{J}_L(r_<; E) \mathcal{H}_L(r_>; E),
\end{aligned}
\tag{3.12}
$$

where $\mathcal{P}_l$ and $\mathcal{R}_l^+ = \mathcal{Q}_l + i\mathcal{P}_l$ are the regular and the irregular solution of the radial Schrödinger equation, eq.(1.5), and the definition of $\mathcal{J}_L$ and $\mathcal{H}_L$ are understood; $\mathcal{P}_l$ and $\mathcal{Q}_l$ (hence $\mathcal{P}_l$ and $\mathcal{R}_l^+$) satisfy the Wronskian relation

$$W\left[\mathcal{P}_l, \mathcal{Q}_l\right] = \sqrt{E}. \tag{3.13}$$

4. Multiple scattering by muffin-tin potentials

4.1. Integral equation for the Green function

Suppose that the system is composed of an assembly of non-overlapping spherical potential (muffin-tin potential) centered on each lattice site of a crystal.

The crystal Green function $G(\boldsymbol{r}, \boldsymbol{r}'; E)$ can be calculated from the free space Green function $g(\boldsymbol{r}, \boldsymbol{r}'; E)$ by

$$G(\boldsymbol{r}, \boldsymbol{r}') = g(\boldsymbol{r}, \boldsymbol{r}') + \int d\boldsymbol{r}''\, g(\boldsymbol{r}, \boldsymbol{r}'')V(\boldsymbol{r}'')G(\boldsymbol{r}'', \boldsymbol{r}'). \tag{4.1}$$

Hereafter, the explicit notation of the energy dependence of the Green function, etc. is omitted for brevity.

4.2. Cell-centered expansion of the Green function

In eq.(4.1) the potential $V(\boldsymbol{r})$ denotes the assembly of muffin-tin potentials. Practically, eq.(4.1) can not be used for the calculation of G because of the convergence problems. Instead we introduce the cell-centered representation of eq.(4.1). First we consider the cell-centered representation of g;

$$\begin{aligned} g(\boldsymbol{r} + \boldsymbol{R}^m, \boldsymbol{r}' + \boldsymbol{R}^n) &= g(\boldsymbol{r}, \boldsymbol{r}' + \boldsymbol{R}^n - \boldsymbol{R}^m) \\ &= -\sqrt{E}\sum_L J_L(\boldsymbol{r})H_L(\boldsymbol{r}' + \boldsymbol{R}^n - \boldsymbol{R}^m) \qquad (\text{for } m \neq n). \end{aligned} \tag{4.2}$$

Using the addition theorem for H,

$$H(\boldsymbol{x} + \boldsymbol{x}') = 4\pi \sum_{L'L''} i^{l-l'+l''} C_{LL'L''} J_{L'}(\boldsymbol{x}_<)H_{L''}(\boldsymbol{x}_>), \tag{4.3}$$

where $C_{LL'L''}$ is the Gaunt number

$$C_{LL'L''} = \int d\hat{\boldsymbol{r}} Y_L(\hat{\boldsymbol{r}}) Y_{L'}(\hat{\boldsymbol{r}}) Y_{L''}(\hat{\boldsymbol{r}})$$

and $\boldsymbol{x}_>$ and $\boldsymbol{x}_<$ is the bigger and the smaller (in the absolute value) of $\boldsymbol{x}$ and $\boldsymbol{x}'$, we obtain

$$g(\boldsymbol{r}+\boldsymbol{R}^m, \boldsymbol{r}'+\boldsymbol{R}^n) = \sum_{LL'} J_L(\boldsymbol{r}) g_{LL'}^{mn} J_{L'}(\boldsymbol{r}') \qquad (\text{for } m \neq n), \tag{4.4}$$

where

$$g_{LL'}^{mn} = 4\pi i \sqrt{E} \sum_{L''} i^{l-l'+l''} C_{LL'L''} H_{L''}(\boldsymbol{R}^m - \boldsymbol{R}^n). \tag{4.5}$$

Defining $g_{LL'}^{mm} = 0$, cell-centered representation of g may be expressed as

$$g(\boldsymbol{r}+\boldsymbol{R}^m, \boldsymbol{r}'+\boldsymbol{R}^n) = \delta_{mn} g(\boldsymbol{r}, \boldsymbol{r}') + \sum_{LL'} J_L(\boldsymbol{r}) g_{LL'}^{mn} J_{L'}(\boldsymbol{r}'). \tag{4.6}$$

Similarly the crystal Green function has the cell-centered representation

$$G(\boldsymbol{r}+\boldsymbol{R}^m, \boldsymbol{r}'+\boldsymbol{R}^n) = \delta_{mn} G_s^m(\boldsymbol{r}, \boldsymbol{r}') + \sum_{LL'} \mathcal{J}_L^m(\boldsymbol{r}) G_{LL'}^{mn} \mathcal{J}_{L'}^n(\boldsymbol{r}'). \tag{4.7}$$

Here G_s^m is the Green function for the system of a single muffin-tin potential V^m at m-th site given by

$$G_s^m(\boldsymbol{r}, \boldsymbol{r}') = -i\sqrt{E} \sum_L \mathcal{J}_L^m(r_<; E) \mathcal{H}_L^m(r_>; E), \tag{4.8}$$

which is exactly the same Green function as defined by eq.(3.12).

4.3. Dyson-type equation for multiple scattering

In eq.(4.7) the second term represents the contribution of the multiple scattering (or "back scattering") to the Green function and giving rise to the band structure. The relation between $G_{LL'}^{mn}$ and $g_{LL'}^{mn}$ is obtained from the cell-centered representation of eq.(4.1). By direct insertion of eqs.(4.6) and (4.7) into eq.(4.2) and using the integral equations which are satisfied by $\mathcal{J}_L^m$ and G_s^m for the single muffin-tin potential V^m, it is proven that $G_{LL'}^{mn}$ is related to $g_{LL'}^{mn}$ by

$$G_{LL'}^{mn} = g_{LL'}^{mn} + \sum_{L''m'} g_{LL''}^{mm'} t_{L''}^{m'} G_{L''L'}^{m'n}. \tag{4.9}$$

For periodic systems eq.(4.9) is solved by Fourier transform as

$$G_{LL'}(\boldsymbol{k}) = \sum_{L''} g_{LL''}(\boldsymbol{k})\,[1 - tg(\boldsymbol{k})]^{-1}_{L''L'}\,. \tag{4.10}$$

The crystal Green function is then given by

$$\begin{aligned} G(\boldsymbol{r} + \boldsymbol{R}^m, \boldsymbol{r}' + \boldsymbol{R}^n) &= \delta_{mn} G^m_s(\boldsymbol{r}, \boldsymbol{r}') + \sum_{LL'} \mathcal{J}^m_L(\boldsymbol{r}) \\ &\times \int_\tau \frac{d\boldsymbol{k}}{\tau} \exp(-i\boldsymbol{k}\cdot(\boldsymbol{R}_m - \boldsymbol{R}_n)) \sum_{L''} g_{LL''}(\boldsymbol{k})\,[1 - tg(\boldsymbol{k})]^{-1}_{L''L'}\, \mathcal{J}^n_{L'}(\boldsymbol{r}'), \end{aligned} \tag{4.11}$$

where τ is the Brillouin zone volume.

5. Band structure calculations

5.1. Traditional KKR method

Standard KKR band structure calculation is performed by finding the zero of the determinant of the matrix appearing in eq.(4.11) (called KKR matrix) for each $\boldsymbol{k}$;

$$\det|\delta_{LL'} - t_L(E) g_{LL'}(\boldsymbol{k}; E)| = 0. \tag{5.1}$$

This procedure gives the energy eigenvalues as a function of $\boldsymbol{k}$ and hence determines an energy dispersion relation $E(\boldsymbol{k})$. The reason why the energy eigenvalues are obtained in this way is the following: The zeros of the KKR matrix gives the poles of the Green function (it actually is a one-to-one correspondence); each pole however corresponds to the eigenstate of the Hamiltonian, as understood from the eigenfunction expansion of the Green function.

In actual calculations, a numerical difficulty arises when the $E(\boldsymbol{k})$ falls near the free-state branches or the atomic energy levels. Both the free states and the atomic states cause poles in the determinant (poles of the structural Green function $g_{LL'}(\boldsymbol{k}; E)$ or those of the t-matrix), changing the sign of the determinant. This can be a big trouble (however difficult to imagine!) in a root-finding procedure. For this reason, the KKR-method is sometimes referred to as an unstable method. Though such a statement may not be quite faire, it certainly is true that careless use of KKR sometimes leads to funny conclusions.

5.2. An alternative

A more direct way to obtain the electronic structure may be to calculate the crystal Green function following eq.(4.11). Such a method is especially attractive because it enable us to apply the KKR technique to various other classes of problem, e.g., impurity problems, disordered alloys, surfaces, interfaces, LEED states, and other spectroscopic properties.

The k-space integration appearing in eq.(4.11), however, causes a tough problem: Since the imaginary part of the integrand is the δ-function, it is very hard to perform the integration literally (actually impossible!). A conceivable way to overcome this problem is to work with complex energies. For the complex energy the integrand, as a function of $\boldsymbol{k}$, becomes quite dull and the integration can be performed accurately.

Such a trick is possible since, first, the back scattering term is the difference between two Green functions, both of them being analytic, and hence analytic in the upper complex half plane and, secondly, all we need in the self-consistent band structure calculation is not the Green function but its energy integral. Owing to these facts, we can safely deform the energy integration path toward the upper complex plane and still can hold all necessary information. This also increases the accuracy of the energy integration because the Green function is quite structureless off the real axis as a function of E.

Contrary to the traditional method mentioned in the previous subsection, this alternative way is free from the spurious poles. Moreover numerical steps needed for this procedure increase, roughly speaking, as N^2, where N is the number of atoms per unit cell, which is compared with N^3 needed for the traditional method.

Another big advantage of this method is that the procedure is quite efficiently vectorized in the sense of the vector processing of the supercomputers. This point, though nothing much physics, is important in actual calculations.

5.3. Total-energy calculation

Once we obtain the Green function we can calculate, in principle, all the ground state electronic properties in the framework of the muffin-tin potential model. For instance, the spin dependent local charge distributions are calculated from the imaginary part of energy integral of the site diagonal Green function:

$$\rho(\boldsymbol{r}) = -\frac{1}{\pi} \Im \int_{-\infty}^{E_{\mathrm{F}}} dE G(\boldsymbol{r}, \boldsymbol{r}\,; E), \tag{5.2}$$

where $G(\boldsymbol{r},\boldsymbol{r};E)$ is given by eq.(4.11) with $m = n = 0$. In order to calculate the total energy of the system we exploit the muffin-tin charge model where the spherical symmetric charge distribution inside the muffin-tin sphere and the uniform charge distribution for interstitial region is assumed. In this case we can express the total energy per atom as a sum of various separate contributions:

$$E_{\rm tot} = E_{\rm band} - E_{\rm pot} + E_{\rm stat} + E_{\rm xc} \tag{5.3}$$

To calculated the band energy, we introduce a function $Z(E)$, whose imaginary part gives the total number of states (per atom) below a real energy E:

$$\begin{aligned} Z(E) = &\int_\tau \frac{d\boldsymbol{k}}{\tau} \left\{ \ln\det|-E+(\boldsymbol{k}+\boldsymbol{g})^2| + \ln\det|1-tg(\boldsymbol{k};E)| \right\} \\ &- \ln\det\left|\frac{\exp(i\eta_L(E))}{\Lambda_L(E)}\right| \end{aligned} \tag{5.4}$$

Here $\Lambda_L(E)$ is defined by eq(1.19), giving a normalization for the phase shift η_L. Such a normalization of the phase shift makes the analytic continuation of $Z(E)$ to the upper complex half plain possible; the procedure removes all singularities which $\exp(i\eta_L(E))$ will have in the upper half plain at the resonances in the single site scattering.

The band energy is now calculated by integrating $Z(E)$ with respect to E up to the Fermi level:

$$E_{\rm band} = -\frac{1}{\pi}\Im\left\{ Z(E_{\rm F})E_{\rm F} - \int_{-\infty}^{E_{\rm F}} Z(E)dE \right\} \tag{5.5}$$

We subtract from the band energy the potential energy

$$E_{\rm pot} = \int_0^{r_0} r^2 dr \rho(r) V^0(r), \tag{5.6}$$

which is the expectation value of the single site potential at 0-th site V^0, to obtain the kinetic energy of the non-interacting system in the sense of the local density functional theory. The electrostatic energy $E_{\rm electrostatic}$ (par atom, in atomic unit) is obtained as

$$\begin{aligned} E_{\rm stat} = 32\pi^2 \int_0^{r_0} dr\, r\rho(r) \int_0^{r} dr'\, r'^2 \rho(r') - 8\pi\, Q \int_0^{r_0} r\rho(r)dr \\ - \frac{1}{2}\, C\, \frac{Q_{\rm out}^2}{a}, \end{aligned} \tag{5.7}$$

where a is the lattice constant and the constant C, depending on the crystal structure, is given as, e.g., C =4.8320664, 4.085521 and 3.1166857 for fcc, bcc and sc lattice, respectively; Q is the nuclear charge and Q_{out} is the number of electrons per atom accumulated at the interstitial region, i.e.,

$$Q_{\mathrm{out}} = Q - \int_0^{r_0} r^2 dr \rho(r). \tag{5.8}$$

The exchange-correlation energy (per atom) is given by the LSD approximation as

$$E_{\mathrm{xc}} = \int_0^{r_0} r^2 dr \rho \epsilon_{\mathrm{xc}}(\rho) + Q_{\mathrm{out}} \epsilon_{\mathrm{xc}}(\rho_{\mathrm{out}}), \tag{5.9}$$

where ϵ_{xc} is the exchange-correlation energy suitable for the homogeneous electron gas. All the core contributions should be included in the above expression.

5.4. Pressure

For pressure we use a mixture of the pressure cell-boundary relation of Liberman–Pettifor and the usual expression which relates the pressure to a sum of twice the kinetic energy and the potential energy with an additional exchange-correlation contribution. We apply the former inside the muffin-tin sphere and use the latter for the interstitial region:

$$\begin{aligned}
3P\Omega = & \sum_L \int_{-\infty}^{E_{\mathrm{F}}} dE\, \rho_L(r_0, E) r_0 \left\{ (E - V(r_0))\, r_0^2 + (D_L - l)(D_L + l + 1) \right\} \\
& + E_{\mathrm{band}} - \sum_L \int_{-\infty}^{E_{\mathrm{F}}} dE\, E \int_0^{r_0} r^2 dr\, \rho_L(r, E) \\
& - 4\pi r_0^3 \rho(r_0) \left\{ \epsilon_{\mathrm{xc}}\big(\rho(r_0)\big) - \mu_{\mathrm{xc}}\big(\rho(r_0)\big) \right\} \\
& - \frac{1}{2} C \, \frac{Q_{\mathrm{out}}^2}{a} - 3Q_{\mathrm{out}} \left\{ \epsilon_{\mathrm{xc}}(\rho_{\mathrm{out}}) - \mu_{\mathrm{xc}}(\rho_{\mathrm{out}}) \right\}
\end{aligned} \tag{5.10}$$

Here, $\rho_L(r, E)$ is the partial density of states inside the muffin-tin sphere, i.e., the L-th component of the negative imaginary part of the Green function divided by π (see eqs.(4.11) and (5.2)), $D_L = r_0 \mathcal{J}_L'(r_0, E)/\mathcal{J}_L(r_0, E)$ is related to the logarithmic derivative of the radial wave functions at $r = r_0$ and μ_{xc} is the exchange correlation potential.

An advantage of this mixture is that in this way we can avoid the numerical problem caused by a big cancellation between kinetic and potential energies without introducing the atomic sphere approximation which the Liberman–Pettifor approach (usually used in LMTO) had to use for a surface integral. Furthermore, we can use this method both for non-relativistic and relativistic cases. The usual treatment, on the otherhand, fails for a relativistic case since the sum of twice the kinetic energy and the potential energy never corresponds to the energy cost for the volume dilation in this case. The reason why the present method works even for the relativistic treatment is that we calculate the pressure at the muffin-tin sphere from the momentum flow across the sphere; the procedure is valid both for relativistic and non-relativistic cases. For the interstitial region the relativistic effects are not important any more, which allows us to apply the second method. A key point is that we need not use the atomic sphere approximation, in contrast to the Liberman–Pettifor approach, for the second method and thus can avoid the additional approximation.

6. Application of the KKR method

6.1. Impurity problems

Suppose an impurity atom located, say, at the origin is embedded in an otherwise perfect host crystal. Now let us assume that the potentials at the neighboring host sites are not affected by the presence of the impurity atom (single site approximation). In this case, all we have to know is the site diagonal Green function at the origin $G(\boldsymbol{r},\boldsymbol{r})$, where G is given by eq.(4.7). This problem is immediately solved if the back scattering term of eq.(4.7) for the perfect host crystal $\tilde{G}^{00}_{LL'}$ (i.e. $m = n = 0$) is known:

$$G^{00}_{LL'} = \sum_{L''} \tilde{G}^{00}_{LL''} \left[1 - (t_{\text{impurity}} - t_{\text{host}})\, \tilde{G}^{00}\right]^{-1}_{L''L'}, \tag{6.1}$$

where

$$\tilde{G}^{00}_{LL'} = \int_{\tau} \frac{d\boldsymbol{k}}{\tau} \tilde{G}_{LL'}(\boldsymbol{k}) = \int_{\tau} \frac{d\boldsymbol{k}}{\tau} \sum_{L''} g_{LL''}(\boldsymbol{k})\, [1 - t_{\text{host}} g(\boldsymbol{k})]^{-1}_{L''L'} \tag{6.2}$$

may be calculated for the host crystal once and while. The above treatment might not be enough when the perturbation caused by the impurity extends beyond the single site. More sophisticated treatment which can deal with not only the impurity site but also the surrounding host sites simultaneously is required in these cases; the extension of eq.(6.1) is rather straightforward.

6.2. KKR-coherent potential approximation

For disordered systems, the coherent potential approximation (CPA) is one of the most efficient way to solved the problem. What are discussed about the disordered systems are averaged properties. In the present context, it is the configuration average of the Green function. In CPA, averaged Green function is expressed in terms of the effective medium; it is the assembly of the fictitious atoms whose atomic potential is specified by the coherent t-matrix $\tilde{t}(E)$. Once the coherent t-matrix is known, any ground state properties are calculated within the single site approximation (actually it is proven to be the best single site treatment).

To determine the coherent t-matrix, we consider the following impurity problem: Let the disordered system be $\mathrm{A}_{1-x}\mathrm{B}_x$. Suppose we put either A or B atom in the effective medium as an impurity. The impurity problems in these cases are solved if $\tilde{t}$ is known (see the preceding subsection); the site diagonal Green function is then given by

$$G^{\mathrm{A\,(or\,B)}}_{LL'} = \sum_{L''} \tilde{G}^{00}_{LL''} \left[1 - \left(t_{\mathrm{A\,(or\,B)}} - \tilde{t}\right) \tilde{G}^{00}\right]^{-1}_{L''L'}, \tag{6.3}$$

where

$$\tilde{G}^{00}_{LL'} = \int_\tau \frac{d\boldsymbol{k}}{\tau} \tilde{G}_{LL'}(\boldsymbol{k}) = \int_\tau \frac{d\boldsymbol{k}}{\tau} \sum_{L''} g_{LL''}(\boldsymbol{k}) \left[1 - \tilde{t} g(\boldsymbol{k})\right]^{-1}_{L''L'}. \tag{6.4}$$

Now the CPA prescription determining $\tilde{t}$ is

$$(1-x) G^{\mathrm{A}}_{LL'} + x G^{\mathrm{B}}_{LL'} = \tilde{G}^{00}_{LL'}. \tag{6.5}$$

In other words, the $\tilde{t}$ should be determined in such a way that the scattering disappears if the single site scattering by A and by B impurity located at the origin in the effective medium is configurationally averaged.

All the average quantities are easily calculated if $\tilde{t}$ is obtained by solving the above self-consistent equation. As for the problems associated to the numerical treatment of the CPA equation and some efficient techniques to get the procedure run, see elsewhere.