Multiple Scattering and Tight-Binding

Connecting the formalisms

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Abstract

These notes (from my boyhood in Bristol) use multiple scattering theory (**MST**) to solve the perfect lattice and single impurity problems (see [1], [2]). I also give the corresponding derivations in tight-binding theory (**TBT**) and show how similar in structure they are to MST. This connection was suggested by Shiba [3] and Anderson's paper [4] on magnetic impurities. The classic TBT treatment of the impurity problem is by Slater and Koster [5].

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1 Fundamental equations

The **MST** problem refers to a system of non-overlapping spherical scatterers located at points $\{\mathbf{R}_i\}$ and described by t-matrices $t_{i,L}(\varepsilon)$ - note that $L \equiv (l,m)$. The scattering path matrix is given by

$$\tau^{ij}_{LL'}(\varepsilon) = t_{i,L}(\varepsilon) + \sum_{L''}\sum_{k\neq i} t_{i,L}(\varepsilon) G_{LL''}(\mathbf{R}_{ik},\varepsilon)\tau^{kj}_{L''L'}(\varepsilon) \tag{1.1}$$

with $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. For what follows we don't need to display the full angular momentum indices and energy variables – only the site indices come into the development. So we'll use an obvious simplified notation and rewrite (1.1) as

$$\tau^{ij} = t_i\delta_{ij} + \sum_{k\neq i} t_i G^{ik}\tau^{kj} \tag{1.2}$$

When put on the energy shell, G^{ij} becomes the real-space structure constant matrix [6] which acts as a propagator linking sites *i* and *j*. This is why the term $k = i$ is excluded from the sum in (1.2); all repeated scatterings from the potential at site *i* are included in t_i. Indeed G^{ij} depends on the Hankel functions $h_l(\mathbf{R}_i - \mathbf{R}_j)$ [6] and these are infinite when $i = j$. Therefore, to simplify the formulae, we modify the structure constants such that the site diagonal term is defined to be zero [6] and then we can write

$$\tau^{ij} = t_i\delta_{ij} + \sum_{k} t_i G^{ik}\tau^{kj} \tag{1.3}$$

in which G^{ik} is understood to mean this modified structure constant matrix.

The **TBT** treatment, on the other hand, starts with the Hamiltonian

$$\mathcal{H} = \sum_i \varepsilon_i a_i^\dagger a_i + \sum_{ij} T_{ij} a_i^\dagger a_j \tag{1.4}$$

where ε_i is a single-site energy[1], T_{ij} is the hopping integral between sites i and j and $a_i^\dagger$ is the creation operator for the Wannier state $|i\rangle$ on site i. The Green's function, or resolvent, is, as usual,

$$\mathcal{G}(\varepsilon) = (\varepsilon - \mathcal{H})^{-1} \tag{1.5}$$

and in the Wannier state representation

$$G_{ij}(\varepsilon) = \langle i|(\varepsilon - \mathcal{H})^{-1}|j\rangle = \langle 0|a_i(\varepsilon - \mathcal{H})^{-1}a_j^\dagger|0\rangle \tag{1.6}$$

$|0\rangle$ being the vacuum. The basic method of solution is to work with the set of equations

[1] We could/should label the single-site energy by atomic quantum numbers, in particular the angular momentum. Then ε_i would become a vector $\boldsymbol{\varepsilon}_i$ and T_{ij} a matrix $\mathbf{T}_{ij}$ in these labels. However, in the spirit of (1.2), we will suppress these labels in TBT and focus only on site labels.

$$\sum_k \langle i|(\varepsilon - \mathcal{H})|k\rangle G_{kj}(\varepsilon) = \delta_{ij} \tag{1.7}$$

This is how Anderson [4] did the impurity problem. Indeed, the perfect lattice is easily treated using the lattice Fourier transform of (1.7). Here, however, I'm going to write it in a different way, one in which the mathematical connection with MST is clear.

First, define the following operators

$$\begin{aligned} \mathcal{L}(\varepsilon) &= \varepsilon - \sum_i \varepsilon_i a_i^\dagger a_i \\ \mathcal{T} &= \sum_{i,j} T_{ij} a_i^\dagger a_j \end{aligned} \tag{1.8}$$

Hence, omitting the energy arguments, we can write the Green's function operator (1.5) as

$$\mathcal{G} = (\mathcal{L} - \mathcal{T})^{-1} = \left(1 - \mathcal{L}^{-1}\mathcal{T}\right)^{-1} \mathcal{L}^{-1} \tag{1.9}$$

and this in turn can be written

$$\mathcal{G} = \mathcal{L}^{-1} + \mathcal{L}^{-1}\mathcal{T}\mathcal{G} \tag{1.10}$$

This already has the look of a Dyson equation, and resemblance becomes closer when we put it in a site representation:

$$\langle i|\mathcal{L}^{-1}|j\rangle = \langle i|\left(\varepsilon - \sum_i \varepsilon_i a_i^\dagger a_i\right)^{-1}|j\rangle = (\varepsilon - \varepsilon_i)^{-1}\delta_{ij} = \boldsymbol{\ell}_i(\varepsilon)\delta_{ij} \tag{1.11}$$

The quantity

$$\boldsymbol{\ell}_i^{-1}(\varepsilon) \equiv \frac{1}{\varepsilon - \varepsilon_i} \tag{1.12}$$

is called (by Shiba [3]) the ***locator*** of site i. Further,

$$\langle i|\mathcal{T}|j\rangle = \langle i|\sum_{k,l} T_{kl} a_k^\dagger a_l|j\rangle = T_{ij} \tag{1.13}$$

Equation (1.10) thus reads, in a site representation,

$$G_{ij} = \boldsymbol{\ell}_i^{-1}\delta_{ij} + \boldsymbol{\ell}_i^{-1}\sum_k T_{ik}G_{kj} \tag{1.14}$$

This is our "fundamental" equation of **TBT**. A glance at (1.3) reveals the equivalence, as regards the site indexing, to **MST**. For convenience, here's a translation table between the two approaches:

MST	**TBT**
τ	G
G	T
t	$\boldsymbol{\ell}^{-1}$

2 The perfect lattice

Consider first the **MST** approach to band theory, the KKR method. The set of vectors $\{\mathbf{R}_i\}$ now form a periodic lattice in which (in the simplest case) each site has t-matrix t ie $t_i = t \quad \forall i$. The scattering path matrix (1.3) is thus given by

$$\tau^{ij} = t\delta_{ij} + t\sum_k G^{ik}\tau^{kj} \tag{2.1}$$

We exploit translational invariance by using lattice Fourier transforms:

$$\begin{aligned} \tau^{ij} &= \Omega^{-1}\int_{BZ} d\mathbf{q}\, e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\tau(\mathbf{q}) \\ G^{ij} &= \Omega^{-1}\int_{BZ} d\mathbf{q}\, e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}G(\mathbf{q}) \end{aligned} \tag{2.2}$$

The integrals are carried out over the Brillouin zone whose volume is Ω. Equation (2.1) is then solved to give

$$\tau(\mathbf{q}) = t + tG(\mathbf{q})\tau(\mathbf{q}) = \left(t^{-1} - G(\mathbf{q})\right)^{-1}$$

The scattering path matrix for the perfect lattice is thus, in all its variables and indices,

$$\tau^{ij}_{LL'}(\varepsilon) = \Omega^{-1}\int_{BZ} d\mathbf{q}\, e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\left[\left(t^{-1}(\varepsilon) - G(\mathbf{q},\varepsilon)\right)^{-1}\right]_{LL'} \tag{2.3}$$

The KKR condition is now easily deduced. We seek poles of the Green's function, which are also the poles of the T-matrix and thus of the $\tau(\mathbf{q},\varepsilon)$. But by the rules of matrix inversion

$$\begin{aligned} \tau_{LL'}(\mathbf{q},\varepsilon) &= \left[\left(t^{-1}(\varepsilon) - G(\mathbf{q},\varepsilon)\right)^{-1}\right]_{LL'} \\ &= \frac{\left[\text{cofactor of } \left(t_l^{-1}(\varepsilon)\delta_{LL'} - G_{LL'}(\mathbf{q},\varepsilon)\right)\right]}{\left\|t^{-1}(\varepsilon) - G(\mathbf{q},\varepsilon)\right\|} \end{aligned}$$

Hence, the eigenvalues of the perfect lattice, ie the bands, are given by the zeros of the so-called KKR determinant:

$$\left\|t^{-1}(\varepsilon) - G(\mathbf{q},\varepsilon)\right\| = 0 \tag{2.4}$$

In **TBT**, the equivalent perfect lattice is defined by a single site energy ε_a, the same on all sites, and hopping integrals which depend only on $\mathbf{R}_{ij} \equiv \mathbf{R}_i - \mathbf{R}_j$. Hence, from (1.12)

$$\begin{aligned} \boldsymbol{\ell}_i^{-1}(\varepsilon) &= \frac{1}{(\varepsilon - \varepsilon_a)} \equiv \boldsymbol{\ell}^{-1} \quad \forall i \\ T_{ij} &= T(\mathbf{R}_i - \mathbf{R}_j) = \Omega^{-1}\int_{BZ} d\mathbf{q}\, e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}T(\mathbf{q}) \end{aligned}$$

and from (1.13) we can again introduce lattice Fourier transforms

$$T_{ij} = T\left(\mathbf{R}_i - \mathbf{R}_j\right) = \Omega^{-1} \int_{BZ} d\mathbf{q} e^{i\mathbf{q}\cdot\left(\mathbf{R}_i - \mathbf{R}_j\right)} T\left(\mathbf{q}\right)$$

$$G_{ij}\left(\varepsilon\right) = G\left(\mathbf{R}_i - \mathbf{R}_j, \varepsilon\right) = \Omega^{-1} \int_{BZ} d\mathbf{q} e^{i\mathbf{q}\cdot\left(\mathbf{R}_i - \mathbf{R}_j\right)} G\left(\mathbf{q}, \varepsilon\right)$$

Hence the correspondences noted in section 1, together with (2.3), yield

$$G\left(\mathbf{q}, \varepsilon\right) = \frac{1}{\left(\boldsymbol{\ell}\left(\varepsilon\right) - T\left(\mathbf{q}\right)\right)} = \frac{1}{\left(\varepsilon - \varepsilon_a - T\left(\mathbf{q}\right)\right)}$$

The TB bands are obviously given by

$$\varepsilon\left(\mathbf{q}\right) = \varepsilon_a + T\left(\mathbf{q}\right) \tag{2.5}$$

which is the analogue of (2.4)[2]. For example, a [1D] chain of lattice spacing a with nearest-neighbour hopping, ie $T_{ij} = T\left(\delta_{i,j+1} + \delta_{i,j-1}\right)$, gives $T\left(q\right) = 2T\cos\left(qa\right)$. Thus $\varepsilon\left(q\right) = \varepsilon_a + 2T\cos\left(qa\right)$ which is the familiar result from elementary TBT.

3 The single impurity

This problem is defined by a lattice $\left\{\mathbf{R}_i\right\}$ in which each site has an A atom, except site *i* which has a B atom. In MST, then,

$$t_j = t_A + \left(t_A - t_B\right)\delta_{ji} \tag{2.6}$$

The Green's function at the impurity site is determined by the *i*-site-diagonal element of τ, which is given by (1.3) and (2.6) as

$$\tau^{ii} = t_B + t_B \sum_k G^{ik}\tau^{ki}$$

But it's obvious that for $j \neq i$

$$\tau^{ji} = \left[\sum_k \tau^{jk} G^{ki}\right] t_B$$

so that

$$\tau^{ii} = t_B + t_B \left[\sum_{j,k} G^{ij}\tau^{jk} G^{ki}\right] t_B \tag{2.7}$$

This can be written as follows:

[2] Recall footnote 1: if we retained the atomic quantum numbers (angular momenta etc) on the site energies then (2.5) for the band energies would be replaced by the determinantal condition $\left\|\varepsilon\left(\mathbf{q}\right) - \boldsymbol{\varepsilon}_a - \mathbf{T}\left(\mathbf{q}\right)\right\| = 0.$

$$\tau^{ii} = t_B + t_B F^i t_B$$
$$F^i = \sum_{j,k} G^{ij} \tau^{jk} G^{ki} \tag{2.8}$$

F^i represents the contribution from all paths starting and ending at site *i*. Call f_n^i the sum over all paths with *n* steps, so that

$$F^i = \sum_n f_n^i$$

The corresponding quantity for the perfect, pure A, lattice, having an A atom on site *i*, is

$$F_0^i = \sum_{jk} G^{ij} \tau_0^{jk} G^{ki} = \sum_n f_{0,n}^i$$

Here the subscript 0 denotes the perfect lattice. Now comes the trick. Let $\tilde{f}_{0,n}^i$ be the sum over all paths of length *n* which avoid site *i* as an intermediate step. Then, of all the paths which contribute to f_n^i, those which avoid site *i* altogether are included in $\tilde{f}_{0,n}^i$, while the rest hit site *I* for the first time at the m^{th} step $(m < n)$, pick up a scattering t_B, and move off again, possibly to return later in the path. Hence

$$f_n^i = \tilde{f}_{0,n}^i + \sum_m^n \tilde{f}_{0,m}^i t_B f_{n-m}^i$$

and if $\tilde{F}_0^i \equiv \sum_n \tilde{f}_{0,n}^i$ we find

$$F^i = \tilde{F}_0^i + \tilde{F}_0^i t_B F^i \tag{2.9}$$

Similarly, for the corresponding paths, $f_{0,n}^i$, of the pure A lattice, we have

$$f_{0,n}^i = \tilde{f}_{0,n}^i + \sum_m^n \tilde{f}_{0,m}^i t_A f_{0,n-m}^i$$

and

$$F_0^i = \tilde{F}_0^i + \tilde{F}_0^i t_A F_0^i \tag{2.10}$$

Now do some careful matrix algebra. Write, using (2.8),

$$\tau_B \equiv \tau^{ii} = t_B + t_B F^i t_B$$
$$\tau_A \equiv \tau_0^{ii} = t_A + t_A F_0^i t_A \tag{2.11}$$

From (2.9) and (2.10), we have

$$F^i = \left[1 - \tilde{F}_0^i t_B\right]^{-1} \tilde{F}_0^i$$
$$F_0^i = \left[1 - \tilde{F}_0^i t_A\right]^{-1} \tilde{F}_0^i$$

Thus

$$\tau_B = t_B + t_B\left[1-\tilde{F}_0^i t_B\right]^{-1}\tilde{F}_0^i t_B = t_B\left[1-\tilde{F}_0^i t_B\right]^{-1}$$
$$\tau_A = t_A\left[1-\tilde{F}_0^i t_A\right]^{-1}$$

Therefore

$$t_B^{-1} - \tau_B^{-1} = \tilde{F}_0^i = t_A^{-1} - \tau_A^{-1}$$

This allows us to write τ_B in terms of $\tau_A = \tau_0^{ii}$ which, in turn, is just the site-diagonal element of the pure A lattice τ matrix and is therefore given by the result (2.3) of section 2. Thus the exact solution to the MST impurity problem is

$$\tau_B = \tau_A\left[1+\left(t_B^{-1}-t_A^{-1}\right)\tau_A\right]^{-1} \tag{2.12}$$

where

$$\left[\tau_A(\varepsilon)\right]_{LL'} = \Omega^{-1}\int_{BZ} d\mathbf{q}\left[\left(t_A^{-1}(\varepsilon) - G(\mathbf{q},\varepsilon)\right)^{-1}\right]_{LL'} \tag{2.13}$$

The corresponding model **TBT** impurity system has site energies ε_A everywhere on the periodic lattice except site *i* which has site energy ε_B. If we take the hopping integrals T_{ij} to be the same as in the pure A lattice, then the problem is specified by the locators

$$\boldsymbol{\ell}_j = \varepsilon - \varepsilon_j$$
$$\varepsilon_j = \varepsilon_A + \left(\varepsilon_B - \varepsilon_A\right)\delta_{ji}$$

or

$$\boldsymbol{\ell}_j = \boldsymbol{\ell}_A + \left(\boldsymbol{\ell}_B - \boldsymbol{\ell}_A\right)\delta_{ji}$$
$$\boldsymbol{\ell}_{A(B)} \equiv \varepsilon - \varepsilon_{A(B)}$$

Substituting this into the fundamental equation (1.14) gives

$$G_B \equiv G_{ii} = \boldsymbol{\ell}_B^{-1} + \boldsymbol{\ell}_B^{-1}\left[\sum_{jk} T_{ij}G_{jk}T_{ki}\right]\boldsymbol{\ell}_B^{-1}$$

with a corresponding expression for the pure A lattice. This is just the analogue of the **MST** expression (2.7). The whole tricky argument about paths carries through, and we can leap to the answer:

$$\begin{aligned} G_B &= G_A\left[1+\left(\boldsymbol{\ell}_B - \boldsymbol{\ell}_A\right)G_A\right]^{-1} \\ G_A(\varepsilon) &= \Omega^{-1}\int_{BZ} d\mathbf{q}\left[\boldsymbol{\ell}_A(\varepsilon) - T(\mathbf{q})\right]^{-1} \end{aligned} \tag{2.14}$$

Finally, note that (2.12) is at the heart of the KKRCPA method [1] for random substitutional alloys, and (2.14) is a key result for the Anderson model [4]. I wrote out this relatively complicated derivation, mainly as an example of the "combinatorial" approach (scattering path classification and counting) pioneered by, for example, John Beeby [2]. In my "Multiple Scattering Theory Primer" [6], using the general treatment of reference systems, I give a much simpler and shorter derivation of the impurity result in MST, which applies to the entire impurity τ matrix (not just its impurity site-diagonal component τ^{ii}).

References

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[6] *“My Multiple Scattering Theory Primer”*, post 11.1 in this series, PJD (DL 2021).