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ELECTRONS IN SOLIDS - III

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REAL SPACE METHODS

The localized tight-binding bases described earlier do not necessarily need long-ranged translational symmetry. Systems without translational symmetry : surfaces, alloys, glasses and amorphous material are often described as well by local chemistry, but have translational symmetry broken in one or many directions. Here, purely real space methods are useful.

See. Solid State Physics, (Academic Press) ed. Seitz and Turnbull vol35

The hamiltonian in the tight-binding basis is a matrix of infinite rank. We may wish to study the Green function, or the resolvent :

$$G_{nm}(z) \ = \ \langle n|(z\mathbf{I} \ - \ \mathbf{H})^{-1}|m\rangle$$

For example,

The spectrum corresponds to the singularities of the Green function. The Green function satisfies the following properties :

1. G_{nn}(z) has singularities only on the real z axis.
2. The sign of the imaginary part of G_{nn}(z) is always negative if the sign of Im z >0, and always positive if Im z <0.
3. G_{nn}(z) $\sim$ 1/E as z$\rightarrow$ $\pm\infty$ along the real axis.

Functions which obey these properties are called herglotz functions.

Note also.

$$\begin{aligned}
G_{nn}(z) &= \langle n|(zI-H)^{-1}|n\rangle \\
\text{If } H|\lambda\rangle &= \lambda|\lambda\rangle \\
G_{nn}(z) &= \sum_{\lambda}\sum_{\lambda'}\langle n|\lambda\rangle\langle\lambda|(zI-H)^{-1}|\lambda'\rangle\langle\lambda'|n\rangle \\
&= \sum_{\lambda}\sum_{\lambda'}\langle n|\lambda\rangle\{1/(z-\lambda)\}\delta_{\lambda\lambda'}\langle\lambda'|n\rangle \\
&= \sum_{\lambda}|\langle\lambda|n\rangle|^2\{1/(z-\lambda)\} \\
\text{So that} & \\
Tr\ Im\ G_{nn}(E-\imath 0^+) &= \sum_{\lambda}-\pi\delta(E-\lambda) \\
\text{That is} & \\
-(1/\pi)\ Im\ Tr\ G_{nn}(E^+) &= n(E) \quad \rightarrow \textbf{Density of States}
\end{aligned}$$

The calculation of the Green function involves finding the matrix elements of the inverse of an infinite matrix. Let us change the basis once more and generate a new basis $\{|n)\}$ from a linear combination of $\{|n\rangle\}$ recursively,

$$\begin{aligned}
|1) &= |n\rangle \\
|2) &= H\,|1) - a_1|1) \\
b_{n+1}|n+1) &= H\,|n) - a_n|n) - b_n|n-1)
\end{aligned}$$

Mutual orthogonality leads to :

$$\begin{aligned} a_n &= \{(n|H|n)/(n|n)\} \\ b_n &= \{(n-1|H|n)/(n-1|n-1)\} \end{aligned}$$

The a-s and b-s can be derived recursively from $|1)$ and H. It is easy to see that $(m|H|n) = 0$ if m > n+1 or m < n-1. In other words in this new basis the hamiltonian is tridiagonal.

Such a tridiogonalization has been first used by Chebyshev for the uniform approximation of a function in an interval in 1859, by Lanczos for matrix diagonalization in 1950, by Whitehead in nuclear physics (1977) and Mori in statistical mechanics in 1965.

Not only is the matrix tridiagonal, it is also semi-infinite. We may begin to calculate $(1|(EI-H)^{-1}|1) = \langle n|(EI-H)^{-1}|n\rangle$. Let D_0 be the determinant of the full hamiltonian matrix, D_1 the determinant of the matrix with the first row and column peeled, ... D_N the one with the first N rows and columns peeled.

$$\begin{aligned} G_{nn}(E) &= [D_1/D_0] \\ &= [1/(D_0/D_1)] \end{aligned}$$

Now expand D$_0$ as $(E - a_1)D_1 \; - \; b_2^2D_2$. The denominator becomes :

$$E \; - \; a_1 \; - \; b_2^2D_2/D_1$$

Again, rewrite D_2/D_1 as $1/(D_1/D_2)$ and expand D$_1$ as $(E - a_2D_2 \; - \; b_3^2D_3$

If we go on doing this, the expression for the Green function becomes a continued fraction :

$$G_{nn}(E) \;\; = \;\; \mathbf{K}_{n=1}^{\infty}1/(e - a_n - b_{n+1}^2|$$

To sum the continued function we generate orthogonal polynomials :

$$\begin{aligned} P_{-1}(E) \;\; &= \;\; 0; P_0(E) \;\; = \;\; 1 \\ b_{n+1}P_{n+1}(E) \;\; &= \;\; (E - a_n)P_n(E) - b_nP_{n-1}(E) \end{aligned}$$

and another set from the same recurrence relation but :

$$Q_0(E) \;\; = \;\; 0; Q_1(E) \;\; = \;\; 1$$

If T(z) is the terminator after N steps of the continued fraction :

$$G_{nn}(E) \;\; = \;\; \{Q_{N+1}(E) \;\; - \;\; T(E)Q_N(E)\}/\{P_{N+1}(E) \;\; - \;\; T(E)P_N(E)\}$$

It is easy to check that the essential singularities of T(E) and G(E) coincide. The rest of the expression merely redistributes the spectral weight over the spectrum.

The choice of the terminator should reflect the asymptotic properties of the continued fraction. This involves the band edges (determined by the essential singularities of T(z) and the band weights. In case it is known that the band edges are E1 and E2, then a T(z) with a_n=a and b_{n+1}=b for all n>N may be used :

$$T(z) = 1/(E-a-b^2T(z))$$

and

$$T(z) = \frac{(E-a)}{2b^2} - \frac{\sqrt{(E-a)^2-4b^2}}{2b^2}$$

$$E1 = a-2b \quad E2 = a+2b$$

This terminator has a inverted parabolic spectral weight distribution. Other more sophisticated terminators which are determined from the first few continued fraction coefficients have been proposed by Nex, Haydock and Lucini.

A herglotz terminator always ensures a herglotz Green function. In this sense the terminator approximation is a controlled approximation which does not violate the essential herglotz analytic properties of the Green function.

This method has been used for Surfaces : Mike Kelly (Vol 35); chemi-absorbed atoms on surfaces (Burke, Pettifor). for amorphous semiconductors (Kelly. Mookerjee), for complex compounds using the chemical pseudo-potential Bullett (vol35), for phase stability by Pettifor et.al. ; for alloys Mookerjee (Electronic Structure of Metals and Alloys : World Scientific) : for rough surfaces (Mookerjee : Gordon Breach) ; for clusters (Kanhere : Gordon Breach).