"Multiple Scattering Approach to Electronic Structures"

7/7/03

[W.Kohn & N.Rostoker, PR 94, 1111 (54)]

Bloch boundary condition

\[ \psi(n_r) = \exp(i k \cdot \tau_{r_0}) \psi(n_r) \]  \hspace{1cm} (1)

Lippmann-Schwinger equation

Set the unperturbed state, \( \psi_0(n_r) = 0 \), in the Lippmann-Schwinger equation, the following resonant equation for bound states is satisfied for selected energies, \( \kappa = \sqrt{E} \):

\[ \psi(n_r) = 0 + \sum_{\text{only 1 unit cell}} G_0(n_r, n'_r; E) \psi(n'_r) \]  \hspace{1cm} (2)

where the free Green's function satisfies the same Bloch boundary condition as \( \psi(n_r) \) and is given by

\[ G_0(n_r, n'_r; E) = -\frac{1}{4\pi^2} \sum_{\text{sum over all images}} \frac{\exp(i k |n_r - n'_r - r_s|)}{|n_r - n'_r - r_s|} \exp(i k \cdot r_s) \]  \hspace{1cm} (3)

Variational principle

The solution of Eq.(2) is obtained via the variational principle,

\[ \delta \Lambda = 0 \]  \hspace{1cm} (4)

where

\[ \Lambda[\psi] = \int_{\Omega} \psi^*(n_r) V(n_r) \psi(n_r) \, dn_r - \int_{\Omega} \int_{\Omega} \psi^*(n_r) V(n_r') \psi(n_r') G(n_r, n'_r; E) V(n_r') \psi(n_r) \]  \hspace{1cm} (5)
Muffin-tin approximation

\[ V(r) = \begin{cases} V(|r|) & (r \leq r_c) \\ 0 & (r > r_c) \end{cases} \]  

(6)

We take the trial wave function

\[ \psi(r) = \sum_{l=0}^{\lambda_{\text{max}}} \sum_{m=-l}^{l} C_{lm} R_l(r) Y_{lm}(r, \theta, \phi) \quad (r \leq r_c) \]  

(7)

(Wave-function matching at \( r = r_c \); cf. Kondo problem)

Determine \( E(k) \) from the secular equation,

\[ \det \begin{vmatrix} A_{lm, l'm'} + V \delta_{ll'} \delta_{mm'} \frac{\tau(l) - \tau(l')}{j_l(r_c) - j_{l'}(r_c)} L_{l'} & \frac{\tau(l) - \tau(l')}{j_l(r_c) - j_{l'}(r_c)} L_{l'} \\ \frac{\tau(l) - \tau(l')}{j_l(r_c) - j_{l'}(r_c)} L_{l'} & \frac{\tau(l) - \tau(l')}{j_l(r_c) - j_{l'}(r_c)} L_{l'} \end{vmatrix} = 0 \]  

(8)

where the logarithmic derivative is

\[ L_{l'} = \left. \frac{dR_{l'}}{dr} \right|_{r=r_c} \]  

(9)

and \( A_{lm, l'm'}(k, E) \) is defined through

\[ G(k, r') = \sum_{l'm'} \sum_{lm} \left[ A_{lm, l'm'} j_{l'}(kr) j_{l'}(kr') + V \delta_{ll'} \delta_{mm'} j_{l'}(kr) \eta_{l'}(kr') \right] Y_{lm}(\theta, \phi) Y_{l'm'}^{*}(\theta', \phi') \]  

(10)

"How to determine the band structure from a knowledge of purely geometric structure constants \( (A_{lm, l'm'}) \) and a small number (\( \sim 3 \)) of scattering phase shifts \( (L_l) \) of the potential in a single sphericalized cell."

[Kohn, Nobel autobiography]
Faulkner Multiple-Scattering Formulation

[L.S. Faulkner, PRB 12, 6186 (1975)]

Lippmann-Schwinger equation and T-matrix

(Lippmann-Schwinger equation)

\[ |\psi\rangle = |\psi_0\rangle + G_0 V |\psi\rangle \quad (|\psi\rangle = (1 - G_0 V)^{-1} |\psi_0\rangle) \]  

(1)

where the free Green's function is

\[ G_0 = (E - H_0 + i0)^{-1} \]  

(2)

(T-matrix)

Rewrite Eq. (1) as

\[ |\psi\rangle = |\psi_0\rangle + G_0 T |\psi_0\rangle \]  

(3)

then the T-matrix, \( T \), satisfies

\[ T = V (1 + G_0 T) \quad (T = (1 - G_0 V)^{-1} V) \]  

(4)

From Eq. (1),

\[ |\psi\rangle = [1 + G_0 V + (G_0 V)^2 + \ldots] |\psi_0\rangle \]

Comparing this with Eq. (3),

\[ T = V + VG_0 V + V(G_0 V)^2 + \ldots \]

which is the same series as is obtained from Eq. (4).

(Bound States)

Bound (resonance) states are obtained from the condition,

\[ |\psi\rangle \neq 0 \text{ and } T |\psi_0\rangle = 0, \text{ or} \]

\[ |\psi\rangle = G_0 V |\psi\rangle \]  

(5)

or \( T \) is singular (see Eq. (2)); this leads to a secular equation to be satisfied for only selected \( E = E_n \).
Multiple scatterers

\[ V = \sum_n V_n \]  \hspace{1cm} (6)

In this multiple-scattering case,

\[ T = \sum_n Q_n \]  \hspace{1cm} (8)

where

\[ Q_n = t_n \left(1 + G_0 \sum_m \frac{Q_m}{t_m} \right) \]  \hspace{1cm} (8)

\[ \text{single-site environment scattering} \]

and the single-site scattering matrix is

\[ t_n = v_n \left(1 + G_0 t_n \right) \]  \hspace{1cm} (9)
"Locally Self-Consistent Multiple Scattering"

[Y.-W. Wang, G.M. Stocks, et al., PRL 75, 2867 ('95)]

\[ \rho_i(\mathbf{r}) = \sum_j \rho^i_M(\mathbf{r}) \sigma^i(\mathbf{r}) \]  \hspace{1cm} (1)

where \( \sigma^i(\mathbf{r}) \) is the Voronoi support function containing atom \( i \), \( \rho^i_M(\mathbf{r}) \) is the density of an \( M \)-atom cluster (local interaction zone) around atom \( i \):

\[ \rho^i_M(\mathbf{r}) = \frac{2}{\pi} \text{Im} \int_{-\infty}^{\infty} \text{d} \epsilon \left\{ \sum_{i,i'} \frac{Z^i_{i'}(\mathbf{r}; \epsilon)}{Z^i_{i'}(\epsilon)} \right\} \left\{ \frac{1}{Z^i_{i'}(\epsilon)} - \frac{1}{Z^i_{i'}(\epsilon)} \right\} \]  \hspace{1cm} (2)

where \( T \) matrix \( \rightarrow \) free Greens function

\[ \tau^i_M(\epsilon) = \left[ T^{-1}_M(\epsilon) - G_M(i; \epsilon) \right]^{-1} \]  \hspace{1cm} (3)

with the free Greens function, \( G_M(i; \epsilon) \), composing of a \( M \times M \) array of free-particle Greens function subblocks \( g^{jk}(\epsilon) \) connecting sites \( j \) and \( k \), and the \( T \) matrix, \( T_M(\epsilon) \), composing of \( M \) diagonal subblocks, \( t^j(\epsilon) \).

In Eq. (2), \( Z^i_{i'}(\mathbf{r}; \epsilon) \) and \( J^i_{i'}(\mathbf{r}; \epsilon) \) are regular (\( \sim j_{i}(\mathbf{r}; \epsilon) \)) and irregular (\( \sim N_{i}(\mathbf{r}; \epsilon) \)) solutions of the single-site Schrödinger equation.
Introducing the Fermi distribution with finite temperatures,

\[ f(e) = \frac{1}{\exp[\beta(e-\mu)] + 1} \]  

Equation (2) in P.5 may be rewritten as

\[ \rho_H^\nu(r) = \frac{2}{\pi} \text{Im} \int_{-\infty}^{\infty} \text{d}e \hat{f}(e) \left\{ \sum_{LL'} \frac{Z_{L'}^* e^{iL' \tau} [Z_{L'}(e)]^*}{Z_L^* e^{iL \tau}} - \sum_{LL'} \frac{Z_{L'}(e) e^{iL' \tau}}{Z_L^* e^{iL \tau}} \right\} \]  

The energy integral in Eq.(5) may be converted to a finite sum off the real axis:

\[ \rho_H^\nu(r) = \sum_{\nu} \left\{ \sum_{LL'} \frac{Z_{L'}(e) e^{iL' \tau}}{Z_L^* e^{iL \tau}} - \sum_{LL'} \frac{Z_{L'}^* e^{iL' \tau} [Z_{L'}(e)]^*}{Z_L^* e^{iL \tau}} \right\} \]  

Note

\[ f(z) \sim f_p(z) = \frac{1}{[(z-\mu+\sigma)/\sigma]^{2p+1}} \]  

Has 2p poles on the circle of radius \( \sigma \).

Advantages

1. Only \( \approx 10 \) poles are enough; much fewer integration points.
2. Free Green's function \( G_H(r; \tau, z) \) off the real-axis is short-ranged!

Note

\[ G_0^{\mu}(r; r'; \tau, \theta) = \frac{e^{i e^{i\theta} |r-r'|}}{4\pi |r-r'|} \]  

(exponential decay off the real-axis)
"Screened Multiple-Scattering Approach"

[A.V. Smirnov, D.D. Johnson, PRB 64, 235129 (901)]

- Dyson's equation via a reference system

\[
G_{\text{ref}}(r, r'; E) = G_{\text{ref}}(r, r'; E) + \int dr'' G_{\text{ref}}(r, r''; E) [V_{\text{eff}}(r'') - V_{\text{ref}}(r'')] G_{\text{ref}}(r'', r'; E)
\]  

(1)

\[
G_{\text{ref}}(r, r'; E) = G_0(r, r'; E) + \int dr'' G_0(r, r''; E) V_{\text{ref}}(r'') G_{\text{ref}}(r'', r'; E)
\]

(2)

where \( G_0(r, r'; E) \) is the free-space Green's function

\[
G_0(r, r'; E) = -\frac{e^{iE|r-r'|}}{4\pi |r-r'|}
\]

(3)

- Well-localized reference system

Non-overlapping hard spheres (constant repulsive potential \( V_{\text{ref}} \) with radius \( \eta_{\text{HS}} \) ) centered at atoms produce screened (exponentially decayed) \( G_{\text{ref}}(r, r'; E) \) making \( E \) in Eq. (3) negative.