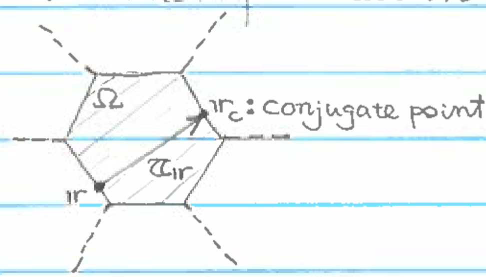
"Multiple Scattering Approach to Electronic Structures"

7/7/03

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

— Bloch boundary condition



$$\psi(\mathbf{r}_c) = \exp(i\mathbf{k}\cdot\tau_{\mathbf{r}})\,\psi(\mathbf{r}) \tag{1}$$

— Lippmann–Schwinger equation

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

$$\psi(\mathbf{r}) = 0 + \underbrace{\int_{\Omega}}_{\Omega\text{, only 1 unit cell}} G_0(\mathbf{r},\mathbf{r}';E)\,V(\mathbf{r}')\,\psi(\mathbf{r}')\,d\mathbf{r}' \tag{2}$$

where the free Green's function satisfies the same Bloch boundary condition as $\psi(\mathbf{r})$ and is given by

$$G_0(\mathbf{r},\mathbf{r}';E) = -\frac{1}{4\pi}\sum_{\mathbf{s}} \frac{\exp(i\kappa|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{r}_s|}\exp(i\mathbf{k}\cdot\mathbf{r}_s) \tag{3}$$

Sum over all images; "environment" effects $\in G(\mathbf{r},\mathbf{r}';E)$

— Variational principle

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

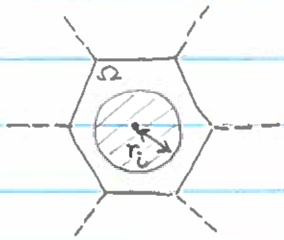
$$\delta\Lambda = 0 \tag{4}$$

where

$$\Lambda[\psi] = \int_{\Omega}\psi^*(\mathbf{r})V(\mathbf{r})\psi(\mathbf{r})\,d\mathbf{r} - \int_{\Omega}d\mathbf{r}\int_{\Omega}d\mathbf{r}'\,\psi^*(\mathbf{r})V(\mathbf{r})G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}') \tag{5}$$

– Muffin-tin approximation

$$V(\mathbf{r}) = \begin{cases} V(|\mathbf{r}|) & (r \le r_i) \\ 0 & (r > r_i) \end{cases} \qquad (6)$$



We take the trial wave function

$$\psi(\mathbf{r}) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} C_{lm} R_l(r) Y_{lm}(\theta,\varphi) \qquad (r \le r_i) \qquad (7)$$

(Wave-function matching at $r = r_i$; cf. Kondo problem)

Determine $E(\mathbf{k})$ from the secular equation,

$$\det \left| \underbrace{A_{lm,l'm'}}_{\text{structural}} + \kappa\, \delta_{ll'} \delta_{mm'} \underbrace{\frac{n_l'(r_i) - n_l(r_i) L_l}{j_l'(r_i) - j_l(r_i) L_l}}_{\text{the same as the phase-shift matching in the Kondo problem}} \right| = 0 \qquad (8)$$

where the logarithmic derivative is

$$L_l = \left. \frac{dR_l/dr}{R_l(r)} \right|_{r=r_i} \qquad (9)$$

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

$$G_0(\mathbf{r},\mathbf{r}') = \sum_{l,m} \sum_{l',m'} \left[A_{lm,l'm'}\, j_l(\kappa r) j_{l'}(\kappa r') + \kappa\, \delta_{ll'} \delta_{mm'}\, j_l(\kappa r) n_l(\kappa r') \right] Y_{lm}(\theta,\varphi) Y^*_{l'm'}(\theta',\varphi')$$

$$(r < r' < r_i) \qquad (10)$$

"How to determine the band structure from a knowledge of purely geometric structure constants ($A_{lm,l'm'}$) & a small number (~ 3) of scattering phase shifts (L_l) of the potential in a single sphericalized cell."
[Kohn, Nobel autobiography]

"Faulkner Multiple-Scattering Formulation"

[J.S. Faulkner, PRB 19, 6186 ('79)]

- Lippmann-Schwinger equation and T-matrix

(Lipmann-Schwinger equation)

$$|\psi\rangle = |\psi_0\rangle + G_0 V |\psi\rangle \qquad \left(|\psi\rangle = (1-G_0V)^{-1}|\psi_0\rangle \right) \tag{1}$$

where the free Green's function is

$$G_0 = (E - H_0 + i0)^{-1} \tag{2}$$

(T-matrix)

Rewrite Eq. (1) as

$$|\psi\rangle = |\psi_0\rangle + G_0 T |\psi_0\rangle \tag{3}$$

then the T-matrix, T, satisfies

$$T = V(1 + G_0 T) \qquad \left(T = (1-G_0V)^{-1} V \right) \tag{4}$$

☺ From Eq. (1),

$$|\psi\rangle = [1 + G_0V + (G_0V)^2 + \cdots]|\psi_0\rangle$$

Comparing this with Eq. (3),

$$T = V + VG_0V + V(G_0V)^2 + \cdots$$

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

(Bound states)

Bound (resonance) states are obtained from the condition,

$|\psi\rangle \neq 0$ and $|\psi_0\rangle = 0$, or

$$|\psi\rangle = G_0 V |\psi\rangle \tag{5}$$

or T is singular (☺see Eq. (3)); this leads to a secular equation to be satisfied for only selected $E = E_n$.

– Multiple scatterers

$$V = \sum_n v_n \tag{6}$$

In this multiple-scattering case,

$$T = \sum_n Q_n \tag{7}$$

where

$$Q_n = \underbrace{t_n}_{\substack{\text{single-site}\\\text{scattering}}} \Big(1 + \underbrace{G_0 \sum_{m \neq n} Q_m}_{\substack{\text{environment}\\\text{scattering}}}\Big) \tag{8}$$

and the single-site scattering matrix is

$$t_n = v_n (1 + G_0 t_n) \tag{9}$$

"Locally Self-Consistent Multiple Scattering"

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

$$\rho(\mathbf{r}) = \sum_i \rho_M^i(\mathbf{r})\,\sigma^i(\mathbf{r}) \tag{1}$$

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

$$\rho_M^i(\mathbf{r}) = -\frac{2}{\pi}\,\mathrm{Im}\int_{-\infty}^{\epsilon_F} d\epsilon \left\{ \sum_{\substack{LL' \\ \hookrightarrow (l,m)}} Z_L^i(\mathbf{r};\epsilon)\,[\tau_M(\epsilon)]^{ii}_{LL'}\,Z_{L'}^i(\mathbf{r};\epsilon) - \sum_L Z_L^i(\mathbf{r};\epsilon)\,J_L^i(\mathbf{r};\epsilon) \right\} \tag{2}$$

where

$$\tau_M(\epsilon) = [\underbrace{T_M^{-1}(\epsilon)}_{\text{T matrix}} - \underbrace{G_M(i;\epsilon)}_{\text{free Green's function}}]^{-1} \tag{3}$$

with the free Green's function, $G_M(i;\epsilon)$, composing of a $M\times M$ array of free-particle Green's 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), $Z_L^i(\mathbf{r};\epsilon)$ and $J_L^i(\mathbf{r};\epsilon)$ are regular ($\sim j_l(\kappa r)$) and irregular ($\sim n_l(\kappa r)$) solutions of the single-site Schrödinger equation.

"Introduction of Finite Temperatures"

[D.M.C. Nicholson, G.M. Stocks, et al., PRB 50, 14686 ('94)]

Introducing the Fermi distribution with finite temperatures,

$$f(\epsilon) = \frac{1}{\exp[\beta(\epsilon-\mu)]+1} \tag{4}$$

Eq. (2) in P.⑤ may be rewritten as

$$\rho_M^i(\mathbf{r}) = -\frac{2}{\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} d\epsilon\, f(\epsilon)\left\{\sum_{LL'} Z_L^i(\mathbf{r};\epsilon)\,[\tau_M(\epsilon)]_{LL'}^{ii}\, Z_{L'}^i(\mathbf{r};\epsilon) - \sum_L Z_L^i(\mathbf{r};\epsilon)\, J_L^i(\mathbf{r},\epsilon)\right\} \tag{5}$$

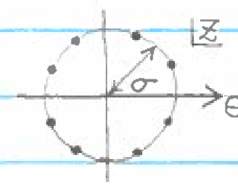
The energy integral in Eq. (5) may be converted to a finite sum off the real axis:

$$\rho_M^i(\mathbf{r}) \sim \sum_{\nu}^{\#\text{ of poles}} \left\{\sum_{LL'} Z_L^i(\mathbf{r};z_\nu)\,[\tau_M(z_\nu)]_{LL'}^{ii}\, Z_{L'}^i(\mathbf{r};z_\nu) - \sum_L Z_L^i(\mathbf{r};z_\nu)\, J_L^i(\mathbf{r};z_\nu)\right\} \tag{6}$$

Note

$$f(z) \simeq f_P(z) = \frac{1}{[(z-\mu+\sigma)/\sigma]^{2P}+1} \tag{7}$$

has 2P poles on the circle of radius σ.



Advantages

1. Only ~10 poles are enough; much fewer integration points.
2. Free Green's function $G_M(i;z_\nu)$ off the real-axis is short-ranged!

Note

$$G_0(\mathbf{r},\mathbf{r}';E) = -\frac{e^{i\sqrt{E}\,|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} \quad \text{(exponential decay off the real-axis)} \tag{8}$$

"Screened Multiple-Scattering Approach"

[A.V. Smirnov, D.D. Johnson, PRB 64, 235129 ('01)]

— Dyson's equation via a reference system

$$\begin{cases} G(\mathbf{r},\mathbf{r}';E) = G_{ref}(\mathbf{r},\mathbf{r}';E) + \int d\mathbf{r}'' G_{ref}(\mathbf{r},\mathbf{r}'';E)[V(\mathbf{r}'') - V_{ref}(\mathbf{r}'')]\, G(\mathbf{r}'',\mathbf{r}';E) & (1) \\ G_{ref}(\mathbf{r},\mathbf{r}';E) = G_0(\mathbf{r},\mathbf{r}';E) + \int d\mathbf{r}'' G_0(\mathbf{r},\mathbf{r}'';E) V_{ref}(\mathbf{r}'')\, G_{ref}(\mathbf{r}'',\mathbf{r}';E) & (2) \end{cases}$$

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

$$G_0(\mathbf{r},\mathbf{r}';E) = -\frac{e^{i\sqrt{E}|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|} \qquad (3)$$

— Well-localized reference system

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