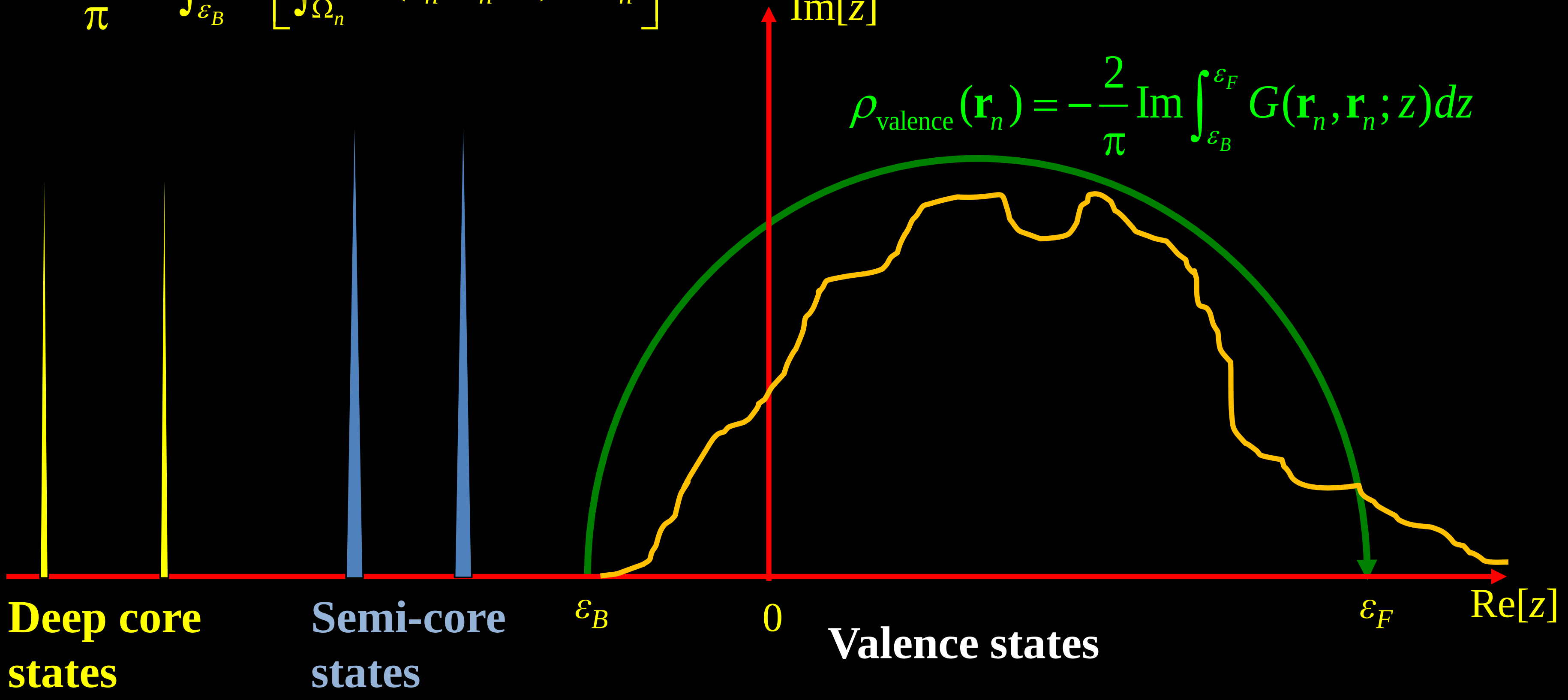
Green Function Method and Contour Integration

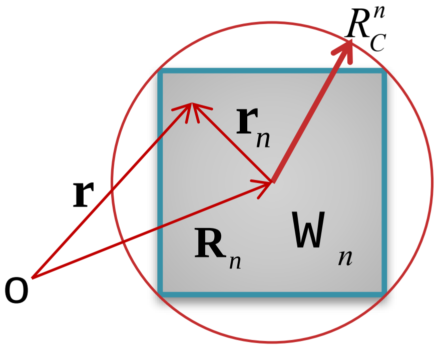
$$\rho(\mathbf{r}_n) = \rho_{\text{core}}(\mathbf{r}_n) + \rho_{\text{valence}}(\mathbf{r}_n)$$

$$E = \sum_c \varepsilon_c + \sum_{n=1}^{N} \int_{\varepsilon_B}^{\varepsilon_F} \varepsilon \rho_n(\varepsilon) dz - \sum_{n=1}^{N} \int_{\Omega_n} \rho(\mathbf{r}_n) V_{\text{eff}}(\mathbf{r}_n) d^3\mathbf{r}_n + U\left[\rho(\mathbf{r})\right] + E_{\text{XC}}[\rho(\mathbf{r})]$$

$$\int_{\varepsilon_B}^{\varepsilon_F} \varepsilon \rho_n(\varepsilon) dz = -\frac{2}{\pi} \operatorname{Im} \int_{\varepsilon_B}^{\varepsilon_F} z \left[\oint_{\Omega_n} G(\mathbf{r}_n, \mathbf{r}_n; z) d^3\mathbf{r}_n \right] dz$$



Green Function in Multiple Scattering Theory



$$V^n(\mathbf{r}_n)=\begin{cases}V_{\text{eff}}(\mathbf{r}), & \text{for } \mathbf{r}\in\Omega_n;\\ 0, & \text{else.}\end{cases}$$

$$G(\mathbf{r}_n,\mathbf{r}'_n;\varepsilon)=\sum_{L,L'}Z_L^n(\mathbf{r}_<;\varepsilon)\tau_{LL'}^{nn}(\varepsilon)Z_{L'}^{n*}(\mathbf{r}_>;\varepsilon)-\sum_L Z_L^n(\mathbf{r}_<;\varepsilon)J_L^{n*}(\mathbf{r}_>;\varepsilon)$$

where $L=\{l,m\}$, $\mathbf{r}_n,\mathbf{r}'_n\in\Omega_n$, $r_<=\min\{r_n,r'_n\}$, and $r_>=\max\{r_n,r'_n\}$. $Z_L^n(\mathbf{r}_n;\varepsilon)$ and $J_L^n(\mathbf{r}_n;\varepsilon)$ are the single site regular and irregular solutions, respectively, corresponding to $V^n(\mathbf{r}_n)$.

$$\left[-\nabla^2+V^n(\mathbf{r}_n)\right]Z_L^n(\mathbf{r};\varepsilon)=\varepsilon Z_L^n(\mathbf{r};\varepsilon)$$

τ-matrix:
$$\underline{\tau}^{nn}(\varepsilon)=\begin{bmatrix}\underline{t}_1^{-1}(\varepsilon) & -\underline{g}_{12}(\varepsilon) & \cdots & -\underline{g}_{1N}(\varepsilon)\\ -\underline{g}_{21}(\varepsilon) & \underline{t}_2^{-1}(\varepsilon) & \cdots & -\underline{g}_{2N}(\varepsilon)\\ \vdots & \vdots & \ddots & \vdots\\ -\underline{g}_{N1}(\varepsilon) & -\underline{g}_{N2}(\varepsilon) & \cdots & \underline{t}_N^{-1}(\varepsilon)\end{bmatrix}_{nn}^{-1}$$

$\underline{M}(\varepsilon)$ matrix

For periodic crystal, $\underline{t}^n(\varepsilon)=\underline{t}(\varepsilon)$, we take **k**-space approach:

$$\underline{\tau}(\varepsilon;\mathbf{k})=\left[\underline{t}^{-1}(\varepsilon)-\underline{g}(\mathbf{k};\varepsilon)\right]^{-1},$$

where $\underline{g}(\mathbf{k};\varepsilon)$ is a lattice Fourier transform of $\underline{g}_{nm}(\varepsilon)$ and is called structure constant matrix.

The τ-matrix is given by: $\underline{\tau}^{nm}(\varepsilon)=\frac{1}{\Omega_{BZ}}\int_{BZ}\underline{\tau}(\varepsilon;\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}d^3\mathbf{k}$.

$\underline{g}_{nm}(\varepsilon)$ is real space structure constant matrix.

$$\rho(\mathbf{r})=\rho_{\text{core}}(\mathbf{r})-\frac{2}{\pi}\operatorname{Im}\int_{\varepsilon_b}^{\varepsilon_F}G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)d\varepsilon,$$

$$\rho(\varepsilon)=-\frac{2}{\pi}\operatorname{Im}\int_{\Omega_n}G(\mathbf{r}_n,\mathbf{r}_n;\varepsilon)d^3\mathbf{r}_n.$$

There is no need for band structure ($\varepsilon_{n\mathbf{k}}$) and wave function ($\Psi_{n\mathbf{k}}(\mathbf{r})$) calculations

The Structure Constant Matrices in the Multiple Scattering Theory

$$\left[\underline{g}_{n_\alpha m_\beta}(\varepsilon)\right]_{LL''} = g^{n_\alpha m_\beta}_{LL''}(\varepsilon) = -4\pi\sqrt{\varepsilon}\sum_{L'} i^{l-l''-l'+1} C^{L'}_{L''L} h^{(1)}_l\left(\sqrt{\varepsilon}\left|\mathbf{a}_\beta + \mathbf{R}_m - \mathbf{a}_\alpha - \mathbf{R}_n\right|\right) Y^*_{L'}(\mathbf{a}_\beta + \mathbf{R}_m - \mathbf{a}_\alpha - \mathbf{R}_n)$$

$$B^{\alpha\beta}_{LL''}(\mathbf{k};\varepsilon) = \sum_{\substack{n \\ m_\beta \neq n_\alpha}} g^{n_\alpha m_\beta}_{LL''}(\varepsilon) e^{i\mathbf{k}\cdot(\mathbf{R}_m - \mathbf{R}_n)} - i\sqrt{\varepsilon}\delta_{\alpha\beta}\delta_{LL''} = g^{\alpha\beta}_{LL''}(\mathbf{k};\varepsilon) - i\sqrt{\varepsilon}\delta_{\alpha\beta}\delta_{LL''} = 4\pi\sum_{L'} i^{l-l''} C^{L'}_{L''L} D^{\alpha\beta}_{L'}(\mathbf{k};\varepsilon)$$

$\underline{B}^{\alpha\beta}(\mathbf{k};\varepsilon)$ is called KKR structure constant matrix

$L = (l,m)$

$h^{(1)}_l(r)$ is spherical Hankel function, $Y_L(\mathbf{r})$ is spherical harmonics

$$C^{L'}_{L''L} = \int_{4\pi} Y_{L''}(\mathbf{r}) Y^*_L(\mathbf{r}) Y_{L'}(\mathbf{r}) d\hat{\mathbf{r}}$$

is called Gaunt factor

$$D^{\alpha\beta}_{L'}(\mathbf{k};\varepsilon) = D^{\alpha\beta,(1)}_{L'}(\mathbf{k};\varepsilon) + D^{\alpha\beta,(2)}_{L'}(\mathbf{k};\varepsilon) + D^{\alpha\beta,(3)}_{L'}(\mathbf{k};\varepsilon)$$

$$D^{\alpha\beta,(1)}_{L'}(\mathbf{k};\varepsilon) = -\frac{4\pi}{\Omega_{\text{unit}}\sqrt{\varepsilon}^{\,l'}} \sum_{\mathbf{K}_n} e^{-i(\mathbf{k}+\mathbf{K}_n)\cdot(\mathbf{a}_\beta - \mathbf{a}_\alpha)} \frac{\left|\mathbf{K}_n + \mathbf{k}\right|^{l'} e^{-\left(\left|\mathbf{K}_n+\mathbf{k}\right|^2 - \varepsilon\right)/\eta}}{\left|\mathbf{K}_n + \mathbf{k}\right|^2 - \varepsilon} Y^*_{L'}(\mathbf{K}_n + \mathbf{k})$$

$$D^{\alpha\beta,(2)}_{L'}(\mathbf{k};\varepsilon) = -\frac{2^{l'+1} i^{-l'}}{\sqrt{\pi}\sqrt{\varepsilon}^{\,l'}} \sum_{\substack{\mathbf{R}_n \\ \mathbf{a}_\beta - \mathbf{a}_\alpha + \mathbf{R}_n \neq 0}} \left|\mathbf{a}_\beta - \mathbf{a}_\alpha + \mathbf{R}_n\right|^{l'} Y^*_{L'}(\mathbf{a}_\beta - \mathbf{a}_\alpha + \mathbf{R}_n) e^{i\mathbf{k}\cdot\mathbf{R}_n} \int_{\sqrt{\eta}/2}^{\infty} d\xi \cdot \xi^{2l'} e^{-\left|\mathbf{a}_\beta - \mathbf{a}_\alpha + \mathbf{R}_n\right|^2 \xi^2 + \varepsilon/4\xi^2}$$

$$D^{\alpha\beta,(3)}_{L'}(\mathbf{k};\varepsilon) = -\delta_{l'0}\delta_{\alpha\beta}\frac{\sqrt{\eta}}{2\pi}\sum_{n=0}\frac{(\varepsilon/\eta)^n}{n!(2n-1)}$$

$$\underline{\tau}^{\alpha\beta}(\varepsilon;\mathbf{k}) = \left[\underline{\underline{t}}^{-1}(\varepsilon) - \underline{\underline{g}}(\mathbf{k};\varepsilon)\right]^{-1}_{\alpha\beta} = \left[\underline{\underline{t}}^{-1}(\varepsilon) - i\sqrt{\varepsilon} - \underline{\underline{B}}(\mathbf{k};\varepsilon)\right]^{-1}_{\alpha\beta}$$

$$\underline{\tau}^{\alpha\beta}(\varepsilon) = \frac{1}{\Omega_{BZ}}\int_{BZ} \underline{\tau}^{\alpha\beta}(\varepsilon;\mathbf{k}) d^3\mathbf{k}.$$