The Theory behind MuST

Yang Wang
Pittsburgh Supercomputing Center
Carnegie Mellon University

Acknowledgment: The MuST project is supported in part by NSF Office of Advanced Cyberinfrastructure and the Division of Materials Research within the NSF Directorate of Mathematical and Physical Sciences under award number 1931367 (Terletska), 1931445 (Tam), and 1931525 (Wang).

What is MuST?

MuST stands for **Mu**ltiple **S**cattering **T**heory

- Multiple Scattering Theory is a method for solving the Kohn-Sham equation, which is the one-electron Schrödinger equation that governs the electronic structure of solids
- Specifically, it calculate the Green function of the Kohn-Sham equation, and determine the electron density by taking the imaginary part of the Green function

MuST is a computational tool for *ab initio* electronic structure calculations

- So called *ab initio*, it implies that the electronic structure is determined based on fundamental physical law, which in this case is quantum mechanics, rather than on empirical models with adjustable parameters
- Other popular *ab initio* software packages include VASP, WIEN2K, ELK, Abinit, Quantum Espresso, etc., which are based on different methods (other than multiple scattering theory) for solving the Kohn-Sham equation.

Obtain and Install MuST

Obtaining the package

```
$ git clone https://github.com/mstsuite/MuST
```

A directory called `MuST` is created in your local space

Requirements

- Linux, including Mac OS X and Microsoft Windows Subsystem for Linux
- Fortran/C/C++ compilers, e.g., gcc
- MPI message library, e.g., openmpi

Installation steps

- Described in “`MuST/INSTALLATION`”

Further information can be found at the following web site:

`https://github.com/mstsuite/MuST/wiki/MuST-Framework-Project`

As a many-electron problem

With Born-Oppenheimer approximation, the wave function for the N electrons in a solid satisfies the following Schrödinger equation (in the atomic units: $\hbar = 1$, $m_e = 1/2$, $e^2 = 2$):

$$\left[-\sum_{\alpha=1}^{N} \nabla_\alpha^2 + \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} \frac{1}{\left|\mathbf{r}_\alpha - \mathbf{r}_\beta\right|} + \sum_{\alpha=1}^{N} V_{\text{ext}}(\mathbf{r}_\alpha) \right] \Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N) = E\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N)$$

where $V_{\text{ext}}(\mathbf{r}_\alpha) = -\sum_n \frac{2Z_n}{\left|\mathbf{r}_\alpha - \mathbf{R}_n\right|}$

The electron density with spin s is given by

$$\rho_s(\mathbf{r}) = N \sum_{s_2 \ldots s_N} \int_\infty \left|\Psi(\mathbf{r}, s; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N)\right|^2 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \ldots d^3\mathbf{r}_N .$$

$$\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$$

and the electronic total energy is

$$E = \sum_{s_1, s_2, \ldots s_N} \int_\infty \Psi^*(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N) \left[-\sum_{\alpha=1}^{N} \nabla_\alpha^2 + \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}} \frac{1}{\left|\mathbf{r}_\alpha - \mathbf{r}_\beta\right|} + \sum_{\alpha=1}^{N} V_{\text{ext}}(\mathbf{r}_\alpha) \right] \Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N .$$

Total energy of the solid: $E_{\text{T}} = E + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{\left|\mathbf{R}_n - \mathbf{R}_m\right|}$

As a one-electron problem in DFT

At the ground state, the electronic total energy E is a functional of the electron density ρ

$$E = T_0[\rho] + \int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} + \int_\infty \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3\mathbf{r} + E_{\text{XC}}[\rho] \qquad \boxed{\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})}$$

The electron density ρ can be calculated by $\rho_s(\mathbf{r}) = \sum_\alpha f_T(\varepsilon_{\alpha,s} - \varepsilon_F)\psi^*_{\alpha,s}(\mathbf{r})\psi_{\alpha,s}(\mathbf{r})$

where the Kohn-Sham orbital $\psi_{\alpha,s}(\mathbf{r})$ is the self-consistent solution of the following one-electron Schrödinger equation, known as the Kohn-Sham equation,

$$\boxed{V_{\text{ext}}(\mathbf{r}) = -\sum_n \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}}$$

$$\left[-\nabla^2 + V_{\text{H}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + V^s_{\text{XC}}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]\right]\psi_{\alpha,s}(\mathbf{r}) = \varepsilon_{\alpha,s}\psi_{\alpha,s}(\mathbf{r})$$

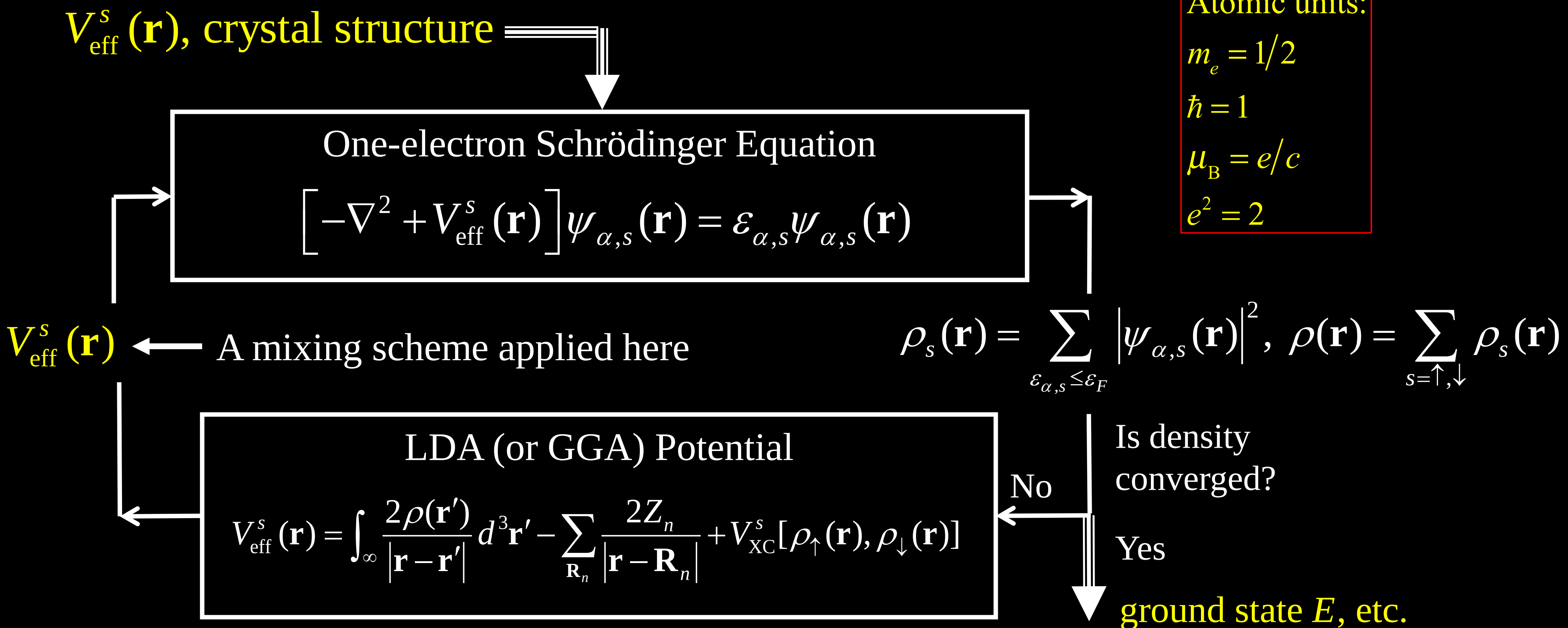
and α is the orbital index. For periodic system, $\alpha = \{n, \mathbf{k}\}$, with n the band index, and **k** the Bloch wave **k**-vector. The Hartree potential is

$$V_{\text{H}}(\mathbf{r}) = \int_\infty \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' \qquad \boxed{f_T(\varepsilon_{\alpha,s} - \varepsilon_F) = \frac{1}{1 + e^{(\varepsilon_{\alpha,s} - \varepsilon_F)/k_B T}}}$$

The many-body problem becomes a one-electron problem with effective potential given by

$$V^s_{\text{eff}}(\mathbf{r}) = \boxed{V_{\text{H}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r})} + V^s_{\text{XC}}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]$$

The Self-consistent Process in an *Ab initio* Electronic Structure Calculation



$V_{\text{eff}}^{s}(\mathbf{r})$, crystal structure

One-electron Schrödinger Equation

$$\left[-\nabla^2 + V_{\text{eff}}^{s}(\mathbf{r})\right]\psi_{\alpha,s}(\mathbf{r}) = \varepsilon_{\alpha,s}\psi_{\alpha,s}(\mathbf{r})$$

$$\rho_s(\mathbf{r}) = \sum_{\varepsilon_{\alpha,s}\le\varepsilon_F} \left|\psi_{\alpha,s}(\mathbf{r})\right|^2, \quad \rho(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \rho_s(\mathbf{r})$$

Is density converged?

No

Yes

ground state E, etc.

LDA (or GGA) Potential

$$V_{\text{eff}}^{s}(\mathbf{r}) = \int_{\infty} \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_{\mathbf{R}_n} \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|} + V_{\text{XC}}^{s}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]$$

$V_{\text{eff}}^{s}(\mathbf{r})$ ← A mixing scheme applied here

Atomic units:

$m_e = 1/2$

$\hbar = 1$

$\mu_{\text{B}} = e/c$

$e^2 = 2$

$$E[\rho_\uparrow, \rho_\downarrow] = \sum_{s=\uparrow,\downarrow} \int_{-\infty}^{\varepsilon_F} \varepsilon \rho_s(\varepsilon) d\varepsilon - \int_{\infty} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' - \sum_{s=\uparrow,\downarrow} \int_{\infty} V_{\text{XC}}^{s}(\mathbf{r})\rho_s(\mathbf{r}) d^3\mathbf{r} + E_{\text{XC}}[\rho_\uparrow, \rho_\downarrow]$$

Electron density and Green function

Consider the electron density which is given by

$$\rho_s(\mathbf{r}) = \sum_\alpha f_T(\varepsilon_{\alpha,s} - \varepsilon_F)\left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = \sum_\alpha \left[\int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)\delta(\varepsilon - \varepsilon_{\alpha,s})d\varepsilon\right]\left|\psi_{\alpha,s}(\mathbf{r})\right|^2$$

$$= \int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)\left[\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s})\left|\psi_{\alpha,s}(\mathbf{r})\right|^2\right]d\varepsilon$$

$$\boxed{\lim_{\eta\to 0}\frac{1}{z+i\eta} = \mathrm{P.V.}\left(\frac{1}{z}\right) - i\pi\delta(z),}$$

Using relation: $\mathrm{Im}\lim_{\eta\to 0}\frac{1}{z+i\eta} = -\pi\delta(z)$, we have

$$\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s})\left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = -\frac{1}{\pi}\mathrm{Im}\lim_{\eta\to 0}\sum_\alpha \frac{\left|\psi_{\alpha,s}(\mathbf{r})\right|^2}{\varepsilon - \varepsilon_{\alpha,s} + i\eta} = -\frac{1}{\pi}\mathrm{Im}\,G_s(\mathbf{r},\mathbf{r};\varepsilon)$$

$$\boxed{G_s(\mathbf{r},\mathbf{r}';\varepsilon) = \lim_{\eta\to 0}\sum_\alpha \frac{\psi^*_{\alpha,s}(\mathbf{r})\psi_{\alpha,s}(\mathbf{r}')}{\varepsilon - \varepsilon_{\alpha,s} + i\eta}}$$

Therefore, in terms of the Green function, the electron density is given by

$$\rho_s(\mathbf{r}) = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)G(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon.$$

At $T = 0$, we have: $\rho_s(\mathbf{r}) = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon$

Electronic density of state and Green function

The density of states is given by

$$\rho_s(\varepsilon) = \sum_{\alpha} \delta(\varepsilon - \varepsilon_{\alpha,s}) \int_{\infty} \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 d^3\mathbf{r} = \int_{\infty} \left[\sum_{\alpha} \delta(\varepsilon - \varepsilon_{\alpha,s}) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 \right] d^3\mathbf{r}$$

Applying the relation shown from the previous slide

$$\sum_{\alpha} \delta(\varepsilon - \varepsilon_{\alpha,s}) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = -\frac{1}{\pi} \operatorname{Im} G_s(\mathbf{r},\mathbf{r};\varepsilon)$$

we have

$$\rho_s(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \int_{\infty} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r} = -\frac{1}{\pi} \operatorname{Im} \sum_{n} \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r}$$

The density of states in space domain Ω_n is given by $\rho_s^n(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r}$

The lattice site Green function $G_n(\varepsilon)$ can be obtained by $G_n(\varepsilon) = \sum_{s=\uparrow,\downarrow} \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r}$

Contour integration

The electron density calculation can be carried out along a contour in the complex plane

$$\rho_s(\mathbf{r}) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d\varepsilon$$

$$= \sum_c \rho_{c,s}(\mathbf{r}) - \frac{1}{\pi}\,\mathrm{Im}\int_{\varepsilon_b}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d\varepsilon$$

$$= \sum_c \rho_{c,s}(\mathbf{r}) - \frac{1}{\pi}\,\mathrm{Im}\oint_{\varepsilon_b}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};z)\,dz$$

$\rho_{c,s}(\mathbf{r})$ is the electron density of core state c with spin s.

$$\rho_{\mathrm{core}}(\mathbf{r}) = \sum_{s=\uparrow,\downarrow}\sum_c \rho_{c,s}(\mathbf{r})$$

$$\rho_{\mathrm{valence}}(\mathbf{r}) = -\frac{1}{\pi}\sum_{s=\uparrow,\downarrow}\mathrm{Im}\int_{\varepsilon_b}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};z)\,dz$$

$$m_z(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})$$

So is the band energy calculation,

$$\int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\rho(\varepsilon)\,d\varepsilon = -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\left(\int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d^3\mathbf{r}\right)d\varepsilon$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \oint_{\varepsilon_b}^{\varepsilon_F} z\left(\int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};z)\,d^3\mathbf{r}\right)dz$$

The density of states (DOS):

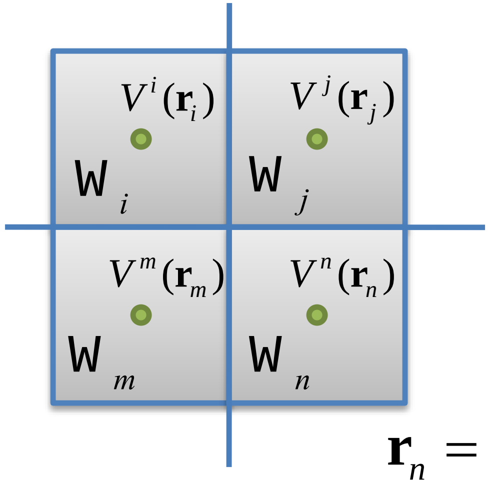
$$\rho(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d^3\mathbf{r}$$

with $\varepsilon_b \le \varepsilon \le \varepsilon_F$.

Multiple Scattering Theory (MST) Approach

- Also known as the KKR method, or Green function method
- The LDA potential is considered as a collection of non-overlapping electronic scattering potentials centered at each atom
- The Bloch states are the standing wave solution of the one-electron multiple scattering processes
- All electron (including core states)
- Unlike other *ab initio* methods, it is Not based on Rayleigh-Ritz variation
- Allows convenient calculation of the Green function

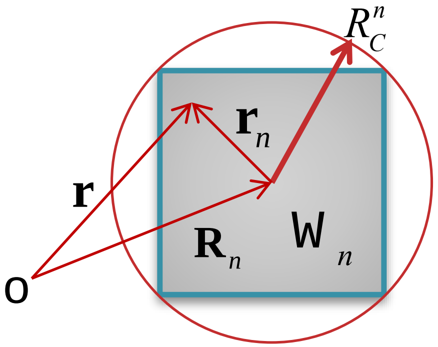
$$V^n(\mathbf{r}_n) = V_{\text{eff}}(\mathbf{r}), \quad \text{for } \mathbf{r} \in \Omega_n$$



$$\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$$

For a matter of convenience, the spin index *s* is dropped off from the expressions in here and the rest of the slides.

Green Function in Multiple Scattering Theory



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

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

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 $V^n(\mathbf{r}_n)$.

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

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

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.

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

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

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

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

Assuming a crystal with N atoms per unit cell

We use α (and β) to denote the atom in the unit cell, $\alpha, \beta = 1, 2, \ldots, N$

We use n (and m) to denote the nth unit cell, and $\mathbf{R}_n$ (and $\mathbf{R}_m$) for a Bravais lattice vector

We use n_α to denote atom α in the nth unit cell, and its position is $\mathbf{a}_\alpha + \mathbf{R}_n$

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

$L = (l,m)$, $h^{(1)}_l(r)$ 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

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

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

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

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

The KKR Structure Constant Matrix

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

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

$\alpha, \beta = 1, 2, \ldots, N$; where N is the number of atoms in the unit cell

$$B^{\alpha\beta}_{LL''}(\mathbf{k};\varepsilon) = 4\pi\sum_{L'} i^{l-l''} C^{L'}_{L''L} D^{\alpha\beta}_{L'}(\mathbf{k};\varepsilon)$$

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

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

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

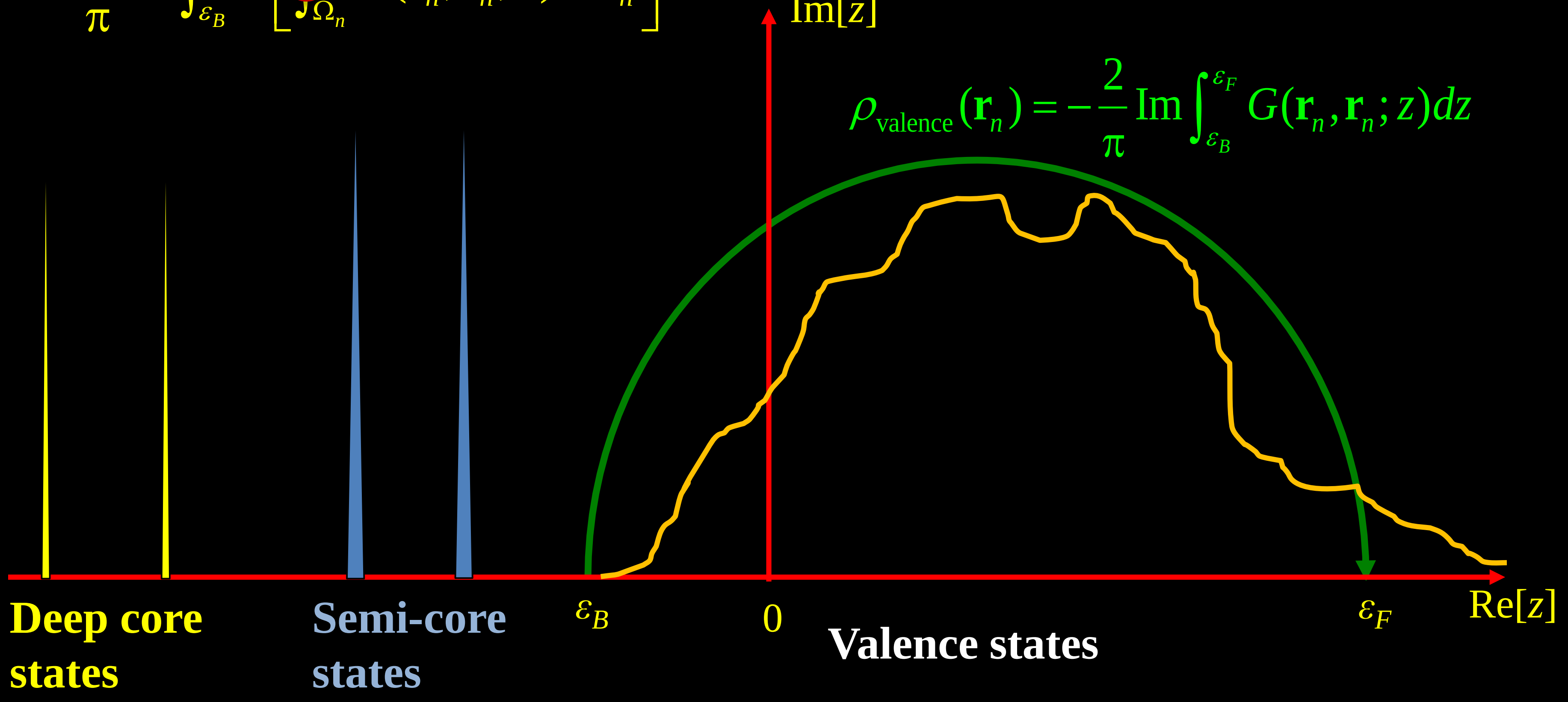
$$D^{\alpha\beta,(3)}_{L'}(\mathbf{k};\varepsilon) = -\delta_{l'0}\delta_{\alpha\beta}\frac{\sqrt{\eta}}{2\pi}\sum_{n=0}\frac{\left(\varepsilon/\eta\right)^n}{n!(2n-1)}$$

Green Function Method and Contour Integration

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

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

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



$$\rho_{\text{valence}}(\mathbf{r}_n) = -\frac{2}{\pi}\,\text{Im} \int_{\varepsilon_B}^{\varepsilon_F} G(\mathbf{r}_n, \mathbf{r}_n; z)\,dz$$

The Self-consistent Process in the Green function based *Ab initio* Electronic Structure Calculation

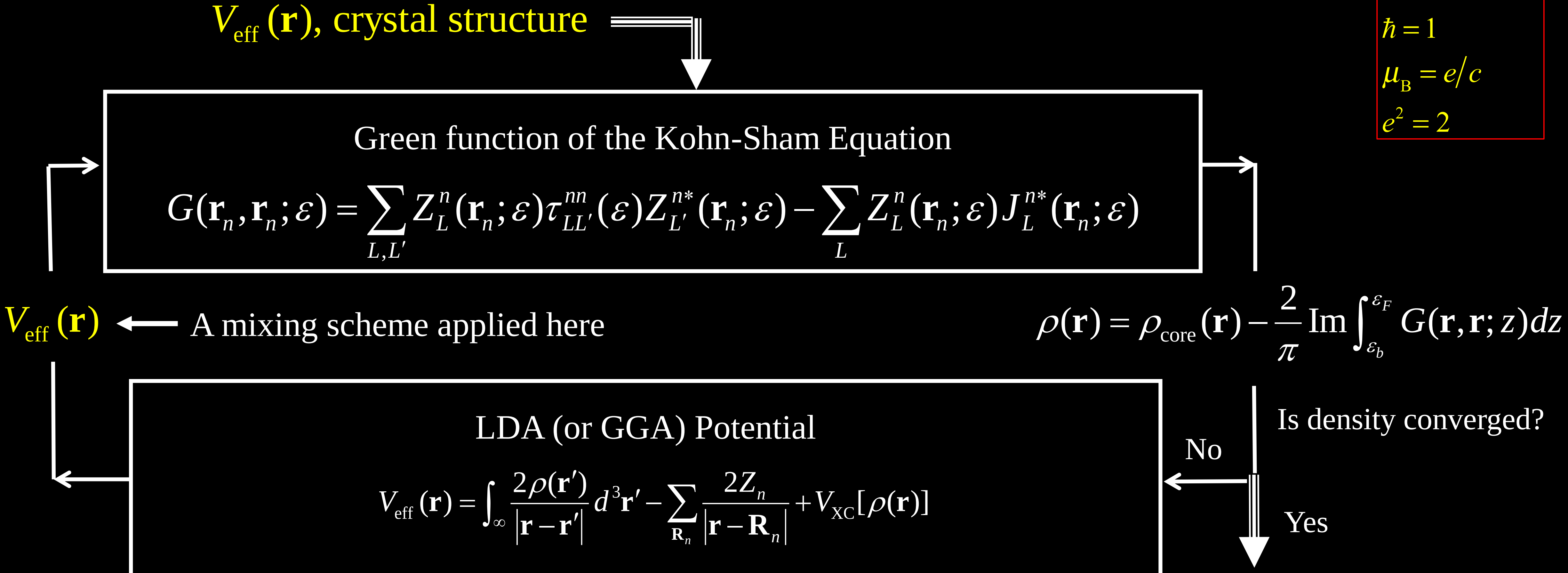
Atomic units:

$m_e = 1/2$

$\hbar = 1$

$\mu_B = e/c$

$e^2 = 2$



$V_{\text{eff}}(\mathbf{r})$, crystal structure

Green function of the Kohn-Sham Equation

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

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

Is density converged?

No

Yes

ground state E, etc.

LDA (or GGA) Potential

$$V_{\text{eff}}(\mathbf{r})=\int_\infty \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'-\sum_{\mathbf{R}_n}\frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}+V_{\text{XC}}[\rho(\mathbf{r})]$$

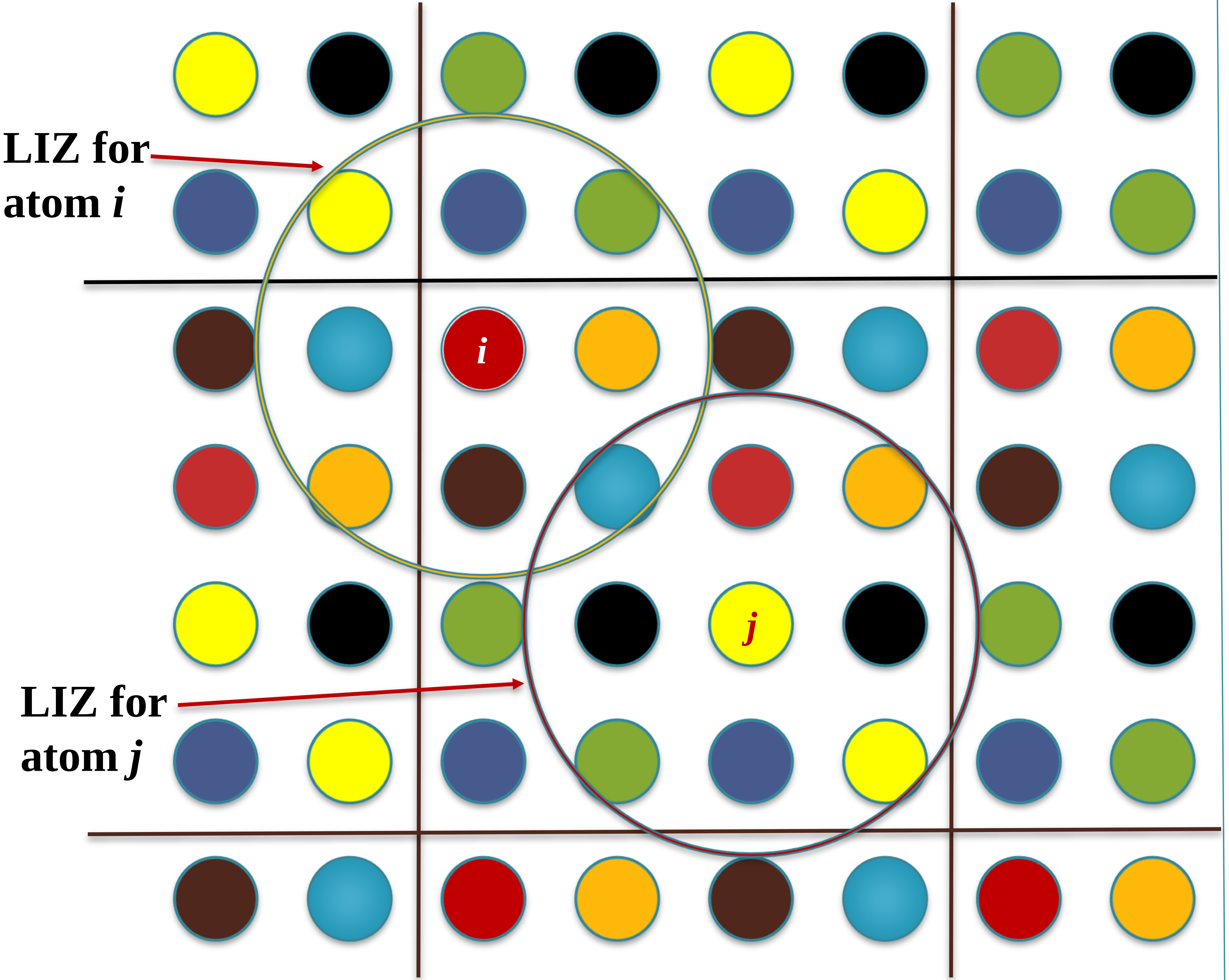
$V_{\text{eff}}(\mathbf{r})$ ← A mixing scheme applied here

$$E[\rho]=\int_{-\infty}^{\varepsilon_F}\varepsilon\rho(\varepsilon)d\varepsilon-\int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'-\int_\infty V_{\text{XC}}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r}+E_{\text{XC}}[\rho]$$

Ab initio Approaches to Random Alloys

- Supercell approach
  - LSMS (linear scaling allow to study very large unit cell containing 10,000 atoms or more)
- Cluster expansion approach, e.g., special quasi-random structures (SQS)
  - KKR + SQS
- Effective medium approach with coherent potential approximation (CPA)
  - KKR-CPA

Locally Self-consistent Multiple Scattering (LSMS) Method



The LIZ cluster with *M* atoms around each site is considered being embedded in vacuum. The τ-matrix for site *i* is given by

$$\underline{\tau}^{11}(\varepsilon)=\begin{bmatrix} \underline{t}_1^{-1}(\varepsilon) & \cdots & -\underline{g}_{1M}(\varepsilon) \\ \vdots & \ddots & \vdots \\ -\underline{g}_{M1}(\varepsilon) & \cdots & \underline{t}_M^{-1}(\varepsilon) \end{bmatrix}_{11}^{-1}$$