Single Scattering Theory

A Preparation for the Understanding of KKR Method

Yang Wang
Pittsburgh Supercomputing Center
Carnegie Mellon University

Outline

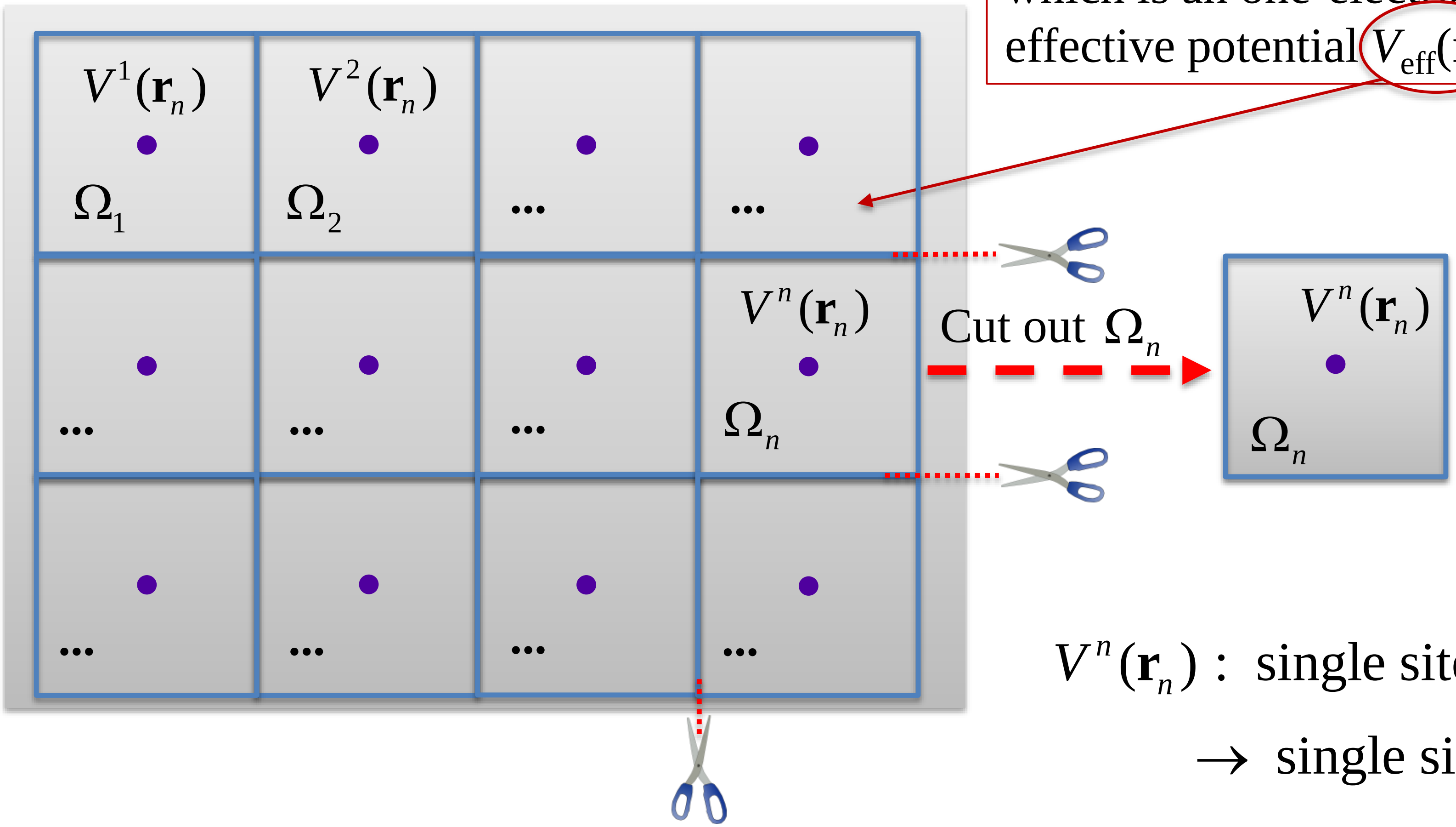
- How the single site scattering problem arises
- What quantities we need to calculate
  - Single site wavefunctions
  - Single site scattering matrices
  - ~~Single site Green function~~
- How these quantities are calculated numerically

From Solid to Atom

In the point of view of multiple scattering theory

Density function theory with LDA/GGA approximation enables us to find the electron density of the ground state of solids

This is achieved by solving the Kohn-Sham equation, which is an one-electron Schrödinger equation with effective potential $V_{\text{eff}}(\mathbf{r})$



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

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

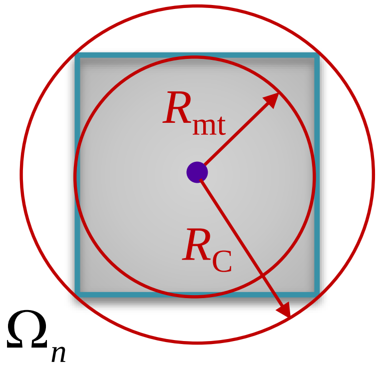
$$V_{\text{eff}}(\mathbf{r})=\sum_n V^n(\mathbf{r}_n)$$

$V^n(\mathbf{r}_n)$: single site scattering potential.

→ single site scattering t-matrix, $\underline{t}^n(\varepsilon)$.

Geometrical Shape of Single Site Potential

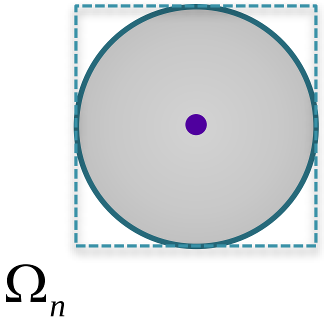
Full potential



Muffin-tin approximation

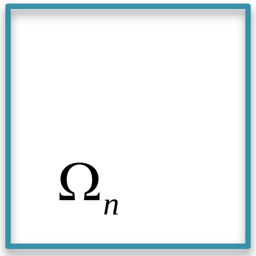
$$\approx$$

Muffin-tin potential



$$V^n(\mathbf{r}_n) = \begin{cases} V_{\mathrm{mt}}(r_n), & \text{if } r_n \le R_{\mathrm{mt}}; \\ 0, & \text{else.} \end{cases}$$

Shape function for domain Ω_n



$$\sigma^n(\mathbf{r}_n) = \begin{cases} 1, & \text{if } \mathbf{r}_n \in \Omega_n; \\ 0, & \text{else.} \end{cases}$$

It is usually called step function for domain Ω_n

From Kohn-Sham Equation to Schrödinger Equation with Single Site Potential

- Kohn-Sham equation in DFT in atomic units ($e^2 = 2$, $m_e = 1/2$, $\hbar = 1$)

$$\left[-\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_\alpha(\mathbf{r}) = \varepsilon_{\alpha}\psi_\alpha(\mathbf{r}) \qquad V_{\text{eff}}(\mathbf{r}) = \sum_n V^n(\mathbf{r}_n)$$

Kohn-Sham orbital index: (n,**k**)

- The Schrödinger equation for single site potential $V^n(\mathbf{r}_n)$, which is centered at $\mathbf{R}_n$,

$$\left[-\nabla^2 + V^n(\mathbf{r}_n)\right]\phi_L^n(\mathbf{r}_n;\varepsilon) = \varepsilon\phi_L^n(\mathbf{r}_n;\varepsilon) \qquad V^n(\mathbf{r}_n) = \begin{cases} V_{\text{eff}}(\mathbf{r}), & \text{if } \mathbf{r}\in\Omega_n; \\ 0, & \text{else.} \end{cases}$$

A single site solution index. Call it “orbital”?

energy is discrete

- For bound states, e.g., the cores states of the atom in Ω_n, we have $\phi_L^n(\mathbf{r}_n;\varepsilon_L) \to 0$ as $r_n \to \infty$.

- For the regular solutions $\phi_L^n(\mathbf{r}_n;\varepsilon)$ are finite at $r_n = 0$. They form complete solutions so that

$$\psi_\alpha(\mathbf{r}) = \sum_L a_L^\alpha \phi_L(\mathbf{r}_n;\varepsilon_\alpha) \quad \text{for } \mathbf{r}\in\Omega_n.$$

Learned in Modern Physics Textbook

For spherical potential, e.g., the muffin-tin potential

$$V^n(\mathbf{r}_n)=V^n(r_n),\quad \text{where } V^n(r_n)=0 \ \text{ for } r_n > R^n_{\mathrm{mt}}.$$

It is possible to apply variable separations, so that the solution of the Schrödinger equation can be written as

$$\phi_L^n(\mathbf{r}_n;\varepsilon)=\varphi_l^n(r_n;\varepsilon)\cdot\boxed{Y_{l,m}(\hat{\mathbf{r}}_n)} \longleftarrow \text{Spherical harmonics}$$

$\hat{\mathbf{r}}_n$ is a unit vector

We now can associate single site "orbital" index *L* with (*l*, *m*), which is a combination of orbital angular momentum quantum number *l* and magnetic quantum number *m*.

We define L = 1, 2, 3, 4, …, corresponding to (0, 0), (1, –1), (1, 0), (1, 1), …, respectively.

The 3-D Schrödinger equation can be reduce to a radial Schrödinger equation

$$\left[-\frac{1}{r_n^2}\frac{\partial}{\partial r_n}r_n^2\frac{\partial}{\partial r_n}+\frac{l(l+1)}{r^2}+V^n(r_n)\right]\varphi_l^n(r_n;\varepsilon)=\varepsilon\varphi_l^n(r_n;\varepsilon)$$

Scattering Theory Taught in Quantum Mechanics Textbook

Assuming spherical potential

- Spherical waves in free space (solution of free space Schrödinger equation)

Spherical standing wave: $j_l(\sqrt{\varepsilon}r_n)Y_{l,m}(\hat{\mathbf{r}}_n)$, where $j_l(\sqrt{\varepsilon}r_n)$ is spherical Bessel function

Spherical outgoing wave: $h_l^{(+)}(\sqrt{\varepsilon}r_n)Y_{l,m}(\hat{\mathbf{r}}_n)$, where $h_l^{(+)}(\sqrt{\varepsilon}r_n)$ is spherical hankel function of the first kind

Spherical incoming wave: $h_l^{(-)}(\sqrt{\varepsilon}r_n)Y_{l,m}(\hat{\mathbf{r}}_n)$, where $h_l^{(-)}(\sqrt{\varepsilon}r_n)$ is spherical hankel function of the second kind

$$h_l^{(-)}(\sqrt{\varepsilon}r)\xrightarrow[r\gg1]{}\frac{i}{\sqrt{\varepsilon}}\frac{e^{-i(\sqrt{\varepsilon}r-l\pi/2)}}{r};$$

$$h_l^{(+)}(\sqrt{\varepsilon}r)\xrightarrow[r\gg1]{}-\frac{i}{\sqrt{\varepsilon}}\frac{e^{i(\sqrt{\varepsilon}r-l\pi/2)}}{r}.$$

$S_l^n(\varepsilon)$: S-matrix

$t_l^n(\varepsilon)$: t-matrix

- The planewave of momentum **k** and energy $\varepsilon = \mathbf{k}^2$ (in atomic units, $\hbar = 0$ and $m_e = 1/2$) is a sum of incoming and outgoing spherical wave

The phase shift $-l\pi/2$ here is caused by $l(l+1)/r^2$ term in the radial Schrödinger equation.

scattering amplitude:
$f_l^n(\varepsilon) = -t_l^n(\varepsilon)$

incoming wave

outgoing wave

$$e^{i\mathbf{k}\cdot\mathbf{r}_n} = 2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\left[h_l^{(-)}(\sqrt{\varepsilon}r_n)+h_l^{(+)}(\sqrt{\varepsilon}r_n)\right]Y_{l,m}^*(\mathbf{k})Y_{l,m}(\hat{\mathbf{r}}_n)\xrightarrow{r_n\gg1}2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\left[\frac{i}{\sqrt{\varepsilon}}\frac{e^{-i(\sqrt{\varepsilon}r_n\boxed{-l\pi/2})}}{r_n}-\frac{i}{\sqrt{\varepsilon}}\frac{e^{i(\sqrt{\varepsilon}r_n\boxed{-l\pi/2})}}{r_n}\right]Y_{l,m}^*(\mathbf{k})Y_{l,m}(\hat{\mathbf{r}}_n).$$

- Scattering potential (with a range up to R_{mt}^n) causes a change in the phase of each partial wave

$$\psi(\mathbf{r}_n;\varepsilon)\xrightarrow{r_n\gg R_{\mathrm{mt}}^n>1}2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l A_l^n\left[\frac{i}{\sqrt{\varepsilon}}\frac{e^{-i(\sqrt{\varepsilon}r_n-l\pi/2\boxed{+\eta_l^n(\varepsilon)})}}{r_n}-\frac{i}{\sqrt{\varepsilon}}\frac{e^{i(\sqrt{\varepsilon}r_n-l\pi/2\boxed{+\eta_l^n(\varepsilon)})}}{r_n}\right]Y_{l,m}^*(\mathbf{k})Y_{l,m}(\hat{\mathbf{r}}_n)$$

$$S_l^n(\varepsilon) = e^{2i\eta_l^n(\varepsilon)},\quad A_l^n = e^{i\eta_l^n(\varepsilon)};$$

$$t_l^n(\varepsilon) = -\frac{1}{\sqrt{\varepsilon}}e^{i\eta_l^n(\varepsilon)}\sin\eta_l^n(\varepsilon).$$

$$S_l^n(\varepsilon) = 1-2i\sqrt{\varepsilon}\cdot t_l^n(\varepsilon)$$

$$\psi(\mathbf{r}_n;\varepsilon)\big|_{r_n>R_{\mathrm{mt}}^n} = 2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\left[h_l^{(-)}(\sqrt{\varepsilon}r_n)+\boxed{S_l^n(\varepsilon)}h_l^{(+)}(\sqrt{\varepsilon}r_n)\right]Y_{l,m}^*(\hat{\mathbf{k}})Y_{l,m}(\hat{\mathbf{r}}_n) = e^{i\mathbf{k}\cdot\mathbf{r}_n}\boxed{-}4\pi i\sqrt{\varepsilon}\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l\boxed{t_l^n}(\varepsilon)h_l^{(+)}(\sqrt{\varepsilon}r_n)Y_{l,m}^*(\hat{\mathbf{k}})Y_{l,m}(\hat{\mathbf{r}}_n)$$

Partial wave phase shifts and *t*-matrix

It is easy to obtain the relation between the scattering amplitude and the phase shift of the partial wave

$$t_l^n(\varepsilon) = -\frac{1}{\sqrt{\varepsilon}} e^{i\eta_l^n(\varepsilon)} \sin \eta_l^n(\varepsilon) \longrightarrow \left| f_l^n(\varepsilon) \right|^2 = \left| t_l^n(\varepsilon) \right|^2 = \frac{1}{\varepsilon} \sin^2 \eta_l^n(\varepsilon).$$

- With $l = 0, 1, 2, \ldots$, and $m = -l, \ldots, +l$, $t_l^n(\varepsilon)\delta_{ll'}\delta_{mm'}$ are elements of the *t*-matrix, $\underline{t}^n(\varepsilon)$, which is diagonal.
- Obviously, at the energies where $\eta_l^n(\varepsilon) = (2k+1)\pi/2,\ k = 0,1,2,\ldots,$ the scattering amplitude is the highest. These energies are called **resonance** energy.
- It implies that, at the resonance energies (> 0), the electronic scattering states have high probability, and consequently there is a high **density of states** around the resonance energies.
- Near a resonance energy, the density of states usually forms a Lorentzian function.

Consider the inverse of $t_l^n(\varepsilon)$, we have

$$\left[t_l^n(\varepsilon) \right]^{-1} = -\sqrt{\varepsilon}\, e^{-i\eta_l^n(\varepsilon)} \big/ \sin \eta_l^n(\varepsilon) = i\sqrt{\varepsilon} - \sqrt{\varepsilon} \cos \eta_l^n(\varepsilon) \big/ \sin \eta_l^n(\varepsilon)$$

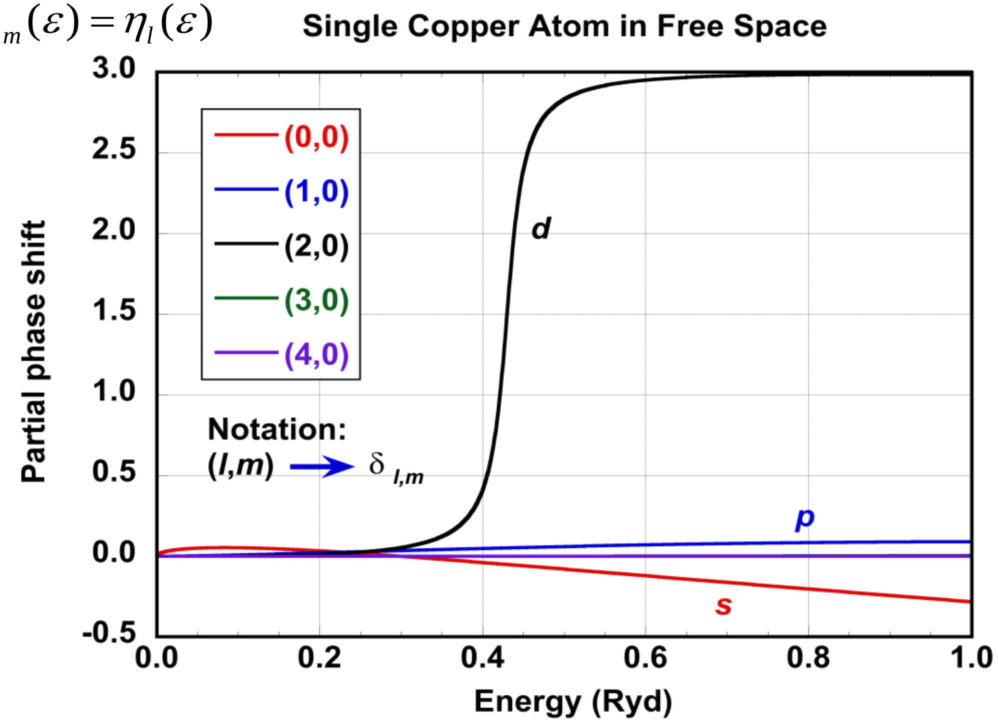
In the matrix form: $\left[\underline{t}^n(\varepsilon) \right]^{-1} = i\sqrt{\varepsilon} - \sqrt{\varepsilon}\, \underline{c}^n(\varepsilon) \cdot \left[\underline{s}^n(\varepsilon) \right]^{-1}$

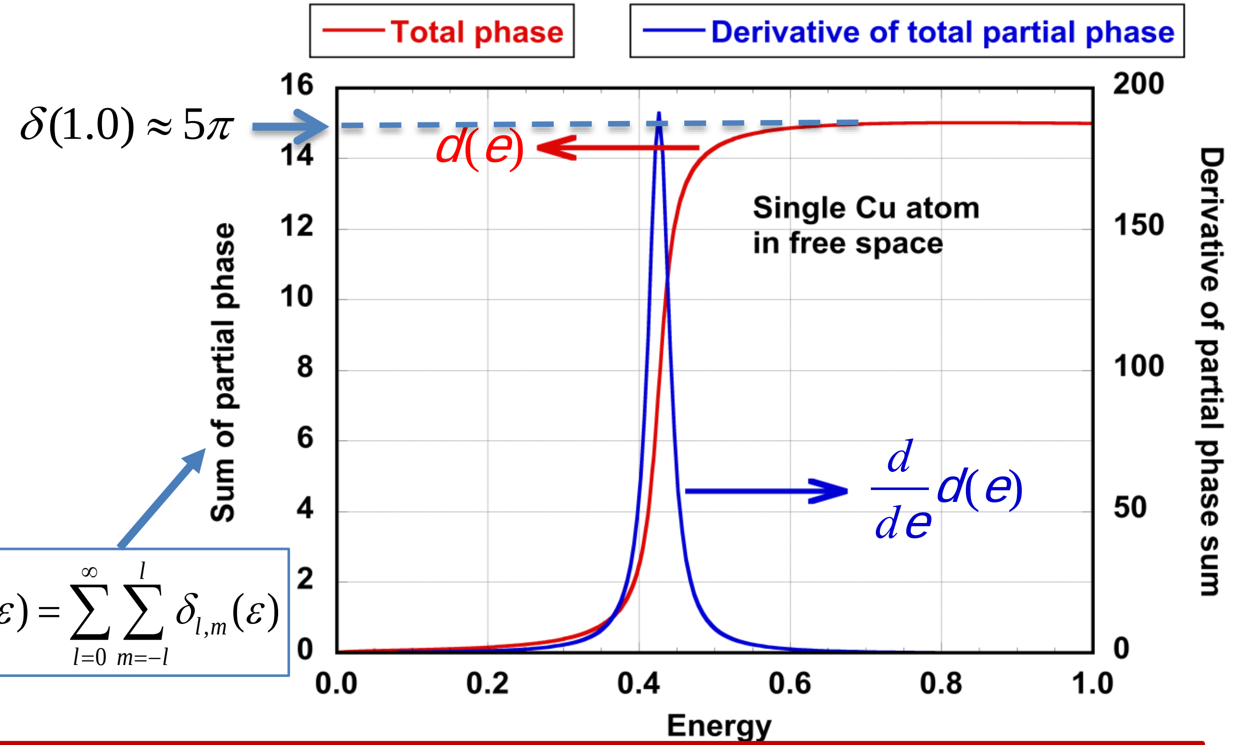
$\sin \eta_l^n(\varepsilon) \cdot \delta_{ll'}\delta_{mm'}$ form a diagonal matrix called sine-matrix $\underline{s}^n(\varepsilon)$

$\cos \eta_l^n(\varepsilon) \cdot \delta_{ll'}\delta_{mm'}$ form a diagonal matrix called cosine-matrix $\underline{c}^n(\varepsilon)$

Physical meaning of partial phase shifts - not told in QM textbook

$\delta_{l,m}(\varepsilon)=\eta_l(\varepsilon)$





$$\delta(\varepsilon)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\delta_{l,m}(\varepsilon)$$

$\eta(\varepsilon)/\pi$ is the additional integrated density of states (IDOS) of entire space, relative to the free electron IDOS

$\eta(0)/\pi$ = number of core electrons

For spherical potential: $S_l(\varepsilon)=e^{2i\eta_l(\varepsilon)}\rightarrow\eta_l(\varepsilon)=\dfrac{1}{2i}\ln S_l(\varepsilon)$

Put in matrix form: $\dfrac{\eta(\varepsilon)}{\pi}=\dfrac{1}{2\pi i}\ln\left(\det\underline{S}(\varepsilon)\right).$

Sorry for the confusion of notations in this slide: $\eta\leftrightarrow\delta$

$t_l(\varepsilon)=1-2i\sqrt{\varepsilon}S_l(\varepsilon)$ → $\underline{t}(\varepsilon)=1-2i\sqrt{\varepsilon}\underline{S}(\varepsilon)$

For non-spherical potential, the *S*- and *t*- matrices are no longer diagonal. The concept of partial phase shifts needs to be generalized. “Generalized partial phase shift” can be obtained by diagonalizing the *S*-matrix.

Matrix Form

Muffin-tin potential case

$$\underline{t} = \begin{bmatrix} t_{11} & 0 & 0 & \cdots \\ 0 & t_{22} & 0 & \cdots \\ 0 & 0 & t_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

Full-potential case

$$\underline{t} = \begin{bmatrix} t_{11} & t_{12} & t_{13} & \cdots \\ t_{21} & t_{22} & t_{23} & \cdots \\ t_{31} & t_{32} & t_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}$$

Each element $t_{LL'}$ corresponds to $t_{(l,m)(l',m')}$, where L is a combination of (l, m).

$L = 1, 2, 3, 4, \ldots, L_{\max}$, corresponding to (0, 0), (1, –1), (1, 0), (1, 1), …, $(l_{\max}, l_{\max})$, respectively.

The number of rows or columns of the matrix = $(l_{\max} + 1)^2$.

For the energy range of our interests, we usually choose $l_{\max} = 3$ or 4.

How to calculate the *t*-matrix

For a given energy ε, which could be a complex value, we may take

- Dyson’s equation approach (Jülich approach)
  1. Calculate a regular solution of the Schrödinger equation by solving the Dyson’s equation, which is an integral equation that is solved iteratively.
  2. Apply this regular solution to the calculation of the *t*-matrix by integrating the regular solution multiplied by the single site potential and the spherical Bessel function over the single site domain Ω.

It might have been called
Bristol approach in the past

- Variable phase approach (Oak Ridge approach)
  1. Calculate a regular solution by solving the Schrödinger equation with a boundary condition at the origin
  2. Apply this regular solution to the calculation of sine- and cosine- matrices
  3. Calculate the *t*-matrix by applying $\left[\underline{t}^{n}(\varepsilon)\right]^{-1} = i\sqrt{\varepsilon} - \sqrt{\varepsilon}\,\underline{c}^{n}(\varepsilon)\cdot\left[\underline{s}^{n}(\varepsilon)\right]^{-1}$

Some Technical Details

Regular solutions for potential $V^n(\mathbf{r}_n)$:

Again, ε could be complex

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

with boundary condition $\phi_L^n(\mathbf{r}_n;\varepsilon) \xrightarrow[r_n\to 0]{} j_l(\sqrt{\varepsilon}r_n)Y_{l,m}(\mathbf{r}_n).$

The boundary condition is legit since

$j_l(\sqrt{\varepsilon}r_n)Y_{l,m}(\mathbf{r}_n)$ is a free electron solution

Near the origin, the dominating term, $-Z_n e^2/r_n$, in $V^n(\mathbf{r}_n)$ is no longer relevant, so that $V^n(\mathbf{r}_n)$ can be ignored and the solution approaches to a free electron solution

It turns out that the sine- and cosine- matrices can be calculated from $\phi_L^n(\mathbf{r}_n;\varepsilon)$

$$\boxed{s_{LL'}^n(\varepsilon) = \sqrt{\varepsilon}\int_{\Omega_n} j_l(\sqrt{\varepsilon}r_n)Y_{l,m}^*(\hat{\mathbf{r}}_n)V^n(\mathbf{r}_n)\phi_{L'}^n(\mathbf{r}_n;\varepsilon)d^3\mathbf{r}_n}$$

$$\boxed{c_{LL'}^n(\varepsilon) = \sqrt{\varepsilon}\int_{\Omega_n} n_l(\sqrt{\varepsilon}r_n)Y_{l.m}^*(\hat{\mathbf{r}}_n)V^n(\mathbf{r}_n)\phi_{L'}^n(\mathbf{r}_n;\varepsilon)d^3\mathbf{r}_n - \delta_{LL'}.}$$

$n_l(x)$: spherical Neumann function

How to calculate the regular solution numerically

We expand the regular solution on spherical harmonics so that we only need to perform calculations on a radial grid (~ 1000) and store the 1-D radial functions $\phi^n_{L'L}(r_n;\varepsilon)$

$$\phi^n_L(\mathbf{r}_n;\varepsilon)=\sum_{L'}\phi^n_{L'L}(r_n;\varepsilon)Y_{L'}(\mathbf{r}_n),\quad \text{with}\quad \phi^n_{L'L}(r_n;\varepsilon)\xrightarrow[r_n\to 0]{} j_l(\sqrt{\varepsilon}r_n)\delta_{LL'}$$

One can prove that the radial functions $\phi^n_{L'L}(r_n;\varepsilon)$ satisfy following coupled differential equations

$$\phi^n_{L'L}(r_n;\varepsilon)=n_{l'}(\sqrt{\varepsilon}r_n)s^n_{L'L}(r_n;\varepsilon)-j_{l'}(\sqrt{\varepsilon}r_n)c^n_{L'L}(r_n;\varepsilon)$$

$$\frac{d}{dr_n}s^n_{L'L}(r_n;\varepsilon)=\sqrt{\varepsilon}\sum_{L'',L_p}C^{L_p}_{L''L'}j_{l'}(\sqrt{\varepsilon}r_n)V^n_{L_p}(r_n)\phi^n_{L''L}(r_n;\varepsilon)$$

$$\frac{d}{dr_n}c^n_{L'L}(r_n;\varepsilon)=\sqrt{\varepsilon}\sum_{L'',L_p}C^{L_p}_{L''L'}n_{l'}(\sqrt{\varepsilon}r_n)V^n_{L_p}(r_n)\phi^n_{L''L}(r_n;\varepsilon)$$

With boundary conditions: $s^n_{L'L}(0;\varepsilon)=0;\ c^n_{L'L}(0;\varepsilon)=\delta_{LL'}$

Here $V^n_{L_p}(r_n)$ is the expansion of the single site potential $V^n(\mathbf{r}_n)$ on spherical harmonics

$$V^n(\mathbf{r}_n)=\sum_{L_p}V^n_{L_p}(r_n)Y_{L_p}(\hat{\mathbf{r}}_n)$$

$C^{L_p}_{L''L'}$ is called Gaunt factor: $C^{L_p}_{L''L'}=\int_{4\pi}Y_{L''}(\hat{\mathbf{r}}_n)Y^*_{L'}(\hat{\mathbf{r}}_n)Y_{L_p}(\hat{\mathbf{r}}_n)d\hat{\mathbf{o}}_n$.

We use 4th-order Adams-Bashforth formula as a predictor, and 4th order Adams-Moulton formula as corrector, for integrating $s^n_{L'L}(r_n;\varepsilon)$ and $c^n_{L'L}(r_n;\varepsilon)$ along the radial grid, and in the mean time we calculate $\phi^n_{L'L}(r_n;\varepsilon)$