

Application of DFT to crystals

| Method | Range of Applicability | Number of Atoms | Obtainable Properties | Methodological Characteristics |
|------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|--------------------------|---------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| Empirical potentials (force fields) | Organic molecules, liquids, polymers, ionic compounds, silicates | Several millions | Molecular structures, densities, compressibilities, vibrational properties (infrared spectra) diffusion, adsorption | Atom-specific parameters electrons not treated explicitly, computationally fast, limited predictive capabilities |
| Effective medium theory and embedded atom method | Metals (bulk, surfaces, interfaces) without directional bonding | Several hundred thousand | Atomistic structures, diffusion, segregation, mechanical properties | Includes local electron density in total energy, best used for noble metals |
| Extended Hückel method, empirical tight-binding, bond order potentials | Covalent compounds, e.g. organic molecules, semiconductors and transition metal compounds | Several thousand | Atomistic structures, diffusion, segregation, mechanical properties; electrical and optical properties | Includes quantum mechanical description of electronic structures, relies on empirical parameters |
| Semi-empirical quantum chemical methods (e.g. MNDO) | Organic molecules, some inorganic systems | Several hundred (*) | Atomistic structures, heats of formation, charges, electronic and optical properties | Atom-specific parameters, well tested for organic molecules |
| Harris functional | All atoms | Several hundred (*) | Bonding topologies for unknown systems, estimation of electrical and optical properties | No adjustable empirical parameters, no self-consistency required; based on density functional theory |

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|------------------------------------------------------------------------------------|--------------------------------------------------------------------------|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| Density functional theory | All atoms, solids, surfaces, interfaces, molecules, clusters | A few hundred (*) | Ground state structures, thermochemical properties (e.g. binding energies), vibrational properties, electrical, optical, and magnetic properties, some dynamical properties | Most commonly used electronic structure method in solid state physics, good overall performance, no systematic improvements towards exact result |
| Hartree-Fock | organic and main-group inorganic compounds, molecular and ionic crystals | One hundred (*) | Ground state and transition state structures, thermochemical properties (e.g. binding energies), vibrational properties | Most commonly used ab initio quantum chemical method, very well tested for organic molecules, conceptual difficulties with metals |
| Hartree-Fock + second order perturbation (MP2) | Mostly small organic molecules | A few tens | Structures and thermochemical properties | Fairly high accuracy still reasonable computational effort |
| Coupled cluster, configuration interaction, and other correlated ab initio methods | Small organic and inorganic molecules | About ten atoms | Structures and binding energies | High computational effort, benchmark quality results, systematic (but slow) convergence towards exact solution |
| Quantum Monte Carlo methods | Small organic and inorganic molecules and clusters | A few tens of atoms | Structures and binding energies | Still in research stage, only single-point energies, possibly promising for accurate benchmarks |

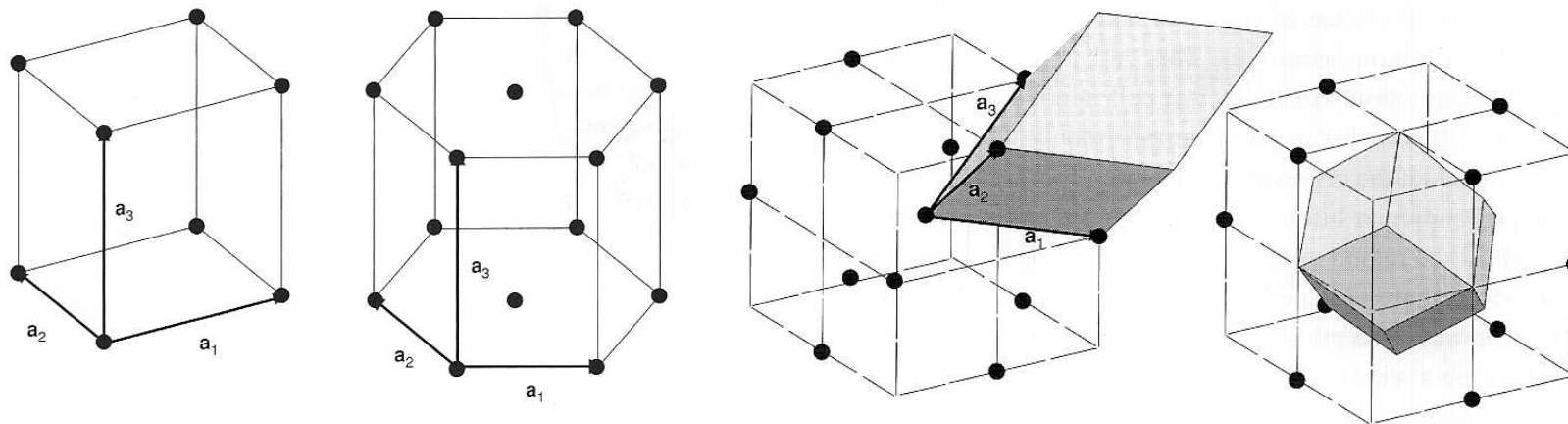
| Method | Acronym | Systems | Atom types | Obtainable Properties | Methodological Characteristics |
|------------------------------------------------|---------|---------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Pseudopotential plane wave | | Periodic structures, metals, semi-conductors, insulators | All main group elements and transition metals; not well tested for rare-earth and actinides | Crystallographic structures, binding energies, phonon spectra, elastic constants, band gaps, band offsets | Only valence electrons treated explicitly, systematic convergence of basis set, computationally efficient |
| Full-potential linearized augmented plane wave | FLAPW | Periodic structures and thin films; all bonding types | All atoms of the periodic table including rare earth atoms and actinides | Crystallographic structures, binding energies, elastic constants, energy band structures, work functions, core level shifts, magnetic moments, magneto-optical properties, hyperfine fields, field gradients | All-electron method, includes relativistic effects explicitly, highly flexible basis set, no shape approximation to the potential ("full-potential" method) |
| Linearized muffin-tin orbital | LMTO | Close-packed periodic structures | All atoms | Energy band structures, substitutional energies, electrical, magnetic and optical properties | Often used in connection with atomic-sphere-approximation (ASA), computationally fast, but restricted to close-packed solids |
| Full-potential linearized muffin-tin orbital | FP-LMTO | Close-packed and open periodic structures | All atoms | same as LMTO + geometry optimizations | More accurate than LMTO-ASA, but computationally more demanding |
| Augmented spherical wave | ASW | same as LMTO | All atoms | same as LMTO | Similar to LMTO |
| Linear combination of atomic orbitals | LCAO | Periodic structures, molecules, and clusters; molecules on surfaces | All atoms | Crystal and molecular structures, binding energies, energy band structures, band gaps, core level shifts | Implemented with Gaussians, Slater-type-orbitals, and numerical atomic orbitals |

Few points about the periodic solid:

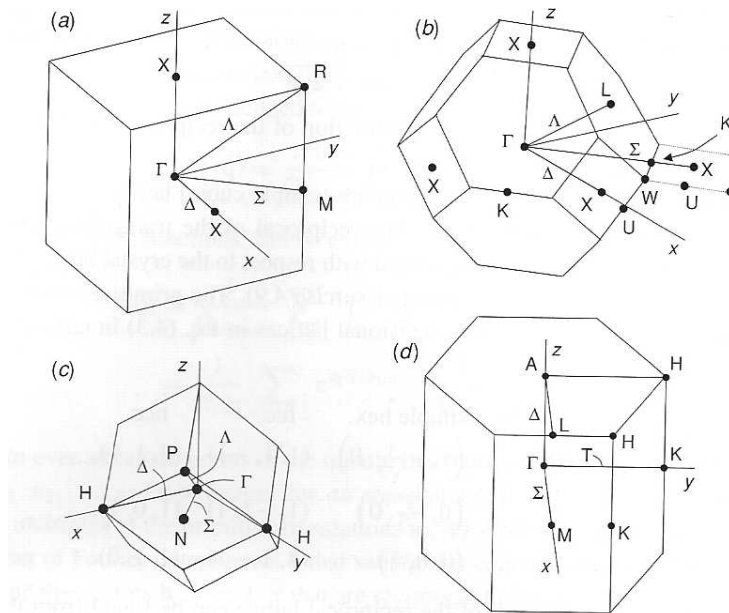
- Any translation of a Bravais lattice can be written as an integral multiple of primitive vectors

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3.$$

Here \mathbf{a}_i are primitive translations.



- The reciprocal lattice vectors $\mathbf{K} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$ also form a Bravais lattice and the reciprocal primitive vectors are $\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$ and permutations.



- Any periodic function in a crystal satisfying $f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r})$, has nonzero Fourier components only for reciprocal lattice vectors \mathbf{K} .
Example: Nuclear position, electron density,...
- The wave function in a solid satisfies the Bloch theorem $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ where $u_{\mathbf{k}}(\mathbf{r})$ is periodic function $u(\mathbf{r} + \mathbf{R}) = u(\mathbf{r})$. Momentum \mathbf{k} is a good quantum number. (Translation commutes with Hamiltonian).
- Any momentum can be written as a sum of a vector from a first Brillouin zone $\mathbf{k} = \frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3$ and reciprocal lattice vector \mathbf{K} , i.e. $\mathbf{q} = \mathbf{k} + \mathbf{K}$. Here

N_i is number of all lattice points in i -th direction and n_i is integer between 0 and $N_i - 1$. Obviously, number of \mathbf{k} -points is the same as number of lattice points.

- Effective potential $V_{eff}(\mathbf{r})$ is periodic therefore

$$\begin{aligned} \langle q' | V_{eff} | q \rangle &= \int_{\Omega_{crystal}} e^{i(\mathbf{q}-\mathbf{q}')\mathbf{r}} V_{eff}(\mathbf{r}) d\mathbf{r} = \sum_{\mathbf{R}} e^{i(\mathbf{q}-\mathbf{q}')\mathbf{R}} \int_{\Omega_{cell}} e^{i(\mathbf{q}-\mathbf{q}')\mathbf{r}'} V_{eff}(\mathbf{r}') d\mathbf{r}' \\ &= \delta_{\mathbf{q}-\mathbf{q}', \mathbf{K}} V_{eff}(\mathbf{K}). \end{aligned} \quad (1)$$

By writing $\psi(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} C_{\mathbf{q}}$ and $V(\mathbf{r}) = \sum_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}} V_{\mathbf{K}}$ the Schroedinger equation becomes

$$\left[\frac{1}{2}(\mathbf{k} + \mathbf{K})^2 - \varepsilon_{\mathbf{k}} \right] C_{\mathbf{k}+\mathbf{K}} + \sum_{\mathbf{K}'} V_{\mathbf{K}-\mathbf{K}'} C_{\mathbf{k}+\mathbf{K}'} = 0. \quad (2)$$

Note that vector \mathbf{k} from first Brillouin zone does not couple to any other \mathbf{k}' from the first Brillouin zone. Only reciprocal vectors \mathbf{K} and \mathbf{K}' couple. Hamiltonian can thus be considered a matrix in $H_{\mathbf{K}, \mathbf{K}'}(\mathbf{k})$ with \mathbf{k} as parameter (H is periodic operator).

The wave function can thus be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} C_{\mathbf{k}+\mathbf{K}} = e^{i\mathbf{k}\mathbf{r}} \sum_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}} C_{\mathbf{k}+\mathbf{K}} = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad (3)$$

where $u_{\mathbf{k}}(\mathbf{r})$ is periodic (Bloch theorem).

Plane waves

Plane waves are the simplest possible bases for the DFT calculation and are becoming more and more popular due to their simplicity and increase in computational power.

- Plane waves are good when potential is slowly varying \rightarrow not so many plane waves needed
- Core electrons in the inner shell can not be described by reasonable (finite) number of plane waves.
- Idea: Divide electrons into core and valence electrons and describe the effect of core electrons and nucleus on valence electrons as a pseudopotential.
 - empirical pseudopotentials
 - Norm-conserving *ab initio* pseudopotentials
 - ultrasoft pseudopotentials

Some all-electron methods

- Linear Muffin Tin Orbitals (LMTO)
- Linear Augmented Plane Wave method (LAPW)
- Full-potential Linear Muffin Tin Orbitals (LMTO) - Savrasov's LMTART
- Full-potential Linear Augmented Plane Wave method (LAPW) - Wien2k code

Units used in calculation

Two conventions are very popular in DFT community: **Hartree** and **Rydberg** → sometimes confusion in units.

We will always use Hartree units in which Hydrogen ground state energy is -0.5 as opposed to Rydberg units where hydrogen ground state energy is -1 Ry = -13.6058 eV.

The Schroedinger equation of hydrogen is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze_0^2}{r}\right)\psi = \varepsilon\psi \quad (4)$$

If we introduce dimensionless variables $\tilde{r} = r/a_0$ and $\tilde{\varepsilon} = \varepsilon/\varepsilon_0$

$$\left(-\frac{\hbar^2}{2ma_0^2}\tilde{\nabla}^2 - \frac{e_0^2 Z}{a_0 \tilde{r}}\right)\psi = \varepsilon_0\tilde{\varepsilon}\psi \quad (5)$$

Choosing Bohr-radius as unit of length $a_0 = \hbar^2/(me_0^2) = 0.5292\text{\AA}$ we are left with

$$\left(-\frac{1}{2}\tilde{\nabla}^2 - \frac{Z}{\tilde{r}}\right)\psi = \frac{\varepsilon_0 a_0}{e_0^2}\tilde{\varepsilon}\psi. \quad (6)$$

In Hartree convention one chooses $\varepsilon_0 = \frac{e_0^2}{a_0} \equiv 1H = 27.2114\text{eV}$ leading to

$$\left(-\frac{1}{2}\tilde{\nabla}^2 - \frac{Z}{\tilde{r}}\right)\psi = \tilde{\varepsilon}\psi. \quad (7)$$

Alternatively, one can choose $\varepsilon_0 = \frac{e_0^2}{2a_0} \equiv 1Ry = 13.6057\text{eV}$ and the Schroedinger equation than takes the form

$$\left(-\tilde{\nabla}^2 - \frac{2Z}{\tilde{r}}\right)\psi = \tilde{\varepsilon}\psi. \quad (8)$$

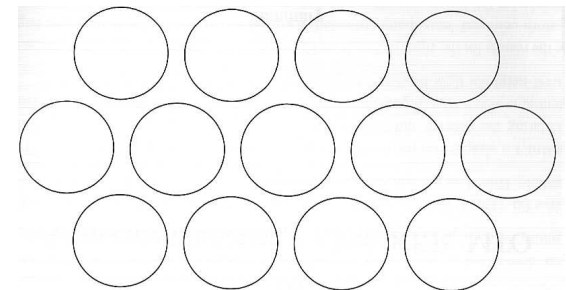
Augmented Plane Wave Method (APW)

Is today probably most precise method in its full potential linear form (Win2k).

It is somewhat involved and therefore harder extendable for purposes like Car-Parinelo molecular dynamics.

Basic idea:

- divide the space into spheres around each nucleus (Muffin Tins) and the rest (Interstials).
- The potential slowly varying in the interstitial \rightarrow use plane waves
- In Muffin Tin spheres, use atomic-like basis functions (Solve Schroedinger equation for the atom)



The solution for DFT equations in crystal is constructed as a linear combination (linear differential equation) of the APW basis functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} A_{\mathbf{K}}(\mathbf{k}) \chi_{\mathbf{k}+\mathbf{K}}^{APW}(\mathbf{r}) \quad (9)$$

where

$$\chi_{\mathbf{k}+\mathbf{K}}^{APW}(\mathbf{r}) = \begin{cases} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} & r > S \\ \sum_L C_L(\mathbf{k} + \mathbf{K}) \psi_L(\varepsilon, \mathbf{r}) & r < S \end{cases} \quad (10)$$

Here L stands for l, m and $\psi_L(\varepsilon, \mathbf{r})$ is solution of the atomic Schroedinger equation

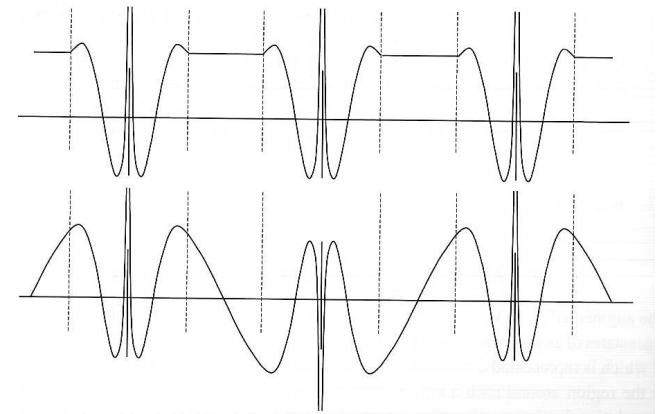
$$\psi_L(\varepsilon, \mathbf{r}) = i^L Y_L(\hat{\mathbf{r}}) \psi_l(\varepsilon, r)$$

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - \varepsilon \right) r \psi_l(r) = 0 \quad (11)$$

Energy ε is determined from the solution of the problem $H\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\psi_{\mathbf{k}}$ and $\varepsilon = \varepsilon_{\mathbf{k}}$.

Hence equations became nonlinear (although we are solving linear differential equation).

Basis functions have one matching parameter C_L and can therefore be match only in value. When applying the kinetic energy operator, one needs to take the discontinuity of the derivative into account.



There exist a well known expansion of a plane wave in spherical coordinates

$$e^{i\mathbf{q}\mathbf{r}} = 4\pi \sum_L i^l j_l(qr) Y_L^*(\hat{\mathbf{q}}) Y_L(\hat{\mathbf{r}}) \quad (12)$$

where j_l are spherical Bessel functions. Matching in value at $r = S$ than fixes parameters C_L to

$$C_L(\mathbf{q}) = 4\pi j_l(qr) \frac{Y_L^*(\hat{\mathbf{q}})}{\psi_l(\varepsilon, S)} \quad (13)$$

The secular equation in APW base takes the form

$$\sum_{\mathbf{K}} \langle \chi_{\mathbf{k}+\mathbf{K}'}^{APW} | H - \varepsilon_{\mathbf{k}} | \chi_{\mathbf{k}+\mathbf{K}}^{APW} \rangle A_{\mathbf{K}}(\mathbf{k}) = 0. \quad (14)$$

The integral can be separated into three terms

- Muffin Tin (MT) part
- Interstitial (I) part
- derivative discontinuity part (DDT)

The MT part vanishes because the base function is already solution of the Schroedinger equation.

The interstitial region contributes

$$P_{\mathbf{K}'\mathbf{K}}^I = \int_I d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} = \int_{V_{cell}} d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} - \int_{r < S} d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} (H - \varepsilon_{\mathbf{k}}) e^{i(\mathbf{k}+\mathbf{K})\mathbf{r}} \quad (15)$$

The first integral can be extended over the whole space because H is periodic. We get

$$P_{\mathbf{K}'\mathbf{K}}^{I,1} = V_{cell} \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS}^I (\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) \delta_{\mathbf{K}\mathbf{K}'} \quad (16)$$

In the second part, we use the above expansion of plane wave and get

$$P_{\mathbf{K}'\mathbf{K}}^{I,2} = \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS}^I (\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) 4\pi \int_0^S j_0(|\mathbf{K} - \mathbf{K}'|r) r^2 dr \quad (17)$$

$$= \left(\frac{1}{2}(\mathbf{k} + \mathbf{K})^2 + V_{KS}^I(\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{|\mathbf{K} - \mathbf{K}'|} \quad (18)$$

The interstitial contribution is therefore

$$P_{\mathbf{K}'\mathbf{K}}^I = \left(\frac{1}{2}(\mathbf{k} + \mathbf{K})^2 + V_{KS}^I(\mathbf{K} - \mathbf{K}') - \varepsilon_{\mathbf{k}} \right) \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell}|\mathbf{K} - \mathbf{K}'|} \right) \quad (19)$$

The last contribution due to discontinuous derivative can be evaluated using Green's identity

$$\int_V \nabla[\chi_i^* \nabla \chi_j] d\mathbf{r} = \oint_{S_V} \chi_i^* \nabla \chi_j d\mathbf{S} = \int_V \nabla \chi_i^* \nabla \chi_j d\mathbf{r} + \int_V \chi_i^* \nabla^2 \chi_j d\mathbf{r} \quad (20)$$

Integral over space V needs to be divided into MT part and the interstitials. We see that the operator ∇^2 needs to act on left and right, i.e., $\nabla \chi_i^* \nabla \chi_j$ when evaluating volume integrals. This changes the above term to more symmetric form

$(\mathbf{k} + \mathbf{K})^2 \rightarrow (\mathbf{k} + \mathbf{K})(\mathbf{k} + \mathbf{K}')$. In addition, on the boundary between the two regions we get an additional contribution

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{1}{2} S^2 \int d\Omega \chi_i^*(r = S, \hat{\mathbf{r}}) \left[\frac{\partial}{\partial r} \chi_j(r = S^-, \hat{\mathbf{r}}) - \frac{\partial}{\partial r} \chi_j(r = S^+, \hat{\mathbf{r}}) \right] \quad (21)$$

To evaluate this term, we first rewrite it using logarithmic derivative

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{1}{2}S^2 \int d\Omega \chi_i^*(S, \hat{\mathbf{r}}) \chi_j(S, \hat{\mathbf{r}}) \left[\frac{\partial}{\partial r} \ln(\chi_j(r = S^-, \hat{\mathbf{r}})) - \frac{\partial}{\partial r} \ln(\chi_j(r = S^+, \hat{\mathbf{r}})) \right] \quad (22)$$

The logarithmic derivatives are $\partial \ln \chi(S^-)/\partial r = \psi'_l(S)/\psi_l(S)$ and $\partial \ln \chi(S^+)/\partial r = j'_l(qS)/j_l(qS)$. The angle integral $d\Omega$ gives as nonzero contribution only if $L_i = L_j$ therefore the derivative discontinuity contribution is

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \sum_L \frac{1}{2}S^2 (4\pi)^2 j_l(|\mathbf{k} + \mathbf{K}'|S) j_l(|\mathbf{k} + \mathbf{K}|S) Y_L(\hat{\mathbf{k}} + \hat{\mathbf{K}}') Y_L(\hat{\mathbf{k}} + \hat{\mathbf{K}}) \Delta D_{l,\mathbf{K}}/S \quad (23)$$

where $\Delta D_{l,\mathbf{K}}$ is dimensionless logarithmic derivative

$$\Delta D_{l,\mathbf{K}} = S \left(\frac{\psi'_l(S)}{\psi_l(S)} - \frac{j'_l(|\mathbf{k} + \mathbf{K}|S)}{j_l(|\mathbf{k} + \mathbf{K}|S)} \right). \quad (24)$$

Using another well known relation

$$\sum_m Y_{lm}(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{q}}') = \frac{2l+1}{4\pi} P_l(\hat{\mathbf{q}} \cdot \hat{\mathbf{q}}') \quad (25)$$

we finally get

$$P_{\mathbf{K}'\mathbf{K}}^{DDT} = \frac{2\pi S}{V_{cell}} \sum_l (2l+1) j_l(|\mathbf{k} + \mathbf{K}'|S) j_l(|\mathbf{k} + \mathbf{K}|S) P_l((\hat{\mathbf{k}} + \hat{\mathbf{K}}') \cdot (\hat{\mathbf{k}} + \hat{\mathbf{K}})) \Delta D_{l,\mathbf{K}}. \quad (26)$$

The secular equation of APW method reads

$$\sum_{\mathbf{K}} (H_{\mathbf{K}'\mathbf{K}} - \varepsilon_{\mathbf{k}} O_{\mathbf{K}'\mathbf{K}}) A_{\mathbf{K}} = 0 \quad (27)$$

where

$$O_{\mathbf{K}'\mathbf{K}} = \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \quad (28)$$

$$H_{\mathbf{K}'\mathbf{K}} = \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})(\mathbf{k} + \mathbf{K}') + V_{KS}^I (\mathbf{K} - \mathbf{K}') \right) O_{\mathbf{K}'\mathbf{K}} + P_{\mathbf{K}'\mathbf{K}}^{DDT} \quad (29)$$

A serious problem with this method is that the Schroedinger equation is non-linear and is therefore numerically less stable to solve. The non-linear term is hidden in the logarithmic derivative $\Delta D_{l,\mathbf{K}}$ which depends on the solution of the Schroedinger equation $\psi_l(r)$ at energy $\varepsilon = \varepsilon_{\mathbf{k}}$.

Linear Augmented Plane Wave Method (LAPW)

The basic idea of any method starting with **L** (LAPW or LMTO) is to solve the Schroedinger equation for fixed energy E_ν rather than for the eigen-energy $\varepsilon_{\mathbf{k}} = \varepsilon$ (which would need to be determined self-consistently). To keep the good precision of the solution, one expands the solution of the Schroedinger equation in Taylor series (usually only to the linear order), i.e.,

$$\psi_l(\varepsilon, r) = \psi_l(E_\nu) + (\varepsilon - E_\nu) \frac{\partial}{\partial \varepsilon} \psi_l(E_\nu, r) \equiv \psi_l(E_\nu) + (\varepsilon - E_\nu) \dot{\psi}_l(E_\nu, r) \quad (30)$$

This energy derivative has very nice properties

- Since the atomic Hamiltonian does not depend on ε and $(H - \varepsilon)\psi_l = 0$, we have $(H - \varepsilon)\dot{\psi}_l = \psi_l$.
- The wave function ψ is normalized $\langle \psi_l | \psi_l \rangle = 1$, therefore $\dot{\psi}_l$ and ψ_l are orthogonal $\rightarrow \langle \dot{\psi}_l | \psi_l \rangle = 0$.

By including $\dot{\psi}$ in the basis, one can achieve accuracy of the total energy of the order of $(\Delta\varepsilon)^2$ where $\Delta\varepsilon$ is $\varepsilon_{\mathbf{k}} - E_\nu$. The resulting wave function is correct up to $\Delta\varepsilon$. At first it looks like the choice of E_ν has to be close to the actual energy $\varepsilon_{\mathbf{k}}$ to get good results. It turns out, however, that the solution is not very sensitive to the choice of E_ν as long as it is not very far from the center of the band $\langle\varepsilon_{\mathbf{k}}\rangle$. In practical calculation E_ν is usually chosen to be in the center of the occupied part of the band.

The classical choice of the LAPW basis functions is

$$\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}} = \sum_L \frac{4\pi i^l}{\sqrt{V}} j_l(|\mathbf{k} + \mathbf{K}|r) Y_L^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) Y_L(\hat{\mathbf{r}}) & r > S \\ \sum_L Y_L(\hat{\mathbf{r}}) [a_L(\mathbf{k} + \mathbf{K})\psi_l(r) + b_L(\mathbf{k} + \mathbf{K})\dot{\psi}_l(r)] & r < S \end{cases} \quad (31)$$

Here L stands for l, m and $\psi_l(r)$ is solution of the atomic Schroedinger equation at fixed energy E_ν

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - E_\nu\right) r \psi_l(r) = 0 \quad (32)$$

$$\left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{KS}(r) - E_\nu\right) r \dot{\psi}_l(r) = \psi_l(r) \quad (33)$$

In classical method, we have two matching parameters $a_L(\mathbf{k} + \mathbf{K})$ and $b_L(\mathbf{k} + \mathbf{K})$,

therefore $\chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$ can be made continuous and differentiable at the muffin-tin sphere S . The two conditions are satisfied with the following 2×2 linear system of equations

$$\begin{pmatrix} a_L \\ b_L \end{pmatrix} = \frac{4\pi i^l}{\sqrt{V}} Y_L^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) \begin{pmatrix} \frac{d}{dr} \psi_l(S) & -\psi_l(S) \\ -\frac{d}{dr} \psi_l(S) & \psi_l(S) \end{pmatrix} \frac{1}{\psi_l(S) \frac{d}{dr} \psi_l(S) - \psi_l(S) \frac{d}{dr} \psi_l(S)} \begin{pmatrix} j_l(|\mathbf{k} + \mathbf{K}|S) \\ \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \end{pmatrix}$$

Note that in practice the sum over L is limited to rather small l . These LAPW basis functions are in practice not strictly continuous. One can correct that by the trick of Soler & Williams <http://link.aps.org/doi/10.1103/PhysRevB.40.1560>.

From the differential equation for ψ and $\dot{\psi}$, and after integration by parts, one can derive the following identity

$$\dot{\psi}_l(S) \frac{d}{dr} \psi_l(S) - \psi_l(S) \frac{d}{dr} \dot{\psi}_l(S) = \frac{1}{S^2} \quad (35)$$

This leads to the simplified expression

$$\begin{pmatrix} a_L \\ b_L \end{pmatrix} = \frac{4\pi i^l}{S^2 \sqrt{V}} Y_{lm}^*(\hat{\mathbf{k}} + \hat{\mathbf{K}}) \begin{pmatrix} \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \\ \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \end{pmatrix} \quad (36)$$

The linear method is more robust, numerically easier to solve and also has "nicer" basis

functions which are continuous in slope.

The solution is again a linear combination of basis functions

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} \chi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) A_{\mathbf{K}}(\mathbf{k}) \quad (37)$$

with coefficients $A_{\mathbf{K}}$ determined from the solution of the secular equation

$$\sum_{\mathbf{K}} \langle \chi_{\mathbf{K}'+\mathbf{k}} | H - \varepsilon_{\mathbf{k}} | \chi_{\mathbf{K}+\mathbf{k}} \rangle A_{\mathbf{K}}(\mathbf{k}) = 0. \quad (38)$$

For convenience, we will choose zero of energy at the linearization energy E_{ν} so that

$$\varepsilon'_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - E_{\nu}$$

$$\sum_{\mathbf{K}} (\langle \chi_{\mathbf{K}'+\mathbf{k}} | H - E_{\nu} | \chi_{\mathbf{K}+\mathbf{k}} \rangle - \varepsilon'_{\mathbf{k}} \langle \chi_{\mathbf{K}'+\mathbf{k}} | \chi_{\mathbf{K}+\mathbf{k}} \rangle) A_{\mathbf{K}}(\mathbf{k}) = 0. \quad (39)$$

We thus have three terms to evaluate

- Muffin tin part $H_{\mathbf{K}'\mathbf{K}}^{MT} \equiv \langle \chi_{\mathbf{K}'+\mathbf{k}}^{MT} | H - E_{\nu} | \chi_{\mathbf{K}+\mathbf{k}}^{MT} \rangle$
- Interstitial part $H_{\mathbf{K}'\mathbf{K}}^I \equiv \langle \chi_{\mathbf{K}'+\mathbf{k}}^I | H - E_{\nu} | \chi_{\mathbf{K}+\mathbf{k}}^I \rangle$
- The total overlap matrix $O_{\mathbf{K}'\mathbf{K}} \equiv \langle \chi_{\mathbf{K}'+\mathbf{k}} | \chi_{\mathbf{K}+\mathbf{k}} \rangle$.

The MT part is

$$\begin{aligned}
 H_{\mathbf{K}'\mathbf{K}}^{MT} &= \sum_L \langle a_L(\mathbf{k} + \mathbf{K}')\psi_l + b_L(\mathbf{k} + \mathbf{K}')\dot{\psi}_l | H - E_\nu | a_L(\mathbf{k} + \mathbf{K})\psi_l + b_L(\mathbf{k} + \mathbf{K})\dot{\psi}_l \rangle \\
 &= \frac{1}{2} \sum_L a_L^*(\mathbf{k} + \mathbf{K}')b_L(\mathbf{k} + \mathbf{K}) + b_L^*(\mathbf{k} + \mathbf{K}')a_L(\mathbf{k} + \mathbf{K})
 \end{aligned} \tag{40}$$

Using relation Eq. (25), we can further simplify

$$H_{\mathbf{K}'\mathbf{K}}^{MT} = \frac{4\pi(2l+1)}{S^4V} \sum_l P_l((\hat{\mathbf{K}}' + \hat{\mathbf{k}}) \cdot (\hat{\mathbf{K}} + \hat{\mathbf{k}})) \frac{1}{2} (a_{l,\mathbf{K}'} b_{l,\mathbf{K}} + a_{l,\mathbf{K}} b_{l,\mathbf{K}'})$$

where

$$a_{l,\mathbf{K}} = \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \tag{41}$$

$$b_{l,\mathbf{K}} = \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \tag{42}$$

The interstitial is again evaluated by integrating first over whole space and subtracting integral within Muffin-tin

$$\begin{aligned}
 H_{\mathbf{K}'\mathbf{K}}^I &= \frac{1}{V} \int d\mathbf{r} e^{-i(\mathbf{k}+\mathbf{K}')\mathbf{r}} \left(-\frac{1}{2} \nabla^2 + V_{KS} - E_\nu \right) e^{i(\mathbf{K}+\mathbf{k})\mathbf{r}} \\
 &= \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS} - E_\nu \right) \int \frac{d\mathbf{r}}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} = \\
 &= \left(\frac{1}{2} (\mathbf{k} + \mathbf{K})^2 + V_{KS} - E_\nu \right) \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V|\mathbf{K} - \mathbf{K}'|} \right)
 \end{aligned} \tag{43}$$

Finally the overlap is

$$\begin{aligned}
 O_{\mathbf{K}'\mathbf{K}} &= \left(\delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell}|\mathbf{K} - \mathbf{K}'|} \right) \\
 &+ \sum_L \langle a_L(\mathbf{k} + \mathbf{K}')\psi_l + b_L(\mathbf{k} + \mathbf{K}')\dot{\psi}_l | a_L(\mathbf{k} + \mathbf{K})\psi_l + b_L(\mathbf{k} + \mathbf{K})\dot{\psi}_l \rangle \\
 &= \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell}|\mathbf{K} - \mathbf{K}'|} + \\
 &+ \sum_L a_L^*(\mathbf{k} + \mathbf{K}') a_L(\mathbf{k} + \mathbf{K}) + b_L^*(\mathbf{k} + \mathbf{K}') b_L(\mathbf{k} + \mathbf{K}) \langle \dot{\psi}_l | \dot{\psi}_l \rangle
 \end{aligned} \tag{44}$$

and using Eq. (25) we get

$$O_{\mathbf{K}'\mathbf{K}} = \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell}|\mathbf{K} - \mathbf{K}'|} + \\ + \frac{4\pi(2l+1)}{S^4 V} \sum_l P_l((\hat{\mathbf{K}}' + \hat{\mathbf{k}}) \cdot (\hat{\mathbf{K}} + \hat{\mathbf{k}})) (a_{l,\mathbf{K}'} a_{l,\mathbf{K}} + b_{l,\mathbf{K}'} b_{l,\mathbf{K}} \langle \dot{\psi}_l | \dot{\psi}_l \rangle)$$

The results of the above calculation can be grouped together as follows:

$$\sum_{\mathbf{K}} (H_{\mathbf{K}'\mathbf{K}} - \varepsilon'_{\mathbf{K}} O_{\mathbf{K}'\mathbf{K}}) A_{\mathbf{K}} = 0 \quad (45)$$

$$O_{\mathbf{K}'\mathbf{K}} = O_{\mathbf{K}'\mathbf{K}}^I + \sum_l \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) (a_{l,\mathbf{K}'} a_{l,\mathbf{K}} + b_{l,\mathbf{K}'} b_{l,\mathbf{K}} \langle \dot{\psi}_l | \dot{\psi}_l \rangle) \quad (46)$$

$$H_{\mathbf{K}'\mathbf{K}} = H_{\mathbf{K}'\mathbf{K}}^I + \sum_l \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) \frac{1}{2} (a_{l,\mathbf{K}'} b_{l,\mathbf{K}} + a_{l,\mathbf{K}} b_{l,\mathbf{K}'}) \quad (47)$$

$$O_{\mathbf{K}'\mathbf{K}}^I = \delta_{\mathbf{K}\mathbf{K}'} - \frac{4\pi S^2 j_1(|\mathbf{K} - \mathbf{K}'|S)}{V_{cell} |\mathbf{K} - \mathbf{K}'|} \quad (48)$$

$$H_{\mathbf{K}'\mathbf{K}}^I = \left\{ \frac{1}{4} [(\mathbf{k} + \mathbf{K})^2 + (\mathbf{k} + \mathbf{K}')^2] + V_{KS} - E_{\nu} \right\} O_{\mathbf{K}'\mathbf{K}}^I \quad (49)$$

$$\mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) = \frac{4\pi(2l+1)}{S^4 V} P_l((\hat{\mathbf{K}}' + \hat{\mathbf{k}}) \cdot (\hat{\mathbf{K}} + \hat{\mathbf{k}})) \quad (50)$$

$$a_{l,\mathbf{K}} = \dot{\psi}_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) - \frac{d}{dr} \dot{\psi}_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) \quad (51)$$

$$b_{l,\mathbf{K}} = \frac{d}{dr} \psi_l(S) j_l(|\mathbf{k} + \mathbf{K}|S) - \psi_l(S) \frac{d}{dr} j_l(|\mathbf{k} + \mathbf{K}|S) \quad (52)$$

The equations were symmetrized $H_{\mathbf{K}\mathbf{K}'} \rightarrow \frac{1}{2}(H_{\mathbf{K}\mathbf{K}'} + H_{\mathbf{K}'\mathbf{K}})$ for numerical efficiency.

Chemical potential

The chemical potential is defined by requiring the number of electrons to be equal to the number of occupied states

$$N/2 = \sum_{\mathbf{k},p} f(\varepsilon_{\mathbf{k}p} - \mu) \quad (53)$$

Here N is the number of valence electrons and factor two comes from spin.

Electron Density

The solution of the LAPW equations which corresponds to the p -th eigenvalue $\varepsilon_{\mathbf{k}}^p$ is

$$\psi_{\mathbf{k}p}(\mathbf{r}) = \sum_{\mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \quad (54)$$

the electron density takes the form

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) |\psi_{\mathbf{k}p}|^2 = \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) A_{\mathbf{K}}^p(\mathbf{k}) \chi_{\mathbf{k}+\mathbf{K}'}^*(\mathbf{r}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \\ &\equiv \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) A_{\mathbf{K}}^p(\mathbf{k}) \end{aligned} \quad (55)$$

Inside the MT sphere, we can average charge over the angle

$$w_{\mathbf{K}\mathbf{K}'}^{MT}(\mathbf{k}, \mathbf{r}) = \int \frac{d\Omega}{4\pi} \chi_{\mathbf{k}+\mathbf{K}'}^*(\mathbf{r}) \chi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) \quad (56)$$

resulting in

$$w_{\mathbf{K}\mathbf{K}'}^{MT}(\mathbf{k}, \mathbf{r}) = \frac{1}{4\pi} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) [\mathbf{a}_{l,\mathbf{K}'} \psi_l(r) + \mathbf{b}_{l,\mathbf{K}'} \dot{\psi}_l(r)] [\mathbf{a}_{l,\mathbf{K}} \psi_l(r) + \mathbf{b}_{l,\mathbf{K}} \dot{\psi}_l(r)] \quad (57)$$

The interstitial region contributes

$$w_{\mathbf{K}\mathbf{K}'}^I(\mathbf{k}, \mathbf{r}) = \frac{1}{V} e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} \quad (58)$$

The final result for the electronic charge weight is

$$w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) = \begin{cases} \frac{e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}}}{V_{cell}} & r > S \\ \frac{\mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K})}{4\pi} [\mathbf{a}_{l,\mathbf{K}'} \psi_l(r) + \mathbf{b}_{l,\mathbf{K}'} \dot{\psi}_l(r)] [\mathbf{a}_{l,\mathbf{K}} \psi_l(r) + \mathbf{b}_{l,\mathbf{K}} \dot{\psi}_l(r)] & r < S \end{cases}$$

In case of Muffin-Tin approximation, the charge in the interstitials is approximated by a constant. The integral over the space gives exactly $O_{\mathbf{K}\mathbf{K}'}^I$. The weight in the interstitial is thus equal to overlap in the interstitials.

One can check that the volume integral of $w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r})$ is the total overlap matrix $O_{\mathbf{K}\mathbf{K}'}$. Since the eigenvectors in this non-orthogonal base are orthogonalized in the following way $A^\dagger O A$, we get the total charge per momentum per band quantum number $\mathbf{k}p$ to be exactly unity.

The electron charge is finally

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}p, \mathbf{K}\mathbf{K}'} f(\varepsilon_{\mathbf{k}p} - \mu) A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) A_{\mathbf{K}}^p(\mathbf{k}) \quad (59)$$

which can also be written as

$$\rho(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int d\omega f(\omega) \sum_{\mathbf{k}p, \mathbf{K}\mathbf{K}'} \frac{\sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{p*}(\mathbf{k}) w_{\mathbf{K}\mathbf{K}'}(\mathbf{k}, \mathbf{r}) A_{\mathbf{K}}^p(\mathbf{k})}{\omega + \mu - \varepsilon_{\mathbf{k}p}} \quad (60)$$

For actual calculation, it is good idea to separate radial loop from the \mathbf{k} -loop to speed up the calculation. It is obvious that the radial functions ψ_l and $\dot{\psi}_l$ depend only on l and radius but not on \mathbf{K} , \mathbf{k} or p . Therefore we will define the following weight functions

$$w_{\mathbf{k}pl}^{(0)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) a_{l, \mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) a_{l, \mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \quad (61)$$

$$\begin{aligned}
w_{\mathbf{k}pl}^{(1)} &= \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) \mathbf{a}_{l,\mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) \mathbf{b}_{l,\mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \\
&+ \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) \mathbf{b}_{l,\mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) \mathbf{a}_{l,\mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k})
\end{aligned} \tag{62}$$

$$w_{\mathbf{k}pl}^{(2)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) \mathbf{b}_{l,\mathbf{K}'} \mathcal{P}_l^{\mathbf{k}}(\mathbf{K}', \mathbf{K}) \mathbf{b}_{l,\mathbf{K}} A_{\mathbf{K}}^p(\mathbf{k}) \tag{63}$$

$$w_{\mathbf{k}p}^{(I)} = \sum_{\mathbf{K}\mathbf{K}'} A_{\mathbf{K}'}^{*p}(\mathbf{k}) O_{\mathbf{K}'\mathbf{K}}^I A_{\mathbf{K}}^p(\mathbf{k}) \tag{64}$$

These sums can be done by matrix multiplication using very efficient LAPACK routines.

After determination of the chemical potential, the weights can be compressed

$$w_l^{(x)} = \sum_{\mathbf{k}p} f(\varepsilon_{\mathbf{k}p} - \mu) w_{\mathbf{k}pl}^{(x)} \tag{65}$$

and the electron charge can finally be obtained by

$$\rho^{MT}(r) = \frac{1}{4\pi} \sum_l w_l^{(0)} \psi_l(r) \psi_l(r) + w_l^{(1)} \psi_l(r) \dot{\psi}_l(r) + w_l^{(2)} \dot{\psi}_l(r) \dot{\psi}_l(r) \tag{66}$$

$$\rho^I(r) = \frac{1}{V_{interstitial}} w^{(I)} \tag{67}$$

Muffin-Tin zero

There is another important detail when doing self-consistent calculation. In every step, potential tends to change quite dramatically and is very hard to achieve self-consistency if we do not fix zero of the potential - the chemical potential varies dramatically and core states with them. The way it is usually done is by requiring that the potential is zero at the Muffin-Tin boundary.

From total electronic charge we calculate Hartree potential by solving Poisson equation and also add exchange-correlation potential in exactly the same way as in atom calculation (see previous lecture). Finally we add nucleous contribution Z/r to Hartree and exchange potential to get total V_{KS} . And the requirement is that $V_{KS}(S) = 0$. Note that this is not an approximation but only our choice of zero for the potential.

Lattice sums

It is important to find chemical potential precisely and therefore one needs to use many \mathbf{k} points in first Brillouin zone. Due to group operations, only a small subset of \mathbf{k} -points is independent (irreducible part of 1st BZ). It is therefore a good idea to use only the irreducible points and assign them weights $w_{\mathbf{k}}$. For cubic lattices, there are 48 space group

operations that commute with H . They are of the form

$$(a, b, c) \rightarrow (-a, b, c), (a, -b, c), \dots (b, a, c), (-c, -b, a) \quad (68)$$

Each permutation of components of a vector gives an equivalent vector. There are $3! = 6$ possibilities. In addition, each component can have either + or minus sign resulting in $2^3 = 8$ possibilities. Together thus $3! 2^3 = 48$ equivalent vectors. Thus for most of non-special points, there are 48 equivalent points and we need to calculate only for one point and multiply the result by 48. Special points have lower weight. For example, $\Gamma = (0, 0, 0)$ point has smallest weight equal to 1.

Tetrahedron method

The above "improved" summation is called special points method. There exists more advanced method to calculate integral over k points called Tetrahedron Method of Lambin and Vigneron. Basic idea is to interpolate energies linearly between two k -points and "pretend" we do calculation for infinite number of k -points and can therefore integrate over k .

First step consist of dividing 1st Brillouin zone into tetrahedra which fill up whole space. Each thrahedra has 4 corners in 3 dimensions. The energy is thus interpolated

$E = E_1 + a(E_2 - E_1) + b(E_3 - E_1) + c(E_4 - E_1)$, where a , b and c run between 0 and 1 when visiting corners of tetrahedra.

For electron density and chemical potential we need integral of the form

$$\text{Im} \sum_{\mathbf{k}} \int_{-\infty}^{\mu} d\omega \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (69)$$

and for density of states the form is

$$\text{Im} \sum_{\mathbf{k}} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (70)$$

The integral is then written as the sum over all tetrahedra and integral in the interior of tetrahedra.

$$\text{Im} \sum_{\mathbf{k}} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} = \sum_{\text{tetrahedra}} \int_{\text{tetrahedra}} d^3\mathbf{k} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (71)$$

The trick is to separately linearly interpolate nominator and denominator as follows

$$\int_{\text{tetrahedra}} d^3\mathbf{k} \frac{C_{\mathbf{k}}}{\omega - \varepsilon_{\mathbf{k}}} \quad (72)$$

$$\begin{aligned}
&= 6 \int_0^1 dc \int_0^{1-c} db \int_0^{1-b-c} da \frac{C_1 + a(C_2 - C_1) + b(C_3 - C_1) + c(C_4 - C_1)}{\omega - E_1 - a(E_2 - E_1) - b(E_3 - E_1) - c(E_4 - E_1)} \\
&\equiv C_1 r_1 + C_2 r_2 + C_3 r_3 + C_4 r_4
\end{aligned}$$

Weights r_i are the same for each function $C_{\mathbf{k}}$ and can be calculated ones for many quantities. The expression for DOS weights is

$$r_i = 6 \int_0^1 dc \int_0^{1-c} db \int_0^{1-b-c} da \frac{(1 - a - b - c)\delta_{i,1} + a\delta_{i,2} + b\delta_{i,3} + c\delta_{i,4}}{\omega - E_1 - a(E_2 - E_1) - b(E_3 - E_1) - c(E_4 - E_1)} \quad (73)$$

and for density

$$q_i = 6 \int_{-\infty}^{\mu} d\omega \int_0^1 dc \int_0^{1-c} db \int_0^{1-b-c} da \frac{(1 - a - b - c)\delta_{i,1} + a\delta_{i,2} + b\delta_{i,3} + c\delta_{i,4}}{\omega - E_1 + a(E_2 - E_1) + b(E_3 - E_1) + c(E_4 - E_1)} \quad (74)$$

The integrals are analytic and a closed expression can be written down

$$r_i = \sum_{j \neq i} \frac{\omega - E_j}{\prod_{k \neq i, j} (E_k - E_j)} \text{lv} \left(\frac{\omega - E_j}{E_j - E_i} \right) \quad (75)$$

where

$$\text{lv}(x) = x \left[1 - x \log \left(1 + \frac{1}{x} \right) \right] \quad (76)$$

$$q_1 = \begin{cases} \frac{1}{4} & \omega > E_1 \\ \frac{\Theta(E_2 < \omega < E_1) \omega_2^4}{4E_{12}^2 E_{32} E_{42}} + \frac{\Theta(E_3 < \omega < E_1) \omega_3^4}{4E_{13}^2 E_{23} E_{43}} + \frac{\Theta(E_4 < \omega < E_1) \omega_4^4}{4E_{14}^2 E_{24} E_{34}} & \omega < E_1 \end{cases} \quad (77)$$

$$q_2 = \begin{cases} \frac{1}{4} & \omega > E_2 \\ \frac{\Theta(E_3 < \omega < E_2) \omega_3^4}{4E_{23}^2 E_{43} E_{13}} + \frac{\Theta(E_4 < \omega < E_2) \omega_4^4}{4E_{24}^2 E_{34} E_{14}} + \frac{\Theta(E_1 < \omega < E_2) \omega_1^4}{4E_{21}^2 E_{31} E_{41}} & \omega < E_2 \end{cases} \quad (78)$$

$$q_3 = \begin{cases} \frac{1}{4} & \omega > E_3 \\ \frac{\Theta(E_4 < \omega < E_3) \omega_4^4}{4E_{34}^2 E_{14} E_{24}} + \frac{\Theta(E_1 < \omega < E_3) \omega_1^4}{4E_{31}^2 E_{41} E_{21}} + \frac{\Theta(E_2 < \omega < E_3) \omega_2^4}{4E_{32}^2 E_{42} E_{12}} & \omega < E_3 \end{cases} \quad (79)$$

$$q_4 = \begin{cases} \frac{1}{4} & \omega > E_4 \\ \frac{\Theta(E_1 < \omega < E_4) \omega_1^4}{4E_{41}^2 E_{21} E_{31}} + \frac{\Theta(E_2 < \omega < E_4) \omega_2^4}{4E_{42}^2 E_{12} E_{32}} + \frac{\Theta(E_3 < \omega < E_4) \omega_3^4}{4E_{43}^2 E_{13} E_{23}} & \omega < E_4 \end{cases} \quad (80)$$

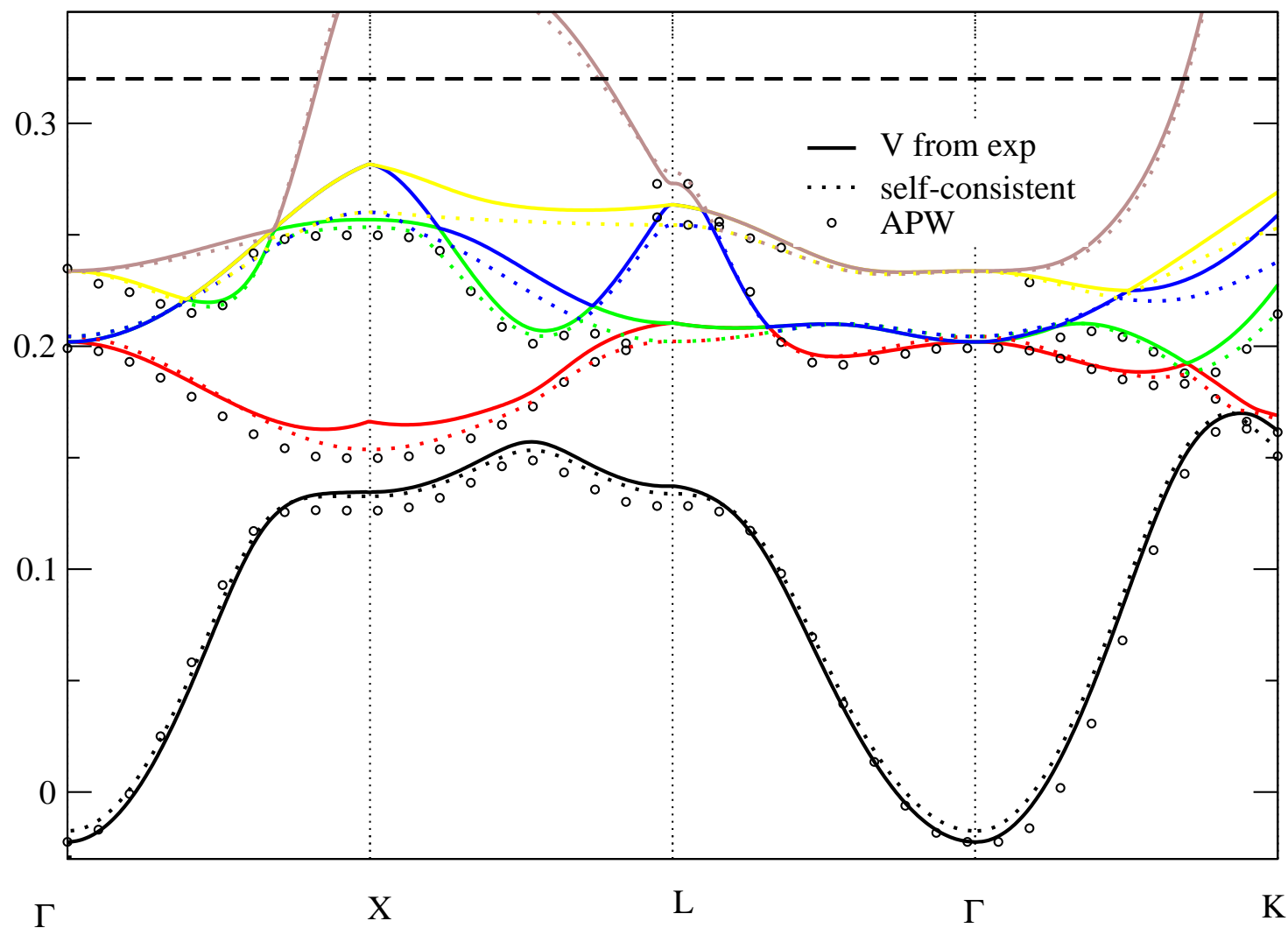
Here we used $\omega_i = \omega - E_i$, $E_{ij} = E_i - E_j$.

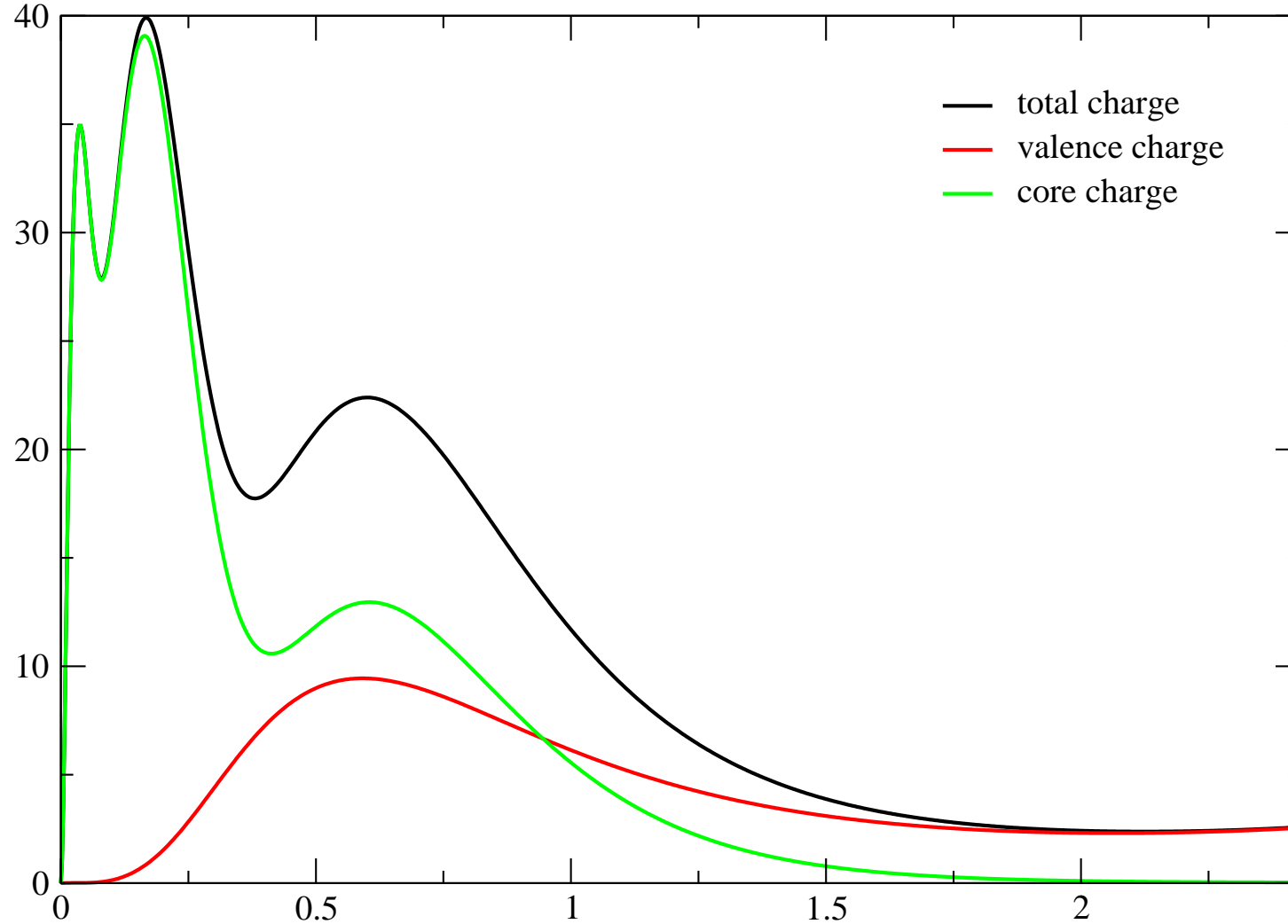
1 Putting it all together

This is the band structure obtained for the C++ program with only few hundred lines of code. The dots show the APW calculation (first part of the lecture where linearization LAPW is not yet done). The full curve correspond to the non-self consistent calculation of band structure with LAPW where the potential was obtained with the fit to experiments (see Thissen book). Finally, the dotted line corresponds to the fully-self consistent calculation with LAPW. The chemical potential is marked with the dashed line.

Cu with LAPW

#K(59), #k(8x8x8), a=6.8219117





Python and C++ code can be downloaded from the webpage under src directory.